## The Radiolytic Hydrogen Production from TODGA and Associated Reprocessing Systems

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## Glossary

- ACSEPT Actinide Recycling by Separation and Transmutation. 22, 24
- AHA Acetohydroxamic acid. 22, 25, 131, 133
- ALSEP An-Ln Separation. 22, 32
- An Actinide. 21, 24
- ARTIST Amide based Radioresources Treatment with Interim Storage of Transuranics. 23
- **CA-BTP** Bis-2,6 (5,6,7,8 tetrahydro 5,9,9 trimethyl 5,8 methano-1,2,4 benzotriazin-3-yl) pyridine. 23, 25, 131, 133
- CDTA 2,2',2",2"" [(1R,2R) 1,2-cyclohexane diyldinitrilo] tetra-acetic acid. 22, 25, 131, 133
- CEA Commissariat a l'energie atomique et aux energies alternatives. 23, 24, 32
- CEA GANEX CEA GANEX process. 24
- CHALMEX Chalmers GANEX. 24
- CMPO N octyl(phenyl) N, N diisobutyl-carbamoyl-methyl-phosphine oxide. 21-23, 131, 134
- **CyMe**<sub>4</sub>-**BTBP** 6,6' bis(5,5,8,8-tetramethyl, 5,6,7,8-tetrahydrobenzo [1,2,4] triazin 3-yl) [2,2']bipyridine. 23, 24, 131, 135
- DEHBA N,N di(2-ethyl-hexyl) butanamide. 24, 131, 136
- DEHiBA N,N di(2-ethyl-hexyl) isobutyramide. 131, 136
- DEHPA (HDEHP) Di 2-ethylhexyl phosphoric acid. 21–25, 131, 136
- DGA Diglycolamide Agent. 22
- DH2EHA N,N di(hexyl-2-ethyl) hexanamide. 24, 131, 136
- DHOA N,N dihexyloctanamide. 24, 30, 131, 137
- DIAMEX Diamide extraction. 22, 23
- DIDPA Di-isodecyl phosphoric acid. 24, 131, 137
- DIPB Di-iso propoxy-benzen. 21, 131, 137
- DMDBTDMA dimethyl-dibutyl tetra-decyl-malonamide. 23, 131, 137

- DMDCATHP 2,6 bis((N-methyl N-dodecyl) carboxamide) 4-methoxy tetra-hydro-pyran. 30
- **DMDOHEMA** N,N' dimethyl N,N' dioctyl-hexyl-ethoxy malonamide. 14, 23–25, 79, 86, 131, 138
- **DTPA** Pentetic acid. 21–24, 131, 138
- EURO-GANEX European GANEX. 17, 24, 34, 38
- EXAm Extraction of Americium. 23, 32
- GANEX Grouped Actinide Extraction. 24, 25
- GC Gas Chromatograph(y). 122
- GFR Gas-cooled Fast Reactor. 20
- HAL Highly Active Liquor. 19
- HEDTA N-(2-hyroxyethly)-ethylenediamine N,N',N'-triacetic acid. 22, 23, 131, 138
- HEH[EHP] 2-ethyl-hexyl-phosphonic acid mono-2-ethyl-hexyl-ester. 22, 131, 139
- HLW High Level Waste. 17, 19, 20, 24, 32
- **ISC** Intersystem Crossing. 33
- JAERI Japan Atomic Energy Research Institute. 23, 24
- LDR Low Dose Region. 14, 37, 41–44, 46, 48, 52, 53, 77–79, 81
- Ln Lanthanide. 21, 24, 25
- MA's Minor Actinides. 17, 20
- MOx Mixed Oxide. 17
- MSR Molten Salt Reactors. 20
- NDA Nuclear Decommissioning Authority. 19
- OK Odourless Kerosene. 19, 24, 32, 33
- PUREX Plutonium and Uranium Redox Extraction. 17, 19, 21–23, 32, 33
- P&T Partitioning and Transmutation. 24
- RHP Radiolytic Hydrogen Production (mol/g). 54, 125
- SACSESS Safety of Actinide Separation Processes. 17, 22–24
- SANEX Selective Actinide Extraction. 22, 23

- SESAME Selective Extraction of Americium by Electrochemical Method. 23
- **SETFICS** Solvent Extraction for Trivalent f-elements Intragroup Separation in CMPOcomplexant System. 23, 32
- SFR/LFR Sodium/Lead-cooled Fast Reactor. 20
- SI International System of Units. 27
- SNF Spent Nuclear Fuel. 17, 19, 20, 22, 29, 81, 85
- **SO**<sub>3</sub>-**Ph-BTP** 2,6-bis (5,6-di-(sulfophenyl) 1,2,4-triazin 3-yl) pyridine. 25, 131, 139
- **TALSPEAK** Trivalent Actinide Lanthanide Separation by Phosphorus reagent Extraction from Aqueous Komplexes. 21
- **TALSQUEAK** Trivalent Actinide Lanthanide Separation using Quicker Extractants and Aqueous Komplexes. 22
- **TBP** Tri-butyl phosphate. 19, 21, 23, 24, 29, 131, 139
- TdDDGA N,N,N',N'-tetradodecyl diglycolamide. 25
- TEDGA Tetra-ethyl diglycolamide. 23, 131, 140
- TEHDGA N,N,N'N'-tetra-2-ethylhexyl diglycolamide. 22, 30, 131, 140
- **TODGA** N,N,N',N' tetraoctyl diglycolamide. 14, 17, 22–25, 29–31, 35, 37, 38, 40, 46–49, 56, 78, 79, 81, 86, 125, 132, 140
- TPF Third Phase Formation. 29
- TRPO Trialkyl Phosphine Oxides. 23
- TRU Transuranic. 24
- TRUEX Transuranic Extraction. 21–23

**TRUSPEAK** TRUEX and TALSPEAK. 21, 22

TRUSQUEAK TRUEX and TALSQUEAK. 22

TWE21 2-(2-dioclylamino-2-oxoethoxy) N,N dioctlypropanamide. 22, 25, 132, 140

- **UREX** Uranium Extraction. 21, 23
- VHTR Very High Temperature Reactor. 20

## The Radiolytic Hydrogen Production from TODGA and Associated Reprocessing Systems

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#### Abstract

Research was conducted into the radiolytic hydrogen production from the gamma radiolysis of *n*-dodecane and N,N,N',N' tetraoctyl diglycolamide (TODGA). Experiments were conducted to determine the value of  $G(H_2)$  for neat *n*-dodecane, TODGA, and mixtures of the two. Variables investigated were the dependence of  $G(H_2)$  on dose, the effect of purging with argon, and the dose rate (between 21 and 360 Gy/min).

The value of  $G(H_2)$  for *n*-dodecane was observed to be dependent on the dose, the dose rate, and exposure to the atmosphere. When the absorbed dose increased to above 5kGy, the value of  $G(H_2)$  decreased. Increasing the dose rate was observed to decrease the value of  $G(H_2)$ . Purging *n*-dodecane with argon resulted in an increased value of  $G(H_2)$ .

When neat TODGA was irradiated, purging the system with argon did not cause an effect on the yield of hydrogen. When the absorbed dose increased above 5kGy, the value of  $G(H_2)$  increased; the opposite behaviour to *n*-dodecane.

Irradiating mixtures of *n*-dodecane and TODGA results in a decreased yield of hydrogen when compared to extrapolations of from neat *n*-dodecane and TODGA.

A model was constructed for hydrocarbon radiolysis, using an iterative approach to solving a set of simultaneous equations, based on the reactions of hydrocarbon radicals after radiolysis. The model did not include a mechanism for the experimentally observed dependence of  $G(H_2)$  on the dose rate of the incident  $\gamma$ -irradiation.

In the future reprocessing system EURO-GANEX, a solution of 0.2M TODGA and 0.5M DMDOHEMA in a hydrocarbon based diluent is expected to be used as the organic extractant phase. The experimentally determined values of  $G(H_2)$  for 0.2M TODGA in *n*-dodecane were as follows. Under aerated conditions:  $(0.208 \pm 0.004)\mu$ mol/J during the Low Dose Region (LDR),  $(0.158 \pm 0.003)\mu$ mol/J for absorbed doses above 5kGy; and  $(0.32 \pm 0.01)\mu$ mol/J for argon purged solutions in the LDR.

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Introduction

### 1 The Nuclear Fuel Cycle and Reprocessing

Safety of Actinide Separation Processes (SACSESS) was a European wide project focussing on the safety of future actinide separation systems. SACSESS had chosen to move forwards with the development of EURO-GANEX (formerly NNL-GANEX) that utilizes TODGA, the novel ligand, as an extractant. As part of researching into the safety of the future reprocessing system EURO-GANEX, the radiolytic hydrogen production of TODGA was investigated.

Hydrogen build up in reprocessing systems presents serious hazards, such as an increased risk of flammability. Hydrogen production must not only be estimated for expected working conditions, but also for non-equilibrium, or mal-operation, situations (such as a blockage in extractant flow).

#### **1.1 Nuclear Fuel Cycle**

The details of the nuclear fuel cycle depend heavily on the type of reactor being used, but all fuel cycles have four main categories: Mining, Fuel Fabrication, Energy Extraction and Waste Treatment.

Fuel cycles that use a thermal reactor, and use steel in the construction of the fuel cladding requires the enrichment of uranium to around 2%-5% U-235 to achieve criticality. This enrichment is achieved by exploiting the weight difference of U-235 and U-238, by methods such as gaseous diffusion and gas centrifuge [24, 31, 38].

The open, or once-through, fuel cycle does not recycle Spent Nuclear Fuel (SNF) back into the reactors. Instead, once cooling is completed, the SNF is either directly disposed of, or processed to reduce the volume of High Level Waste (HLW) (i.e. highly radioactive). This is achieved by separating out lower activity constituents before disposal. This results in the majority of the available energy of the fuel being lost to waste products.

The closed fuel cycle requires only a single (or very small) amount of new material, see Figure 1.1. This scheme requires a large investment into the building and running of reprocessing facilities and the development of reactors capable of using reprocessed SNF as fuel.

As countries begin to make moves towards developing a closed fuel cycle, the reprocessing of SNF can be stepped up to stockpile material suitable for future fuel fabrication.

In the UK, reprocessing of SNF is currently conducted using the PUREX process. It was initially developed to obtain weapons-grade plutonium from thermal SNF. As the civil nuclear energy sector has grown, PUREX has been adapted to recover the materials necessary to fabricate MOx fuel. In addition, the removal of plutonium and uranium from SNF greatly reduces the long term radioactivity of the bulk of the waste, see Figure 1.2. However, the Minor Actinides (MA's) (neptunium, americium and curium) also provide a large contribution to the decay heat, and the long term radioactivity of the majority of the waste could be further



**Figure 1.1:** The Fuel Cycle. The red arrows refer to processes unique to the closed fuel cycle. The closed fuel cycle reduces both the amount of final waste and the amount of material that must be mined. Reprocessing SNF allows the recovery of fissile material. The small amount of the SNF that cannot be recycled is separated and processed for disposal. The mining of new material is significantly reduced but cannot be eliminated due to the slow loss of material from the cycle.



**Figure 1.2:** The activity levels of SNF as a function of time. The activity of the fission products decays quickly and is negligible after a few hundred years. The actinides, however, continue to decay well into the 1000's of years, producing significant levels of radioactivity. Whilst Pu-240 is the longest lived, it is Am-241 which causes the majority of the decay heat at the level of 1000 years. Removal of the actinides would drastically reduce the time until background levels of radiation are reached from 1000's to 100's of years. Reproduced from *Sustainable and Safe Nuclear Fission Energy* [32].

lowered by their separation.

#### 1.1.1 PUREX Process

The PUREX system uses Tri-butyl phosphate (TBP) in a hydrocarbon diluent, such as Odourless Kerosene (OK), as an organic phase to extract plutonium and uranium from SNF which has been dissolved in nitric acid. Undissolved parts of the SNF, such as structural material, are removed and dealt with separately. Uranium and plutonium are extracted from the aqueous phase, by TBP, into the organic phase.

The aqueous phase waste (Highly Active Liquor (HAL)) then goes on to be concentrated by evaporation, and undergo vitrification into glass to form HLW. The organic phase, loaded with uranium and plutonium, goes through further stages to achieve separation and purification. The used organic phase is recycled and used again.

#### 1.1.2 The UK's High Level Waste Inventory

Nuclide	Half-life	Activity
	(yr)	(TBq)
Co-60	5.27	$1.6 \times 10^4$
Sr-90	29.1	$3.2 \times 10^{7}$
Ru-106	1.01	$1.8 \times 10^{5}$
Sb-125	2.73	$9.2 \times 10^{4}$
Te-125	0.159	$2.3 \times 10^4$
Cs-134	2.06	$1.4 \times 10^{5}$
Cs-137	30	$4.2 \times 10^{7}$
Ce-144	0.78	$1.0 \times 10^{5}$
Pm-147	2.62	$1.9 \times 10^{6}$
Sm-151	88.7	$1.3 \times 10^{5}$
Eu-154	8.6	$2.9 \times 10^5$
Eu-155	4.96	$6.6 \times 10^4$
Pu-241	14.4	$2.4 \times 10^{4}$
Am-241	433	$3.7 \times 10^{5}$
Cm-244	18.1	$1.2 \times 10^{5}$
Beta/gamma daughters	-	$3.7 \times 10^{7}$

**Table 1.1:** The radionuclides that contribute significantly ( $\gtrsim 0.1\%$ ) to the activity of HLW [52].

HLW in the UK makes up 95% of the total activity of the inventory of radioactive waste, but only 0.02% by volume [52, 53]. All of the HLW in the UK is processed and handled at Sellafield, mainly from the HAL produced as a waste product from the PUREX process, and the current inventory has an activity of approximately  $7.8 \times 10^7$ TBq [52]. As a comparison, the accidents at Chernobyl, Fukishima and Three-Mile Island released 5200PBq, 770PBq and 0.062PBq repectively [2,82]. The predicted reduction in activity of this HLW over time is shown in Figure 1.3.

Reports by the NDA on the UK's Radioactive Waste Inventory in 2013 allow us to estimate the specific activity of the HAL [51–53]. A total activity for the HAL is estimated at  $\approx 2.4 \times 10^4 \text{TBqm}^{-3}$ , with alpha and beta/gamma contributions of  $\approx 1.61 \times 10^2 \text{TBqm}^{-3}$  and  $\approx 2.38 \times 10^4 \text{TBqm}^{-3}$  respectively. The radionuclides that contribute significantly ( $\gtrsim 0.1\%$ ) to the activity of the HLW are listed in Table 1.1.



**Figure 1.3:** The decay of the activity of HLW. This is the activity of the total inventory of HLW, at a volume of  $\approx 1080 \text{m}^3$  and a mass of  $\approx 2900$  tonnes. Reproduced from the NDA's report on the UK's 2013 Radioactive Waste Inventory - Radioactivity Content of Waste [52].

#### 1.2 Future Nuclear Reprocessing Systems

The development of Gen IV reactors (those currently under research by the Generation IV International Forum) has given rise to research into new reprocessing systems which will be able to handle the new types of SNF. Designs of Gen IV include the Very High Temperature Reactor, Molten Salt Reactors, Sodium/Lead-cooled Fast Reactor and Gas-cooled Fast Reactor. Fast, or breeder, reactors are those that are capable of producing more fissile material than they consume. Some of the new reactor designs include the transmutation of the MA's via excess neutrons inside the reactor [3, 75].

Research into new reprocessing systems has also been sparked by the growing need to deal with the current inventory of SNF and HLW. As can be seen in Figures 1.2 and 1.3 the actinides continue to produce a significant amount of radioactivity long after the fission products have decayed to below the level of natural uranium. The separation of the actinides from the rest of the SNF and HLW would reduce the volume of waste that will be active for 1000's rather than 100's of years. This is of particular advantage when considering the placement of geological repositories, where there is concern that contamination of ground water could occur or that the site may be unwittingly breached by future generations.

The time required for americium to reach an activity below that of natural uranium is longer than the time since the last glacial maximum, see Figure 1.4. For plutonium this reaches back to a time comparable to the last super-eruption of the Yellowstone caldera, over half a million years ago. The separation and separate storage and/or treatment of the ac-



**Figure 1.4:** A comparison between historic events and the amount of time required for radiotoxicity to reach the levels of natural uranium. This is for 1 tonne of SNF from a Pressurised Water Reactor (PWR) with a 40,000 MWd/t burnup from an initial enrichment of 4% [32].

tinides (such as plutonium, americium and curium) would greatly reduce the amount of time for the majority of the volume of waste to reach the activity of natural uranium, subsequently reducing the risk of containment breaches. These considerations have led to an increased interest in developing new reprocessing systems to meet the requirements of separating future fuel types and the reduction of the waste radioactivity levels and duration of its radiotoxicity.

There are two main categories of future reprocessing systems: Homogeneous and Inhomogeneous (or Heterogeneous). Homogeneous systems extract all of the desired elements at the same time and produce a product in which the elements are mixed. Inhomogeneous systems separate each element into a different stream, allowing for greater flexibility of the final destinations. Many systems used a combination of the two, such as systems where major actinides (U and Pu) are separated from minor actinides, but each grouping remains mixed.

The contamination of Pu by other actinides is desirable due to the reduction in in the risk of nuclear proliferation as extra steps would be required to achieve weapons grade plutonium from the waste streams.

#### 1.2.1 Systems Under Active Research

Figure 1.5 displays a selection of the most promising reprocessing streams to be performed on the raffinate of existing reprocessing systems (Figure 1.5a), and the stages required for the standalone ARTIST process (Figure 1.5b). The various reprocessing systems are discussed in further detail below.

Diagrams of the molecules mentioned can be found in Appendix E (Chapter 13).

#### In the US

TRUEX has been developed at the Argonne National Laboratory, and is based on PUREX. It is aimed at extracting the actinides; specifically plutonium, uranium, americium and curium. A solution of 1.4M TBP and 0.2M CMPO is used as the organic extractant phase [61].

TALSPEAK aims at producing separate product streams of the An's and the Ln's from UREX raffinate. DEHPA (HDEHP) and DIPB is used to extract the actinides and lanthanides to-gether. DTPA is then used to extract the trivalent actinides by complexation.

TRUSPEAK combines the processes of TRUEX and TALSPEAK and has been put forward as an alternative to the American UREX+.



(b) The standalone ARTIST process.

**Figure 1.5:** The above figure lists some of the most promising reprocessing systems under research to be conducted on the raffinate of existing reprocessing systems (PUREX, UREX, COEX). Uranium, plutonium and neptunium are removed in the first step. The ARTIST reprocessing system developed in Japan is a standalone reprocessing system, in which uranium and the transuranic elements are removed by ARTIST. DIDPA then extracts the actinides and lanthanides. DTPA finally produces an actinide product. Diagrams adapted from [28].

The combination of TRUEX and Trivalent Actinide Lanthanide Separation using Quicker Extractants and Aqueous Komplexes (TALSQUEAK) is known as TRUSQUEAK and aims to separate the minor actinides from the SNF and is an alternative to the TRUSPEAK process. Instead of the DEHPA (HDEHP) in TRUSPEAK, HEH[EHP] is used as an extracting agent along with CMPO.

ALSEP was patented by the US Department of Energy in January 2013. The solvent is composed of a DGA extractant and HEH[EHP]. Two DGA's are being investigated as candidates: TODGA and TEHDGA. The solvent (DEHPA (HDEHP) or HEH[EHP] with TEHDGA or TODGA in *n*-dodecane) is mixed with the feed and HEDTA. HEDTA and oxalic acid is then used as a scrub for the organic phase. DTPA is used as an stripping agent.

#### In the EU

SANEX has two main variations: i-SANEX, or innovative-SANEX, and 1c-SANEX.

i-SANEX was developed during the ACSEPT project and aims to selectively extract the minor actinides from a PUREX raffinate without the need for a preliminary DIAMEX step. TODGA is used as an extractant for the trivalent actinides and lanthanides with CDTA used to prevent the extraction of zirconium and palladium. AHA is used to selectively strip the actinides [80]. Within the SACSESS project, TWE21 is being considered as an alternative to TODGA, with HEDTA instead of CDTA.

1c-SANEX is aimed at extracting the minor actinides from PUREX raffinate, much like i-SANEX. The organic phase contains a mixture of  $CyMe_4$ –BTBP and TODGA in TPH/1- octanol to extract the minor actinides. L-cysteine is used to scrub the solution of Pd.

DIAMEX has been developed to co-extract trivalent actinides and trivalent lanthanides from PUREX raffinate. 0.5M DMDBTDMA is used as an extractant. The feed contains 0.1M oxalic acid and 0.02M HEDTA. The ATALANTE facility achieved separation factors of 99.9% in a laboratory setting [3, 40, 76, 77]. The diluent for the organic phase is a mixture of kerosene and 1-octanol [54].

R-SANEX aims to selectively extract the minor trivalent actinides from a DIAMEX raffinate. The solvent contains a mixture of  $CyMe_4$ -BTBP and TODGA in 1-octanol. Previous iterations of R-SANEX used DMDOHEMA instead of TODGA. An alternative to  $CyMe_4$ -BTBP, CA-BTP, has been investigated as part of the SACSESS project. Efficiencies of >99% for the recovery of the trivalent actinides have been achieved at a laboratory scale [3, 34, 74, 76, 79, 80].

SANEX-2 systems, occurring after DIAMEX and R-SANEX, use a variety of extractants and stripping agents. They aim to separate the actinides from the lanthanides. Their efficiency is varied and research continues. Separation factors of 99% and above have been achieved by multiple chemical separation systems. The SESAME system has reached efficiencies above 99.9% [3]; other systems include LUCA and those utilising CyMe<sub>4</sub>-BTBP. TRPO has been used, achieving 99.9%, whilst mixtures of TODGA and CyMe<sub>4</sub>-BTBP have reached 99% [41, 45, 73, 81, 90].

EXAm is under development by the CEA under the French 2006 Waste Management Act and aims to extract americium from the raffinate of current waste reprocessing streams. The process is based on TEDGA blended with DMDOHEMA and DEHPA (HDEHP) in HTP. HEDTA is the stripping agent for Am.

#### In China

TRPO is being developed at the Tsinghua University in Beijing, and uses tri-alkyl phosphinoxides (Cyanex 923) in kersosene. The mixture of the two molecules that makes up Cyanex 923 is also known as TRPO. The TRPO system aims to co-extract the trivalent actinides and lanthanides from a PUREX raffinate stream. Separation factors achieved at a laboratory scale were very encouraging at > 99.9% [89].

Following after TRPO, the Cyanex-301 system uses a mixture of TBP and Cyanex-301 to achieve separation factors of > 99.9% in laboratory scale tests [26, 44, 90]. It has been developed by Tsinghua University and has also been investigated by the Argonne Laboratory in the USA when researching the UREX+ process.

#### In Japan

SETFICS has been under development since 1997 in Japan. It is based on the same solvent mixture as TRUEX (CMPO and TBP in *n*-dodecane) with the addition of DTPA.

ARTIST (Amide based Radioresources Treatment with Interim Storage of Transuranics) is a standalone process comprised of three stages. It has been under development by JAERI since 2000 and aims to recover and store all actinides, uranium and several transuranics separately. A flow chart of the processes in the ARTIST system is shown in Figure 1.5b.

Initially, hexavalent uranium is extracted exclusively. This step requires a branched-alkyl monoamide. Under current research the molecules are DEHBA and DH2EHA. A combination of TODGA and DHOA in *n*-dodecane is used to extract the remaining transuranic elements as the last stage of the ARTIST process. The DIDPA process is developed by JAERI and utilizes 0.5M DIDPA and 0.1M TBP [23,47,48]. DTPA is conducted after DIDPA, and the two combined are often known as DIDPA/DTPA. This system uses DTPA to selectively strip the An's from the Ln's. Tests on HLW have achieved separation factors of 99.9% for the An's (Np, Pu, Am and Cm) on a laboratory scale [35, 47].

#### GANEX

GANEX systems are expected to be formed of two stages; the first stage would remove bulk uranium, whilst the second stage would recover the Transuranic (TRU) elements. Figure 1.6 shows the three main options under research for the GANEX-2 cycle. All of these cycles produce a grouped actinide product containing plutonium, neptunium, americium and curium.



