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function in that electrons are delivered to a preformed catalyst–substrate complex by a transition metal redox couple that cycles between oxidation states. That polymer coatings on electrodes might be used to mimic such systems and that the biological catalysts themselves could be incorporated in the coatings to produce catalyzed conversions of substrates by mechanisms such as that shown in Figure 7 are possibilities that deserve continued experimental testing.

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Registry No. $Ru(NH_3)_6^{2+}$, 19052-44-9; $Ru(NH_3)_6^{3+}$, 18943-33-4; CoTPP, 14172-90-8; H_4TPP^{2+}, 50849-35-9; H_2TPP, 917-23-7; O_2, 7782-44-7; Nafion 1200, 87901-14-2; graphite, 7782-42-5.

Free Radical Decay in Adamantane

A. T. Tegowski and D. W. Pratt*

Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260.

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Abstract: Kinetic electron paramagnetic resonance (EPR) techniques have been used to characterize the decay behavior of the "stable" free radical 2-cyclohexanonyl in the plastic crystal phase of an adamantane matrix over the temperature range 257–313 K. Typical plots of the EPR signal intensity as a function of time are biexponential in nature, suggesting the existence of at least two channels for free radical decay. The activation parameters for both processes have been measured in both protonated and deuterated samples. A comparison of these results with those in other systems suggests that the host does, as expected, considerably reduce the preexponential factors for decay of the radical by bimolecular processes but has relatively little influence on the corresponding activation energies.

Adamantane (tricyclo[3.3.1.1]decane, $C_{10}H_{16}$) has been widely employed as a matrix for studies of free radicals by electron paramagnetic resonance (EPR) and optical spectroscopy.[1] Radicals generated by ultraviolet or X-ray irradiation of suitable precursors in this host are randomly distributed and apparently isolated from one another. As "substitutional" impurities, they exist in cavities within the matrix which are of sufficient size that radicals no larger than the molecules they replace can rotate freely, at least in the plastic phase of adamantane. This means that sharp, "isotropic" EPR spectra whose line shapes do not change with time are obtained over a wide temperature range. Further, as adamantane is transparent to visible and near-UV light, the medium can also be used for a variety of optical experiments.

It occurred to us that the adamantane matrix technique might also prove useful for kinetic studies of free radicals. Thus, radical rearrangements, isomerizations, and other unimolecular processes, normally obscured in gas phase or solution experiments by more rapid recombination reactions, might be detectable in an adamantane matrix where the rates of diffusion-controlled bimolecular reactions could be reduced considerably.[2] In this report, we describe some preliminary experiments which were designed to test these ideas. Specifically, we have incorporated the relatively stable free radical 2-cyclohexanonyl in adamantane, made measurements of its decay behavior at different temperatures with EPR methods, and used these data to establish the kinetic and thermodynamic parameters governing radical decay in this system. Both protonated and deuterated guest and host molecules have been employed.

Experimental

A detailed description of our experimental procedures has been given earlier.[3] Briefly, samples were prepared by recrystallizing adamantane from cyclohexanone and irradiating them, in air and at room temperature, with use of an XRD-1 X-ray generator with a Cu-target tube. EPR spectra were obtained with a Varian E4 spectrometer and E257 variable temperature accessory. Temperatures are believed accurate to ±2 K. Decay measurements were performed by tuning the field into resonance with a strong line in the spectrum and monitoring its intensity as a function of time following temperature equilibration of the sample. Kinetic data were determined by constructing semilog plots of intensity vs. time; fitting by least squares the linear long lifetime component; subtracting this component from the total, normally biexponential, decay; and fitting by least squares the linear short lifetime component. Fits characterized by correlation coefficients less than 0.999 were rejected.

