Radical Formation and Radiation Damage in Adamantane

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Unequivocal samples of the 1-adamantyl (1-Ad) and 2-Ad radicals have been prepared in a matrix of adamantane (Ad) by the simultaneous deposition of atomic sodium, 1- and 2-bromoadamantane, and adamantane at 77 K. The EPR spectrum of the 1-Ad radical contrary to previous reports has a clearly resolved hyperfine structure that can be analyzed in terms of the solution parameters of Krusic et al., and the spectrum of the 2-Ad radical is identical with that previously reported by Ferrell et al. It is also shown that conditions of purification and irradiation can greatly affect the spectra obtained upon x irradiation of Ad itself. Depending upon conditions, allylic radicals that are primary products of ring-opening reactions or benzyl-type radicals that are probably secondary reaction products can also be obtained in addition to 1-Ad and 2-Ad radicals.

Introduction

The use of adamantane (Ad) as a matrix for the production and stabilization of free radicals generated from deliberately introduced impurities by the action of ionizing radiation has become widely accepted. Recent observations of hydrogen atom addition to, or abstraction from, aromatic systems (as desired) has added to its usefulness for EPR studies. The advantages of adamantane as a matrix for optical studies have also been discussed. However, the products from the X irradiation of pure adamantane have resisted unambiguous assignment. One of the major obstacles has been its greatest virtue, the ability to trap organic impurities and transfer the radiation damage to them, which makes it extremely difficult to study a pure sample. This ability has often been unrecognized by many workers and has therefore led to considerable confusion in attempts to identify the radical products of the irradiation of adamantane itself. A second obstacle to the understanding of radical formation processes in Ad has been the failure to realize that the details of the sample preparation can influence the nature of the radicals obtained. For example, when Ad is recrystallized from toluene, either the benzyl radical (hydrogen abstraction) or the methycyclohexadienyl radical (hydrogen addition) may be obtained depending upon sample preparation. The following is a summary of our present level of understanding of the Ad matrix technique and of the formation of radicals from adamantane itself.

Bowers et al. reported a spectrum that was attributed to the adamantane anion radical obtained by the reduction of Ad by Na-K alloy in THF-DME. That spectrum was shown in fact to be the benzene anion radical generated from benzene present in the Ad as an impurity. Assignments of radicals to spectra obtained by the action of ionizing radiation on solid Ad have been much more confusing. Gee et al. first observed EPR spectra from Ad that was purified by vacuum sublimation and X-irradiated at 77 K, and they analyzed the 77 K spectrum in terms of a mixture of the 1- and 2-Ad radicals. Bonazzola and Marx obtained similar spectra but, on the basis of the observed temperature dependence between 81 and 233 K, postulated a radical formed by ring opening of the Ad molecule. They stated that there was no evidence for the formation of the 1- and 2-Ad radicals.

Filly and Gunther took great care in purifying their Ad and in analyzing impurity levels. The procedure consisted of double recrystallization with activated carbon in hexane (<1% impurities), vacuum sublimation (~0.05% impurities), and finally recrystallization (<0.01% impurities). Electron and γ irradiation of the final material at 77 K did not give any analyzable spectra, but they did assign the spectrum observed following room-temperature irradiation to the 1-Ad radical. However, Marx pointed out that their hyperfine splitting (hfs) did not agree with the parameters reported by Krusic et al., who unambiguously generated the 1-Ad radical by photolytic decomposition of the peroxy ester in cyclopropane at 120 K.

Ferrell et al. published an EPR spectrum of X-irradiated Ad, which consisted of a broad line (width = 22.5 G) with a partially resolved triplet of ~5 G. The spectrum was stable to 280 K and was attributed to the 2-Ad radical. In an ENDOR experiment on the same radical, Lloyd and Rogers reported an accurate measurement of the small triplet splitting as 3.35 G. On the basis of an INDO calculation and geometric consideration, this was attributed to the two equivalent δ bridgehead protons in the 2-Ad radical.