**Figure 1.6:** The GANEX-1 cycle extracts uranium. There are three main GANEX-2 cycles options: CEAGANEX, EURO-GANEX, and CHALMEX. All of the candidates are under development in Europe. Adapted from [28].

CEA GANEX has shown promising results by using a combination of DMDOHEMA and DEHPA (HDEHP) and is being tested at the laboratory scale [18, 28, 42].

CHALMEX is a variation of CEA GANEX, developed during ACSEPT. CHALMEX utilizes CyMe<sub>4</sub>-BTBP and TBP. An alternative to TBP, DEHBA, is also being investigated. Neither hot nor cold tests have been conducted, and research is continuing at Chalmers, Sweden [28].

EURO-GANEX uses a combination of TODGA and DMDOHEMA in an OK diluent as the organic extractant [6, 18].

#### **1.3 EUROGANEX**

The GANEX process is formed of two cycles. A candidate for the GANEX-2 cycle is EURO-GANEX, developed though ACSEPT and SACSESS, both part of the Seventh Framework Program (FP7) of the European Commission (Euratom - Fission). SACSESS was a follow-up to the project ACSEPT.

SACSESS was a collaborative project, coordinated by the CEA, aimed at providing a structured framework to enhance the safety of the fuel cycles associated with Partitioning and Transmutation (P&T). Selected processes were studied to identify weak points and to optimize flowsheets.

EURO-GANEX is based on the option first put forward by NNL during ACSEPT, during the early development stages it was referred to as NNL-GANEX. It uses a combination of TODGA and DMDOHEMA in an OK diluent as the organic extractant [6,18,71]. It aims to be a complete reprocessing system, avoiding the mixing of acidic and neutral extractants and eliminating

the need for a buffer by using a highly acidic stripping step [8–10, 16, 17, 25, 42, 43, 45, 55, 71, 76]. A flowsheet diagram of the process is shown in Figure 1.7.



**Figure 1.7:** The solvent extraction cycle for EURO-GANEX with the aqueous feeds specified. The solvent feed is comprised of 0.2M TODGA and 0.5M DMDOHEMA in OK. Red arrows indicate the flow of the aqueous streams. The blue arrows indicate the flow of the organic stream: the initial solvent feed and then the solvent carrying the extracted metal ions which are re-extracted by the stripping process. The used solvent is then removed and recycled for further use [71].

0.5M DMDOHEMA, as a modifier to 0.2M TODGA, was chosen to maximize the initial aqueous concentration of plutonium. In addition, this combination increases the loading capacitiy and reduces the risk of third phase formation from metal loading. Other promising mixtures include the addition of 0.5M DEHPA (HDEHP) to 0.2M TODGA, or the alternative organic mixture of 0.2M TdDDGA with 0.5M DMDOHEMA [12, 18, 70, 71]. EURO-GANEX underwent successful hot tests at ITU in 2014, though with some significant losses observed. A modified process is in development replacing TODGA with TWE21 and SO<sub>3</sub>-Ph-BTP with CA-BTP [28].

Plutonium and the other actinides are selectively stripped by AHA (or  $SO_3$ -Ph-BTP) to remove them from the Ln's (Lanthanide). The addition of CDTA acts as a masking agent to prevent the co-extraction of the fission products, such as Pd, Zr and Ag [6].

To alleviate concerns over proliferation, the reprocessing product is designed to be unsuitable for the production of nuclear weapons as further extraction steps would be necessary to achieve the required purity [32].

In the GANEX-2 cycle the organic phase of the extraction will be subject to multi component irradiation. The main two sources of irradiation will be gamma and alpha. Alpha irradiation from the extracted metal ions will have only a small radius of effect, whilst gamma will effect the entire solution.

Understanding the production of hydrogen in nuclear reprocessing systems is of great importance when considering safety cases and the risk posed by a build up of this flammable and explosive gas. In particular it is a necessity when designing safety systems involving ventilation and gas monitoring.

The 2011 Fukushima accident involved damage to four reactor buildings by hydrogen gas explosions. The cause of this build up of hydrogen was the exposure of heated fuel rods to steam, causing the exothermic production of hydrogen. Systems designed to regulate the amount of hydrogen by burning the excess failed to function due to the loss of electrical power, highlighting the need for passive safety systems, such as catalytic recombiners [83].

### 2 Radiation Chemistry

#### 2.1 Sources of Radiation

With the exception of nuclides formed by cosmic radiation, natural nuclides fall into two categories: long-lived nuclides, those with half-lives comparable to the age of the earth; and the daughter products of the long lived nuclides.

Co-60 is produced by the neutron irradiation of Co-59 in nuclear reactors and has a halflife of 5.27 years. Co-60 decays by  $\beta$  emission to the stable isotope Ni-60, and produces two  $\gamma$ -rays with energies 1.17 and 1.33 MeV.

$${}^{59}\text{Co} + n \to {}^{60}\text{Co} \tag{2.1}$$

$$^{50}\text{Co} \rightarrow ^{50}\text{Ni} + e^- + \bar{\nu_e} + 2\gamma$$
 (2.2)

The long half-life and easily shielded low energy  $\beta$  decay make Co-60 preferable to other  $\gamma$  sources of similar intensity for laboratory work.

#### 2.2 Measuring Dose

The absorbed dose,  $A_D$ , is defined as the mean energy, E, imparted to an amount of matter, m. The SI unit is the Gray (Gy), equivalent to  $Jkg^{-1}$ . Units previously in use included the rad and the erg/g.

$$A_{\rm D} = \frac{\rm E}{\rm m} \tag{2.3}$$

$$1 \,\mathrm{Gy} = 6.24 \times 10^{15} \,\mathrm{eV/g} = 100 \,\mathrm{rad}$$
 (2.4)

$$1 \operatorname{rad} = 100 \operatorname{erg}/\operatorname{g} \tag{2.5}$$

To measure the amount of energy imparted to a system dosimetry is used. There are two main methods of measuring a dose rate: Chemical, where the rate of a known reaction is observed; and Physical, where an effect of the incident energy is detected, such as by the inducement of an electrical current.

A well known chemical dosimeter is the Fricke Solution, where the oxidation of ferrous ions to ferric ions ( $Fe^{2+}$  to  $Fe^{3+}$ ) is observed by means of the absorption peak of the ferric ions at 304 nm. The amount of ferric ions produced is linear for a dose of up to 400 Gy. This method

relies on the extrapolation from a limited dose range to higher doses, and has the drawback that the solution is sensitive to visible light as well, and therefore has a limited shelf-life.

#### 2.3 G-Value

The G-Value is a useful concept in radiation chemistry. It measures the yield (produced or destroyed) of a substance per unit of imparted energy.

$$G(X) = \frac{dn_X}{dE}$$
(2.6)

where  $n_X$  is the the amount of the substance being produced or destroyed. The SI unit is  $mol J^{-1}$ , but the value is often reported as molecules / 100 eV. The conversion is given below.

$$1 \mu \text{mol} \text{J}^{-1} = 9.65 \,\text{molecules} / \,100 \,\text{eV}$$
 (2.7)

$$1 \,\mathrm{molecule} \,/\,100 \,\mathrm{eV} = 0.1036 \,\mu\mathrm{molJ}^{-1}$$
 (2.8)

To avoid confusion, when quoting values they will be given as:  $\# \mu mol J^{-1}$  (# molecules / 100 eV).

### 3 TODGA - N,N,N',N'-tetraoctyl-diglycolamide



Figure 3.1: The structure of TODGA, showing the one etheric and two amidic oxygen atoms.

TODGA (N,N,N',N' tetraoctyl diglycolamide) was first developed by Sasaki *et al.* as part of the research into novel ligands for the extraction of the actinide and lanthanide groups from SNF [60]. It has since been studied extensively and has been used as an extractant in the hot tests of the EURO-GANEX reprocessing system [6, 16, 18].

It is fully soluble in *n*-dodecane, and many other hydrocarbon based diluents, and has been shown to have high extraction efficiency for the minor actinides and rare earths when in contact with a highly acidic aqueous phase [46]. As a diamide derivative it is completely incinerable, producing no solid radioactive waste upon combustion, making final disposal simpler [66].

As an organic phase, TODGA exists of small spherical reverse miscelles with a water core, with or without  $HNO_3$ , surrounded by four TODGA molecules. TODGA contains three donor oxygen atoms, one etheric and two amidic, with which it bonds to ions, see Figure 3.1 [50].

The extraction reaction of a metal ion  $M^{n+}$  by a ligand, L, from an aqueous solution containing nitric acid can be written as:

$$\mathbf{M}^{n+} + p\mathbf{L}_{\mathrm{org}} + n(\mathbf{NO}_{3}^{-}) \leftrightarrows \mathbf{M}(\mathbf{L}_{p})(\mathbf{NO}_{3})_{\mathrm{n,org}}$$
(3.1)

where *p* is the stoichiometry ratio, specific for each metal ion. The valency preference order is III > IV > VI > V [13, 15, 68].

In the high loading region TODGA has a tendency to form a third phase, limiting the efficiency of any extract. This can be very low for some metal ions, especially Nd(III). Extraction of nitric acid can reduce the threshold for TPF [50,60,68,69]. Suppression of TPF has been succesfully achieved using modifiers such as 1-octanol, monoamides, dialkylamides, and TBP. Other modifiers can be added to suppress the extraction of undesired elements [11,46,69,80].

Some future reprocessing systems are theorized to use ligands based on TODGA, such as

#### DMDCATHP [54].

Structural changes of ligands and diluents from degradation processes play a crucial role in the efficiency of extraction, selectivity, and the possibility of solvent recycling [54].

Extraction processes are expected to have high acidity of the aqueous phase, a high intensity radiation field, and long application times in centrifugal contactors [54].

#### 3.1 Radiolytic Studies of TODGA

Due to the large amount of ionizing radiation in a nuclear reprocessing stream, significant degradation is expected. This degradation is expected to adversely affect the ability of TODGA to extract the minor actinides as bonds within the molecule are broken. Doses of 100kGy almost completely impair the efficiency of TODGA [54]. The bonds broken are expected to include the bonds within the long hydrocarbon chains.

It was thought that the long hydrocarbon chains would provide radiolytic stability to the molecule by acting as 'sacrificial' bonds [87]. However, if this was the case, then it could be expected that the radiolytic degradation of the TODGA would include many of the same products as from a hydrocarbon chain, including hydrogen gas. Branched alkanes have been found to degrade at a higher rate than straight alkanes. However, when comparing TODGA and TEHDGA, which contains branched hydrocarbon chains, no significant differences were found in the rate of degradation or the final yields of the degradation products. These two pieces of evidence give strong evidence that the majority of the irradiation is received by the diglycolamide centres, and that most bond cleavage occurs there as well [87]. See Appendix E (Chapter 13) for molecular diagrams of TODGA (Figure 13.81) and TEHDGA (Figure 13.80).

A value of  $G(H_2)$  for TODGA has not been reported, but its value is of crucial importance for the modelling of safety cases in reprocessing flowsheets. This study aimed to identify the value of  $G(H_2)$  for TODGA under gamma radiolysis, and to identify the effects of the concentration of TODGA when in a solution with *n*-dodecane.

In general, the acidity of the aqueous phase enhances radiolysis, as do aliphatic saturated diluents, whilst aromatic diluents depress the effect of radiolysis [7, 14, 48, 49, 72]. However, it has been observed that nitric acid has an insignificant effect on radiolysis of TODGA [66]. The degradation of neat TODGA occurs at a slower rate than for TODGA-*n*-dodecane systems, leading to the conclusion that *n*-dodecane has a sensitization effect on TODGA, as it does for most amides in amide-*n*-dodecane systems. This is possibly due to a charge transfer reaction from the radical cations of *n*-dodecane to TODGA [65, 66, 87].

TODGA has been observed to have a four-fold radiation resistance to  $\alpha$  compared to  $\gamma$ irradiation. The decomposition of TODGA has been measured to have a decomposition G value of  $G_{\alpha} = 0.022 \pm 0.0001 \,\mu \text{mol J}^{-1}$  and  $G_{\gamma} = 0.080 \pm 0.0003 \,\mu \text{mol J}^{-1}$  by Sugo *et al.* [66,67]. This observed radiation resistance to  $\alpha$  leads to the conclusion that extrapolating from  $\gamma$  radiolysis alone will result in an overestimate of the decomposition of the organic phase. The addition of benzene or DHOA has been observed to offer a protecting effect against radiolysis [21, 39, 58, 62, 67, 87].

There is experimental evidence that the degradation of TODGA is dependent on dose, with a relation of the form  $G=G_0e^{-kD}$ , and so the use of a G value is not appropriate. However, the initial value of G,  $G_0$ , can be used, calculated from the initial concentration and a dose

constant, d (kGy<sup>-1</sup>). Table 3.1 displays some of the values of dose constant and G<sub>0</sub> in literature [87].

$$G_0 = d[TODGA] \times 1.3 \tag{3.2}$$

**Table 3.1:** Initial degradation G values and dose constants for various TODGA systems in the available literature. Values of  $G_0$  were calculated using the Equation 3.2 [87].

Sample Constituents	Go	Dose Constant d	Ref
Sumple Constituents	11-1		
	$\mu$ molj <sup>+</sup>	KGY 1	
0.05M TODGA	0.29	4.5	[66]
0.05M TODGA	0.27	$4.1 \pm 0.3$	[87]
$0.05M$ TODGA/ $0.1M$ HNO $_3$	0.3	$4.5 \pm 0.2$	[87]
$0.05M$ TODGA/ $2.5M$ HNO $_3$	0.25	$3.8 \pm 0.3$	[87]

Coexisting HNO<sub>3</sub> in the organic phase appears to have a negligible effect on the radiolytic stability of TODGA. It has commonly been reported that the favoured bond to rupture under radiolysis is affected by the presence of nitric acid but experimental evidence is unclear if this is the case. The most susceptible bonds are the N–C<sub>carbonyl</sub> bond, the C–C<sub>carbonyl</sub> bond, and the C–O<sub>ether</sub> [87].

## 4 Hydrocarbon Radiolysis

The radiolysis of hydrocarbons is a subject that has been of much interest over the past several decades, especially in the context of nuclear reprocessing, where the hydrocarbon containing organic phase is subject to not only a high intensity multi-component radiation field, but also in contact with a highly acidic aqueous phase for long durations [54].

Hydrocarbons are often chosen for use in high radiation areas over other substances due to lower radiolysis yields than other functionalized solvents [84]. With respect to nuclear reprocessing, several hydrocarbon based solvents have been proposed for use in various future reprocessing systems. Examples include: OK mixed with modifiers such as 1-octanol; HTP for the CEA EXAm process; and *n*-dodecane for processes such as SETFICS (Japan) and ALSEP (US) [3, 54]. OK is used as the diluent in the PUREX process, and is a candidate for many proposed future systems [6, 16, 18]. Understanding the underlying reaction mechanisms of hydrocarbons, when subject to ionising radiation, is of crucial importance when considering the safe operating of future reprocessing plants.

#### 4.1 The Response to Ionising Radiation

Estimates of average dose received by the organic solvent in a reprocessing plant will vary, but it is expected to be in the region of 100kGy per year, depending on fuel type and burn up [54]. Table 1.1 lists the radionuclides in HLW which contribute significantly to the activity, and includes various decay routes, including alpha, beta, and gamma. As the organic phase of a solvent extraction system moves metal ions from the aqueous phase into the organic, a significant amount of the dose will occur via more localized alpha and beta irradiation than the system wide gamma.

There is a large body of work on the photolysis of hydrocarbons. However, extrapolating from photolysis to radiolysis is suspect at best. The upper energy limit of photolysis is 11.6 eV, and it is thought that the main routes of dissociation alter significantly at energies over 12 eV [4]. There is experimental evidence that suggests that the rupture of C–C bonds is unimportant for hydrocarbons [64].

In a hydrocarbon, ionization occurring upon radiolysis resulting in either a direct excitation (accounting for 10% to 20% of excited state production), or the formation of a geminate radical cation and electron [86]. The ionization of hydrocarbons has a G-value for the loss of the ground state parent molecule of around  $0.31 - 0.83 \mu mol/J$  (3-8 molecules/100 eV). For liquid cyclohexane it is  $0.57 \mu mol/J$  (5.5 molecules/100 eV) [4].

In non polar liquids, such as hydrocarbons, geminate pair recombination is the dominant process, as proton transfer involving the ground state radical cation is too slow to compete [29,63,64]. The rate of this recombination is limited by diffusion for solvated electrons, but not

for free or quasi-free electrons [88]. In a liquid phase 90-99% of the positive ions recombine with the geminate electrons to produce excited molecules and radicals [4].

The excited states can take a singlet or triplet form. Recombination in multiple ion pair groups will produce larger amounts of triplet state products [29].

In alkanes and cycloalkanes of molecular weights above n-decane, the chance of a singlet excited state being formed upon recombination is greatly increased, resulting in approximately a three-fold increase in the yield of the singlet state. As such, the triplet state is less likely to form and the yield is diminished, indicating that it takes a less significant role in the chemistry of the system [4].

The lifetime of the excited state is dependent on the whether the excited state is in the singlet or triplet state with the lifetime of the triplet state being much longer than the singlet state. The lifetimes of the singlet excited states increases along with hydrocarbon chain length from around 0.7ns in *n*-hexane, to 4ns for *n*-dodecane for the singlet excited state [30, 86].

Once formed, the excited states seek to relax and discard their energy. One route is Intersystem Crossing (ISC) where the spin on the excited electron is reversed, this causes a singlet to become a triplet, or a triplet to relax to a singlet. The transition of a triplet to a singlet state is known as phosphorescence due to accompanying release of energy as a photon. ISC is a slow process and it is expected that other routes will be much more likely.

For the excited singlet state of cyclohexane there is a probability of 0.8 that it will dissociate to yield molecular hydrogen [4]. Molecular hydrogen elimination from an excited linear chain hydrocarbon molecule,  $RH_2^*$ , takes the form shown below.

$$\mathrm{RH}_{2}^{*} \rightarrow \mathrm{R}(=) + \mathrm{H}_{2} \tag{4.1}$$

A triplet excited state is less likely to undergo molecular hydrogen elimination, but is more likely than the singlet excited state to undergo H-atom detachment by:

$$\mathrm{RH}_{2}^{*} \rightarrow \mathrm{RH}^{\bullet} + \mathrm{H}^{\bullet} \tag{4.2}$$

These radical states can then undergo further reactions with each other, the excited molecules, and ground state molecules of the system to produce various products.

#### 4.2 *n*-Dodecane

Cyclohexane had previously been considered the paradigm for hydrocarbon radiolysis, and the final products and effects of various chemical additives on the final products of cyclohexane have been thoroughly studied. Most hydrocarbons do not produce high mobility ions when exposed to ionizing radiation, however, cyclohexane, methlycyclohexane, and the decalins have been observed to produce these high mobility ions. This unusual property of cyclohexane makes it, along with methlycyclohexane and the decalins, a poor choice for a representative of the hydrocarbons as a whole [29].

OK is a mixture of hydrocarbons, one of which is dodecane. As such, *n*-dodecane ( $C_{12}H_{26}$ ) is often used in laboratory research as a substitute [84]. OK is used as a diluent in PUREX

reprocessing and is a candidate diluent for EURO-GANEX reprocessing system [6, 16, 18].

#### 4.2.1 Radiolysis of *n*-Dodecane

When *n*-dodecane is subject to gamma radiation, 94.7% of radiolytic events result in the formation a geminate pair. Of these, only 5% go on to avoid recombination [78]. As a result a large number of excited states are formed, which can be expected to mainly take the singlet spin state as the molecular weight is above that of *n*-decane [4].

The radiolytic yield of hydrogen from the gamma radiolysis of *n*-dodecane has been investigated previously. Values of this yield have been reported between 0.29 and 0.699  $\mu$ mol/J (2.8 and 6.71 molecules/100 eV), as shown in Table 4.1.

	Dose Rate	G(H <sub>2</sub> )	G(H <sub>2</sub> )
	Gy/min	molecules/100eV	µmol/J
Cundall and Griffiths [19]	16.7	5	0.52
Dewhurst, H.A. [20]	-	4.9	0.51
Rappoport and Gumann [57]	5	4.9	0.51
Holland <i>et al</i> . [27]	7.2	6.71	0.699
Barelko <i>et al.</i> $[5]^a$	145-245	2.8	0.29

**Table 4.1:** Values of  $G(H_2)$  in the literature.

<sup>*a*</sup>: Value for the production of all gases.

Where a dose rate was specified in Table 4.1, the value of  $G(H_2)$  was plotted as a function of dose rate, shown in Figure 4.1. This figure could lead us to conclude that there may be a dose rate dependence on the value of  $G(H_2)$ . A dose rate dependence of  $G(H_2)$  would have to be taken account of in any safety case modelling of reprocessing flowsheets where it could be expected that the dose rate may be extremely variable. This possibility was investigated further in this study, collecting values of  $G(H_2)$  for dose rates between 21 and 360 Gy/min.



a: [57] b: [27] c: [19] d: [5]

**Figure 4.1:** Values from Table 4.1 plotted as a function of the dose rate. This plot suggests that there may be a dose rate dependence on the production of  $H_2$ . This dose rate dependence was investigated further in this study in the range 21-360 Gy/min.

Previous studies have indicated that *n*-dodecane interacts with TODGA to alter the radiolytic stability of the molecule. The reaction of the radical cation with TODGA is expected to take the form:

$$C_{12}H_{26}^{++} + TODGA \rightarrow C_{12}H_{26} + [TODGA]^{++}/other products$$
 (4.3)

with a measured reaction rate of  $(9.72 \pm 1.10) \times 10^9 \text{ M}^{-1} \text{s}^{-1}$ . This is considerably slower than the reaction rate reported for the radical cation of *n*-dodecane with the geminate ion of  $3.3 \times 10^{11} \text{ M}^{-1} \text{s}^{-1}$  by Zarzana *et al.* [87]. From this we may expect that the production of singlet and triplet excited states of *n*-dodecane is affected very little by the presence of TODGA and that the main reactions with TODGA will occur with the other radical products of *n*-dodecane.

## Part II

# Experimentation
### **5** Experimental Details

To investigate the production of hydrogen from TODGA and *n*-dodecane, small amounts of solution were placed in glass vials and sealed using a crimp cap, see Figure 5.1. Vials were placed inside a Co-60 irradiator and periodically removed for samples of the headspace to be removed and analysed by gas chromatography.

#### 5.1 Investigated Variables

Variables under investigation were dose, dose rate, the presence of air, and the concentration of TODGA.

The value of  $G(H_2)$  is defined as the amount of hydrogen produced per unit of absorbed energy, see Section 2.3. This can be rewritten as:

$$G(H_2)(\text{mol}/J) = \frac{\text{RHP}(\text{mol}/g)}{\text{Dose}(kGy)}$$
(5.1)

where RHP is the Radiolytic Hydrogen Production, the amount of hydrogen produced per gram of irradiated solution. When a linear fit is appropriate to the data collected, the gradient of RHP as a function of dose is used as the value of  $G(H_2)$ .

To gain a measure of any dependence on dose, linear fits through the origin were constructed to data collected at doses below 5 kGy, the Low Dose Region (LDR), and to all of the available data. Due to time constraints, it was not always possible to gain a value from both the LDR and doses above 5kGy.

Group #	Minimum	Maximum
(DRG)	Gy/min	Gy/min
2	21	32
3	32	47
4	47	71
5	71	107
6	107	160
7	160	240
8	240	360

Dose rates used were between 21 and 360 Gy/min. To investigate the dependency of  $G(H_2)$  on the dose rate, this range was split into several smaller dose rate groups (DRG's) and values of  $G(H_2)$  calculated for each group. The values of these groups are shown in Table 5.1

The effect of the presence of air was determined by comparing values of  $G(H_2)$  from samples exposed to the atmosphere before being sealed (aerated) and those which once sealed were purged using argon (deaerated).

