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The reactions of hydrogen atoms, generated by ultraviolet photolysis of hydrogen iodide, with solid ethane and propane at 10 K are investigated using electron spin resonance (ESR) to identify the reaction products. Although the results are generally similar to those found by others for these tunneling hydrogen abstraction reactions in dilute solutions of the alkanes in xenon, there also are significant differences, most notably, evidence that only the secondary hydrogen of propane is abstracted in its tunneling reaction with an H atom. Also notable is the high degree of crystalline order in the ethane matrix, which is preserved in the ethyl radical product of the H atom–ethane reaction.

I. INTRODUCTION

Matrix isolation spectroscopy, commonly used to investigate the molecular structures of free radicals and other unstable species, is also an important method for investigating solid state reactions.[1] These reactions often differ markedly from the analogous gas phase reactions due to such factors as temperature, the effects of the solid environment on the approach of reactants and separation of products (matrix cage effect) and differences in the manner and rate of energy distribution prior to and during reaction.[1,2] Of special interest are tunneling processes that often predominate in solids, especially at low temperatures where thermally activated reaction pathways are excluded.[1] Such reactions, especially those involving hydrogen atoms, have been extensively studied.[3–6] Here, previous electron spin resonance (ESR) studies of the reactions of photolytically generated hydrogen atoms with alkanes in xenon matrices[5,6] are extended to reactions in the solid alkanes themselves.

II. EXPERIMENTAL

The apparatus used to prepare the matrices has been described previously,[7] and need only be briefly summarized here. It consists of a 250 ml sample bulb, with a stopcock controlled port at the top for filling with appropriate gas mixtures from a vacuum line, and another stopcock controlled port at the bottom for connection to a 4 mm o.d. fused silica sample deposition tube. Gas flow from the bulb into the sample tube is constrained to a 1 mm i.d. tube located inside the sample tube, thereby minimizing deposition of the sample in regions other than the bottom. After filling with the desired gas mixture, this apparatus is removed from the vacuum line, and its sample deposition tube inserted into an Air Products Helitran flow—through cryostat that passes through the center of the microwave cavity of the ESR spectrometer. This cryostat is equipped with a temperature controller that varies the sample temperature between 8 and 295 K by controlling the temperature of the cold helium gas flowing over the sample. The sample is deposited simply by opening the stopcock between the bulb and the sample tube, thus allowing the gaseous sample to expand into and deposit at the bottom of the sample tube. Here, all samples were deposited at around 10 K.

After deposition, the sample is photolyzed in situ through the slotted port in the back of the microwave cavity. All photolyses used a 200 W high pressure mercury arc lamp. The ESR spectra, which can be observed during photolysis, were taken on a home-built X-band ESR spectrometer.

III. RESULTS AND DISCUSSION

A. Ethane

Ultraviolet photolysis of an $HI/C_2H_6=2/98$ matrix for 25 min at 9 K yielded a strong, if somewhat poorly resolved, ethyl radical ESR spectrum. No H atoms were observed, indicating that all the H atoms had reacted with ethane molecules. This is in marked contrast to a methane matrix, whose reaction with photogenerated H atoms is so limited that it can be used to investigate the reactions of H atoms with traces of other molecules in the matrix (e.g., $H+CO\rightarrow HCO$).[6,7] A further indication that H atoms react completely with the ethane matrix at 10 K is that no formyl (HCO) was observed upon replacing methane by ethane in the foregoing procedure used to produce HCO in a methane matrix.[6] Barring the unlikely event that, contrary to the situation in methane, the energetic ("hot") H atoms present immediately after the HI photodissociation react completely with ethane before being thermally equilibrated, this result supports previous work concluding that the observed ethyl radical is the product of tunneling abstraction of H from ethane by thermally equilibrated (i.e., "cold") H atoms.[4]

On warming to around 30 K, spectral resolution improved markedly to the spectrum shown in Fig. 1(a). Upon continued warming, the spectrum began weakening above 40 K and disappeared at around 50 K. This is due to some reaction of the radicals because the spectrum did not reappear on recooling. The improved resolution on warming is due to annealing of the matrix because it is not lost on recooling to 9 K. Cooling did, however, produce interesting changes in the widths and intensities of some individual lines, as shown in Fig. 1(c). There was, however, no change
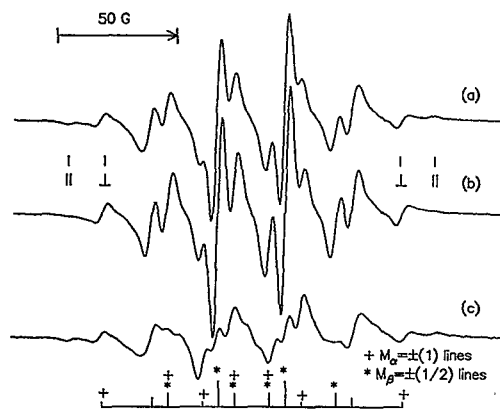
FIG. 1. ESR spectra of the ethyl radical produced by ultraviolet photolysis of HI in ethane for 25 min at 10 K. (a) Spectrum after warming to 30 K with the sample tube in its original photolysis position. (b) Spectrum at 30 K after the sample tube is rotated 90° about its axis. (c) Spectrum after cooling to 10 K with the sample tube in its original position. The stick spectrum at the bottom gives the calculated relative intensities of the perpendicular components of the anisotropic spectrum.