Results

Figure 1 shows the EPR spectra, recorded at 135 K, of the 2-cyclohexanonyl (A) and 2-cyclohexanonyl-*1,3,3'*-d_3 (B) radicals in a $C_{10}D_{16}$ host matrix. The former, having a single α proton ($a_1^H = 18.0$ G) and two magnetically inequivalent β protons ($a_6^H = 23.5$, $a_6^{H'} = 43.7$ (G), exhibits an eight-line spectrum at this temperature. Weak lines attributable to the 2-cyclohexanonyl-*1*-d_1 radical, produced by exchange between the guest and host, are also observed. The spectrum of the 2-cyclohexanonyl-*1,3,3'*-d_3 radical is similar except that the α-proton hyperfine splitting (hfs) is replaced by hfs due to the α deuteron ($a_1^D = 6.4$ G). A small **g** tensor anisotropy is detectable in the spectra of Figure 1. At higher temperatures, the increased reorientational mobility of the radical leads to a more nearly symmetrical spectrum. In addition, increasing the temperature produces an alternating line width effect owing to ring interconversion.[4] However, neither the widths nor the positions of the wing lines in these spectra are significantly

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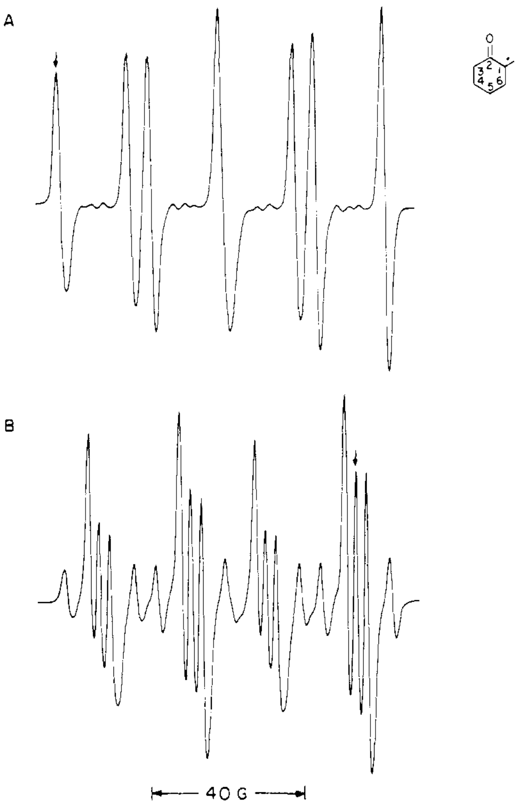

Figure 1. EPR spectra of the 2-cyclohexanonyl (A) and the 1,3,3′-trideuteriocyclohexanonyl (B) radicals in perdeuterioadamantane at 135 K. Arrows denote field positions used for decay measurements.

influenced by changes in temperature above 230 K where the radical decay proceeds at a measurable rate. Hence, we used the peak heights of these lines of determine the behavior of the radical concentration as a function of time.

Kinetic measurements were performed on four different types of samples: 2-cyclohexanonyl in $C_{10}H_{16}$ (HH), 2-cyclohexanonyl in $C_{10}D_{16}$ (HD), 2-cyclohexanonyl-*1,3,3′*-d_3 in $C_{10}H_{16}$ (DH), and 2-cyclohexanonyl-*1,3,3′*-d_3 in $C_{10}D_{16}$ (DD). The spectra in $C_{10}H_{16}$ are, apart from the extra line width due to unresolved intermolecular hyperfine splittings, similar to those in $C_{10}D_{16}$. Shown in Figure 2 are typical plots of the EPR signal intensity as a function of time for three different HH samples at 313 K. In all cases, the decay behavior can be fit by an expression of the form

$$I(t) = I_f^0 e^{-k_f t} + I_s^0 e^{-k_s t}$$

That is, the decay is composed of two different and easily distinguishable exponential components, fast (with rate constant k_f and intercept I_f^0) and slow (with rate constant k_s and intercept I_s^0). The values of these four parameters depend on both the concentration of the radical precursor and the irradiation time, as illustrated in Figure 2. Here, curves A and B show the decay behavior at 313 K of HH samples prepared from a 10% solution of cyclohexanone in *n*-heptane and irradiated for 1 and 10 min, respectively, while curve C refers to an HH sample, also at 313 K, which was prepared from neat cyclohexanone and irradiated for 10 min. Fits of data of this type showed that the relative contribution of the fast component to the overall decay, as determined from the ratio I_f^0/I_s^0, is enhanced in low concentration samples irradiated for long times. The rate constant k_f has its largest values (typically 1 min^{-1}) in low concentration samples irradiated for short times, whereas the rate constant k_s has its largest values (typically 0.05 min^{-1}) in high concentration samples irradiated for long times. Qualitatively similar behavior was observed for the remaining three sample types.