The concentrations of TODGA studied are shown in Table 5.2. These values were chosen based on the expected concentration of TODGA when used in EURO-GANEX: 0.2M TODGA. The various concentrations of TODGA should give a good indication of the interaction between *n*-dodecane and TODGA under  $\gamma$ -radiolysis.

**Table 5.2:** The concentrations of TODGA studied in this research, with the corresponding mole fraction. EURO-GANEX is expected to use a TODGA concentration of 0.2 M [6].

Concentration	TODGA Volume	TODGA Weight	Mole Fraction	Mole Fraction
mol/L	%	%	TODGA	<i>n</i> -Dodecane
0	0	0	0	1
0.01	0.64	0.77	0.00227	0.99773
0.2	12.77	15.09	0.049524	0.950476
0.4	25.54	29.40	0.108807	0.891193
1.0	63.84	68.19	0.385934	0.614066
1.546	100	100	1	0

#### 5.2 Reagents and Chemicals

TODGA was obtained from Technocomm with a putrity of 99%, determined by HPLC. *n*-Dodecane was obtained from Sigma Aldrich with a purity of 99%. TODGA and *n*-dodecane were used without further purification.

The argon gas used as the carrier gas for gas chromatography analysis and purging of samples had a percentage purity of 99%.

#### 5.3 Sample Preparation

The volume of the vials used were measured by using the weight difference between an empty sealed vial and a sealed vial filled with water. From this measurement, the vial volumes were approximated at  $11.99 \pm 0.02$  ml and  $21.7 \pm 0.2$  ml.

Solutions were prepared by weighing out the necessary weight of TODGA for a set volume and then adding *n*-dodecane to reach the required volume. These solutions are then mixed by shaking by hand. Smaller volumes of the solution were placed into glass vials using a volumetric pipette.

The glass vials were sealed with a crimp cap containing a butyl rubber septum, see Figure 5.1a. Solution volumes used were 1ml, 2ml, 5ml, and 10ml. No noticeable effect on the value of  $G(H_2)$  from the sample volume or vial size was observed.

To deaerate samples, a needle was placed through the septum to the bottom of the vial and argon was fed in, see Figure 5.1b. argon was chosen to deaerate the sample as it was the carrier gas for the gas chromatograph. This process of deaeration does result in damage to the septum resulting in a less gas-tight system than would be ideal. In addition, the shelf-life of irradiated samples is significantly reduced, and headspace samples must be taken promptly.



**Figure 5.1:** The method of sampling the headspace and deaerating the solution. Headspace gas samples were removed through the septum using a gas tight syringe. To deaerate the solution, a needle is inserted through the septum to the bottom of the vial and argon fed in, bubbling through the solution to purge the system. The headspace gas is allowed to escape through a chimney in the septum. Once the argon has bubbled through, the inlet and chimney needles are removed.

For deaerated samples the vials were re-capped and deaerated again after each sampling before being placed back inside the Irradiator.

#### 5.4 Gamma Irradiation

A Co-60  $\gamma$ -irradiator was used to conduct  $\gamma$ -radiolysis studies of samples. The irradiator used was a Foss Therapy Model 512 Co-60 Irradiator. The irradiation chamber was divided by a rack into which the sample vials could be placed over two vertical levels. Details of the irradiator and sample rack are available in Appendix D (Chapter 13). Dosimetry for the irradiation by Co-60 was conducted using the Radcal high intensity gamma radiation detector 10X6-0.18 attached to the Accu-Gold+ Digitizer. It is capable of detecting dose rates between 500 nGy/s and 6.31 Gy/s for a dose between 2µGy and 17 kGy with an error of ±5% [56]. Measurements of the dose rate for the 'cells' were taken at the beginning of each irradiation session. Details of the dosimeter are available in Appendix D (Chapter 13).



**Figure 5.2:** Two colour maps of the dose rate measurements in the irradiation chamber. Each map is divided into grid representing the rack used to hold sample vials. Note the bottom rack does not contain any measurements for row 8 as samples were not placed in these positions.

Colour, or heat, maps showing the variation in dose rate across the irradiation cell were produced using measured values, Figure 5.2. These assumed that the measurements were taken at the centre of each 'cell'. Dose rates measured varied between a maximum of 360 Gy/min and a minimum of 21 Gy/min. For comparison, it is expected that average considered annual dose for the organic phase is 100kGy, depending on fuel type and burn up [54]. This would equate to approximately 0.19Gy/min if the dose rate was constant throughout each year. However, reprocessing systems are expected to be run in batches, where the dose rate will be significantly higher for short amounts of time, followed by long periods of very low dose rates.

When analysing the data, the dose rate has been assumed to be the same throughout each vial and unaffected by the presence of other vials between them and the source rods. This naturally leads to a small level of error, which is increased for the vials nearest the sources where the dose rate is large and will decay quickly with increasing distance.

Another source of error is the speed at which the two sources are raised. It was typically the case that one source would raise 5-10 seconds late. This is thought to have little effect on the experimental irradiation, due to these lasting several minutes. However, due to the shorter duration time, 1-2 minutes, when measuring the dose rate, this could potentially result in a lower dose rate being measured.

#### 5.5 Gas Analysis

To determine if  $G(H_2)$  has any dependencies other than the expected (linear with dose), several parameters were investigated. These parameters were: dose rate (between 21 and 360 Gy/min), concentration of TODGA, and aeration vs. deaeration of the solution.

Samples of  $100\mu$ l were taken from the headspace with a gas tight syringe through the septum. Analysis of the hydrogen content of the sampled gas was conducted through the use of a gas chromatograph (SRI Model 8610C with a Thermal Conductance Detector), with argon as a carrier gas. This method has been used by other researchers, such as P.A. Yakabuskie *et al.* (2010) [85].

Vials were irradiated multiple times to build a picture of the gas evolution. With aerated samples, once a sample of the headspace had been taken the vials were irradiated again. Corrections for the decrease in the amount of hydrogen and the change in pressure were applied to the measured values of subsequent samples. For samples initially exposed to oxygen, a solubility of oxygen in the solution was assumed of 0.74mM, the solubility of oxygen in *n*-dodecane [59]. Deaerated samples required a different set of calculations to correct subsequently collected samples, taking into account the hydrogen lost whilst re-capping and deaerating. For more information on the calculations used, see Appendix C (Chapter 13).

#### **5.6 Determining a Value of** $G(H_2)$

Data points of the amount of hydrogen produced were averaged when taken at similar doses, this was done separately when taking the data as a whole and when looking a the effect of dose rate.

The averaged values of the amount of hydrogen produced was then plotted against the

dose absorbed by the system and a linear fit constructed. The gradient of a linear fit of the number of mols of hydrogen produced per gram of solution as a function of the absorbed dose is  $G(H_2)$ . Linear fits are constructed for the LDR (< 5kGy) and to the entirety of the data, known as the limiting value of  $G(H_2)$ . An example of this is shown in Figure 5.3. See Appendix C (Chapter 13) for more details on how a value of  $G(H_2)$  is determined.



**Figure 5.3:** Example of Method of Determining  $G(H_2)$ . The amount of hydrogen (mol) produced per gram of solution is plotted as a function of the absorbed dose (kGy). The gradient of the linear fit gives the value of  $G(H_2)$  (mol/J). Two linear fits are constructed, one to the data collected below 5kGy for the LDR and one to the entirety of the data.

## 6 Radiolytic Molecular Hydrogen Production from *n*-Dodecane

#### 6.1 Dose and Dose Rate

#### Dose

Figure 6.1 shows the amount of molecular hydrogen produced (mol/g) for different values of absorbed dose (kGy). The largest absorbed dose reached for *n*-dodecane was  $\approx$  37kGy.

The values of the linear fits in Figure 6.1 are  $(0.34 \pm 0.01)\mu$ mol/J for the LDR, and  $(0.30 \pm 0.01)\mu$ mol/J for all doses, these values are also shown on Figure 6.2 by the arrows on the right hand side of the Figure.



**Figure 6.1:** The molecular hydrogen produced at various absorbed doses of gamma-irradiation for aerated *n*-dodecane. Two linear fits have been constructed; one for all of the data, and one to the data within the LDR (the fit line has been extended for clarity).

#### **Dose Rate**

Table 6.1 lists the experimentally determined values of  $G(H_2)$  for neat *n*-dodecane, along with the difference between the value for LDR and the limiting value of  $G(H_2)$ . Figure 6.2 shows the values of  $G(H_2)$  calculated from the gradients of linear fits for the amount of molecular hydrogen produced against the absorbed dose as a function of the incident gamma-radiation

Group #	LDR	Limiting G(H <sub>2</sub> )	$\Delta G(H_2)$
	$\mu$ mol/J	$\mu$ mol/J	$\mu$ mol/J
2	$0.44 \pm 0.02$	$0.33\pm0.01$	$0.11\pm0.02$
3	$0.422 \pm 0.009$	$0.327\pm0.004$	$0.10 \pm 0.01$
4	$0.387\pm0.004$	$0.34 \pm 0.01$	$0.05 \pm 0.01$
5	$0.401\pm0.005$	$0.296\pm0.007$	$0.105 \pm 0.009$
6	$0.32\pm0.01$	$0.236\pm0.007$	$0.08 \pm 0.01$
7	-	$0.21 \pm 0.01$	-
8	$0.316\pm0.006$	$0.252\pm0.009$	$0.06 \pm 0.01$

**Table 6.1:** Experimentally determined values of  $G(H_2)$  for *n*-dodecane split by dose rate and the dose range examined, along with the difference between the value for LDR and the limiting value of  $G(H_2)$ .

dose rate. The arrows on the right hand side of the figure indicate the values calculated from a fit to the entirety of the data as shown in Figure 6.1.

Table 6.1 and Figure 6.2 indicate a decrease in the value of  $G(H_2)$  as the dose rate increases. The reduction in  $G(H_2)$  with the dose rate is more pronounced for the LDR. For the LDR, the largest difference in  $G(H_2)$  over the different dose rates is  $(0.19\pm0.02) \mu \text{mol/J}$ . For the limiting value of  $G(H_2)$ , the maximum difference over the dose rate range investigated is  $(0.13\pm0.01)\mu \text{mol/J}$ .



**Figure 6.2:** Determined values of  $G(H_2)$  for aerated and deaerated *n*-dodecane along with exponential fits to the aerated data and values from literature. The arrows on the right hand side indicate the values of  $G(H_2)$  determined from the data not split by dose rate. It is clear that deaeration results in an increase in the rate of molecular hydrogen production. The exponential fits are given in Equations (6.1) and (6.2). Literature values are listed in Table 4.1.

When values of  $G(H_2)$  for the lower dose rate groups are compared to those for the entirety of the data, it can be seen that at dose rates of  $\leq 100 \text{ Gy/min}$  the rate of molecular hydrogen production is elevated in comparison to the average; in the LDR significantly so. Above  $\approx$ 100 Gy/min there is a depressed rate of production of molecular hydrogen compared to the average. There appears to be less variation above  $\approx 100 \,\text{Gy/min}$ . This may be a result of the larger size of the dose rate groups, but may also be a feature of higher dose rates.

Values of  $G(H_2)$  are consistently and significantly larger for the LDR for aerated samples, as shown in Figure 6.2. As the largest dose received by samples was  $\approx 37 \text{ kGy}$  (see Figure 6.1), it is impossible to give an informed opinion as to how this decrease in  $G(H_2)$  will continue.

When the dose rate is increased the value of  $G(H_2)$  for *n*-dodecane decreases, possibly following an exponential decay, as shown in Figure 6.2. The exponential fits shown in Figure 6.2 follow the relations:

$$G(H_2) = (0.4 \pm 0.3) - 1.5468 \left( 1 - \exp\left(\frac{\text{Dose Rate (Gy/min)}}{166 \pm 7}\right) \right) < 5kGy \quad (6.1)$$
  

$$G(H_2) = (0.36 \pm 0.07) - 1.4464 \left( 1 - \exp\left(\frac{\text{Dose Rate (Gy/min)}}{115 \pm 4}\right) \right) \qquad \text{All Doses} \quad (6.2)$$

#### 1.2E-6 Deaerated n-Dodecane Radiolytic Hydrogen Production (mol/g) Linear fit (<5kGy) 1.0E-6 8.0E-7 6.0E-7 4.0E-7 2.0E-7 0.0 0.5 1.5 0.0 1.0 2.0 Absorbed Dose (kGy)

#### 6.2 Deaeration of the Samples

**Figure 6.3:** The amount of molecular hydrogen produced per gram of irradiated solution for various absorbed doses. A linear fit through the origin gives a value for  $G(H_2)$  of  $(0.58\pm0.02)\mu$ mol/J.

Deaerated samples were irradiated in a much smaller range of dose rates: (36 - 50)Gy/min. This puts the data collected in two dose rate groups: 3 and 4, see Table 5.1, however, the data were not separated.

Figure 6.3 shows the data collected from samples that were deaerated before irradiation. A linear fit through the origin has been constructed, giving a value for  $G(H_2)$  of (0.58±0.02)  $\mu$ mol/J. Due to time constraints, the absorbed dose did not go above 2kGy.

Figure 6.2 shows the value of  $G(H_2)$  for deaerated *n*-dodecane in relation to the aerated data. It is very clear that deaeration of the sample before irradiation results in a significantly increased rate of the production of molecular hydrogen gas.

The decrease in the value of  $G(H_2)$  when the sample is aerated before irradiation is most

likely due to the reactions of the *n*-dodecane radicals,  $H^{\bullet}$ ,  $RH^{\bullet}$ , and R(=) with  $O_2$  which would otherwise go on to produce molecular hydrogen. The relevant reactions with  $O_2$  are listed below.

$$\mathrm{H}^{\bullet} + \mathrm{O}_2 \to \mathrm{HO}_2 \tag{6.3}$$

$$\mathrm{RH}^{\bullet} + \mathrm{O}_2 \longrightarrow \mathrm{RHO}_2 \tag{6.4}$$

$$R(=) + O_2 \to RO_2 \tag{6.5}$$

It could be expected that once the available oxygen in the aerated samples has been used, the production of hydrogen would match that seen in deaerated samples. However, upon reaching the doses where the oxygen concentration could be assumed to be significantly reduced the value of  $G(H_2)$  decreases rather than increases. This indicates that the mechanism affecting the dependence on dose is not due to the availability of oxygen.

## 7 Radiolytic Molecular Hydrogen Production from Neat TODGA

#### 7.1 Dose and Dose Rate

Figure 7.1 shows the values of  $G(H_2)$  calculated from linear fits, where appropriate, as a function of the dose rate of the incident gamma radiation. The same data, with the addition of the values collected from the data as a whole, both aerated and deaerated, are displayed in Table 7.1. The rate of production of molecular hydrogen is consistently and significantly lower during the LDR, but varies very little with dose rate.



**Figure 7.1:** The molecular hydrogen production from irradiated aerated neat TODGA and *n*-dodecane as a function of dose rate. Whilst for TODGA the LDR has consistently lower values for  $G(H_2)$ , this trend is the reverse *n*-dodecane exhibits. The arrows on the right hand side indicate the value of  $G(H_2)$  determined where the data were not split by dose rate.

Figure 7.2 displays the entirety of the data collected for TODGA, without any separation into the dose rate groups, with the two linear fits plotted. Figure 7.3 displays a selection of the data in Figure 7.2 with both linear fits visible but the x-axis limited to 5kGy. It is easy to see the difference between the rate of molecular hydrogen production in the LDR and higher doses.

 $G(H_2) = 0.123 \pm 0.002 \ \mu \text{mol/J}$ (7.1)  $G(H_2) = 0.056 \pm 0.001 \ \mu \text{mol/J}$ For <5kGy Dose (7.2)



**Figure 7.2:** The molecular hydrogen production from irradiated aerated TODGA as a function of dose with linear fits through the origin. The two fits show the marked difference between the rate of molecular hydrogen production in the LDR and above.  $G(H_2)=(0.123\pm0.002)\mu \text{mol/J}$ . LDR  $G(H_2)=(0.056\pm0.001)\mu \text{mol/J}$ .



Figure 7.3: The same data and fits as shown in Figure 7.2 but with a maximum dose of 5kGy.

The value of  $G(H_2)$  approximately doubles when aerated TODGA is exposed to doses above 5kGy. This increase in the rate of molecular hydrogen production could be expected from an increase in the rate of TODGA degradation with dose. However, over the dose range investigated, the rate of molecular hydrogen production does not increase in an exponential manner as the rate of TODGA degradation has been observed to do (G(destruction)=G<sub>0</sub> e<sup>-kD</sup>) [87].

Headspace	Dose	$G(H_2)$
Contents	Region	$\mu$ molJ $^{-1}$
Argon	< 5kGy	$0.050 \pm 0.004$
Air	< 5kGy	$0.056 \pm 0.001$
Air	All Doses	$0.123 \pm 0.002$

**Table 7.1:** The values of  $G(H_2)$  for neat TODGA.

#### 7.2 Deaeration of the Samples

The amount of molecular hydrogen produced per gram of solution as a function of the absorbed dose for argon purged samples is shown in Figure 7.4.



**Figure 7.4:** The molecular hydrogen production from irradiated deaerated TODGA, as a function of dose with a linear fit through the origin.  $G(H_2) = (0.050 \pm 0.004) \mu \text{mol}/\text{J}$ .

Table 7.1 does not show any significant difference between the value of  $G(H_2)$  for deaerated and aerated TODGA in the LDR. This was not expected. For *n*-dodecane, purging the sample with argon before irradiation resulted in an increased value of  $G(H_2)$ . If the increase in the value of  $G(H_2)$  in aerated samples as the dose increases is due to the loss of oxygen, it would be expected that deaeration of TODGA would result in a higher value of  $G(H_2)$ . As this is not the case, see Table 7.1, the increase in  $G(H_2)$  as the dose increases is not caused by a loss of oxygen.

# 8 Radiolytic Molecular Hydrogen Production from Mixtures of TODGA and *n*-Dodecane

Mixtures of TODGA and *n*-dodecane were gamma-irradiated, as detailed in Chapter 5. Four different concentrations of TODGA in *n*-dodecane were investigated, in addition to neat *n*-dodecane and TODGA, as listed in Table 5.2. Tables 8.1, 8.2, and 8.3 list the values of  $G(H_2)$  calculated from linear fits of the amount of hydrogen produced per gram of solution (mol/g) as a function of the absorbed dose (kGy).

**Table 8.1:** List of all of the values of  $G(H_2)$  collected for mixtures of *n*-dodecane and TODGA where no splitting of the data by Dose Rate Group # occurred.

[TODGA]	Mole Fraction	$G(H_2)$ (LDR)	Limiting G(H <sub>2</sub> )
mol/litre	TODGA	$\mu$ mol/J	$\mu \mathrm{mol}/\mathrm{J}$
0	0	$0.34\pm0.01$	$0.30 \pm 0.01$
0.01	0.00227	-	$0.336 \pm 0.003$
0.2	0.049524	$0.208\pm0.004$	$0.158\pm0.003$
0.4	0.108807	$0.22\pm0.02$	$0.143\pm0.004$
1.0	0.385934	$0.143\pm0.003$	$0.110\pm0.002$
1.546	1.0	$0.056\pm0.001$	$0.123\pm0.002$

**Table 8.2:** List of all of the values of  $G(H_2)$  collected for mixtures of *n*-dodecane and TODGA irradiated which were purged with argon before irradiation.

[TODGA]	Mole Fraction	$G(H_2)$ (LDR)	Limiting G(H <sub>2</sub> )
mol/litre	TODGA	µmol/J	$\mu$ mol/J
0	0	$0.58\pm0.02$	-
0.2	0.049524	$0.32\pm0.01$	-
1.0	0.385934	$0.096 \pm 0.002$	$0.127\pm0.006$
1.546	1.0	$0.050 \pm 0.004$	-

[TODGA]	Mole Fraction	Dose Rate	$G(H_2)$ (LDR)	Limiting G(H <sub>2</sub> )
mol/litre	TODGA	Group #	$\mu$ mol/J	µmol/J
0	0	2	$0.44 \pm 0.02$	$0.33 \pm 0.01$
0	0	3	$0.42\pm0.009$	$0.327 \pm 0.004$
0	0	4	$0.387\pm0.004$	$0.34\pm0.01$
0	0	5	$0.401 \pm 0.005$	$0.296 \pm 0.007$
0	0	6	$0.32 \pm 0.01$	$0.236 \pm 0.007$
0	0	7	-	$0.21 \pm 0.01$
0	0	8	$0.316 \pm 0.006$	$0.252 \pm 0.009$
0.01	0.00227	2	$0.24\pm0.01$	-
0.01	0.00227	3	$0.27 \pm 0.01$	-
0.01	0.00227	4	$0.339 \pm 0.009$	-
0.01	0.00227	5	$0.40 \pm 0.04$	$0.33\pm0.01$
0.01	0.00227	6	$0.365 \pm 0.003$	-
0.01	0.00227	7	$0.358\pm0.004$	-
0.01	0.00227	8	$0.362\pm0.008$	-
0.2	0.049524	2	$0.18\pm0.02$	-
0.2	0.049524	3	$0.230\pm0.008$	$0.281\pm0.004$
0.2	0.049524	4	$0.22 \pm 0.01$	$0.20 \pm 0.01$
0.2	0.049524	5	$0.216\pm0.004$	$0.25\pm0.02$
0.2	0.049524	6	$0.250\pm0.009$	$0.180\pm0.005$
0.2	0.049524	7	$0.219\pm0.002$	$0.189\pm0.002$
0.2	0.049524	8	$0.23\pm0.01$	$0.153 \pm 0.002$
0.4	0.108807	2	$0.33\pm0.01$	-
0.4	0.108807	3	$0.21\pm0.01$	$0.20\pm0.01$
0.4	0.108807	4	$0.17\pm0.02$	$0.103\pm0.009$
0.4	0.108807	5	$0.205 \pm 0.003$	$0.132 \pm 0.006$
0.4	0.108807	6	$0.160\pm0.009$	$0.164\pm0.002$
0.4	0.108807	7	$0.16\pm0.03$	$0.128\pm0.002$
0.4	0.108807	8	$0.220\pm0.005$	$0.200\pm0.003$
1.0	0.385934	3	$0.148\pm0.004$	$0.150 \pm 0.002$
1.0	0.385934	4	-	$0.141\pm0.001$
1.0	0.385934	5	$0.149\pm0.005$	$0.116\pm0.006$
1.0	0.385934	6	$0.123\pm0.007$	$0.125 \pm 0.006$
1.0	0.385934	7	$0.141\pm0.009$	$0.118\pm0.002$
1.546	1.0	3	-	$0.131 \pm 0.003$
1.546	1.0	4	-	$0.105\pm0.002$
1.546	1.0	5	$0.045\pm0.003$	$0.116\pm0.001$
1.546	1.0	6	$0.062\pm0.005$	$0.131\pm0.006$
1.546	1.0	7	$0.077\pm0.003$	$0.139\pm0.006$
1.546	1.0	8	-	$0.119 \pm 0.007$

**Table 8.3:** List of all of the values of  $G(H_2)$  collected for mixtures of *n*-dodecane and TODGA, where the data were split by Dose Rate Group # (as described in Table 5.1).

#### 8.1 G(H<sub>2</sub>) as a Function of Dose and Dose Rate: [TODGA]=0.01M

Figure 8.1 displays the calculated values of  $G(H_2)$  as a function of the dose rate of the incident gamma irradiation. The value indicated by the arrow on the right hand side is from Table 8.1.

An initial increase in the value of  $G(H_2)$  as the dose rate increases is observed for dose rates below 100 Gy/min.

Whilst the value of  $G(H_2)$  is similar to that for *n*-dodecane when the data are not split by dose rate (see Table 8.1), the values of  $G(H_2)$  for dose rates above 100Gy/min are significantly higher for a solution of 0.01M [TODGA] in *n*-dodecane and significantly lower for dose rates below 50 Gy/min when compared to neat *n*-dodecane (see Table 8.3).

Despite the mole fraction for TODGA being only  $1.5 \times 10^{-5}$  for a concentration of 0.01M TODGA in *n*-dodecane, the effect on the dependence of G(H<sub>2</sub>) on the dose rate is significant.