More recently Hyfantis and Ling X-irradiated Ad itself and 1- and 2-substituted adamantane derivatives, both neat and doped into Ad. They attributed the spectra to the 1- and 2-Ad radicals stable at room temperature, contrary to the results of Ferrell et al. The spectrum of the 1-Ad radical was a single line of ~50-G peak-to-peak width (first derivative presentation) and without resolvable hfs. Further radical scavenging experiments revealed a 3:1 yield of 1-Ad to 2-Ad radicals from the X irradiation of neat Ad.

Dismukes and Willard made careful studies of the effects of microwave power and of annealing time at 77 K on the EPR spectra of γ-irradiated Ad. They obtained evidence for the formation of the 2-Ad radical that was in agreement with the observations of Ferrell et al. However, their evidence for the formation of the 1-Ad radical does not seem to be consistent with the spectrum of this radical in solution.

In view of the confusing and inconsistent results discussed above, we have prepared unambiguous samples of...
the 1-Ad and 2-Ad radicals in Ad by the simultaneous deposition of atomic sodium with the 1- or 2-bromo-adamantanes, thus making the radicals without X irradiation. The spectra obtained will be compared with those from X irradiation of purified Ad and of Ad doped with hydrogen atom traps such as p-benzoquinone (PBQ) and tetrafluoro-p-benzoquinone (TFPBQ).

**Experimental Section**

Adamantane (Aldrich Gold Label 99+%) X-irradiated as received gives a variety of EPR signals, which change as the Ad is purified and are therefore not directly attributable to the Ad. Of the various available methods of purification, namely, vacuum sublimation, zone refining, and recrystallization, the first two will not give satisfactory results if used alone. However, recrystallization from straight-chain hydrocarbons (C₆-C₆) following treatment with activated carbon will remove the bulk of impurities, and the other methods will then be effective for removal of the trace amounts left. Cyclohexane is not as useful a solvent for recrystallization because Ad so treated exhibits undesirable in optical studies.

Recrystallizations were performed in the following hydrocarbons: n-pentane (Baker spectra grade), n-hexane, n-nonane (Phillips pure grade), n-heptane (Baker analyzed reagent), and n-octane. The bigger hydrocarbons were chosen because of the size limitations of the matrix, so that there would be less occlusion of solvent. Ad recrystallized from technical grade n-heptane (Mallinckrodt) after activated-carbon treatment appears to selectively occlude the branched heptanes present in low concentrations, as deduced from the EPR signal observed after X irradiation. Some of the Ad purified by recrystallization was further zone refined in a thick-wall 10-mm i.d. Pyrex tubing until used. Sodium (Mallinckrodt) was fractionated, as deduced from the EPR signal observed after activation with a KBr press) to a maximum pressure of -150000 psi. The die could be evacuated to remove oxygen if desired. Two die were used for recrystallization and zone refining.

**Sample preparation for X irradiation** consisted of pressing Ad in a 1/3 in. i.d. X 1.5 in. long die (similar to a KBr press) to a maximum pressure of ~150000 psi. The die could be evacuated to remove oxygen if desired.

The 1- and 2-bromoadamantanes (Aldrich) were vacuum sublimed, and the individual sublimates were mixed with Ad in a 5:1 v/v Ad:BrAd ratio and then kept sealed under vacuum until used. Sodium (Mallinckrodt) was fractionally distilled under vacuum until a bright mirror with blue fringes was obtained. The Ad/BrAd and sodium were simultaneously deposited onto a 77 K surface, the sodium being heated to ~500 K to give it the required vapor pressure, by means of a vacuum deposition apparatus that has been described previously. It was necessary to dilute the BrAd with Ad because depositions of BrAd with sodium alone gave a sample that would not scrape into the sample tube easily but adhered to all glass surfaces, possibly because of static attraction generated by the NaBr in the more polarizable BrAd.

TFPBQ (Aldrich) was purified by vacuum sublimation, mixed with Ad in a Pyrex tube, and sealed under vacuum. They were conublimed by heating one end of the tube to 140 °C in an oil bath. The tube was then broken, and the solid solution obtained was pressed to 150000 psi in the evacuated die (0.01 mmHg) with continuous pumping for ~10 min. This method gave a yellow translucent pellet. The same procedure was used with PBQ (Aldrich).