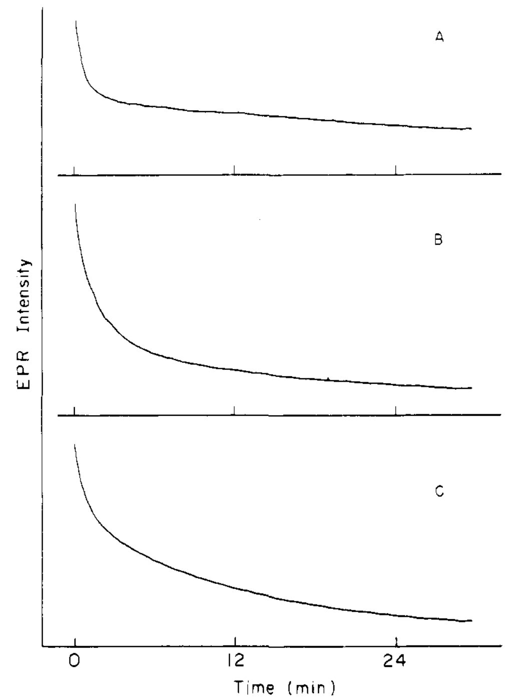

Figure 2. Plots of the EPR signal intensity at 313 K as a function of time. Curve A, 10% HH sample X-irradiated for 1 min; curve B, 10% HH sample X-irradiated for 10 min; curve C, neat HH sample X-irradiated for 10 min.

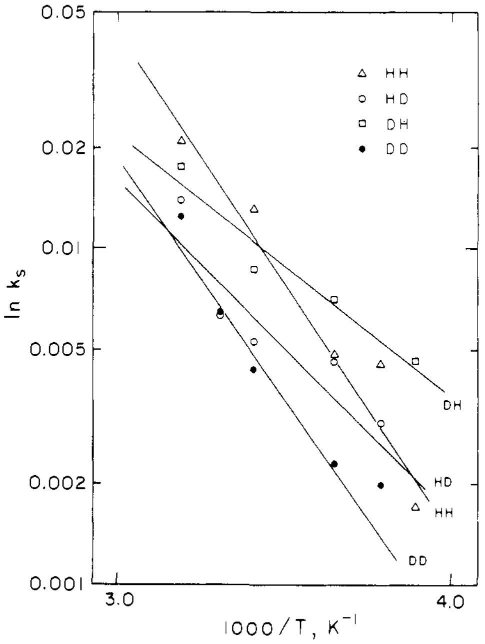

Figure 3. Plots of ln k_s vs. 1/T for the 2-cyclohexanonyl radical in adamantane: (△) HH sample, (○) HD sample, (□) DH sample, (•) DD sample.

We also made careful measurements of the temperature dependence of the decay of the EPR signal intensity over the range 257–313 K in samples prepared with the same concentration of radical precursor and irradiated for equal times. In 10% samples, the quantity I_f^0/I_s^0 increases with increasing temperature, varying from 0.29 at 246 K to 1.4 at 314 K. A semilog plot of I_f^0/I_s^0 vs 1/T is approximately linear with slope −2.5. Similarly, ln k_f and ln k_s also scale approximately linearly with reciprocal temperature, suggesting that both processes are activated ones. The Arrhenius parameters in 10% HH samples irradiated for 10 min are ln A_f = 2.7 ± 1.0, E_a^f = 1.9 ± 1.0, ln A_s = 1.8 ± 1.0, and E_a^s = 3.4 ± 1.0 kcal mol^{-1}. The corresponding parameters for samples prepared from neat cyclohexanone, where the temperature dependence of only the slow component was studied in detail (cf. *Figure* 3), are ln A_s = 7.2 ± 1.0 and E_a^s = 6.8 ± 1.0 (HH samples), ln A_s = 1.5 ± 1.0 and E_a^s = 3.6 ± 1.0 (DH), ln A_s = 2.7 ± 1.0 and E_a^s = 4.5 ± 1.0 (HD), and ln A_s = 5.9 ± 1.0 and