**Figure 8.1:** The value of  $G(H_2)$  as a function of the dose rate for aerated 0.01M TODGA in *n*-dodecane under gamma irradiation. The arrow on the right hand side indicates the value from Table 8.1. The dotted line is an indication only of the trend.

#### 8.2 G(H<sub>2</sub>) as a Function of Dose and Dose Rate: [TODGA]=0.2M



**Figure 8.2:** The value of  $G(H_2)$  as a function of the dose rate for aerated 0.2M TODGA in *n*-dodecane under gamma irradiation. The arrows on the right hand side indicate the values from Table 8.1.

Figure 8.2 displays the calculated values of  $G(H_2)$  as a function of the dose rate. The arrows on the right hand side indicate the values displayed in Table 8.1.

There appears to very little variation in  $G(H_2)$  with dose rate. However, there is a suggestion that above 100Gy/min, the rate of molecular hydrogen production is greater in the LDR. Below 100Gy/min it is less clear whether there is a dependence on the absorbed dose due to the variance in the values of  $G(H_2)$  for doses above 5kGy.

#### 8.3 $G(H_2)$ as a Function of Dose and Dose Rate: [TODGA]=0.4M

Figure 8.3 displays the calculated values of  $G(H_2)$  as a function of the dose rate.

Values calculated from the LDR appear to be consistently higher than for linear fits to all doses. Additionally, at dose rates below 50 Gy/min, the value of  $G(H_2)$  increases significantly, as indicated by the trend line in Figure 8.3.

Above 50Gy/min the value of  $G(H_2)$  increases as the dose rate increases when looking at doses above 5kGy, however, the value for the Dose Rate Group # 3 is significantly higher than the value determined without splitting the data by dose rate. This significant increase in  $G(H_2)$  at low dose rates is also seen in the LDR for Dose Rate Group # 2. This increase in  $G(H_2)$  at low dose rates is also seen for neat *n*-dodecane.



**Figure 8.3:** The value of  $G(H_2)$  as a function of the dose rate for aerated 0.4M TODGA in *n*-dodecane under gamma irradiation. The arrows on the right hand side indicate the values from Table 8.1. The dotted line is an exponential decay fit to the data collected in the LDR.

#### 8.4 $G(H_2)$ as a Function of Dose and Dose Rate: [TODGA]= 1M

Figure 8.4 displays the calculated values of  $G(H_2)$  as a function of the dose rate of the incident gamma irradiation for all Dose Rate Groups apart from # 8. There is almost no change in  $G(H_2)$  with dose rate or dose. There is a slight decrease in the value of  $G(H_2)$  as the dose rate increases.



**Figure 8.4:** The value of  $G(H_2)$  as a function of the incident dose rate for aerated 1M TODGA in *n*-dodecane under gamma irradiation.

For Dose Rate Group # 8, a linear fit which passed through the origin was not possible for the RHP as a function of the absorbed dose, see Figure 8.5. As such, values of  $G(H_2)$  for each point were calculated and plotted against the absorbed dose, shown in Figure 8.6. The value of  $G(H_2)$  increases linearly with dose without showing any signs of levelling off to a constant value. This effect is most likely an artefact and requires re-examination.

The linear fit in Figure 8.5 for the amount of hydrogen produced per gram of solution as a function of absorbed dose has an equation given by:

$$RHP = ((-4.3 \pm 0.1) \times 10^{-7}) + (Dose \times (0.210 \pm 0.004) \times 10^{-6})$$
(8.1)

The linear fits in Figure 8.6 have equations for the dependence of  $G(H_2)$  on the absorbed dose given by:

$$G(H_2) = ((-4 \pm 1) \times 10^{-8}) + (Dose \times (3.2 \pm 0.3) \times 10^{-9})$$
(8.2)

and

$$G(H_2) = \text{Dose} \times (2.3 \pm 0.2) \times 10^{-9}$$
 (8.3)

The value of  $G(H_2)$  calculated from the linear fit in Figure 8.5,  $(0.210 \pm 0.004)\mu mol/J$ , is significantly larger than the value of  $G(H_2)$  determined for any other Dose Rate Group.



**Figure 8.5:** The RHP as a function of the absorbed dose for aerated 1M TODGA in *n*-dodecane under gamma irradiation for Dose Rate Group # 8. Whilst a linear fit can be constructed, it does not pass through the origin. The gradient of the linear fit gives a value for  $G(H_2)$  of  $(0.210 \pm 0.004) \ \mu \text{mol/J}$  with an intercept of  $(-4.3 \pm 0.1) \times 10^{-7} \text{ mol/g}$ .



**Figure 8.6:** The value of  $G(H_2)$  for each point shown in Figure 8.5 as a function of the absorbed dose for aerated 1M TODGA in *n*-dodecane under gamma irradiation. The value of  $G(H_2)$  increases linearly with dose and does not show any signs of levelling off to a constant value of  $G(H_2)$ . The red linear fit has an equation of  $G(H_2) = (-4 \pm 1) \times 10^{-8} + \text{Dose}((3.2 \pm 0.3) \times 10^{-9})$  and the blue linear fit through the origin has a gradient of  $(2.3 \pm 0.2) \times 10^{-9}$  mol/g (or mol/J/kGy).

#### 8.5 $G(H_2)$ as a Function of [TODGA] and the Effect of Deaeration

Figures 8.7 and 8.8 display the calculated value of  $G(H_2)$  against the concentration of TODGA with a linear and logarithmic x-axis scale respectively. Figures 8.9, 8.10, and 8.11 show the data in Figure 8.7 separated by whether the samples were deaerated by argon and the dose regions for which the values of  $G(H_2)$  were determined.

When examining the values of  $G(H_2)$  determined for aerated solutions for doses above 5kGy a logarithmic fit has been constructed, shown in Figure 8.9. This logarithmic fit fits the data for concentrations of TODGA above 0.2M very well, but underestimates the values of  $G(H_2)$  for neat *n*-dodecane and 0.01M TODGA in *n*-dodecane.

The logarithmic fit in Figure 8.9 has the equation:

$$G(H_2) = (0.122 \pm 0.007) - (0.019 \pm 0.009) \ln([TODGA] + (0.00999 \pm 0.00007))$$
(8.4)

 $G(H_2)$  calculated for concentrations of 0.2M TODGA in *n*-dodecane and above are much lower than for neat *n*-dodecane. The rate at which the decrease in  $G(H_2)$  with increasing [TODGA] occurs slows as the concentration approaches neat TODGA.



Figure 8.7: The value of G(H<sub>2</sub>) as a function of [TODGA] for both aerated and deaerated samples.

A linear fit has been constructed to the experimentally determined values of  $G(H_2)$  for aerated solutions for doses below 5kGy. This linear fit agrees well with data for concentrations of TODGA of 0.2M and above, but underestimates the value for neat *n*-dodecane, see Figure 8.10.

The equation of the linear fit in Figure 8.10 is:

$$G(H_2) = (0.26 \pm 0.02) - ([TODGA] \times (0.13 \pm 0.02))$$
(8.5)

For samples purged with argon before irradiation and irradiated to doses below 5 kGy, the



Figure 8.8: The value of  $G(H_2)$  as a function of [TODGA] for both aerated and deaerated samples.



**Figure 8.9:** The value of  $G(H_2)$  as a function of the concentration of [TODGA] for aerated samples for linear fits to data extending to beyond 5 kGy. The values for *n*-dodecane and 0.01M TODGA concentration are very similar.  $G(H_2)$  calculated for concentrations of 0.2M TODGA and above are much lower, but do not vary greatly as the concentration of TODGA increases towards neat TODGA.



**Figure 8.10:** The value of  $G(H_2)$  as a function of the concentration of [TODGA] for aerated samples for linear fits to data collected below 5 kGy. The relationship appears to be a linear decrease in the value of  $G(H_2)$  as [TODGA] increases.

relationship between the value of  $G(H_2)$  and [TODGA] can be approximated by a logramithic fit, given by:

$$G(H_2) = \pm 5 \pm 9 \ln([TODGA] \pm 31)$$
 (8.6)

The behaviour of  $G(H_2)$  as a function of the concentration of TODGA will be most clearly demonstrated in the samples that were purged with argon before gamma-irradiation. The chemistry of the aerated samples will be additionally complicated by the presence of oxygen which can scavenge both H<sup>•</sup> and RH<sup>•</sup> (where RH<sub>2</sub> is the n-dodecane molecule) that can go on to react to produce H<sub>2</sub>.

The logarithmic relation of  $G(H_2)$  to the concentration of TODGA implies that TODGA does not interfere with the excited state of *n*-dodecane which decays to directly produce molecular hydrogen.

i.e. The reaction

$$\mathrm{RH}_2 \rightsquigarrow \mathrm{RH}_2^* \to \mathrm{R}(=) + \mathrm{H}_2 \tag{8.7}$$

is not quenched by the presence of TODGA and the reaction:

$$\mathrm{RH}_{2}^{*} + \mathrm{TODGA} \rightarrow \mathrm{RH}_{2} + \mathrm{TODGA}^{*}$$
 (8.8)

occurs at a very slow rate.

The reaction of TODGA with the radical cation of *n*-dodecane to produce the radical cation of TODGA and a ground state *n*-dodecane molecule has been observed to occur, but at

a rate 2 orders of magnitude slower than the reaction of the cation with the geminate ion [87].



**Figure 8.11:** The value of  $G(H_2)$  as a function of the concentration of [TODGA] for deaerated samples for linear fits to data collected below 5kGy. The relationship appears to be an logarithmic decay as [TODGA] increases.

## Part III

# **Computational Modelling**

## 9 Constructing a Model for the Radiolysis of *n*-Dodecane

The model was constructed using FACSIMILE. A full code printout is provided in Appendix B (Chapter 13).

#### 9.1 The Model

To extend the applicability of the empirical data beyond situations practical to achieve in a laboratory setting, a computational model can be created and fitted to the experimental data.

The model developed within this research uses an iterative approach to finding a numerical solution to a set of simultaneous equations. These equations are constructed from a group of reactions which have been assumed to be applicable in this system, and the corresponding reaction rates. The effect of modifying rate constants can then be examined to provide insights into the underlying chemistry of the system under radiolysis.

Once the computational model can reliably reproduce experimentally determined values, the parameters of the model can be extended to regimes outside of those under experimental study. This ability to extend the model is especially useful when considering safety cases of industrial applications, such as nuclear reprocessing, which are often impractical to replicate in a laboratory setting.

The approach used here towards the set of simultaneous different equations is a numerical and iterative one. The rate of change at any given time for a specific species is dependent on the reactions it is involved in, and the concentration of the species involved.

#### 9.2 Iterative Approach to Simultaneous Equations

A reaction of the general form

$$aA + bB \stackrel{k}{\rightleftharpoons} cC + dD \tag{9.1}$$

has a rate of reaction given by

$$\frac{d[A]}{dt} = -ak[A]^{\alpha}[B]^{\beta}$$
(9.2)

where

k - Rate Constant (M<sup>1-
$$\alpha$$
- $\beta$ )  
v(t) = k[A] <sup>$\alpha$</sup> [B] <sup>$\beta$</sup> 
(9.3)  
 $\alpha,\beta$  - Order or Reaction  
v(t)= $-\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$ 
(9.4)</sup>

When we consider connected reactions, as shown below in Reactions 9.5 to 9.7, we can see that the rate of change becomes dependent on both reactions the species is involved in. This method of constructing coupled differential equations from a reaction scheme has been used to model the change of each molecular species.

$$aA + bB \stackrel{k_1}{\rightleftharpoons} cC + dD \tag{9.5}$$

$$gC \stackrel{k_2}{\rightleftharpoons} eE + fF$$
 (9.6)

$$\frac{d[C]}{dt} = c k_1 [A]^{\alpha} [B]^{\beta} - g k_2 [C]^{\gamma}$$
(9.7)

#### 9.3 The Reaction Scheme

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**Figure 9.1:** A flowchart of the reaction scheme of hydrocarbon radiolysis with the reaction rates labelled. Any reactions which result in the production of molecular hydrogen have been circled.

Figure 9.1 displays the reaction scheme of *n*-dodecane as a flowchart. The excited states

have been excluded from this model. Instead, the yields of C–H scission and H<sub>2</sub> elimination have been used (referred to as GCHSCISSION and GH2ELIMINATION in the code respectively). The yield of C–C scission is expected to be extremely low, with a value of  $\approx 0.003 \ \mu$ mol/J( $\approx 0.03$  molecules/100eV) for cyclohexane, and is neglected in this model [1].

The following reactions were therefore included in the model to represent the outcome of *n*-dodecane under  $\gamma$ -irradiation.

$$\mathrm{RH}_{2} \xrightarrow{K10A} \mathrm{RH}_{2} + \mathrm{h}\nu_{1} \tag{9.8}$$

$$\mathrm{RH}_{2} \stackrel{K7B}{\leadsto} \mathrm{RH}_{2} + \mathrm{h}\nu_{2} \tag{9.9}$$

$$\operatorname{RH}_{2}^{*} \operatorname{RH}_{2}^{*} \operatorname{RH}_{2}^{*} \operatorname{RH}_{2}^{*} \operatorname{RH}_{2}^{\bullet} \operatorname{2}(\operatorname{RH}^{\bullet}) + \operatorname{H}_{2}$$

$$(9.10)$$

$$\mathrm{RH}_{2} \xrightarrow{K7A} \mathrm{R}(=) + \mathrm{H}_{2} \tag{9.11}$$

$$\mathrm{RH}_{2} \xrightarrow{K10B} \mathrm{RH}^{\bullet} + \mathrm{H}^{\bullet} \tag{9.12}$$

$$\operatorname{RH}_{2} \stackrel{K_{24}}{\leadsto} \operatorname{RH}_{2}^{+} + e_{\operatorname{free}}^{-}$$
(9.13)

The species  $hv_1$  represents phosphorscence and  $hv_2$  fluorescence. The equation controlled by reaction rate K10C represent the reaction of an excited state with the ground state of *n*-dodecane and is expected to be very small. The reaction rate K24 is calculated from the G-value for the yield of free ions (GESC in the code), 0.0138  $\mu$ mol/J (0.13 molecules/100eV) [1]. The summation of these yields is equal to 0.623  $\mu$ mol/J (5.88 molecules/100eV) for the degradation rate of the *n*-dodecane.

In the above equations, the reaction rates K10B and K7A are calculated from G-values of 0.394 and 0.176  $\mu$ mol/J (3.8 and 1.7 molecules/100eV) and represent C–H scission and H<sub>2</sub> elimination respectively [1].

To convert from a G-value (molecules/100eV) to a reaction rate a conversion factor is used (referred to as FORM in the code):

FORM = 
$$\frac{\text{Dose Rate (100eV/s)}}{A_v}$$
 (9.14)

where  $A_v$  is Avogadro's number.

In addition there is a reaction which produces a value of excess hydrogen, using a G value, referred to as GEXCESSH2 in the code, which is set to 0  $\mu$ mol/J (0 molecules/100eV) for *n*-dodecane:

$$\stackrel{K23}{\leadsto} H_2 \tag{9.15}$$

Subsequent reactions of the radicals are listed below.

$$\mathbf{R}(=) + \mathbf{R}\mathbf{H}^{\bullet} \xrightarrow{K5} \bullet \mathbf{R} - \mathbf{R}\mathbf{H}$$
(9.16)

$$\mathbf{R}(=) + \mathbf{H}^{\bullet} \stackrel{K6}{\to} \mathbf{R}\mathbf{H}^{\bullet} \tag{9.17}$$

$$2 \operatorname{RH}^{\bullet} \stackrel{K1A}{\to} (\operatorname{RH})_{2}$$

$$\stackrel{K1B}{\to} \operatorname{R}(=) + \operatorname{RH}_{2}$$

$$(9.18)$$

$$(9.19)$$

$$RH^{\bullet} + H^{\bullet} \xrightarrow{K3B} R(=) + H_2$$

$$(9.20)$$

$$\xrightarrow{K3A} RH_2$$

$$(9.21)$$

- $H^{\bullet} + {}^{\bullet}R RH \xrightarrow{K15} (RH)_2$ (9.22)
- $2 \operatorname{H}^{\bullet} \stackrel{K14}{\to} \operatorname{H}_2 \tag{9.23}$
- $H^{\bullet} + RH_2 \xrightarrow{K4} RH^{\bullet} + H_2$ (9.24)
- $\mathrm{H}^{\bullet} + \mathrm{O}_{2} \xrightarrow{K16} \mathrm{HO}_{2} \tag{9.25}$

$\mathrm{RH}^{\bullet} + \mathrm{O}_2 \xrightarrow{K_{17}} \mathrm{RHO}_2$	(9.26)

$$\mathbf{R}(=) + \mathbf{O}_2 \xrightarrow{K_{25}} \mathbf{RO}_2 \tag{9.27}$$

$$2\operatorname{RHO}_2 \xrightarrow{K26} \operatorname{RO} + \operatorname{ROH}_2 + \operatorname{O}_2$$
(9.28)

**Table 9.1:** The non-zero values of the initial concentrations of the various species in the model, where TIMEIRR is equal to 0.001s and FORM is a conversion factor from molecules/100eV to mol/s, see Equation (9.14)

Species	Intial Concentration
	mol/litre
$\rm RH_2^+$ , $\rm e_{free}^-$	GESC × FORM × TIMEIRR
O <sub>2</sub>	O2SOLUBILITY
H <sub>2</sub>	(GEXCESSH2 + GH2ELIMINATION) × FORM × TIMEIRR
R(=)	GH2ELIMINATION × FORM × TIMEIRR
RH●, H●	GCHSCISSION × FORM × TIMEIRR

#### 9.4 Initial Concentrations

An initial dose to the system is assumed, equal to the dose from an irradiation lasting 0.001s (referred to as TIMEIRR in the code). From this, initial concentrations of R(=), H<sub>2</sub>, RH<sup>•</sup>, H<sup>•</sup>, hv<sub>1</sub>, hv<sub>2</sub>, RH<sub>2</sub><sup>+</sup>, and  $e_{free}^-$  are calculated, see Table 9.1. All other concentrations are set to 0M, apart from the concentration of oxygen in the solution, which is equal to the solubility of oxygen in *n*-dodecane 7.4 × 10<sup>-4</sup>M (referred to as O2SOLUBILITY in the code) [59].

The concentration of RH<sub>2</sub> is not included in this model as it is assumed that concentration will not be significantly reduced by irradiation over the dose regions under consideration.

## 10 Results - Computational Modelling

Table 10.1 details the reaction rates used in the model for the reactions shown in Figure 9.1. Unless otherwise specified all data in this chapter were run with a value for the dose rate of 60Gy/min.

Rate Constant	Value	Hydrocarbon	Ref
	/mol/s		
K1	$1.50498 \times 10^{9}$	<i>n</i> -Dodecane	LaVerne J.A. <i>et.al</i> 1994 [36]
K1A	$0.52 \times K1$	<i>n</i> -Dodecane	LaVerne J.A. <i>et.al</i> 1994 [36]
K1B	$0.48 \times K1$	<i>n</i> -Dodecane	LaVerne J.A. <i>et.al</i> 1994 [36]
K3	$2.3 \times 10^{9}$	Cyclooctane	LaVerne J.A. <i>et.al</i> 1997 [37]
КЗА	K3	Cyclooctane	LaVerne J.A. <i>et.al</i> 1997 [37]
K3B	K3	Cyclooctane	LaVerne J.A. <i>et.al</i> 1997 [37]
K4	$2.5 \times 10^{7}$	Cyclooctane	LaVerne J.A. <i>et.al</i> 1997 [37]
K5	$0.75 \times 10^{9}$	<i>n</i> -Dodecane	LaVerne J.A. <i>et.al</i> 1994 [36]
K6	$2.3 \times 10^{9}$	Cyclooctane	LaVerne J.A. <i>et.al</i> 1997 [37]
K14	$3.05 \times 10^{9}$	Cyclooctane	LaVerne J.A. <i>et.al</i> 1997 [37]
K15	$2.3 \times 10^{9}$	Cyclooctane	LaVerne J.A. <i>et.al</i> 1997 [37]
K16	$(K3B/13.2) \times 10^2$	-	Klots C.E. <i>et.al</i> 1964 [33]
K17	K16	-	Klots C.E. <i>et.al</i> 1964 [33]
K25	K16	-	Klots C.E. <i>et.al</i> 1964 [33]
K26	$1 \times 10^{6}$	-	Assumption

Table 10.1: Reaction rates used in the FACSIMILE model, along with the relevant source and Hydr	0-
carbon the reference stated (if applicable).	

#### 10.1 Oxygen Depletion in the Model

Figure 10.1 displays the concentrations of  $H_2$ ,  $O_2$ ,  $RH^{\bullet}$ ,  $H^{\bullet}$ ,  ${}^{\bullet}R-RH$ ,  $(RH)_2$ ,  $ROH_2$ , RO, and  $HO_2$  as a function of the absorbed dose for a dose rate 100Gy/min up to a dose of 2kGy. All other concentrations are too small to be visible on this scale.

The concentration of oxygen becomes negligible within approximately 1.6kGy, so any reactions after this dose are equivalent to those seen when oxygen is not present. In the physical experiments the maximum dose reached was  $\approx$  37kGy for neat *n*-dodecane in the presence of oxygen. Throughout all the physical experiments oxygen was not depleted from the headspace. This is a major difference that should be kept in mind when comparing the experimental and computational results.



**Figure 10.1:** Concentration as a function of dose (0-2kGy). Species represented are  $H_2$ ,  $O_2$ , R(=),  $RH^{\bullet}$ ,  $H^{\bullet}$ ,  ${}^{\bullet}R-RH$ ,  $(RH)_2$ ,  $ROH_2$ , RO, and  $HO_2$ . Other concentrations are too small to be visible on this scale. Dose rate of 60Gy/min. Data points are taken every Gy. The concentration of oxygen decreases to negligible amounts within approximately 1.6kGy. The concentrations of  $ROH_2$  and RO do not decrease as the model does not include any further reactions of these volatile species.



Figure 10.2: Dose Rate 100Gy/min with a duration of 200s, for a dose of 0.33kGy.

**Table 10.2:** The value of  $G(H_2)$  (to 3d.p.) calculated from the model with various values of dose rate, run until a dose of 500Gy was reached. No dependence on the dose rate was found, as was expected for the reactions used within this model.  $[O_2](t=0)=0 \text{ mM}$ 

Dose Rate	$G(H_2)$
Gy/min	$\mu$ mol/J
10	0.464
20	0.464
50	0.464
100	0.464
500	0.464

#### **10.2** Altering the Initial Oxygen Concentration

Altering the initial oxygen concentration and examining the value of  $G(H_2)$  after a set dose allows an examination of the effect of the presence of oxygen. The effect on  $G(H_2)$  of the initial concentration of oxygen is shown in Figure 10.2.

A dose of  $\approx$  330Gy was chosen as there was little variation in the value of G(H<sub>2</sub>) for the model run with a zero initial concentration of oxygen, see Figure 10.4, and is not sufficient to have entirely removed oxygen when starting with a concentration of 0.74mM, see Figure 10.1.

The dependence of  $G(H_2)$  on the initial concentration of oxygen in not linear. The equation of the dotted trendline in Figure 10.2 is given by:

$$G(H_2) \mu(\text{mol/J}) = (0.39 \pm 0.03) + \frac{(0.572 \pm 0.003) - (0.39 \pm 0.03)}{1 + \left(\frac{\text{Solubility (mM)}}{0.6 \pm 0.1}\right)^{2.0 \pm 0.3}}$$
(10.1)

#### **10.3** Altering the Dose Rate

When examining if the model used within this research had any dependence on the dose rate of the incident radiation the value of  $G(H_2)$  was calculated to 3 decimal places. The results are displayed in Table 10.2. There is no change in the value of  $G(H_2)$  when the dose rate is altered, as was expected.

#### **10.4** G-Values as a Function of Dose

The model does not keep track of the concentration of *n*-dodecane, which necessarily limits the dose to which the model can be considered applicable.