**Results**

1-Adamantyl Radical. Figure 1, A and B, shows the EPR spectrum obtained from the sample prepared by the simultaneous deposition of 1-BrAd, Ad, and Na; (B) the same spectrum at 190 K and higher gain; (C) computer simulation based on the parameters of Table I and a mixture of 95% 1-Ad radical and 5% 2-Ad radical; (D) the same with 85% 1-Ad and 15% 2-Ad; (E) the same with 75% 1-Ad and 25% 2-Ad.
Radical Formation in Adamantane


Figure 2. EPR spectrum at 77 K of the sample prepared by the simultaneous deposition of 2-BrAd, Ad, and Na (top), with a computer simulation based on the parameters of Table I (bottom).

Figure 3. (A) EPR spectrum of Ad X-irradiated at 77 K and recorded at 225 K; (B) computer simulation of spectrum A based on the parameters of Table I.

Figure 4. (A) EPR spectrum of Ad X-irradiated at 77 K and recorded at 230 K, showing the strong center line; (B) recorded at 300 K; (C) spectrum of Ad doped with TFPBQ X-irradiated and recorded at 300 K; (D) computer simulation of spectrum C based on the parameters of Table I.

Computer simulations (Figure 1, C-E) based on the parameters of Table I show the effect of increasing fractions of the 2-Ad radical in the spectrum. The best fit to the experimental spectrum was obtained with a mixture of 95% 1-Ad and 5% 2-Ad radicals (Figure 1C).

The introduction of oxygen into the system had no observable effect until a temperature of 195 K was reached. At this temperature a signal consisting of a single line of ~5 G width and a g value characteristic of peroxy radicals was observed. We attribute this to the 1-peroxyadamantyl radical.

2-Adamantyl Radical. The spectrum obtained when 2-BrAd and Ad are codeposited with sodium is shown in Figure 2, along with a computer simulation based on the parameters of Table I. As with the 1-adamantyl radical, there was an abrupt decrease of signal intensity when the PTT was reached. Again, introduction of oxygen had no effect until 200 K was reached, when the formation of the 2-peroxyadamantyl radical was observed. It can be distinguished from the 1-peroxyadamantyl radical because it exhibits a hfs from the a-proton of ~5 G.

X Irradiation of Adamantane. When recrystallized or recrystallized and zone-refined Ad is X-irradiated at 77 K and the EPR spectra are monitored as a function of temperature, a series of radicals is observed as shown in Figures 3-4. The first spectrum to be seen as the temperature is raised exhibits reversible temperature-dependent line-width alternation, and above the PTT it reveals a more detailed hyperfine structure in the limiting high-temperature form (Figure 3, top). The spectrum and its temperature dependence are similar to that reported by Bonazzola and Marx, and the radical responsible for it will be referred to herein as B and M. The EPR parameters are listed in Table I an the computer simulation
As the temperature is raised further to 230 K, the 1-Ad has almost completely disappeared and a broad center line takes its place (Figure 4A). Finally, at 300 K another additional spectrum appears (Figure 4B). The latter spectrum is identical with that produced when Ad doped with TFPBQ is X-irradiated (see below), but with the addition of a center of line width 80% of the total intensity.

When Ad was doped with TFPBQ or PBQ and X-irradiated at 300 K, the spectra obtained could not be assigned to the specifically introduced impurity and were identical for the two compounds. The spectrum is shown in Figure 4C, and its computer simulation in 4D. These parameters were also reported by Filby and Gunther (radicals F and G), and we agree with them that it is stable to high temperatures (~400 K). We did not observe any appreciable intensity of the B and M or 1-Ad radicals when the TFPBQ was present.

Discussion

The results presented here conflict with most previous studies of radiation damage to Ad. It should be apparent that the analysis of radiation-damage products can easily be erroneous if the variety of radicals that can be produced simultaneously and the nature of the matrix are not properly considered. It appears that the only radical to have been correctly assigned is the 2-adamantyl radical. Even the 1-adamantyl radical has not previously been correctly identified in Ad, even though its hfs parameters are known from the accurate solution results of Krusic et al.