$E_a^s = 6.5 \pm 1.0$ kcal mol^{-1} (DD). Thus, the preexponential factors and activation energies of isotopically mixed samples are somewhat smaller than those of the isotopically pure ones.

Discussion

Perhaps the most interesting result of this study is that the decay of the EPR signal intensity of 2-cyclohexanonyl radicals in an adamantane matrix is biexponential in nature. At first sight, this is not a surprising result as there is ample precedent for nonexponential decay of free radicals in solid matrices.[5] The usual explanation for this behavior is that as substantial nuclear displacements are required during the decay, differently oriented radicals in the fixed environment of the host react with different rates. However, there are several reasons for believing that this kind of site effect is not responsible for the decay behavior of free radicals in adamantane. Chief among these is the observation of isotropic EPR spectra at temperatures above the transition to the plastic phase (208 K). As magnetic anisotropies in g and A in free radicals of the 2-cyclohexanonyl type are of the order of MHz,[3] the time required for reorientational motion of the guest must be considerably less than 10^{-6} s. In agreement with this, Berman and Schwartz[6] have measured rotational correlation times of the order of 10^{-10} s for di-*tert*-butyl nitroxide free radicals in adamantane near room temperature. This time scale is many orders of magnitude less than that for free radical decay. Therefore, we believe that the radicals produed by X-irradiation of 2-cyclohexanone in this host may be regarded as "homogeneously" reacting species, i.e., that the measured rate constants and activation parameters are averaged over the large number of nearly degenerate orientations sampled by the radical during its rapid motion in the adamantane "solvent cage".

The clear distinguishability of the fast and slow decays under most conditions shows that there must be (at least) two channels for the disappearance of free radicals in an adamantane matrix. Processes which come immediately to mind are (1) hydrogen atom abstraction from the host, (2) hydrogen atom abstraction from the guest, and (3) radical–radical recombination to form, by hydrogen atom transfer, cyclohexanone and cyclohexenone. Ordinarily, one can distinguish these several possibilities on the basis of the experimental observables, e.g., activation parameters, isotope effects, and product analyses. However, there are serious practical difficulties when such studies are attempted in the solid state. For example, hydrogen atom abstraction reactions in the condensed phase often have apparent activation energies that are much lower than the corresponding reactions in the gas phase. This has been demonstrated most convincingly by Williams and co-workers,[7] who showed that the rate of disappearance of methyl radicals in crystalline acetonitrile and the rate of formation of cyanomethyl radical are governed by identical activation energies of 1.4 kcal mol^{-1} between 77 and 87 K. The corresponding value of E_a for this reaction in the gas phase is 10 kcal mol^{-1}.[8] Quantum mechanical tunneling, whose importance is presumably enhanced by the close proximity and relatively static nature of the reactants in the solid state, was offered as an explanation for the large difference in E_a values.

We do not believe that such large differences will be typical of the plastic phase in molecular crystals. As already noted, the rotational correlation times of small free radicals in adamantane even below the transition temperature are much shorter than those in ordinary solids and more typical of hydrocarbon solutions. Thus, if hydrogen atom abstraction is occurring, tunneling is probably not important, and the measured activation energies should approach the solution or gas-phase values. Further, large isotope effects, such as the $\sim 10^{13}$ reduction in the rate of the reaction $CH_3 + CD_3CN$ observed by Wang and Williams,[7] are not expected, nor are they observed. We therefore conclude that the absence of such effects in our experiments (cf. Figure 3) cannot be taken as evidence that hydrogen atom abstraction is not occurring. Positive evidence for the formation of adamantyl radicals could not be obtained, possibly because such species have very short lifetimes above 240 K.[9] That the matrix is involved is, however, clear from the EPR results demonstrating the formation of deuterated (protonated) 2-cyclohexanonyl radicals in irradiated HD (DH) samples at higher temperatures (cf. Figure 1).