With a dose rate of 100 Gy/min, a degradation rate of 0.623  $\mu$ mol/J (5.88 molecules/100 eV) is equivalent to 0.76  $\mu$ mol/s, and a dose of 100kGy is sufficient to reduce the concentration of *n*-dodecane by 1%.

A reduction of more that 1% could be considered as significant and would necessitate an alteration to the model to track the concentration of *n*-dodecane. A decreased concentration of *n*-dodecane would result in a decreasing amount of dose being delivered to *n*-dodecane molecules per second, resulting in a gradual decrease in the rate of production for the radiolytic products of *n*-dodecane, which are calculated from published G-values.

As such, the model is limited to doses of less than 100kGy, where it can be assumed that any reduction in the concentration of *n*-dodecane is insignificant. In addition, this matches well with the range examined experimentally and the predicted typical dose received by the organic solvent in a reprocessing plant per year [54].

An initial concentration of oxygen within the solution of 0mM mimics an argon purged solution, whilst a value of 0.74mM for the initial concentration of oxygen in the solution represents a solution previously exposed to the atmosphere.

#### **10.4.1** G(H<sub>2</sub>)



**Figure 10.3:**  $G(H_2)$  calculated from the computational model as a function of the absorbed dose (up to 60kGy). Dose rate 60Gy/min.

Figures 10.3 and 10.4 detail the value of  $G(H_2)$  calculated from the computational model as a function of the dose with various dose regions examined. Each Figure displays the value of  $G(H_2)$  for models that started with a zero initial concentration of oxygen, and those that started with an initial concentration of 0.74mM of oxygen.

When oxygen is present the behaviour of  $G(H_2)$  as the dose is increased is significantly altered in comparison to the model when no oxygen is present. Despite oxygen depletion occurring within  $\approx 1.6$ kGy, see Figure 10.1, the rise in the value of  $G(H_2)$  continues until around 5kGy, before it begins to decrease and match the behaviour seen from the model with no initial oxygen. In addition the rate at which  $G(H_2)$  changes appears to vary considerably for the 1st kGy of dose, this is most likely due to the rapidly decreasing concentration of oxygen in the model and the alteration in the preferred reactions.

Figure 10.3 displays the value of  $G(H_2)$  from the model for doses up to 60kGy. After the initial increase in the value of  $G(H_2)$ , during the first 5kGy for the aerated model and almost instantaneously for the deaerated model, there is a continual decrease in the value of  $G(H_2)$ .



**Figure 10.4:**  $G(H_2)$  calculated from the computational model as a function of the absorbed dose (up to 5kGy). Dose rate 60Gy/min.

This decrease continues throughout the entire dose range examined, but the rate of reduction does slow as larger doses are reached.

This decrease in the value of  $G(H_2)$  is examined by considering the reactions that produce molecular  $H_2$ .

$$\operatorname{RH}_{2} \xrightarrow{K10C} \operatorname{RH}_{2}^{*} + \operatorname{RH}_{2} \to 2(\operatorname{RH}^{\bullet}) + \operatorname{H}_{2}$$
(10.2)

$$\mathrm{RH}_{2} \stackrel{K7A}{\leadsto} \mathrm{R}(=) + \mathrm{H}_{2} \tag{10.3}$$

$$RH^{\bullet} + H^{\bullet} \xrightarrow{K3B} R(=) + H_2$$
(10.4)

$$2 \operatorname{H}^{\bullet} \stackrel{K14}{\to} \operatorname{H}_2 \tag{10.5}$$

$$\mathbf{H}^{\bullet} + \mathbf{R}\mathbf{H}_{2} \xrightarrow{K4} \mathbf{R}\mathbf{H}^{\bullet} + \mathbf{H}_{2} \tag{10.6}$$

Reactions (10.2) and (10.3) do not depend on the concentration of the reactants as it is

assumed that concentration of RH<sub>2</sub> remains constant.

Therefore, the reactions that can vary are Reactions (10.4), (10.5), and (10.6). When the concentration of  $H^{\bullet}$  increases, the rate of Reactions (10.4) and (10.6) will increase linearly with  $[H^{\bullet}]$ , whilst the rate of Reaction (10.5) will increase with a quadratic relationship. Reactions (10.5) requires two hydrogen atoms for each molecular hydrogen produced, whilst Reactions (10.4) and (10.6) require only one  $H^{\bullet}$ . The result is that a smaller amount of molecular hydrogen is produced for each hydrogen atom that reacts as the concentration of  $H^{\bullet}$  increases.

This can be seen more clearly when considering the total rate of change of [H<sub>2</sub>].

$$\frac{d[H_2]}{dt} = G_0 + (Y_0 + K3B[RH^{\bullet}])[H^{\bullet}] + K14[H^{\bullet}]^2$$

$$G_0 = (K7A + K10C[RH_2])[RH_2]$$

$$Y_0 = K4[RH_2]$$
(10.7)

The total number of reactions that occur during the model are shown in Figure 10.5. There is an increase in the number of reactions following Reaction (10.5) after the oxygen has been consumed ( $\approx$  1kGy). Almost no reactions follow Reaction (10.4) before  $\approx$  2kGy, due to the very low concentration of RH<sup>•</sup>, but this rapidly increases once oxygen has been depleted.



**Figure 10.5:** The number of reactions (cumulative) that occur as the dose increases. The reactions displayed are those which produce molecular hydrogen (H<sub>2</sub>).  $[O_2](t=0)=0.74$  mM. Dose rate 60Gy/min.

The concentration of H<sup>•</sup> and RH<sup>•</sup> as a function of the absorbed dose is shown in Figure 10.6. Once oxygen has been removed from the system there is an increase in the concentration of H<sup>•</sup> and RH<sup>•</sup>, indicating that these species react much faster with oxygen than each other or other species. Once a maximum is reached their concentration decreases slightly as the dose increases, but remains relatively stable.

Another reason for the decrease in  $G(H_2)$  as the dose increases is the increase in Reaction (10.8).



**Figure 10.6:** The concentration of H<sup>•</sup> and RH<sup>•</sup> as a function of dose. The concentration of H<sup>•</sup> increases much more slowly than the concentration of RH<sup>•</sup>. Once the maimum is reached there is a gradual decrease as the dose increases.  $[O_2](t=0)=0.74$  mM. Dose rate 60Gy/min.

$${}^{\bullet}\mathrm{R}-\mathrm{RH}+\mathrm{H}^{\bullet} \xrightarrow{K_{15}} (\mathrm{RH})_2 \tag{10.8}$$

Reaction (10.8) does not occur when oxygen is present as  $^{\bullet}R-RH$  is not formed in any great quantities. However once oxygen is depleted in the system, Reaction (10.8) begins to occur and removes hydrogen atoms from the system, which could otherwise have gone on to react and produce molecular hydrogen.

#### **10.4.2** G(RO) and G(ROH<sub>2</sub>)

As G(RO) and  $G(ROH_2)$  are produced at the same rate by only one reaction and the model does not include any further reactions their concentration, and therefore their G-values, are equal. Figure 10.7 displays the value of G(RO) and  $G(ROH_2)$  as a function of dose.

Whilst  $O_2$  is present their concentration increases linearly, see Figure 10.1, as the concentration of oxygen decreases linearly.

The set of reactions that produce RO and ROH<sub>2</sub> are:

$$\mathrm{RH}^{\bullet} + \mathrm{O}_2 \xrightarrow{K17} \mathrm{RHO}_2 \tag{10.9}$$

$$2(\text{RHO}_2) \xrightarrow{K26} \text{RO} + \text{ROH}_2 + \text{O}_2$$
(10.10)


**Figure 10.7:** The value of G(RO) and  $G(ROH_2)$  as a function of dose. Whilst oxygen is present the value of G(RO) and  $G(ROH_2)$  increases as the concentration of RH<sup>•</sup> increases. Once the oxygen has been depleted the concentration remains stable and so the value of G decreases as the dose increases.  $[O_2](t=0)=0.74$  mM. Dose rate 60Gy/min.

These reactions indicate that the concentration of  $RH^{\bullet}$  is as important to the production of RO and  $ROH_2$  as the concentration of oxygen is. The amount of oxygen decreases linearly, whilst the concentration of  $RH^{\bullet}$  increases at a faster and faster rate as the dose increases, see Figure 10.6, resulting in a linear increase in the concentration of RO and  $ROH_2$  even as the concentration of oxygen decreases.

#### **10.4.3** G(R(=))

Figure 10.8 displays the value of G(R(=)) as a function of dose. Whilst oxygen is present R(=) is prevented from forming as a stable product as it is used by Reaction (10.11).

$$\mathbf{R}(=) + \mathbf{O}_2 \xrightarrow{K_{25}} \mathbf{RO}_2 \tag{10.11}$$

Once the oxygen has been depleted the above mechanism is no longer applicable. There is a sharp increase in the concentration of R(=), as shown in Figure 10.8 by the peak in G(R(=)). This is followed by a sharp decline in the value of G(R(=)) that tails off as the dose increases. This decline in the value of G(R(=)) is due to Reaction (10.12).

$$\mathbf{R}(=) + \mathbf{H}^{\bullet} \stackrel{K6}{\to} \mathbf{R}\mathbf{H}^{\bullet} \tag{10.12}$$

This reaction is dependent on the concentration not only of R(=), but also H<sup>•</sup>. The concentration of H<sup>•</sup> is small, but increases as the concentration of oxygen decreases, see Figure 10.6. As the dose increases more R(=) is consumed by Reaction (10.12) and the G-value de-



**Figure 10.8:** The value of G(R(=)) as a function of dose.  $[O_2](t=0)=0.74$  mM. Dose rate 60Gy/min.

creases.

#### 10.4.4 G((RH)<sub>2</sub>)

Figure 10.9 shows the value of  $G((RH)_2)$  as a function of dose. The production of  $(RH)_2$  is inhibited by the presence of oxygen. One of the main pathways of formation uses R(=).

$$\mathbf{R}(=) + \mathbf{R}\mathbf{H}^{\bullet} \stackrel{K_5}{\to} \bullet \mathbf{R} - \mathbf{R}\mathbf{H} \tag{10.13}$$

$${}^{\bullet}\mathrm{R}-\mathrm{RH} + \mathrm{H}^{\bullet} \xrightarrow{K15} (\mathrm{RH})_2 \tag{10.14}$$

As discussed in Section (10.4.3), whilst oxygen is present R(=) reacts rapidly with oxygen to produce  $RO_2$ , preventing Reaction (10.13) from occurring.

The other reaction that produces R(=) is Reaction (10.4), which requires both an RH<sup>•</sup> and H<sup>•</sup>, the concentrations of which are very low whilst oxygen is present.

As  $(RH)_2$  does not go on to react any further the concentration can only increase. Figure 10.9 shows that the value of  $G((RH)_2)$  increases with dose as well, indicating that the reactions which produce it become favoured as the dose increases.



Figure 10.9: The value of  $G((RH)_2)$  as a function of dose.  $[O_2](t=0)=0.74$  mM. Dose rate 60Gy/min.

## Part IV

# **Conclusions and Further Work**

## 11 Conclusions

This chapter presents conclusions drawn from the experimental and computational data detailed in Chapter 6, Chapter 7, Chapter 8, and Chapter 10.



#### 11.1 *n*-Dodecane

Figure 11.1: The data as shown in Figure 6.2. Literature values are listed in Table 4.1.

The effect of dose rate can be seen in Figure 11.1. The literature values, in pink, match well with the experimentally determined values for the aerated samples. The first three literature values are at dose rates below those examined in this work, and provide evidence to support the suggestion that the value of  $G(H_2)$  continues to increase as the dose rate decreases.

At higher dose rates, we can expect the concentration of radicals to be increased, and therefore the probability of radical recombination to elevate. A higher chance of radical recombination would reduce the available radicals that could go on to produce molecular hydrogen.

The dose rate effect is of great importance when considering very long durations of exposure; for instance, in mal-operation situations where it may not be possible to remove the solvent from the radiation field for a long period of time.

When linear fits are constructed for data going above the LDR (5kGy), the value of  $G(H_2)$  decreases. No evidence was found that the rate of molecular hydrogen production continues to decrease as the dose increases, however the highest dose reached experimentally for *n*-

dodecane was  $\approx$  37kGy, and conclusions cannot be drawn beyond this dose. The effect of the absorbed dose has not been found to have been commented on in literature, though many other systems display a dependence on the absorbed dose.

The rate of molecular hydrogen production for absorbed doses below 5kGy is elevated in comparison to the average rate for larger absorbed doses.

The average dose per year is estimated to be in the region of 100kGy, so it is likely that the LDR will have relatively little influence [54]. However, the elevation in  $G(H_2)$  from fresh solvent must be taken into account for safety case modelling.

Upon deaeration of the samples, the rate of molecular hydrogen production was significantly increased. A lack of oxygen in the atmosphere the sample is exposed to, and oxygen dissolved in the solution, significantly increases the yield of molecular hydrogen. This effect was expected as oxygen, upon radiolysis of *n*-dodecane, is expected to react with radical species such as  $H^{\bullet}$  and  $RH^{\bullet}$ , reducing the yield of  $H_2$ .

#### **11.2 TODGA**



**Figure 11.2:** Molecular diagram of N,N,N',N' tetraoctyl diglycolamide (TODGA) with the most likely bonds to break highlighted by red lines. 'A' the  $C-C_{carbonyl}$  bond, 'B' the  $C-O_{ether}$  bond, and 'C' is the  $N-C_{carbonyl}$  bond [87].

Table 11.1 displays the value of  $G(H_2)$  calculated for neat TODGA (N,N,N',N' tetraoctyl diglycolamide). The rate of molecular hydrogen production from TODGA is effected very little by the dose rate of the incident gamma irradiation. When examining the change in the rate of molecular hydrogen production, as a function of the absorbed dose, it behaves in the opposite way to neat *n*-dodecane. With TODGA,  $G(H_2)$  increases when the dose increases above 5kGy.  $G(H_2)$  approximately doubles for dose rates above 5kGy.

Doses of 100kGy have been shown to almost entirely impair the function of neat TODGA, so it is expected that fresh TODGA will be introduced several times per year when the annual dose to the organic solvent is in the region of 100kGy [54]. Clean up and recycling of the solvent will play a major role in ensuring continued effectiveness of reprocessing systems.

Deaeration of neat TODGA does not appear to affect the value of  $G(H_2)$ . This lack of response to deaeration of TODGA may be due to the way in which TODGA responds to radiation. The bonds which are most susceptible to breakage under radiation are the  $N-C_{carbonyl}$  bond, the  $C-O_{ether}$  bond and the  $C-C_{carbonyl}$  bond, see Figure 11.2. Any of the bonds which go on to react with OH<sup>•</sup> could equally react with H<sup>•</sup>, and so the lack of oxygen does not significantly effect the reactions of the fragments of TODGA [87].

Headspace	Dose Rate	G(H <sub>2</sub> ) for LDR	Limiting G(H <sub>2</sub> )
Contents	Group	μmol/J	µmol/J
Air	3	-	$0.131 \pm 0.003$
Air	4	-	$0.105 \pm 0.002$
Air	5	$0.045 \pm 0.003$	$0.114 \pm 0.001$
Air	6	$0.062 \pm 0.005$	$0.131 \pm 0.006$
Air	7	$0.077 \pm 0.003$	$0.139 \pm 0.006$
Air	8	-	$0.119 \pm 0.007$
Air	-	$0.056 \pm 0.001$	$0.123 \pm 0.002$
Argon	-	$0.050 \pm 0.004$	-

**Table 11.1:** A list of all the values calculated for  $G(H_2)$  for neat TODGA under gamma irradiation.

#### 11.3 Mixtures of *n*-Dodecane and TODGA

Figure 11.3 shows the experimentally determined values of  $G(H_2)$  with varying concentrations of TODGA. The values presented are for the linear fits to data not split by dose rate group.

For TODGA concentrations of 0.2M and below, deaeration increases the value of  $G(H_2)$  significantly. For 1.0M [TODGA] and above, the effect of deaeration is much smaller. For neat TODGA, as discussed above, the effect is almost negligible. For 1.0M [TODGA], deaeration reduces  $G(H_2)$  in the LDR, but increases  $G(H_2)$  very slightly for absorbed doses above 5kGy. This effect of deaeration for 1.0M [TODGA] may be an effect of errors and scatter.

Literature on the subject suggests that TODGA degrades faster in the presence of *n*-dodecane [66]. If TODGA degrades at a faster rate when mixed with *n*-dodecane, it could be expected that more molecular hydrogen would be produced, as the contribution from TODGA would be proportionally larger than expected. However, experimentally determined values are almost universally lower than would be expected from extrapolating the values of neat TODGA and neat *n*-dodecane, see Figure 11.4. The notable exception to this are the data collected for aerated 0.01M [TODGA] (over all doses), that are not only higher than expected, but larger than the value collected for neat *n*-dodecane, see Figure 11.3.

#### 11.4 Impact in Mal-Operation Situations

From the experimentally collected data we can construct theories as to how the rate of molecular hydrogen production will be altered by various mal-operation situations.

#### 11.4.1 Changes in the Concentration of TODGA in the Organic Phase

If there is a decrease in the concentration of TODGA a smaller amount of metal ions will be extracted into the organic phase, resulting in a smaller dose being received from  $\alpha$ -sources. This will reduce the dose rate and possibly result in an increase in the rate of molecular hydrogen production if the concentration of TODGA becomes low enough. In addition a decrease in the concentration of TODGA will result in a decrease in the viscosity of the organic phase.

Increasing the concentration of TODGA will increase the viscosity of the organic phase. It is likely that a larger amount of metal ions will be extracted, and possibly that a third phase will form when the modifier, DMDOHEMA, is no longer sufficient to counter third phase formation. With increased [TODGA], G(H<sub>2</sub>) decreases.



**Figure 11.3:** The value of  $G(H_2)$  as a function of [TODGA] and whether the sample has been deaerated. The scale of the [TODGA] axis is logarithmic after 0.005 mol/litre.



**Figure 11.4:** The value of  $G(H_2)$  as a function of [TODGA] and whether the sample has been deaerated with argon. In addition, linear predictions are shown, constructed by extrapolating from the data for neat *n*-dodecane and TODGA.

#### 11.4.2 Changes in the Concentration of SNF in the Aqueous Phase

When the concentration of SNF in the aqueous phase is decreased, we can expect that a greater proportion of the nitric acid will be extracted by TODGA and that nitration would be more likely to occur.

When the concentration of SNF in the aqueous phase is increased, we can expect the dose rate to increase. At a concentration of 0.2M TODGA there is little evidence that the dose rate affects the rate of molecular hydrogen production, so we can expect that an increase in dose rate will lead to a linear increase in the amount of molecular hydrogen produced per unit time.

#### 11.4.3 Introduction of a Fresh Organic Phase

By comparing the rate of molecular hydrogen production during the LDR and above 5kGy, for [TODGA] < 0.4M, we can conclude that increasing the dose above 5kGy will result in a decrease in the rate of molecular hydrogen production. For [TODGA] = 1.0M, the rate of molecular hydrogen production decreases above 5kGy when aerated, but increases when deaerated. For neat TODGA, doses above 5kGy have a higher rate of molecular hydrogen production than during the LDR.

Introducing fresh solvent into the reprocessing system will result in a brief increase in the rate of molecular hydrogen production when aerated at a concentration of TODGA below 1.0M.

#### 11.5 Hydrocarbon Radiolysis Model

The method of construction for the hydrocarbon radiolysis model is shown in Chapter 9. The data collected from the computational model are discussed in Chapter 10.

The model was limited to doses of 100kGy. This was due to the model not keeping track of the concentration of  $RH_2$  and so the model needed to keep the change in concentration negligible. However, as this is dose predicted to be delivered to the organic solvent during reprocessing per year, this limit is not unreasonable [54].

The computational model built and discussed within this work does not address the origin of the dose rate dependence of  $G(H_2)$ , and the value of  $G(H_2)$  from the model does not change when the dose rate is altered. The lack of dose rate dependence was expected as the most likely cause of a dose rate dependence would be the existence of triplet-triplet annihilation.

Triplet-triplet annihilation can occur through two reactions:

$$\operatorname{RH}_{2}^{*}(T) + \operatorname{RH}_{2}^{*}(T) \xrightarrow{1/4k_{ann}} \operatorname{RH}_{2}^{*}(S) + \operatorname{RH}_{2}$$
 (11.1)

$$\stackrel{3/4k_{ann}}{\rightarrow} \operatorname{RH}_2^*(\mathsf{T}) + \operatorname{RH}_2 \tag{11.2}$$

where  $k_{ann}$  is the rate at which triplet-triplet annihilation occurs. As the model does not include the singlet and triplet excited states, triplet-triplet annihilation could not be incorporated into this model.

Without the presence of oxygen the largest value of  $G(H_2)$  output by the model is  $\approx$ 

 $0.57\mu$ mol/J. The value determined experimentally was  $(0.58\pm0.02)\mu$ mol/J for doses up to 2kGy. The computational model agrees well with the experimentally determined values for deaerated solutions.

When oxygen is introduced from the model, doses of approximately 1.6kGy were sufficient to deplete oxygen from the system, see Figure 10.1. The effect of oxygen was noticeable for much longer than this. In Figure 11.5 the effect of oxygen is noticeable until doses of around 12-14kGy.



**Figure 11.5:**  $G(H_2)$  calculated from the computational model as a function of the absorbed dose (up to 20kGy). The effect of an initial non-zero oxygen concentration is noticeable until doses of around 12-14kGy. Dose rate 60Gy/min.

The effect of the presence of oxygen is difficult to compare to the experimentally determined values as the model did not include the presence of a headspace, which would have resulted in a continual transference of oxygen between the liquid and gas phases. This transference between the two phases would most likely have resulted in the movement of oxygen from the gas phase to the liquid phase, extending the dose range for which oxygen is present and affecting the value of  $G(H_2)$  for much longer than the results from the model would suggest.

When oxygen is present the values of  $G(H_2)$  output by the model are much larger than those determined experimentally. Possible causes in the model for this include the reaction rates being used, a lack of intersystem crossing reactions and ratios of reaction rates

Many of the reaction rates used in this model were for hydrocarbons other than *n*-dodecane. It is known that the ratio of singlet to triplet excited states formed when a hydrocarbon is subject to irradiation is dependent on the length of hydrocarbon chain. As singlet and triplet states have different preferred methods of relaxation this could have a large effect on the model.

The ratio of certain reaction rates, such as:

$$\frac{k(\mathrm{H}^{\bullet} + \mathrm{O}_2)}{k(\mathrm{H}^{\bullet} + \mathrm{RH}_2)} \tag{11.3}$$

is different for different R's (different hydrocarbons). In the model discussed within this work, the source of the value of  $k(H^{\bullet} + RH_2)$  was cyclooctane [37].

Intersystem crossing could not be included in this model as the singlet and triplet states were not included.

## 12 Improving the Method of Experimentation and Possible Further Work

#### 12.1 Improving Experimentation

#### 12.1.1 In-Line Gas Chromatography

An alternative method of analysing the gaseous products formed by radiolysis is the use of In-line Gas Chromatography.

Samples are placed inside the Irradiator and permanently connected to the gas chromatograph. A rotating valve is used to control where the carrier gas flows. During irradiation the sample is isolated and is a closed system separate from the GC loop. When sampling, the valve rotates and allows the carrier gas to flow through the sample before moving into the column. The rotating valve system is shown in Figure 12.1.



**Figure 12.1:** Arrows show the flow of argon. On the left is the position of the valve during irradiation, where the argon used as the carrier gas moves from the cylinder, through the valve, and to the column of the GC without entering the sample. On the right is the valve position during sampling. Argon flows from the cylinder, bubbles through the sample in the irradiator and flows back to the column, carrying with it any gas produced by the sample, including that dissolved in the solution.

This method of sample collection has a number of advantages over sampling from the headspace. The first is the total collection of all gases produced, allowing for smaller doses and a greater certainty in measurements, this also includes any gases dissolved in the solution as the same is purged during each sampling. The next is the increased reliability of deaeration, without the need for the piercing of a septum, this would reduce the amount of atmospheric leakage that could be expected. Disadvantages include the reduced rate at which data can be collected when compared to the irradiation of multiple vials at a time and the necessity of purging the system.