Adamantyl Radicals. Although we find that the 1- and 2-adamantyl radicals generated from the BrAd disappear at the PTT of Ad and that these radicals formed in neat Ad are stable to ~230 K, other investigators have postulated their existence at 300-400 K. Also, contrary to both the now-well-established ability of Ad to give well-resolved isotropic spectra of freely rotating radicals and the NMR evidence that the individual Ad molecules in crystalline Ad have considerable rotational freedom, the 1-Ad radical in Ad has been said to give a single broad line at 300 K with no resolved hfs. Furthermore, the radical-scavenging experiments that were carried out by dissolving X-irradiated Ad at 300 K in bromine-saturated cyclohexane to yield a 5:1 ratio of 1-BrAd to 2-BrAd, and were thought to demonstrate the existence of the 1- and 2-Ad radicals, are not in fact definitive. Any radical present in the Ad at 300 K can lead to the observed results, as shown by the following mechanism:

R- + Br2 → RBr + Br-
Br- + Ad → HBr + 1-Ad + 2-Ad-
1-Ad (2-Ad) + Br2 → BrAd + Br-

Thus, the 1- and 2-Ad radicals need only have a transient existence. The 3:1 ratio of products has been observed previously for free-radical halogenation of Ad and has also been found to be highly solvent dependent.

As can be seen in Figure 1A, the hyperfine structure of the 1-Ad radical is in fact readily resolvable, and the spectrum is simulated with the same parameters that were found for the radical in solution (Table I). However, if the yield of 2-Ad radicals, formed either as direct irradiation products or as secondary products of hydrogen abstraction by 1-Ad radicals from neighboring Ad molecules, is as low as 25% of the total radical intensity (Figure 1E), there is very little chance of establishing the existence of the 1-Ad radical. In fact, even 15% of 2-Ad (Figure 1D) dominates the appearance of the spectrum.

Other Radicals in Adamantane. In addition to the spectra of the 1-Ad and 2-Ad radicals, whose interpretation is relatively straightforward, we have observed spectra from several other radicals that cannot be dismissed as simply belonging to impurities in the Ad. The radical formed in low yield by 77 K X irradiation of Ad has a spectrum qualitatively similar to those reported by Bonazzola and Marx and also by Gee et al. The simulation of Figure 3D is based, however, on only a 3% yield of the radical relative to the 1-Ad radical. The spectrum exhibits line-width alternation similar to that caused by inversion in cyclic radicals, and in agreement with Bonazzola and Marx we suggest that it is due to a substituted cyclohexyl radical formed by cage opening.

Room-Temperature Radicals. Figure 4C shows the spectrum first observed by Filby and Gunther and assigned by them to the 1-adamantyl radical. It has hyperfine splitting constants closely resembling a benzyl type radical and is stable to 400 K. It is not readily apparent to us why their highly purified adamantane should give the same results as the Ad doped with TFPBQ or PBQ. One would expect to observe the intense center line as shown in Figure 4B. Therefore, our initial assumption of hydrogen-atom scavenging by TFPBQ must be modified to include free-radical scavenging also. The stability of the radical that was observed coupled with its inability to react with TFPBQ lends credence to our assignment to an aromatic π radical species. Since this radical is not present in the low temperature spectra, it may be a product formed by reactions of radicals and dehydrogenated species to form a more stable product. The strong center line that forms when X-irradiated Ad is warmed is probably due to polymerization of the radicals in the Ad.

Conclusion

The following equations summarize the EPR observable products, their conditions of formation and stability, and the resulting spectra that we believe occur upon subjecting Ad to ionizing radiation:

\[
\text{X-ray} \rightarrow \text{Ad} \rightarrow 1\text{-Ad} \text{(stable to 230 K) + 2-Ad} \text{<90%} \text{<77 K)} \\
\text{Ad + TFPBQ \rightarrow an alicyclic radical stable to 245 K (B and M, Figures 3 and 4)} \\
1\text{-Ad} \rightarrow \text{TFPBQ radical + polymeric products}
\]

It must be emphasized that Ad efficiently occludes small traces of unsuspected impurities and that the presence of impurities, although they may not form stable products, may alter the relative yields and to a small extent the stability of the radicals produced by ionizing radiation.

