# ON THE RADIOLYSIS OF ADAMANTANE

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Bromine scavenging experiments, and comparative radiolysis of adamantane and adamantane derivatives, indicate that adamantane forms the 1-adamantyl radical as the predominant species following  $\gamma$ -radiolysis.

### 1. Introduction

The use of adamantane as an isolation matrix is now well established, but there is considerable controversy in the recent literature as to the nature of the majority species produced when purified adamantane is subjected to radiolysis itself [1-8]. The report by Krusic and co-workers [9] yields hyperfine coupling constants for an authentic 1-adamantyl radical produced in solution by photochemical generation and provides a basis for comparison with radiolysis experiments. The most recent report from Filby and Günther [6, 10] indicates that a 1-adamantyl radical is formed, although Marx [7] has pointed out that their reported couplings do not agree with the constants found by Krusic et al. [9]. In opposition to this assignment, Lloyd and Rogers [8] propose that the 2-adamantyl radical is formed, on the basis of data taken from double-resonance ENDOR techniques. As an alternate suggestion to both of these, Bonnazola and Marx [2] propose the formation of a radical via C-C bond cleavage, leading to a substituted cyclohexenyl radical. In view of this controversy, we decided to apply some of the techniques associated with classical radiation chemistry investigations in an attempt to clarify the situation.

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#### 2. Experimental

Adamantane, supplied commercially from various sources, was recrystallized from cyclohexane to remove all possible alien solutes introduced by its synthesis<sup>‡</sup>, dissolved in freshly distilled cyclo-hexane solvent (saturated solution at just above room temperature), and this solution subjected to preparative gas chromatography. The adamantane fraction was redissolved in the cyclohexane fraction, and re-chromatographed. Samples of 1-chloro- and 2-chloro-adamantane, 1-bromo and 2-bromo-adamantane, purchased from commercial sources, were recrystallized from methylcyclohexane prior to use.

Standard vacuum-line techniques were used to prepare samples for radiolysis, and to prepare scavenger solutions at the requisite concentrations. Samples were irradiated (Co-60 source, dose-rate as determined by Fricke dosimetry was ca.  $3 \times 10^{16}$  eV g<sup>-1</sup>, doses of ca.  $10^{18}$  eV g<sup>-1</sup>) both in vacuo and exposed to air, no qualitative differences were seen<sup>†</sup>. Samples irradiated in air were held in a stoppered pyrex vial, and then transferred to an ESR tube after the end of the irradiation period, thus eliminating any possible introduction of colour centres into the quartz envelope of the cell.

\* See footnote in Can. J. Chem. 50 (1972) 3982, for explanation of this procedure.
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Work in progress on radiolysis processes of adamantane, and solutes held in adamantane, while under controlled atmospheres of various gases both before and after radiolysis, will be reported at a later date.

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For samples in vacuo, the cell was inverted and radiolysis carried out of the solid samples at the "pyrex" end of the ESR cell, thus minimizing the introduction of colour centres into the quartz portion of the cell used for ESR monitoring. The ratio of cell signal to sample signal by this method was at least  $10^{-2}$ ; and evacuated ESR cells were used as blank control samples for comparison.

Scavenging experiments were carried out by forming a cell from a "break-seal" device. Into the lower part of the cell was placed approximately 5 ml of a solution of Br<sub>2</sub> in cyclohexane (various concentrations between 1 and 10 mole % were used), this was degassed and sealed off under a vacuum of less than  $10^{-3}$  torr. Into the top half of the cell was placed approximately 300 mg of adamantane, the solid was then degassed and sealed off under vacuum. The top half of this cell was irradiated at room temperature to doses up to 10<sup>19</sup> eV g<sup>-1</sup> although the majority of experiments were performed with doses ca. 1018 eV g<sup>-1</sup>. After the termination of irradiation, the break-seal was punctured, and the adamantane solid allowed to fall into the Br2 scavenger solution, a sample was then extracted and subjected to gas chromatographic analysis (f.i.d.,  $12' \times 1/8''$ i.d. glass column, 5% w/w di-isodecylphthalate on 100-120 mesh chromosorb G at ca. 60°C). Control experiments, where un-irradiated adamantane was added to Br<sub>2</sub>/cyclohexane solutions under identical conditions, disclosed no formation of bromo-adamantanes; bromo-adamantanes produced by radiolysis were identified on the GLC chromatogram by authentic samples purchased from commercial sources, and checked by standard chemical analyses (NMR and IR).

Computer simulations were made via a Fortran IVG program [11] written for an IBM-360/75 Computer and CalComp accessory. ESR spectra were obtained via a Varian E 3 spectrometer, variable temperature accessory and/or quartz dewar sample holder.