#### 12.2 Further Work

#### 12.2.1 Type of Ionising Radiation

There has been an experimentally observed 4-fold radiation resistance to alpha in comparison to gamma irradiation for TODGA [66, 67]. To examine whether this radiation resistance impacts the molecular hydrogen yield it will be necessary to repeat the experiments carried out here with alternative sources of ionising radiation.

Other sources of ionising radiation include alpha radiation from actinides that occur in SNF, He<sup>2+</sup> ions with specific energies from an accelerator, accelerated electrons, and neutrons.

#### 12.2.2 Determining the Cause of the Dose Rate Dependence of *n*-Dodecane

To confirm experimentally that a higher concentration of radicals leads to a decrease in the yield of molecular hydrogen, a scavenger can be added to the solution that would keep the concentration of radicals the same for different dose rates and the yield of molecular hydrogen measured. This would allow the idea that the concentration of radicals effects the yield of molecular hydrogen to be examined.

#### 12.2.3 Modelling Hydrocarbons Under Radiolysis

As the reactions examined in the model discussed within this work are not only applicable to *n*-dodecane, but to all straight chain hydrocarbons, comparisons between various hydrocarbons could be made by altering the values of GEXCESSH2, GH2ELIMINATION, GCHSCIS-SION, and GESC where these are known.

A dose rate effect on the production of hydrogen from hydrocarbons was observed experimentally. A model which could identify the cause of this would be beneficial to predicting the behaviour of *n*-dodecane outside of the conditions studied experimentally.

The most likely causes of the dose rate dependence are triplet-triplet annihilation (discussed in Section 11.5) and the concentration of geminate ion pairs affecting the proportion of singlet and triplet states formed [1].

If the concentration of geminate pairs is the source of the dose rate dependence a model that takes account of the positions of the species, or their local concentration, would be beneficial. If the local concentration is more important than the bulk concentration to the reaction rates, then any model that uses the bulk concentration will be suffer significantly from the neglect of the local concentration.

An approach using finite element analysis would allow for spatial variation in the local concentration without the need to calculate the position of every component in the system. This approach would use boundary conditions between smaller units, each of which acted as a bulk medium, see Figure 12.2.

An alternative would be a model in which the position and motion of each species is calculated and the probability of a reaction occurring is based on the separation between individual components of the system.

A system that takes account of the local concentration variations has the advantage of being adapted to model high LET radiation sources, such as  $\alpha$ -particles, where the energy is



**Figure 12.2:** A large volume is broken down into several smaller volumes. Each unit is then evaluated separately, allowing for variation between them.

deposited in a small region instead of homogeneously throughout the material.

To extend the applicability of a hydrocarbon radiolysis model, the inclusion of reactions with TODGA, DMDOHEMA, and co-exisiting aqueous and gaseous phases would be of great interest to the safety case modelling of future reprocessing systems.

Part V

# Appendices

## **13** Appendices

This section includes the Appendices:

- Appendix A: Graphs of Experimental Data
- Appendix B: Code
- Appendix C: Calculations on Experimental Data
- Appendix D: Co-60 Irradiator
- Appendix E: Molecular Diagrams

### Appendix A: Graphs of Experimental Data



#### Molecular Hydrogen Production - *n*-Dodecane

**Figure 13.1:** Amount of Molecular Hydrogen Produced for Various Doses for Deaerated *n*-Dodecane - Low Dose Region. LDR  $G(H_2) = (0.58 \pm 0.02) \mu \text{mol}/\text{J}$ .



**Figure 13.2:** Amount of Molecular Hydrogen Produced for Various Doses for Aerated *n*-Dodecane.  $G(H_2) = (0.30 \pm 0.01) \mu \text{mol}/\text{J}$ . LDR  $G(H_2) = (0.34 \pm 0.01) \mu \text{mol}/\text{J}$ .



**Figure 13.3:** Amount of Molecular Hydrogen Produced for Various Doses for Aerated *n*-Dodecane - Dose Rate Group 2.  $G(H_2)=(0.33\pm0.01)\mu mol/J$ . LDR  $G(H_2)=(0.44\pm0.02)\mu mol/J$ .



**Figure 13.4:** Amount of Molecular Hydrogen Produced for Various Doses for Aerated *n*-Dodecane - Dose Rate Group 3.  $G(H_2) = (0.327 \pm 0.004) \mu mol/J$ . LDR  $G(H_2) = (0.422 \pm 0.009) \mu mol/J$ .



**Figure 13.5:** Amount of Molecular Hydrogen Produced for Various Doses for Aerated *n*-Dodecane - Dose Rate Group 4.  $G(H_2) = (0.34 \pm 0.01) \mu \text{mol}/\text{J}$ . LDR  $G(H_2) = (0.387 \pm 0.004) \mu \text{mol}/\text{J}$ .



**Figure 13.6:** Amount of Molecular Hydrogen Produced for Various Doses for Aerated *n*-Dodecane - Dose Rate Group 5.  $G(H_2) = (0.296 \pm 0.007) \mu \text{mol}/\text{J}$ . LDR  $G(H_2) = (0.401 \pm 0.005) \mu \text{mol}/\text{J}$ .



**Figure 13.7:** Amount of Molecular Hydrogen Produced for Various Doses for Aerated *n*-Dodecane - Dose Rate Group 6.  $G(H_2) = (0.236 \pm 0.007) \mu \text{mol/J}$ . LDR  $G(H_2) = (0.32 \pm 0.01) \mu \text{mol/J}$ .



**Figure 13.8:** Amount of Molecular Hydrogen Produced for Various Doses for Aerated *n*-Dodecane - Dose Rate Group 7.  $G(H_2)=(0.21\pm0.01)\mu mol/J$ .



**Figure 13.9:** Amount of Molecular Hydrogen Produced for Various Doses for Aerated *n*-Dodecane - Dose Rate Group 8.  $G(H_2) = (0.252 \pm 0.009) \mu \text{mol}/\text{J}$ . LDR  $G(H_2) = (0.316 \pm 0.006) \mu \text{mol}/\text{J}$ .

#### **Molecular Hydrogen Production - TODGA**



**Figure 13.10:** The molecular hydrogen production from irradiated aerated TODGA as a function of dose with linear fits through the origin with the focus on the LDR.  $G(H_2) = (0.123 \pm 0.002) \mu \text{mol/J}$ . LDR  $G(H_2) = (0.056 \pm 0.001) \mu \text{mol/J}$ .



**Figure 13.11:** The molecular hydrogen production from irradiated aerated TODGA, DRG 3, as a function of dose with a linear fit through the origin.  $G(H_2) = (0.131 \pm 0.003) \mu mol/J$ .



**Figure 13.12:** The molecular hydrogen production from irradiated aerated TODGA, DRG 4, as a function of dose with a linear fit through the origin.  $G(H_2)=(0.105\pm0.002)\mu mol/J$ .



**Figure 13.13:** The molecular hydrogen production from irradiated aerated TODGA, DRG 5, as a function of dose with linear fits through the origin.  $G(H_2)=(0.116 \pm 0.001)\mu \text{mol/J}$ . LDR  $G(H_2)=(0.045 \pm 0.003)\mu \text{mol/J}$ .



**Figure 13.14:** The molecular hydrogen production from irradiated aerated TODGA, DRG 5, as a function of dose with linear fits through the origin with the focus on the LDR. LDR  $G(H_2)=(0.045 \pm 0.003)\mu$ mol/J.



**Figure 13.15:** The molecular hydrogen production from irradiated aerated TODGA, DRG 6, as a function of dose with linear fits through the origin.  $G(H_2)=(0.131 \pm 0.006)\mu mol/J$ . LDR  $G(H_2)=(0.062 \pm 0.005)\mu mol/J$ .



**Figure 13.16:** The molecular hydrogen production from irradiated aerated TODGA, DRG 6, as a function of dose with linear fits through the origin with the focus on the LDR. LDR  $G(H_2)=(0.062 \pm 0.005)\mu mol/J$ .



**Figure 13.17:** The molecular hydrogen production from irradiated aerated TODGA, DRG 7, as a function of dose with linear fits through the origin.  $G(H_2)=(0.139 \pm 0.006)\mu \text{mol/J}$ . LDR  $G(H_2)=(0.077 \pm 0.003)\mu \text{mol/J}$ .



**Figure 13.18:** The molecular hydrogen production from irradiated aerated TODGA, DRG 7, as a function of dose with linear fits through the origin with the focus on the LDR. LDR  $G(H_2)=(0.077 \pm 0.003)\mu$ mol/J.



**Figure 13.19:** The molecular hydrogen production from irradiated aerated TODGA, DRG 8, as a function of dose with a linear fit through the origin.  $G(H_2) = (0.119 \pm 0.007) \mu mol/J$ .



**Figure 13.20:** The molecular hydrogen production from irradiated deaerated TODGA, as a function of dose with a linear fit through the origin.  $G(H_2) = (0.050 \pm 0.004) \mu \text{mol/J}$ .

#### Molecular Hydrogen Production - 0.01M TODGA in *n*-Dodecane



**Figure 13.21:** The value of RHP as a function of the absorbed dose for aerated 0.01M TODGA in *n*-dodecane under gamma irradiation.



**Figure 13.22:** The value of RHP as a function of the absorbed dose for aerated 0.01M TODGA in *n*-dodecane under gamma irradiation for DRG # 2.



**Figure 13.23:** The value of RHP as a function of the absorbed dose for aerated 0.01M TODGA in *n*-dodecane under gamma irradiation for DRG # 3.



**Figure 13.24:** The value of RHP as a function of the absorbed dose for aerated 0.01M TODGA in *n*-dodecane under gamma irradiation for DRG # 4.



**Figure 13.25:** The value of RHP as a function of the absorbed dose for aerated 0.01M TODGA in *n*-dodecane under gamma irradiation for DRG # 5.



**Figure 13.26:** The value of RHP as a function of the absorbed dose for aerated 0.01M TODGA in *n*-dodecane under gamma irradiation for DRG # 6.



**Figure 13.27:** The value of RHP as a function of the absorbed dose for aerated 0.01M TODGA in *n*-dodecane under gamma irradiation for DRG # 7.



**Figure 13.28:** The value of RHP as a function of the absorbed dose for aerated 0.01M TODGA in *n*-dodecane under gamma irradiation for DRG # 8.

#### Molecular Hydrogen Production - 0.2M TODGA in *n*-Dodecane



**Figure 13.29:** The value of RHP as a function of the absorbed dose for aerated 0.2M TODGA in *n*-dodecane under gamma irradiation.



**Figure 13.30:** The value of RHP as a function of the absorbed dose for aerated 0.2M TODGA in *n*-dodecane under gamma irradiation, focusing on the LDR.



**Figure 13.31:** The value of RHP as a function of the absorbed dose for deaerated 0.2M TODGA in *n*-dodecane under gamma irradiation.



**Figure 13.32:** The value of RHP as a function of the absorbed dose for aerated 0.2M TODGA in *n*-dodecane under gamma irradiation for DRG # 2.



**Figure 13.33:** The value of RHP as a function of the absorbed dose for aerated 0.2M TODGA in *n*-dodecane under gamma irradiation for DRG # 3.



**Figure 13.34:** The value of RHP as a function of the absorbed dose for aerated 0.2M TODGA in *n*-dodecane under gamma irradiation for DRG # 4.



**Figure 13.35:** The value of RHP as a function of the absorbed dose for aerated 0.2M TODGA in *n*-dodecane under gamma irradiation for DRG # 5.



**Figure 13.36:** The value of RHP as a function of the absorbed dose for aerated 0.2M TODGA in *n*-dodecane under gamma irradiation for DRG # 6.



**Figure 13.37:** The value of RHP as a function of the absorbed dose for aerated 0.2M TODGA in *n*-dodecane under gamma irradiation for DRG # 7.



**Figure 13.38:** The value of RHP as a function of the absorbed dose for aerated 0.2M TODGA in *n*-dodecane under gamma irradiation for DRG # 8.

#### Molecular Hydrogen Production - 0.4M TODGA in *n*-Dodecane



**Figure 13.39:** The value of RHP as a function of the absorbed dose for aerated 0.4M TODGA in *n*-dodecane under gamma irradiation.



**Figure 13.40:** The value of RHP as a function of the absorbed dose for aerated 0.4M TODGA in *n*-dodecane under gamma irradiation for DRG # 2.


**Figure 13.41:** The value of RHP as a function of the absorbed dose for aerated 0.4M TODGA in *n*-dodecane under gamma irradiation for DRG # 3.



**Figure 13.42:** The value of RHP as a function of the absorbed dose for aerated 0.4M TODGA in *n*-dodecane under gamma irradiation for DRG # 4.



**Figure 13.43:** The value of RHP as a function of the absorbed dose for aerated 0.4M TODGA in *n*-dodecane under gamma irradiation for DRG # 5.



**Figure 13.44:** The value of RHP as a function of the absorbed dose for aerated 0.4M TODGA in *n*-dodecane under gamma irradiation for DRG # 6.



**Figure 13.45:** The value of RHP as a function of the absorbed dose for aerated 0.4M TODGA in *n*-dodecane under gamma irradiation for DRG # 7.



**Figure 13.46:** The value of RHP as a function of the absorbed dose for aerated 0.4M TODGA in *n*-dodecane under gamma irradiation for DRG # 8.

## Molecular Hydrogen Production - 1.0M TODGA in *n*-Dodecane



**Figure 13.47:** The value of RHP as a function of the absorbed dose for aerated 1.0M TODGA in *n*-dodecane under gamma irradiation.



**Figure 13.48:** The value of RHP as a function of the absorbed dose for deaerated 1.0M TODGA in *n*-dodecane.

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**Figure 13.49:** The value of RHP as a function of the absorbed dose for aerated 1.0M TODGA in *n*-dodecane under gamma irradiation for DRG # 3.



**Figure 13.50:** The value of RHP as a function of the absorbed dose for aerated 1.0M TODGA in *n*-dodecane under gamma irradiation for DRG # 4.



**Figure 13.51:** The value of RHP as a function of the absorbed dose for aerated 1.0M TODGA in *n*-dodecane under gamma irradiation for DRG # 5.



**Figure 13.52:** The value of RHP as a function of the absorbed dose for aerated 1.0M TODGA in *n*-dodecane under gamma irradiation for DRG # 6.



**Figure 13.53:** The value of RHP as a function of the absorbed dose for aerated 1.0M TODGA in *n*-dodecane under gamma irradiation for DRG # 7.

# **Appendix B: Code**

This appendix contains a printout of the code developed within this research and used in the modelling of the molecular hydrogen production from the  $\gamma$ -radiolysis of *n*-dodecane. This section provides a printout only. For a more detailed discussion of the model please see Chapter 9.

model \*A FACSIMILE program to calculate the reactions for irradiated n-dodecane; \*Very basic setup; \*Does not simulate reactions whilst a dose is received ; \*Sets up production of excited states from a dose ; \*No headspace; PERMIT + - ;COMPILE INSTANT; OPEN 32 "MODELOUT.OUT"; OPEN 31 "MODELOTHEROUT.OUT"; \*\*; \*; VARIABLE RH2EXSING ; VARIABLE RH2EXTRIP ; VARIABLE RH2PLUS ; VARIABLE EFREE ; VARIABLE HNU1 ; VARIABLE HNU2 ; VARIABLE H2 ; VARIABLE REQUAL ; VARIABLE RHDOT ; VARIABLE HDOT ; VARIABLE RHRH ; VARIABLE RDOTRH ; VARIABLE 02 ; VARIABLE HO2 ; VARIABLE RHO2 O RO2 RO RHOH ; VARIABLE RO2H ; VARIABLE HI RHI I2 I ; VARIABLE HI2 RHI2 ; \*VARIABLE GRHO2 GHO2 GO2 GRHRH ; \*VARIABLE GRDOTRH GHDOT GRHDOT GREQUAL ; \*VARIABLE GRH2EXTRIP GRH2EXSING GH2 GRH2 ; \*; \*Parameters ; PARAMETER SV ; Solution volume in litres - specified below PARAMETER HV ; Headspace volume in litres - specified below PARAMETER NDDDENS ; Density of ndd in kg/litre - specified below PARAMETER W ; Solution weight in kg PARAMETER DR ; Dose rate Gy/min - specified below PARAMETER DREV ; Dose rate 100eV/s PARAMETER DOSE ; The Dose delivered to the solution multiples of 100eV PARAMETER TIMEIRR ; Time of Irradiation s - specified below PARAMETER MOLMASS ; kg/mol - specified below PARAMETER NDDMOL ; Molarity of just ndd PARAMETER GMINUSNDD ; Decay rate of ndd molecules/100eV PARAMETER K1 K3 K3A K4 K5 ; PARAMETER K1A K1B ; PARAMETER K6 K7 K10 ; PARAMETER K7A K7B K7C ; PARAMETER K10A K10B K10C ; PARAMETER K3B K14 ;

model PARAMETER K15 K16 K17 ; PARAMETER K18 K19 ; PARAMETER K20 K21 K23; PARAMETER K24 K25 K26 K27 ; PARAMETER K28 ; PARAMETER GSING GTRIP GEXCESSH2 ; PARAMETER GRAY2EV ; PARAMETER AVAGADRO ; Avagadro's constant molecules/mol PARAMETER DOSEEND CONC FORM O2SOLUBILITY ; PARAMETER GH2ELIMINATION GCHSCISSION GESC ; \*; \*Initialise Parameter ; \*; \* ASSUMPTIONS ; \* The amount of radiation does not significantly ; \* effect the concentration of n-dodecane ; \* it is therefore ignored ; \*; COMPILE INSTANT; \*; AVAGADRO = 6.022 \* (10\*\*23); molecules/mol DR = 100.00; Gy/min DOSE RATE SV = 1.00; volume of solution in litres HV = 0.00 ; volume of headspace in litres MOLMASS = 0.17034; kg/mol NDDDENS = 0.75; kg/litre = NDDDENS \* SV ; Weight of solution in kg M \* CONVERSION FACTORS ; GRAY2EV = (6.242 \*(10.0\*\*16)) \* W ; Converts gray to 100eV CONC = (1/SV)\*(1/AVAGADRO) ; Converts number of molecules to concentrations \*; TIMEIRR = 0.001; s Initial time to produce an initial dose DREV = (DR/60.00) \* GRAY2EV ; 100eV/s NDDMOL = NDDDENS/MOLMASS ; mol/L of nDD DOSE = DREV \* TIMEIRR ; Dose delivered - multiples of 100eV ; Formation rate conversion factor G FORM = DREV/AVAGADRO (molecules/100eV) to mol/s \*\*; COMPILE INITIAL; \* G VALUES ; GEXCESSH2 = 0.0 ; K23 molecules/100eV LAVERNEJA1997 0.75 cyclohexane 0.15 Cyclooctane molecules/100eV HUMMELA1992 GH2ELIMINATION = 1.30; K7A (Cyclohexane) page 765 GCHSCISSION = 3.80 ; K10B molecules/100eV HUMMELA1992 (Cyclohexane) molecules/100eV Free ions yield GESC = 0.13 ; HUMMELA1992 (Cyclohexane) \* GMINUSNDD = - GH2ELIMINATION - GCHSCISSION - GESC ; molecules/100eV HUMMELA1992 (Hydrocarbons)

model

```
*;
* REFERENCES ;
* GH2TOTAL = 5 molecules/100eV n-HEXANE; HUMMELA1992
* GH2TOTAL = 5.6 molecules/100eV Cyclohexane ; HUMMELA1992
                = -0.25 *GMINUSNDD
                                   ; K20
* GSING
                                                molecules/100eV HUMMELA1992
(Hydrocarbons)
                = -0.75 *GMINUSNDD
* GTRIP
                                        ; K21
                                                molecules/100eV HUMMELA1992
(Hydrocarbons)
* 1:3 ratio of Singlet to triplet ;
* GEXCESSH2
                = 0.75 molecules/100eV Cyclohexane ; LAVERNEJA1997
* G(C-C) Scission = 1.5 molecules/100eV n-Hexane ; HUMMELA1992
* G(C-C scission) = 0.2 molecules/100eV Cyclohexane ; HUMMELA1992
* GH2ELIMINATION = 1.3 molecules/100eV Cyclohexane ; HUMMELA1992
* GCHSCISSION = 3.8 molecules/100eV Cyclohexane ; HUMMELA1992
* GESC = 0.13 molecules/100eV Cyclohexane ; HUMMELA1992
*;
* Amount of species - in mol/litre ;
* RH2EXSING
               = 0.00
                                ;
* RH2EXTRIP
                = 0.00
                                ;
               = GESC * FORM * TIMEIRR ;
RH2PLUS
02SOLUBILITY
               = 7.4E-4 ; ROLSJL1990427
EFREE
               = GESC * FORM * TIMEIRR ;
                                        ; Phosphoresence
HNU1
                = 0.00
HNU2
              = 0.00
                                        ; Fluoresence
H2 = (GEXCESSH2 + GH2ELIMINATION) * FORM * TIMEIRR; LAVERNEJA1997 (Cyclohexane)
         = GH2ELIMINATION * FORM * TIMEIRR;
REOUAL
               = GCHSCISSION * FORM * TIMEIRR
RHDOT
                                                ;
               = GCHSCISSION * FORM * TIMEIRR
HDOT
RHRH
               = 0.00
                       ;
RDOTRH
               = 0.00
                       ;
               = 0.75 * 02SOLUBILITY ;
02
H02
                = 0.00
                                ;
RHO2
                = 0.00
                                ;
0
                = 0.00
                                ;
12
                = 0.00
                                ;
Ι
                = 0.00
                                ;
ΗI
                = 0.00
                                ;
RHI
                = 0.00
                                ;
                = 0.00
RO2
                                ;
RO
                = 0.00
                                ;
RHOH
                = 0.00
                                ;
*;
* REACTION RATES ;
K1= 1.50498E+9 ; LAVERNEJA1994 2kobs n-dodecane Radical-Radical
K1A= 0.52 * K1 ; LAVERNEJA1994
                                                                RHDOT + RHDOT =
RHRH
K1B= 0.48 * K1
               ; LAVERNEJA1994
                                                                RHDOT + RHDOT =
REQUAL + RH2
K3= 2.3E+9
               ; k(R+H)
                                Cycloctane LAVERNEJA1997
K3A= K3
               ; k(R+H)
                                Cycloctane LAVERNEJA1997
                                                                RHDOT + HDOT
= RH2
K3B= K3
               ; k(R+H)
                                Cycloctane LAVERNEJA1997
                                                                RHDOT + HDOT
```