In summary, we believe that adamantane X-irradiated at 77 K produced mostly 1-Ad radicals with resolvable hyperfine splittings plus a small yield of 2-Ad radicals and an alyclic radical that is probably a ring-opening primary radiation-damaging product. Upon warming or upon irradiation at higher temperatures, the observed radicals are a benzyl radical and a radical with no hfs that we assign to secondary reaction products.

References and Notes

ESCA Studies of Methanation Catalysts Derived from Intermetallic Compounds

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ESCA measurements have been performed on several catalysts: (1) MNi$_5$ (M = Th, U, or Zr), which under reaction conditions convert to Ni/MO$_2$ (2) Ni/ThO$_2$ prepared by conventional means; and (3) ThCo$_5$ which converts during reaction to Co/ThO$_2$. All except the conventionally formed Ni/ThO$_2$ show surfaces rich in the transition metal, accounting for the high methanation activity of these materials. The ESCA results show that the surface of the Ni/ThO$_2$ conventionally formed catalyst is very low in Ni, thus providing an explanation of its weak catalytic activity. Exposure of the MNi$_5$ systems to H$_2$ or mixtures of H$_2$ and CO enhances the surface enrichment of Ni. This is ascribed to the strong interactions between Ni and H or CO.

**TABLE I: Catalytic Behavior of the Catalysts Studied**

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<th>Catalyst</th>
<th>% CO converted at 300 °C</th>
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<tr>
<td>ThNi$_5$</td>
<td>~100</td>
<td>5</td>
</tr>
<tr>
<td>UNi$_5$</td>
<td>12.5</td>
<td>2</td>
</tr>
<tr>
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Table I. As noted above, the decomposed state of ThNi$_5$ (Ni/ThO$_2$) was found to be very active; in addition, it showed high resistance to H$_2$S poisoning. In contrast, ZrNi$_5$ is less active and readily poisoned by H$_2$S. To elucidate these differences ThNi$_5$, UNi$_5$, and ZrNi$_5$ and their decomposition products were examined earlier by Auger spectroscopy. This study showed that during use as a catalyst the surface of the material became progressively enriched in nickel for the Th system but steadily depleted in nickel for the Zr system. It was also observed that the decomposed state of ZrNi$_5$ (Ni/ZrO$_2$) became heavily overlaid with graphite during use, whereas the surface of the Th system did not.

The earlier studies did not provide information concerning the chemical state of Ni in the fresh and used catalytic material. It was presumed from the activity and the results obtained by CO chemisorption measurements that the surface nickel was largely or perhaps exclusively metallic. The present work was undertaken to provide this information in regard to surface composition of these materials, including inter alia information about the chemical state of living nickel. With respect to the latter, Siegmund et al. by photoemission studies have recently found the surface of the closely related material, LaNi$_5$, to consist of LaO$_x$, La(OH)$_{1-x}$, and metallic Ni. The oxide and hy-

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**References**


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**Introduction**

In previous work, principally from this laboratory, a number of intermetallic compounds involving rare earths or actinides combined with Fe, Co, or Ni have been studied in relation to the catalytic conversion of CO/H$_2$ mixtures into hydrocarbons. It has been observed that under reaction conditions the intermetallic compound is extensively transformed into rare earth or actinide oxide plus metallic. The present work was undertaken to provide additional information about the chemical state and activity of these materials. The ESCA results show that the surface of the Ni/ThO$_2$ conventionally formed catalyst is very low in Ni, thus providing an explanation of its weak catalytic activity. Exposure of the MNi$_5$ systems to H$_2$ or mixtures of H$_2$ and CO enhances the surface enrichment of Ni. This is ascribed to the strong interactions between Ni and H or CO.

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