The ratio I_f^0/I_s^0 is a measure of the relative probability of the different reaction pathways.[10] That this quantity is enhanced in low (precursor) concentration samples irradiated for long times suggests that the fast exponential decay is the result of radical–radical recombination [process 3] and that the slow decay is the result of hydrogen atom abstraction from the host [process 1]. Process 2, hydrogen atom abstraction from the guest, should not affect the EPR signal intensity on our time scale if it results in the formation of the 2-cyclohexanonyl radical. A second reason for associating process 3 with the fast component and process 1 with the slow component is that the activation energy for a typical radical–radical recombination reaction is expected to be considerably smaller than that for the typical abstraction reaction, particularly when the secondary radical formed in the latter is less stable than the primary one.[11] Finally, we recall that the ratio I_f^0/I_s^0 is also enhanced by increases in temperature. This result also supports the view that the fast process involves guest free radicals, rather than host molecules, since such a process requires escape from the solvent cage before reaction can occur.

Some evidence exists that a fourth process, intermolecular hydrogen (or deuterium) atom transfer, is also occurring. This is provided by a comparison of the activation parameters of isotopically mixed samples with the isotopically pure ones. Such a process will, again, not affect the EPR signal intensity in HH or DD samples on our time scale. However, in DH or HD samples, the exchange of a D(H) atom at the radical site with an H(D) atom of the host will lead to a loss of signal at the field where the spectrum is being monitored. If this process occurs at a rate which is comparable to that of hydrogen atom abstraction, it will reduce the measured preexponential factors and activation energies in isotopically mixed samples, as observed. This is also the most direct way of accounting for the appearance of deuterated (protonated) radicals in irradiated HD (DH) samples. The Arrhenius parameters associated with the abstraction reaction are, then, on the order of $\ln A_s \sim 6.6$ and $E_a^s \sim 6.7$ kcal mol^{-1}. The value of A_s is many orders of magnitude less than the corresponding values for similar gas-phase reactions, but the value of E_a^s is reduced by only 10–20% in the adamantane host.[11]

It is of interest to compare the measured activation energies for free radical decay in adamantane with those for rotational and diffusional motion in the pure material.[12,13] The activation energy associated with the reorientational motion of host molecules in the plastic phase is $E_a^r = 3.1$ kcal mol^{-1}. While it may become increasingly difficult to describe such motions by simple correlation functions in systems where the solute molecule is much smaller than the molecules of the surrounding medium,[14] the "activation energy" for reorientational motion of 2-cyclohexanonyl radicals in adamantane certainly cannot be larger than E_a^r. Thus, if hydrogen atom abstraction occurs before the guest free radical escapes from the transient solvent cavity, we can conclude that the rate of abstraction is governed primarily by the details of the potential energy surface for the chemical reaction rather than specific solute–solvent interactions since $E_a^s > E_a^r$.

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The activation energy associated with translational diffusion in the plastic phase of adamantane is $E_a{}^d = 36.7$ kcal mol^{-1}, much larger than either of those measured in this work. It is believed that self diffusion in molecular crystals occurs by a vacancy mechanism. If so, then one expects some reduction in the activation energy for diffusion of 2-cyclohexanonyl radicals in adamantane because of the expected decrease in the free energy of formation of vacant lattice sites of the appropriate size. Some decrease in the repulsive part of the intermolecular potential energy function might also be anticipated. However, even in the plastic phase of cyclohexane, the activation energy for self diffusion is of the order of 10 kcal mol^{-1}. This value is still much larger than the measured activation energy for the fast decay process. Thus, if as suggested above, the fast decay is the result of radical–radical recombination, then it would appear that the rate of this reaction is also not strongly influenced by the host. This is not unreasonable, as the time scale for diffusional motion in a system having an activation energy as high as 10 kcal mol^{-1} is still many orders of magnitude faster than the time scale for the fast free radical decay process in adamantane.