= REQUAL + H2 K4= 2.5E+7 ; k(RH+H) Cycloctane LAVERNEJA1997 HDOT + RH2 = RHDOT + H2 K5= 0.75E+9 ; LAVERNEJA1994 kobs Radical-Radical REQUAL + RHDOT= RDOTRH K6= 2.3E+9 ; k(R+H) Cycloctane LAVERNEJA1997 REQUAL + HDOT = RHDOT K14= 3.05E+9 ; k(H+H) Cycloctane LAVERNEJA1997 HDOT + HDOT = H2 K15= 2.3E+9 ; k(R+H) Cycloctane LAVERNEJA1997 HDOT + RDOTRH = RHR \* REACTIONS WITH OXYGEN OR OXYGEN CONTAINING MOLECULES; K16= ((K3B/4.4)/3)\* (10\*\*2) ; KLOTSCE19642040 HDOT + 02 = H02 K17= K16 ; RHDOT + 02 = RH02 K25= K16 ; REQUAL + 02 = RO2 \* Assumption that O2 reacts ; \* equally with all radicals ; RHO2 + RHO2 = RO + RHOH + O2K26= 0.00 ; RHO2 + RHDOT = RO2H + REQUAL K27= 0.00 \* REACTIONS WITH IODINE ; = HI + I HDOT + I2 K18= 1.4E+10 ; k(I2+H) Cycloctane LAVERNEJA1997 RHDOT + I2 K19= 0.66E+10 ; kobs n-dodecane LAVERNEJA1994 = RHI + Ι K28= 0.26E7 ; kobs n-dodecane LAVERNEJA1994 I + I= I2 \* ; \* REACTION RATES FROM G-VALUES ; \* : \* SINGLET REACTION RATES ; K7A= GH2ELIMINATION\*FORM Yield of REOUAL and H2 ; K7B= (k7A/85) \* 15 ; K7 = K7A + K7B; \*; \* TRIPLET REACTION RATES ; ; yield of RHDOT and HDOT (C-H Scission) K10B= GCHSCISSION\*FORM K10A= K10B \* 0 ; K10C= K10B \* (10/90) ; K10= K10A + K10B + K10C ; \*; \* K22=(5.0\*DREV\*0.947\*0.05)/AVAGADRO ; WERSTDW1995 EFREE and RH2PLUS -Alternative to K24 K23= GEXCESSH2\*FORM ; Excess Hydrogen production K24= GESC\*FORM ; EFREE and RH2PLUS \*\*; COMPILE EQUATIONS; %K1A : RHDOT + RHDOT = RHRH ; %K1B : RHDOT + RHDOT = REQUAL ; %K3A : RHDOT + HDOT = ; %K4 : HDOT = RHDOT + H2 ;

model

Page 4

model %K5 : REQUAL + RHDOT = RDOTRH ; %K6 : REQUAL + HDOT = RHDOT ; ; H2 Elimination from irradiation %K7A : = REQUAL + H2 %K7B : = HNU2 = HNU1 %K10A : ; %K10B : = RHDOT + HDOT ; C-H Scission from irradiation = H2 + RHDOT + RHDOT %K10C : ; %K3B : RHDOT + HDOT = REQUAL + H2 ; %K14 : HDOT + HDOT = H2 ; ; %K15 : HDOT + RDOTRH = RHRH ; %K16 : HDOT + 02 = H02 = HO2 = RHO2 ; %K17 : RHDOT + 02 ; %K18 : HDOT + I2 = HI + I ; %K19 : RHDOT + I2 = RHI + I ; ; Excess H2 %K23 : = H2 = RH2PLUS + EFREE ; %K24 : = RO2 ; = RO + RHOH + O2 %K25 : REQUAL + 02 %K26 : RHO2 + RHO2 ; %K27 : RHO2 + RHDOT = RO2 + REQUAL ; %K28 : I + I = I2 ; \*\*; SETPSTREAM 2 32 13; TIME H2 REQUAL RHDOT HDOT RDOTRH RHRH 02 0 RH02 H02 RHOH RO; \*\*; SETPSTREAM 3 31 13 ; TIME I2 I RHI2 HI2 O2 O RHO2 HO2 RHOH RO HNU1 HNU2 ; \*\*; COMPILE PRINT; \* Displays selected results against time; PSTREAM 2; PSTREAM 3; \*\*; \*Output Control; WHENEVER TIME = 0.00 + 0.01\*20000 % CALL PRINT; \*\*; BEGIN; STOP; \*; \* REFERENCES ; \* HUMMELA1992 ; \* Title The Chemistry of Alkanes and Cycloalkanes ; \* Authour A Hummel ; \* Edited Saul Patai and Zvi Rappoport; \* Publisher John Wiley and Sons Ltd ; \* ISBN 0-471-92498-9;

model

```
* LAVERNEJA1997 ;
* Authors Jay A LaVerne and Simon M Pimblott and Laszlo Wojnarovits ;
* Title Diffusion-Kinetic Modelling of the $\gamma$-Radiolyis of Liquid
Cycloalkanes ;
* Journal Journal of Physical Chemistry A;
* Volume 101 ;
* Pages 1628-1634 ;
* Year 1997 ;
* LAVERNEJA1994 ;
* Authors Jay A LaVerne and Laszlo Wojnarovits ;
* Title Rate of Alkyl Radical-Radical, Alkyl Radical-Iodine, ;
* and Iodine Atom-Atom Reactions in Normal Alkanes and Cycloalkanes ;
* Journal Journal of Physical Chemistry;
* Volume 98 ;
* Pages 12635-12640 ;
* Year 1994 ;
* WERSTDW1993 ;
* title = {{Early Events Following Radiolytic and Photogeneration of Radical
Cations in Hydrocarbons}},;
* journal ={{"Radiation Physics and Chemistry}},;
* volume = "41", ;
* number = "1 - 2", ;
* pages = "127 - 133", ;
* year = "1993", ;
* doi = "http://dx.doi.org/10.1016/0969-806X(93)90049-Z", ;
* url = "http://www.sciencedirect.com/science/article/pii/0969806X9390049Z", ;
* author = {D.W. Werst and A.D. Trifunac};
* KLOTSCE19642040 :
* Authors Cornelius E Klots and Y. Raef and Russell H Johnsen ;
* Journal The Journal of Physical Chemistry ;
* Pages 2040-2043 ;
* Volume 68 ;
* Number 8 ;
* Year 1964 ;
* ROLSJL1990427 ;
* author = {Rols, J. L. and Condoret, J. S. and Fonade, C. and Goma, G.}, ;
* title = {Mechanism of enhanced oxygen transfer in fermentation using
emulsified oxygen-vectors}, ;
* journal = {Biotechnology and Bioengineering}, ;
* volume = {35}, ;
* number = {4}, ;
* publisher = {Wiley Subscription Services, Inc., A Wiley Company},;
* issn = {1097-0290}, ;
* url = {http://dx.doi.org/10.1002/bit.260350410}, ;
* doi = {10.1002/bit.260350410}, ;
* pages = {427--435}, ;
* year = {1990} ;
```

# **Appendix C: Calculations on Experimental Data**

This Appendix provides a detailed discussion of the calculations used on the experimentally collected data to achieve the values presented in Chapters 6, 7 and 8.

Error calculations are indicated by **E**:, the respective errors of variables are denoted by an  $\alpha$  with a subscript corresponding to the variable, e.g. for variable *B* the error is  $\alpha_B$ .

## **Measurements of Radiolytic Hydrogen Production**

#### Raw Data from the Gas Chromatograph to a Hydrogen Volume

Using a calibration curve it is possible to convert from the area, A (mVs), of the peak from Gas Chromatograph(y) (GC) to the volume of hydrogen in the analysed sample, V ( $\mu$ L).

A calibration curve is constructed by injecting known volumes of gas into the GC, as shown in Figure 13.54. The linear fit from Figure 13.54 is:

$$A(\mu Vs) = (87 \pm 2)(Vs/L) \times V(\mu L)$$
(13.1)

To calculate a volume from a given area of a peak the following equation is used:

$$V = \frac{A}{a} - \frac{b}{a} \tag{13.2}$$

where  $a = (87 \pm 2)\mu Vs/\mu L$ 

$$b = 0\mu \text{Vs}$$
  
**E:**  $\alpha_V = V \sqrt{\left(\frac{\alpha_A}{A}\right)^2 + \left(\frac{2}{87}\right)^2}$  (13.3)

To then estimate the volume of hydrogen in the headspace the sample fraction,  $F_S$ , is used.

$$F_{\rm S} = \frac{V_{samp}}{V_{head} - V_{liq}} \tag{13.4}$$

$$\mathbf{E:} \, \alpha_{F_{\mathrm{S}}} = F_{\mathrm{S}} \sqrt{\left(\frac{\alpha_{V_{samp}}}{V_{samp}}\right)^2 + \left(\frac{\alpha_{V_{head}}}{V_{head}}\right)^2 + \left(\frac{\alpha_{V_{liq}}}{V_{liq}}\right)^2} \tag{13.5}$$

where  $V_{samp}$ , mL, is the volume of headspace removed and run through the GC (100 ± 5 µL),  $V_{liq}$ , mL, is the volume of the liquid to be irradiated and  $V_{head}$ , mL, is the volume of the empty vial.

The volume of hydrogen in the headspace,  $H_{head}$  (mL), is then:

$$H_{head} = \frac{V}{F_S} \tag{13.6}$$

$$\mathbf{E:} \,\alpha_{H_{head}} = \frac{1}{F_S} \sqrt{\alpha_V^2 + \left(\frac{V\alpha_{F_S}}{F_S}\right)^2} \tag{13.7}$$



**Figure 13.54:** Figure showing the relationship between the area below the hydrogen GC peak and the amount of hydrogen injected. This data was collected using injections of a 5% hydrogen in argon calibration gas at two different column temperatures of 80° and 120°. The fit uses the concatenated data of both temperatures as there is no significant deviation between the two. The data represented here was collected over multiple days, strengthening the assumption that the calibration remains constant; however, this was checked periodically throughout this project.

# Corrections

#### **Corrections for Previous Samplings**

Multiple samples of gas from the headspace may be taken from the same vial through the same septa. This removal necessitates a correction to the amount of hydrogen calculated to be in the headspace, as well as the inclusion of previously removed hydrogen, to the total.

The correction factor,  $C_f$ , is defined below, where  $F_S$  is the sample fraction, and # is the sample number (e.g. # = 2 for the 2nd sample removed from a vial).

$$C_f = \frac{1}{(1 - F_S)^{(\#-1)}} \tag{13.8}$$

 $C_f = 1$  when # = 1 and increases with the value of #. The corrected value of hydrogen in the headspace produced by the irradiated liquid,  $V_c$  (mL), is given as follows,

$$V_c = C_f H_{head} + V_p \tag{13.9}$$

$$\mathbf{E:} \, \alpha_{V_c}^2 = V_c^2 \left[ \left( \frac{\alpha_{H_{head}}}{H_{head}} \right)^2 + \left( \frac{\alpha_{F_S}(\# - 1)}{(1 - F_S)} \right)^2 \right] + \alpha_{V_p}^2 \tag{13.10}$$

where  $V_p$ , mL, is the volume of hydrogen removed by previous samples

#### **Correcting for Hydrogen Produced by the Sample Vessel**

To calculate the amount of hydrogen produced by the irradiated liquid,  $V_S$  (mL), the hydrogen produced from the cap,  $H_{cap}$  (mL), is taken away from the total amount of hydrogen in the headspace,  $V_c$  (mL), using:

$$V_{\rm S} = V_c - H_{cap} \tag{13.11}$$

$$\mathbf{E:} \ \alpha_{V_S} = \sqrt{\alpha_{V_c}^2 + \alpha_{H_{cap}}^2} \tag{13.12}$$

The amount of hydrogen produced by cap has been calculated as function of dose (*D* (kGy)):

$$H_{cap} = (3.900 \pm 0.792) \times 10^{-4} D + (0.15 \pm 0.02)$$
(13.13)

$$\mathbf{E:} \, \alpha_{H_{cap}}^2 = 0.02^2 + D^2 7.92 \times 10^{-5} \tag{13.14}$$

#### **Correcting for Dissolved Hydrogen**

Henry's Law Volatility Constant,  $K_{H}^{px}$  (Pa), of a solute in a solvent is defined by the relation:

$$K_H^{px} = \frac{p}{x} \tag{13.15}$$

where p, Pa is the partial pressure of the solute in the gas phase and x is the molar mixing ratio of the solute and solvent (dimensionless).

The molar mixing ratio, *x*, is defined as:

$$x = \frac{n_{i,liq}}{n_{other,liq}} \tag{13.16}$$

where  $n_{i,liq}$  is the amount of the solute in the solvent, mol, and  $n_{other,liq}$  is the amount of the solvent, moles. When  $n_{i,liq} << n_{other,liq}$  then x is approximately the mole fraction.

The partial pressure, p (Pa), is defined as:

$$p = \frac{V_i}{V_{head}} \frac{n_i RT}{V_i} = \frac{n_i RT}{V_{head}}$$
(13.17)

where  $V_i$  is the volume of the solute in the gas phase, m<sup>3</sup>;  $V_{head}$  is the volume of the gas phase, m<sup>3</sup>;  $n_i$  is the amount of the solute in the gas phase, mol; R is the gas constant ( $\approx 8.314$  Jmol<sup>-1</sup>K<sup>-1</sup>); and T is the temperature of the gas phase, K.

So the amount of the solute in the solvent is given by:

$$n_{i,liq} = \frac{RT n_{other,liq} n_i}{K_H^{px} V_{head}}$$
(13.18)

Data from the work by Gao et al. is extrapolated to 300K to achieve a value of  $K_H^{px}$  of  $\approx$  123 MPa for hydrogen solubility in *n*-dodecane [22]. So to calculate the amount of hydrogen in *n*-dodecane the following equation can be used:

$$n_{i,liq} \approx \frac{n_{other,liq} n_i}{V_{head}} \frac{8.314 \times 300}{123} \approx \frac{n_{other,liq} n_i}{V_{head}} \times 20.28$$
(13.19)

The total amount of hydrogen produced by the solute in each vial is then given by:

$$H_{total} = H_{gas} + n_{i,liq} \tag{13.20}$$

where  $H_{gas}$  is the number of moles corresponding to the volume  $V_S$ 

Notes: The work by Gao et al. was conducted at temperatures between 344 - 410K at pressures up to 13.2MPa, therefore the values calculated from this extrapolation should be treated with a large amount of error. Gao et al. found that Henry's Law Volatility Constant decreased as the temperature increased, this relation was linear over the range they studied and has been assumed to remain linear at lower temperatures. In addition, the values are assumed to be applicable at lower pressures than those used by Gao et al.

When correcting for the hydrogen in *n*-dodecane/TODGA mixtures the solubility is assumed to be the same as in *n*-dodecane alone. Again, this introduces extra uncertainty in the amount of hydrogen calculated to be dissolved in the solution.

### **Calculation of a** $G(H_2)$ -value

The raw data is processed as above in Section 13 and the corrections outlined in Section 13 are applied. A measure of the number of moles of molecular hydrogen gas  $(H_2)$  produced per gram of irradiated liquid is constructed, this quantity is referred to as Radiolytic Hydrogen Production (mol/g) (RHP) and is defined as:

$$RHP = \frac{H_{total}}{M}$$
(13.21)

where M, g, is the mass of the irradiated liquid.

The error on this value is given by:

$$\mathbf{E:} \,\alpha_{RHP} = RHP \sqrt{\left(\frac{\alpha_{H_{total}}}{H_{total}}\right)^2 + \left(\frac{\alpha_M}{M}\right)^2} \tag{13.23}$$

By plotting RHP as a function of Dose (kGy), *D*, the gradient, *g*, of a linear fit to the points gives:

$$g = \frac{\text{RHP}}{D} = \frac{H_{total}}{M \times D}$$
(13.24)

with units of mols/J.

The units of  $G(H_2)$  in literature are either molecules/100 eV or  $\mu$ mol/J. A list of unit conversions are given below.

$$\begin{split} G(H_2)(\mu \text{mol}/J) &= g \times 10^6 \end{split} \tag{13.25} \\ G(H_2)(\text{molecules}/100 \text{ eV}) &= g \times 10^2 \times \frac{A_\nu (\text{molecules}/\text{mol})}{6.24 \times 10^{18} (\text{ev}/J)} \\ &\approx g \times 10^7 \times \frac{6.022}{6.24} \\ &\approx g \times 9.65 \times 10^6 \qquad (13.26) \\ G(H_2)(\text{molecules}/100 \text{ eV}) &\approx 9.65 \times G(H_2)(\mu \text{mol}/J) \qquad (13.27) \end{split}$$

The linear fit is constructed using OriginPro 8.5.1 and Origin 9.1 which uses a weighted fit and calculates the gradient and intercept along with the standard deviation of each value.

There is the option of restricting the linear fit so that it passes through (0,0) as this is the expected intercept if the response is linear at all doses and dose rates, and the vessel initially contained hydrogen at an undetectable level.

# Appendix D: Co-60 Irradiator

This Appendix contains schematics showing the dimensions of the irradiation chamber, the rack used to hold sample vials, and the details of the dosimeter used.



Figure 13.55: Top-down view of the sample rack base plate.



Figure 13.56: Top-down view of the sample rack position on the base plate.



**Figure 13.57:** Side view of the sample rack position on the base plate, with a projection down onto a top-down view of the base plate.





### 10X6-0.18 HIGH DOSE-RATE CHAMBER

The 10X6-0.18 ion chamber is intended for in-beam measurements of high-intensity gamma radiation. It is suitable for cavity gamma irradiators as well as beam type irradiators. The fully guarded chamber is mounted at the end of a 3 meter, low-noise triax cable.

## **Specifications**<sup>1</sup>

Rate Specifications:

Exposure Specifications:

Calibration Accuracy:

Exposure Rate Dependence

Energy Dependence:

Active Length:

Construction:

50 μR/s - 180 R/s 500 nGy/s - 1.58 Gy/s 200 μR - 2 MR 2 μGy - 17 kGy

±4% using 60Co

±2%, 3 mR/s to 180 R/s

±5%, 45 keV to 1.33 MeV

8.1 mm ± 1 mm

C552 air-equivalent walls & electrode; polyacetal exterior cap; 0.18  $\rm cm^3$  active volume; 3 m, low-noise triax cable; 0.1 kg



Dimensions in millimeters



<sup>1</sup>Specifications apply when used with Accu-series control units.

# **Appendix E: Molecular Diagrams**

This appendix contains a list of molecules mentioned throughout this work, complete with molecular diagrams, chemical names and the acronyms most commonly used to refer to them.

Listed are:

- Acetohydroxamic acid (AHA) Figure 13.58
- Bis-2,6 (5,6,7,8 tetrahydro 5,9,9 trimethyl 5,8 methano-1,2,4 benzotriazin-3-yl) pyridine (CA-BTP) Figure 13.59
- 2,2',2",2"" [(1R,2R) 1,2-cyclohexane diyldinitrilo] tetra-acetic acid (CDTA) Figure 13.60
- N octyl(phenyl) N, N diisobutyl-carbamoyl-methyl-phosphine oxide (CMPO) Figure 13.61
- Cyanex 923 Figure 13.62
- Cyanex 301 Figure 13.63
- 6,6' bis(5,5,8,8-tetramethyl, 5,6,7,8-tetrahydrobenzo [1,2,4] triazin 3-yl) [2,2']bipyridine (CyMe<sub>4</sub>-BTBP) Figure 13.64
- N,N di(2-ethyl-hexyl) butanamide (DEHBA) Figure 13.65
- N,N di(2-ethyl-hexyl) isobutyramide (DEHiBA) Figure 13.66
- N,N di(hexyl-2-ethyl) hexanamide (DH2EHA) Figure 13.67
- Di 2-ethylhexyl phosphoric acid (DEHPA (HDEHP)) Figure 13.68
- N,N dihexyloctanamide (DHOA) Figure 13.69
- Di-isodecyl phosphoric acid (DIDPA) Figure 13.70
- Di-iso propoxy-benzen (DIPB) Figure 13.71
- dimethyl-dibutyl tetra-decyl-malonamide (DMDBTDMA) Figure 13.72
- N,N' dimethyl N,N' dioctyl-hexyl-ethoxy malonamide (DMDOHEMA) Figure 13.73
- Pentetic acid (DTPA) Figure 13.74
- N-(2-hyroxyethly)-ethylenediamine N,N',N'-triacetic acid (HEDTA) Figure 13.75
- 2-ethyl-hexyl-phosphonic acid mono-2-ethyl-hexyl-ester (HEH[EHP]) Figure 13.76
- 2,6-bis (5,6-di-(sulfophenyl) 1,2,4-triazin 3-yl) pyridine (SO<sub>3</sub>-Ph-BTP) Figure 13.77
- Tri-butyl phosphate (TBP) Figure 13.78
- Tetra-ethyl diglycolamide (TEDGA) Figure 13.79
- N,N,N'N'-tetra-2-ethylhexyl diglycolamide (TEHDGA) Figure 13.80

- N,N,N',N' tetraoctyl diglycolamide (TODGA) Figure 13.81
- 2-(2-dioclylamino-2-oxoethoxy) N,N dioctlypropanamide (TWE21) Figure 13.82



Figure 13.58: Acetohydroxamic acid (AHA)



**Figure 13.59:** Bis-2,6 (5,6,7,8 tetrahydro 5,9,9 trimethyl 5,8 methano-1,2,4 benzotriazin-3-yl) pyridine (CA-BTP)



Figure 13.60: 2,2',2",2"" [(1R,2R) 1,2-cyclohexane diyldinitrilo] tetra-acetic acid (CDTA)



Figure 13.61: N octyl(phenyl) N, N diisobutyl-carbamoyl-methyl-phosphine oxide (CMPO)



Figure 13.62: Cyanex 923 - A Trialkyl Phosphine Oxide



**Figure 13.64:** 6,6' bis(5,5,8,8-tetramethyl, 5,6,7,8-tetrahydrobenzo [1,2,4] triazin 3-yl) [2,2']-bipyridine (CyMe<sub>4</sub>-BTBP)



Figure 13.65: N,N di(2-ethyl-hexyl) butanamide (DEHBA)



Figure 13.66: N,N di(2-ethyl-hexyl) isobutyramide (DEHiBA)



Figure 13.67: N,N di(hexyl-2-ethyl) hexanamide (DH2EHA)



Figure 13.68: Di 2-ethylhexyl phosphoric acid (DEHPA (HDEHP))



Figure 13.69: N,N dihexyloctanamide (DHOA)



Figure 13.70: Di-isodecyl phosphoric acid (DIDPA)



Figure 13.71: Di-iso propoxy-benzen (DIPB)



Figure 13.72: dimethyl-dibutyl tetra-decyl-malonamide (DMDBTDMA)



Figure 13.73: N,N' dimethyl N,N' dioctyl-hexyl-ethoxy malonamide (DMDOHEMA)



Figure 13.74: Pentetic acid (DTPA)



Figure 13.75: N-(2-hyroxyethly)-ethylenediamine N,N',N'-triacetic acid (HEDTA)



Figure 13.76: 2-ethyl-hexyl-phosphonic acid mono-2-ethyl-hexyl-ester (HEH[EHP])



Figure 13.77: 2,6-bis (5,6-di-(sulfophenyl) 1,2,4-triazin 3-yl) pyridine (SO<sub>3</sub>-Ph-BTP)



Figure 13.78: Tri-butyl phosphate (TBP)



Figure 13.79: Tetra-ethyl diglycolamide (TEDGA)



Figure 13.80: N,N,N'N'-tetra-2-ethylhexyl diglycolamide (TEHDGA)



Figure 13.81: N,N,N',N' tetraoctyl diglycolamide (TODGA)



Figure 13.82: 2-(2-dioclylamino-2-oxoethoxy) N,N dioctlypropanamide (TWE21)

# Bibliography

- The Chemistry of Alkanes and Cycloalkanes. John Wiley and Sons Ltd, 1992. ISBN 0-471-92498-9.
- [2] Three Mile Island, Chernobyl, and Fukushima. *IEEE Spectrum 48*, 11 (November 2011), 92–92.
- [3] 13 Generation IV Reactor Designs, Operation and Fuel Cycle. In *Nuclear Fuel Cycle Science and Engineering*, Crossland, Ian, Ed. Woodhead Publishing, 2012, pp. 333 395.
- [4] AUSLOOS, P., REBBERT, R.E., SCHWARZ, F.P., AND LIAS, S.G. Pulse- and Gamma Ray-Radiolysis of Cyclohexane: Ion Recombination Mechanisms. *Radiation Physics and Chemistry 21*, 1 (1983), 27–43.
- [5] BARELKO, E., SOLYANINA, I., AND TSVETKOVA, Z. Radiation-Chemical Stability of TBP in Solutions of Hydrocarbons. *Soviet Atomic Energy 21*, 4 (1966), 946–950.
- [6] BELL, K., CARPENTIER, C., CARROTT, M., GEIST, A., GREGSON, C., HERES, X., MAGNUSSON, D., MALMBECK, R., MCLACHLAN, F., MODOLO, G., MULLICH, U., SYPULA, M., TAYLOR, R., AND WILDEN, A. Progress Towards the Development of a New GANEX Process. *Procedia Chemistry* 7, 0 (2012), 392 – 397. ATALANTE 2012 International Conference on Nuclear Chemistry for Sustainable Fuel Cycles.
- [7] BELLIDO, A.V AND RUBENICH, M.N. Influence of the Diluent on the Radiolytic Degradation of TBP in TBP % (v/v)-diluent-HNO<sub>3</sub> Systems. *Radiochim. Acta* 36 (1984), 61.
- [8] BONILLO, P. Periodic Report Summary 3 Actinide Recycling by Separation and Transmuation (ACSEPT). Tech. Rep. 56207, European Commission: Cordis, CEA, Bat 400, CEA Marcoule, 30207, BAGNOLS-SUR-CEZE CEDEX, France, 2013.
- [9] BOURG, S. Final Project Report Actinide Recycling by Separation and Transmuation (ACSEPT). Tech. Rep. D0.1.14, European Commission, CEA, Bat 400, CEA Marcoule, 30207, BAGNOLS-SUR-CEZE CEDEX, France, 2013.
- [10] BOURG, S., HILL, C., CARAVACA, C., EKBERG, C., AND RHODES, C. Toward the Future Demonstration of Advanced Fuel Treatments. In *Proceedings of GLOBAL 2009, Paris* (2009), GLOBAL 09.
- [11] BROWN, J., CARROTT, M. J., FOX, O. D., MAHER, C. J., MASON, C., MCLACHLAN, F., SARS-FIELD, M. J., TAYLOR, R. J., AND WOODHEAD, D. A. Screening of TODGA/TBP/OK Solvent Mixtures for the Grouped Extraction of Actinides. *IOP Conference Series: Materials Science and Engineering* 9, 1 (2010), 012075.