3. Results and discussion

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Adamantane samples subjected to radiolysis at room temperature in the solid (polycrystalline) state produce a single, wide, typically "solid state" unresolved ESR signal, with a peak-to-peak separation for the first deriv-

ative of approximately 11-12G, and an overall spectrum width of approximately 50G (Filby and Günther [4] report a spectrum width of 49G), see fig.1A. On radiolysis, and monitoring, at 77°K the ESR spectrum reveals more fine structure (see fig.2A) which can be reasonably represented by a computer simulation using coupling constants from Krusic et al. [9] and a linewidth (first derivative peak-to-peak) of ca. 1.4G (see fig.2B). At linewidths greater than ca. 2.2G, a single featureless peak results from simulations, closely resembling the room temperature spectrum observed experimentally. Further, as reported by Filby et al., no qualitative differences were observed between samples irradiated at 77°K and monitored from 77°K up to room temperatures, and samples irradiated and monitored at room temperatures. Equally, unlike Ferrell et al. [3] but in agreement with Filby et al., our ESR signals were stable at room temperature for several hours, and in decaying did not appear to produce any secondary ESR signal.

The occurrence of dissociative electron attachment reactions by halogen and pseudo-halogen derivatives of non-aromatic hydrocarbons when subjected to radiolysis is well established and we decided to utilize this behavioral pattern and attempt to produce authentic 1-adamantyl and 2-adamantyl radicals from chloro-adamantanes. Accordingly, commercially supplied samples of 1-chloro- and 2-chloro-adamantane were checked for authenticity, and subjected to radiolysis as solid polycrystalline samples under vacuum at temperatures between 77° and 300°K. Ill-resolved, but very characteristic ESR signals were produced from each sample (see figs. 1B and 1C), with a featureless "one-hump" spectrum being obtained from 1-chloro-adamantane, and an equally featureless, but basically "two-hump", spectrum resulting from the 2-chloro-derivative. This is typically the behaviour expected from dissociative electron attachment reactions in both systems; a strong  $\alpha$ -carbon proton coupling producing the characteristic doublet splitting observed in the 2-derivative and probable 2-adamantyl radical, and a broad singlet structure from the expected 1-adamantyl radical derived from the 1-chloro-derivative. Identical results were obtained from radiolysis of commercially supplied, and subsequently authenticated, 1-bromo- and 2-bromo-adamantane samples, and supporting behaviour from oth-

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Fig.1. Room temperature first derivative ESR spectra of  $\gamma$ -irradiated polycrystalline adamantane, 1-chloro-adamantane, and 2-chloro-adamantane.



Fig.2. First derivative ESR spectrum of polycrystalline adamantane taken at 77°K after  $\gamma$  irradiation at 77°K. (a) Experimental spectrum, (b) computer simulation of spectrum using the values reported by Krusic et al. [9] and a linewidth of 1.48G.



Fig.3. GLC chromatogram showing formation of 1-bromo, and 2-bromo-adamantane following  $\gamma$ -radiolysis of adamantane and Br<sub>2</sub> scavenging.

er derivatives<sup>\*\*</sup>. Using arbitrarily selected values for possible coupling constants in 2-adamantyl by analogy with those reported by Krusic et al. [9] for 1-adamantyl, and from general radiation chemistry reports of cage-type molecules [12] (15-20 G for one  $\alpha$ -proton, 6-7 G for two equivalent  $\beta$ -protons, 4--5 G for four of the  $\gamma$ -protons, and ca. 1-2 G for the other 4  $\gamma$ -protons), computer simulations using 0.5 to 2.0 G peak-to-peak linewidths show a gradual degradation into a "two-hump" spectrum closely resembling that obtained from radiolysis of 2-bromo-adamantane at room temperature.

A further established technique in radiation chemistry is the use of halogen scavengers to determine radical identities produced by radiolysis, and although iodine is the preferred scavenger for a variety of reasons, the readily available 1-bromo- and 2-bromo-adamantane derivatives suggested that a Br<sub>2</sub> scavenging experiment be tried. A purified sample of adamantane was  $\gamma$ -irradiated at room temperature under vacuum, and then added to a Br<sub>2</sub>/cyclohexane scavenger system (still un-

\*\* A complete account of radiolyses of several adamantane derivatives (-OH, -NH<sub>2</sub>, -CN), diamantane samples, spin-trapping of radicals derived from adamantane, diamantane, perdeuterated adamantane, and adamantane derivatives, together with radiolyses and photolyses of glassy-matrix isolated adamantane derivatives, is currently being prepared for submission.

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der vacuum) at room temperature. A small sample, ca.  $0.3\lambda$ , was analyzed by GLC and a typical chromatogram is displayed in fig.3. This shows clearly the formation of both 1-bromo- and 2-bromo-adamantane, with relative yields in the ratio of ca. 3:1. This may be a direct indication of initial yields, or it may reflect merely the established stability of the 1-adamantyl radical in solution relative to the 2-adamantyl radical [13, 14], and thus relative scavenging efficiencies. However, the data from Br<sub>2</sub> scavenging experiments, together with the rather more inferential data from the low temperature radiolyses and computer simulations, and the comparative radiolyses of adamantane and adamantane derivatives, seem to indicate that the predominant species formed is the 1-adamantyl radical. One final point, more detailed Br<sub>2</sub> scavenging experiments\*\* seem to indicate that the relative ratio of 1adamantyl to 2-adamantyl radical varies with absorbed dose, and this may perhaps be the explanation for the controversy concerning the identity of the species produced.

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