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Registry No. 2-Cyclohexanonyl radical, 40528-46-9; adamantane, 281-23-2; cyclohexanone, 108-94-1.

Double Metal-to-Metal Bonds in Metal Carbonyl Clusters Formed in the Gas-Phase Negative Ion Chemistry of Iron Pentacarbonyl

John Wronka[†] **and D. P. Ridge***

Contribution from the Department of Chemistry and the Center for Catalytic Science and Technology, University of Delaware, Newark, Delaware 19711. Received May 9, 1983

Abstract: Fe(CO)$_4^-$ is observed to form Fe$_2$(CO)$_8^-$ in a gas-phase reaction with Fe(CO)$_5$. The rate constant for the reaction is log $k = -12 \pm 0.5$, fast enough to account for the Fe$_2$(CO)$_8^-$ which has been reported to form in the condensed phase chemistry of Fe(CO)$_5$. Relative rate constants for clustering reactions of Fe(CO)$_3^-$, Fe$_2$(CO)$_5^-$, Fe$_2$(CO)$_6^-$, Fe$_3$(CO)$_9^-$, Fe$_3$(CO)$_{10}^-$, and Fe$_4$(CO)$_{11}^-$ are reported. Other observed products include Fe$_4$(CO)$_{13}^-$, which is reportedly observed in the condensed phase chemistry of Fe(CO)$_5$ and Fe$_5$(CO)$_{14}^-$. It is concluded from reactivity patterns that Fe$_2$(CO)$_{5,6,7}^-$ each have a double metal–metal bond.

Introduction

It has been known for some years that cationic metal clusters are formed by gas-phase ion–molecule reactions in metal carbonyls.[1-5] Such processes were first reported in the ion–molecule reactions of metal complexes with both CO and cyclopentadienyl ligands.[1] Clustering reactions in Fe(CO)$_5$ have been studied in some detail.[2] Clusters containing up to four iron atoms result from a sequence of reactions beginning with reactions between Fe(CO)$_5$ and Fe(CO)$_n^+$ fragments formed by electron impact. Cations formed from Ni(CO)$_4$,[3] Cr(CO)$_6$,[4] and CoNO(CO)$_3$[5] have also been shown to undergo clustering reactions with their parent neutral compounds. Reactivity of this kind is probably common to all metal carbonyls.

Metal carbonyl cluster compounds have a rich chemistry in the condensed phase. They are useful as models for heterogeneous metal catalysis[6] and as stoichiometric reagents in a number of useful organic syntheses.[7] Parallels between chemistry of the clusters in the gas phase and in the condensed phase have not been extensively studied. One reason for this is that carbonyls form about electron-rich metal centers. Anionic metal carbonyl clusters are quite common in the condensed phase and have an extensive chemistry.[8] Unfortunately, few gas-phase anionic clustering reactions are known. One such reaction in each of Ni(CO)$_4$[9] and Fe(CO)$_5$[2,9] and two in Cr(CO)$_6$[9] have been described.

The present report describes a number of previously unobserved gas-phase anionic clustering reactions in Fe(CO)$_5$. New ion cyclotron resonance techniques make it possible to observe these reactions, several of which have rate constants three orders of magnitude less than the collision rate. The reactions are unique and interesting in several ways. First, the products include such species as Fe$_2$(CO)$_8^-$, and Fe$_4$(CO)$_{13}^-$, which occur in the condensed-phase chemistry of Fe(CO)$_5$.[10] Second, the reactants include a number of highly coordinatively unsaturated species, some formed only by collision-induced decomposition of more saturated ions accelerated by irradiation at their cyclotron frequencies. Third, the kinetics of the reactions suggest that some of the clusters are double metal–metal bonds.

Experimental Section

These studies were done by use of an ion cyclotron resonance spectrometer having a conventional three-region rectangular cell with a square cross section 2.54 × 2.54 cm.[11] The source region is 2.54 cm long

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