- [12] BROWN, J., MCLACHLAN, F., SARSFIELD, M., TAYLOR, R., MODOLO, G., AND WILDEN, A. Plutonium Loading of Prospective Grouped Actinide Extraction (GANEX) Solvent Systems based on Diglycolamide Extractants. *Solvent Extraction and Ion Exchange 30*, 2 (2012), 127–141.
- [13] BRYANT, W. M. D., MITCHELL, J., AND SMITH, D. M. Analytical Procedures Employing Karl Fischer Reagent.1 V. The Determination of Water in the Presence of Carbonyl Compounds. *Journal of the American Chemical Society* 62, 12 (1940), 3504–3505.
- [14] CANVA, J. AND PAGES, M. Effets de Protection et de Sensibilisation dans la Decomposition Radiolytique du Phosphate de Tributyle. *Radiochim. Acta 4* (1965), 88.
- [15] CARROT, M. J., GREGSON, C. R., AND TAYLOR, R. J. Neptunium Extraction and Stability in the GANEX Solvent: 0.2 M TODGA/0.5 M DMDOHEMA/Kerosene. *Solvent Extraction and Ion Exchange 31*, 5 (2013), 463–482.
- [16] CARROTT, M., BELL, K., BROWN, J., GEIST, A., GREGSON, C., HERES, X., MAHER, C., MALM-BECK, R., MASON, C., MODOLO, G., MULLICH, U., SARSFIELD, M., WILDEN, A., AND TAYLOR, R. Development of a New Flowsheet for Co-Separating the Transuranic Actinides: The EURO-GANEX Process. *Solvent Extraction and Ion Exchange 32*, 5 (2014), 447–467.
- [17] CARROTT, M., FOX, D., MAHER, C., MODOLO, G., MCLACHLAN, F., SARSFIELD, M., TAYLOR, R., AND WOODHEAD, D. Extraction and Stripping of Actinides in TBP and TODGA/TBP Systems for Advanced Fuel Processing. In *Proceedings of GLOBAL 2009, Paris* (2009), GLOBAL 09.
- [18] CARROTT, M., GEIST, A., HERES, X., LANGE, S., MALMBECK, R., MIGUIRDITCHIAN, M., MOD-OLO, G., WILDEN, A., AND TAYLOR, R. Distribution of Plutonium, Americium and Interfering Fission Products Between Nitric Acid and a Mixed Organic Phase of TODGA and DMDOHEMA in Kerosene, and Implications for the Design of the EURO-GANEX Process. *Hydrometallurgy 152*, 0 (2015), 139 – 148.
- [19] CUNDALL, R. B., AND GRIFFITHS, P. A. Radiation Induced Cis-Trans Isomerization of 2-Butene in Hydrocarbon Solutions. *Discuss. Faraday Soc.* 36 (1963), 111–123.
- [20] DEWHURST, H. A. Radiation Chemistry of Organic Compounds. I. *n*-Alkane Liquids. *The Journal of Physical Chemistry* 61, 11 (1957), 1466–1471.
- [21] GALAN, H., NUNEZ, A., ESPARTERO, A., SEDANO, R., DURANA, A., AND DE MENDOZA, J. Radiolytic Stability of TODGA: Characterization of Degraded Samples Under Different Experimental Conditions. *Procedia Chemistry* 7 (2012), 195–201.
- [22] GAO, W., ROBINSON, R. L. J., AND GASEM, K. A. M. High Pressure Solubilities of Hydrogen, Nitrogen and Carbon Monoxide in Dodecane from 344 to 410K at Pressures to 13.2MPa. *J. Chem. Eng. Data* 44, 1 (1999), 130–132.
- [23] GOMPPER, K. Zur Abtrennung Langlebiger Nuklide. In *Radioakitvitat und Kernenergie, Forschungszentrum Karlsruhe, Karlsruhe* (2001).
- [24] GRANT, I.S. AND PHILLIPS, W.R. *Electromagnetism*, Second Ed. ed. John Wiley and Sons Inc, 1990.

- [25] HERES, X., SOREL, C., MIGUIRDITCHIAN, M., CAMES, B., HILL, C., BISEL, I., ESPINOUX, D., EYSSERIC, C., BARON, P., AND LORRAIN, B. Results of Recent Counter-Current Tests on Am(III)/Ln(III) Separation using TODGA Extractant. In *Proceedings of GLOBAL 2009*, *Paris* (2009), GLOBAL 09.
- [26] HILL, C., MADIC, C., BARON, P., OZAWA, M., AND TANAKA, Y. Americium(III)/Trivalent Lanthanides Separation Using Organothiophosphinic Acids. In *Proceedings of the International Conference on Future Nuclear Systems* (1997), vol. 2, GLOBAL 97, p. 1490.
- [27] HOLLAND, J., MERKLIN, J., AND RAZVI, J. The Radiolysis of Dodecane-Tributylphosphate Solutions. *Nuclear Instruments and Methods* 153, 2 - 3 (1978), 589 – 593.
- [28] JOLY, P AND BOO, E. ROADMAP Actinide Separation Processes 2015, 2015. Published by SACSESS. Grant agreement No. 323282. Authors from LGI Consulting. Available online at https://t.co/atms88Fhs3.
- [29] JR, M. S., WERST, D., JONAH, C., AND TRIFUNAC, A. Primary Events in Hydrocarbon Radiolysis: Real-time Studies of Radical-cation Chemistry. *International Journal of Radiation Applications and Instrumentation. Part C. Radiation Physics and Chemistry* 37, 3 (1991), 461 – 467.
- [30] KATSUMURA, Y., YOSHIDA, Y., TAGAWA, S., AND TABATA, Y. Study on the Excited State of Liquid Alkanes and Energy Transfer Process by Means of Picosecond Pulse Radiolysis . *Radiation Physics and Chemistry (1977) 21*, 1âĂŞ2 (1983), 103 – 111.
- [31] KESSLER, G. *Sustainable and Safe Nuclear Fission Energy*. Springer, 2012, ch. Uranium Enrichment, pp. 59–71.
- [32] KESSLER, G. Sustainable and Safe Nuclear Fission Energy. Springer, 2012.
- [33] KLOTS, C., RAEF, Y., AND JOHNSEN, R. Commentary on Scavenging Plots in Radiation Chemical Studies of Liquid Cyclohexane. *The Journal of Physical Chemistry* 68, 8 (1964), 2040–2043.
- [34] KOLARIK, Z., MULLICK, U., AND GASSNER, F. Selective Extraction of Am(III) over Eu(III) Nitrates by 2,6,ditriazolyl and 2,6-ditriazinyl Piridines. *Solvent Extraction and Ion Exchange 17* (1999).
- [35] KUBOTA, M., MORITA, Y., YAMAGUCHI, I., FUJIWARA, T., WATANABE, M., MIZOGUCHI, K., AND TATSUGAE, R. Development of the Four Group Partitioning Process at JAERI. In Proceeding of the 5th International Information Exchange Meeting (1998), p. 131.
- [36] LAVERNE, J. A., AND WOJNAROVITS, L. Rates of Alkyl Radical-Radical, Alkyl Radical-Iodine, and Iodine Atom-Atom Reactions in Normal Alkanes and Cycloalkanes. *The Journal of Physical Chemistry* 98, 48 (1994), 12635–12640.
- [37] LAVERNE, J.A., PIMBLOTT, S.M., AND WOJNAROVITS, L. Diffusion-Kinetic Modeling of the  $\gamma$ -Radiolysis of Liquid Cycloalkanes. *J. Phys. Chem. A 101* (1997), 1628–1634.
- [38] LIVERHANT, S.E. *Elementary Introduction to Nuclear Reactor Physics*. John Wiley and Sons Inc, 1960.

- [39] LUMETTA, G. J., GELIS, A. V., CARTER, J. C., NIVER, C. M., AND SMOOT, M. R. The Actinide-Lanthanide Separation Concept. *Solvent Extraction and Ion Exchange 32*, 4 (2014), 333– 347.
- [40] MADIC, C. AND HUDSON, M.J. High level Liquid Waste Partitioning by Means of Completely Incinerable Extractants. Tech. rep., EUR, 1998. Report EUR-18038.
- [41] MALMBECK, R., MAGNUSSON, D., AND GLATZ, J.P. Recovery of MA Using a CYME<sub>4</sub>-BTBP Based SANEX Solvent. In *Proceedings of GLOBAL 2009, Paris* (2009), GLOBAL 09.
- [42] MIGUIRDITCHIAN, M., ROUSSEL, H., CHAREYRE, L., BARON, P., ESPINOUX, D., CALOR, J.N., VIALLESOUBRANNE, C., LORRAIN, B., AND MASSON, M. HA Demonstration in the AT-LANTE Facility of the GANEX 2nd Cycle for the Grouped TRU Extraction. In *Proceedings* of GLOBAL 2009, Paris (2009), GLOBAL 09.
- [43] MIGUIRDITCHIAN, M., SOREL, C., CAMES, B., BISEL, I., BARON, P., ESPINOUX, D., CALOR, J.N., VIALLESOUBRANNE, C., LORRAIN, B., AND MASSON, M. HA Demonstration in the ATLANTE Facility of the GANEX 1st Cycle for the Selective Extraction of Uranium from HLW. In *Proceedings of GLOBAL 2009, Paris* (2009), GLOBAL 09.
- [44] MODOLO, G., AND ODOJ, R. Synergistic Selective Extraction of Actinides(III) over Lanthanides from Nitric Acid Using New Aromatic Diorganyldithiophosphinic Acides and Neutral Organophosphorus Compounds. *Solvent Extraction and Ion Exchange 17*, 1 (1999), 33–53.
- [45] MODOLO, G., KLUXEN, P., AND GEIST, A. Selective Separation of Americium III from Curium III, Californium III and Lanthanides III by the LUCA Process. In *Proceedings* of GLOBAL 2009, Paris (2009), GLOBAL 09.
- [46] MORITA, Y., SASAKI, Y., ASAKURA, T., KITATSUJI, Y., SUGO, Y., AND KIMURA, T. Development of a New Extractant and a New Extraction Process for Minor Actinide Separation. *IOP Conference Series: Materials Science and Engineering* 9, 1 (2010), 012057.
- [47] MORITA, Y., FUJIWARA, T., SHIRAHASHI, K., WATANABE, M., TATSUGAE, R., AND KUBOTA, M. Diisodecylphosphoric Acid, DIDPA, as an Extractant for Transuranium Elements. In *International Conference on Evaluation of Emerging Nuclear Fuel Cycle Systems (GLOBAL* 95) (1995), vol. 2, GLOBAL 95, p. 1163.
- [48] MORITA, Y., KUBOTA, M., AND SHIN, Y.J. Radiolysis of Diisodecyl Phosphoric Acid and its Effect on the Extraction of Neptunium. *Solvent Extraction and Ion Exchange* 8, 4-5 (1990), 529.
- [49] MUSIKAS, C. Potentiality of Nonorganophosphorus Extractants in Chemical Separation of Actinides. *Separation Science and Technology 23*, 12-13 (1988), 1211.
- [50] NAVE, S., MODOL, G., MADIC, C., AND TESTARD, F. Aggregation Properties of N,N,N',N'-Tetraoctyl-3-oxapentanediamide (TODGA) in n-Dodecane. *Solvent Extraction and Ion exchange 22*, 4 (2004), 527–551.
- [51] NUCLEAR DECOMMISIONING AUTHORITY. 2013 UK Radioactive Waste Inventory Radioactive Waste Composition. Tech. rep., Nuclear Decommisioning Authority, Herdus House, Westlakes Science and Technology Park, Cumbria, CA24 3HU, February 2014.
- [52] NUCLEAR DECOMMISIONING AUTHORITY. 2013 UK Radioactive Waste Inventory Radioactivity Content of Wastes. Tech. rep., Nuclear Decommisioning Authority, Herdus House, Westlakes Science and Technology Park, Cumbria, CA24 3HU, February 2014.
- [53] NUCLEAR DECOMMISIONING AUTHORITY. 2013 UK Radioactive Waste Inventory Waste Quantities from All Sources. Tech. rep., Nuclear Decommisioning Authority, Herdus House, Westlakes Science and Technology Park, Cumbria, CA24 3HU, February 2014.
- [54] OSSOLA, A., MACERATA, E., TINONIN, D. A., FAROLDI, F., GIOLA, M., MARIANO, M., AND CASNATI, A. Radiolytic Degradation of a New Diglycol-Diamide Ligand for Actinide and Lanthanide Co-Extraction from Spent Nuclear Fuel. *Radiation Physics and Chemistry* 124 (2016), 246–251.
- [55] POINSSOT, CH., WARIN, D., AND ROSTAING, C. Recent Progress in Advanced Actinide Recycling Processes. In *International Conference on Fast Reactor and Related Fuel Cycle, Kyoto* (2009).
- [56] RADCAL CORPORATION. 10X6-0.18 Specification, July 2016. Accessed 14/07/2016. Available at http://www.radcal.com/10x6-0-18.
- [57] RAPPOPORT, S., AND GAUMANN, T. Radiolyse des Hydrocarbures. 21e Communication. Mecanismes Radicalaires et Non-Radicalaires dans les *n*-Alcanes en Phase Liquide. *Helvetica Chimica Acta* 56, 8 (1973), 2861–2879.
- [58] RAVI, J., VENKATESAN, K., ANTONY, M., SRINIVASAN, T., AND VASUDEVA RAO, P. Feasibility of Using Di-dodecyl-di-octyl Diglycolamide for Partioning of Minor Actinides from Fast Reactor High-Level Waste. *Solvent Extraction and Ion Exchange 32* (2014), 424–436.
- [59] ROLS, J.L., CONDORET, J.S., FONADE, C., AND GOMA, G. Mechanism of enhanced oxygen transfer in fermentation using emulsified oxygen-vectors. *Biotechnology and Bioengineering* 35, 4 (1990), 427–435.
- [60] SASAKI, Y., SUGO, Y., SUZUKI, S., AND TACHIMORI, S. The Novel Extractants, Diglycolamides, for the Extraction of Lanthanides and Actinides in HNO<sub>3</sub>-*n*-Dodecane. *Solvent Extraction and Ion Exchange 19*, 1 (2001), 91–103.
- [61] SCHULZ, W.W. AND HORWITZ, E.P. The TRUEX Process and the Management of Liquid TRU-waste. *Separation Science and Technology 23* (1988), 1355–1372.
- [62] SHARMA, J., RUHELA, R., SINGH, K., JUMAR, M., JANARDHANAN, C., ACHUTAN, P., MONAO-HAR, S., WATTAL, P., AND SURI, A. Studies on Hydrolysis and Radiolysis of Tetra(2thylhecyl)diglycolamide (TEHDGA)/Isodecyl Alcohol/*n*-Dodecane Solvent System. *Rachiochim. Acta.* 98 (2010), 485–491.
- [63] SHKROB, I. A., AND TRIFUNAC, A. D. Pulse Radiolysis of Alkanes: a Time-Resolved EPR Study - Part I. Alkyl Radicals. *Radiation Physics and Chemistry* 46, 1 (1995), 83 – 96.

- [64] SPOTHEIM-MAURIZOT, M., MOSTAFAVI, M., DOUKI, T., AND BELLONI, J., Eds. Radiation Chemistry: From Basics to Applications in Material and Life Sciences. EDP Sciences, Les Ulis Cedex A, France, 2008.
- [65] SUGO, Y., IZUMI, Y., YOSHIDA, Y., NISHIJIMA, S., SASAKI, Y., KIMURA, T., SEKINE, T., AND KUDO, H. Influence of Diluent on Radiolysis of Amides in Organic Solution. *Radiation Physics and Chemistry* 76, 5 (2007), 794 – 800.
- [66] SUGO, Y., SASAKI, Y., AND TACHIMORI, S. Studies on Hydrolysis and Radiolysis of N,N,N ',N'-Tetraoctyl-3-Oxapentane-1,5-Diamide. *Radiochimica Acta* 90, 3 (2002), 161–165.
- [67] SUGO, Y., TAGUCHI, M., SASAKI, Y., HIROTA, K., AND KIMURA, T. Radiolysis Study of Actinide Complexing Agent by Irradiation with Helium Ion Beam. *Radiation Physics and Chemistry 78*, 12 (2009), 1140 – 1144.
- [68] SUZUKI, H., NAGANAWA, H., AND TACHIMORI, S. Role of Hydrophobic Counteranions in the Ion Pair Extraction of Lanthanides(III) with an Electrically Neutral Extractant. *Phys. Chem. Chem. Phys.* 5 (2003), 726–733.
- [69] TACHIMORI, S., SASAKI, Y., AND SUZUKI, S. Modification of TODGA-*n*-Dodecane Solvent with a Monoamide for High Loading of Lanthanides(III) and Actinides(III). *Solvent Extraction and Ion Exchange 20*, 6 (2002), 687–699.
- [70] TASHIRO, Y., KODAMA, R., SUGAI, H., SUZUKI, K., AND MATSUOKA, S. Nonphosphate Degradation Products of Tributyl Phosphate and their Reactivities in PUREX Media under Extreme Conditions. *Nuclear Technology 129*, 1 (JAN 2000), 93–100.
- [71] TAYLOR, R., CARROTT, M., GALAN, H., GEIST, A., HERES, X., MAHER, C., MASON, C., MALM-BECK, R., MIGUIRDITCHIAN, M., MODOLO, G., RHODES, C., SARSFIELD, M., AND WILDEN, A. The EURO-GANEX Process: Current Status of Flowsheet Development and Process Safety Studies . *Procedia Chemistry 21* (2016), 524 529. ATALANTE 2016 International Conference on Nuclear Chemistry for Sustainable Fuel Cycles.
- [72] THIOLLET, G. AND MUSIKAS, C. Synthesis and Uses of the Amides Extractants. *Solvent Extraction and Ion Exchange* 7, 5 (1989), 813.
- [73] USUDA, S., YAMANISHI, K., MIMURA, H., SASAKI, Y., KIRISHIMA, A., SATO, N., AND NIIBORI,
  Y. Separation of Am and Cm by Using TODGA and DOODA(C8) Adsorbents with Hydrophilic Ligand-Nitric Acid Solution. *Journal of Radioanalytical and Nuclear Chemistry* 303, 2 (2015), 1351–1355.
- [74] VITORGE, P. Lanthanides and Trivalent Actinides Complexation by Tripyridyl Triazine. Application to Liquid-Liquid-Extraction. Tech. rep., CEA, 1984. CEA-R-5270.
- [75] WARIN, D. Future Nuclear Fuel Cycles: Prospect and Challenges for Actinide Recycling. IOP Conference Series: Materials Science and Engineering 9, 1 (2010), 012063.
- [76] WARIN, D. Minor Actinide Partitioning. In *1st ACSEPT International Workshop, Lisbon* (2010), ACSEPT.

- [77] WARIN, D., POINSSOT, CH., AND MARTY, P. The CEA ATALANTE Facility: A Laboratory for Fuel Cycle R&D. In *Proceedings of GLOBAL 2009, Paris* (2009), GLOBAL 09.
- [78] WERST, D., AND TRIFUNAC, A. Early Events Following Radiolytic and Photogeneration of Radical Cations in Hydrocarbons. *"Radiation Physics and Chemistry 41*, 1 - 2 (1993), 127 – 133.
- [79] WILDEN, A., SCHREINEMACHERS, C., SYPULA, M., AND MODOLO, G. Direct Selective Extraction of Actinides (III) from PUREX Raffinate using a Mixture of CyMe<sub>4</sub>BTBP and TODGA as 1-cycle SANEX Solvent. *Solvent Extraction and Ion Exchange 29*, 2 (2011), 190–212.
- [80] WILDEN, A. AND MODOLO, G. AND SYPULA, M. AND GEIST, A AND MAGNUSSON, D. The Recovery of An(III) in an Innovative-Sanex Process using a TODGA-based Solvent and Selective Stripping with a Hydrophilic BTP. *Procedia Chemistry* 7, 0 (2012), 418 – 424. ATALANTE 2012 International Conference on Nuclear Chemistry for Sustainable Fuel Cycles.
- [81] WILDEN, A. AND SYPULA, M. AND SCHREINEMACHERS, C. AND KLUXEN, P. AMD MODOLO, G. 1-cycle SANEX Process Development Studies Performed at Forschungszentrum Julich. In 1st ACSEPT International Workshop, Lisbon (2010), ACSEPT.
- [82] WORLD NUCLEAR ASSOCIATION. Chernobyl Accident 1986, November. Accessed 15/03/2017.
- [83] WORLD NUCLEAR ASSOCIATION. Fukushima Accident. Webpage, January 2017. [Online: Accessed 2-February-2017].
- [84] WRIGHT, A., AND PAVIET-HARTMANN, P. Review of Physical and Chemical Properties of Tributyl Phosphate/Diluent/Nitric Acid Systems. *Separation Science and Technology* 45, 12-13 (2010), 1753–1762.
- [85] YAKABUSKIE, P., JOSEPH, J., AND WREN, J. The Effect of Interfacial Mass Transfer on Steady-State Water Radiolysis. *Radiation Physics and Chemistry* 79, 7 (July 2010), 777–785.
- [86] YANG, J., KONDOH, T., NORIZAWA, K., NAGAISHI, R., TAGUCHI, M., TAKAHASHI, K., KATOH, R., ANISHCHIK, S. V., YOSHIDA, Y., AND TAGAWA, S. Picosecond Pulse radiolysis: Dynamics of Solvated Electrons in Ionic Liquid and Geminate Ion Recombination in Liquid Alkanes. *Radiation Physics and Chemistry* 77, 10-12 (2008), 1233 – 1238. The International Symposium on Charged Particle and Photon Interaction with Matter - ASR 2007.
- [87] ZARZANA, C. A., GROENEWOLD, G. S., MINCHER, B. J., MEZYK, S. P., WILDEN, A., SCHMIDT, H., MODOLO, G., WISHART, J. F., AND COOK, A. R. A Comparison of the γ-Radiolysis of TODGA and T(EH)DGA Using UHPLC-ESI-MS Analysis. *Solvent Extraction and Ion Exchange 33*, 5 (2015), 431–447.
- [88] ZHANG, T., LEE, Y. J., KEE, T. W., AND BARBARA, P. F. The Mechanism of Electron-Cation Geminate Recombination in Liquid Isooctane . *Chemical Physics Letters* 403, 4-6 (2005), 257 – 261.

- [89] ZHU, Y., SONG, C., XU, J., YANG, D., LIU, B., AND CHEN, J. The Removal of Actinides from High Level Radioactive Waste by TRPO Extraction. The Extraction of Americium and Some Lanthanides. *Chinese Journal of Nuclear Science and Engineering* 9 (1989), 141–150.
- [90] ZHU, Y., WANG, S., XU, C., WANG, X., AND FENG, X. The Separation of Americium from Light Lanthanides by CYANEX 301 Extraction. *Raciochimica Acta* 68 (1995), 95–98.