FIG. 2. ESR spectrum of the products of the ultraviolet photolysis of an $HI/C_3H_8 = 2/98$ matrix for 25 min at 10 K. The stick spectrum at the bottom gives the calculated relative intensities of an isotropic i-propyl spectrum with equal α- and β-proton hyperfine splittings.

in the integrated intensity of the spectrum. As discussed in detail later, these changes are attributed to the effects of internal tunneling rotations on the methyl-proton hyperfine splittings.

Except for the highest and lowest field lines, which contain the distinct parallel and perpendicular features of a powder spectrum of randomly oriented radicals with axially symmetric g-factor and hyperfine interactions,[8,10] the ethyl spectrum in Fig. 1(a) could be mistaken for an isotropic spectrum whose lines are broadened by superhyperfine interactions with the matrix hydrogens. This point is an important consideration in interpreting ESR spectra under conditions where the relatively weak parallel features of powder spectra may be obscured by stronger lines.

A novel and unexpected feature of this system is that the ethyl radicals are strongly oriented in a partially crystalline ethane matrix, as was revealed by rotating the sample tube 90° about its axis. As shown in Fig. 1(b), this rotation decreased the parallel components of the highest and lowest field lines almost to zero with a corresponding increase in their perpendicular components. Since the rotation axis is perpendicular to the magnetic field, this shows the ethyl radicals initially were preferentially oriented with their magnetic axis (the C–C bond) parallel to the magnetic field. Changes are also observed in the interior lines, especially those subject to the large anisotropic α-proton hyperfine splitting, that is, the $M_\alpha = \pm 1$ lines, as indicated in Fig. 1.[8] Only the perpendicular components of the interior lines are observed, as their weaker parallel components are obscured by nearby lines.

The observed orientation dependence is attributed to a partial crystalline character of the as-deposited ethane matrix which is preserved in the ethyl radicals formed by the H atom abstraction reaction. The alternative explanation of orientational selectivity in the HI photolysis (even unpolarized light is not completely isotropic in this experiment because it has electric vectors only along the sample tube axis and the
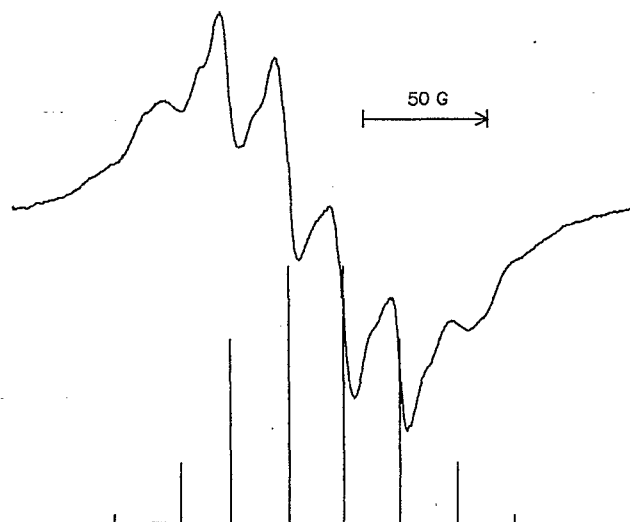
magnetic field) is excluded by the fact that the effect varied somewhat from deposition to deposition. Also, in some matrices the sense of the initial orientation was reversed, that is, the parallel features were increased rather than decreased by the rotation.

That these simple deposition methods can yield partially crystalline matrices requires that care be taken in interpreting ESR spectra in such matrices. For example, the spectrum in Fig. 1(b) easily could be mistaken for a somewhat broadened isotropic ethyl spectrum. On the other hand, the indicated ability to prepare matrices with partial single crystal character could be useful, particularly if the degree of crystallinity can be increased by varying such sample deposition conditions as temperature, deposition rate, etc.

B. Propane

Utraviolet photolysis of an $HI/C_3H_8 = 2/98$ matrix at 10 K for some 25 min yielded the ESR spectrum shown in Fig. 2. This spectrum consists of eight uniformly spaced lines, with some indications of weak secondary lines midway between some of these eight line, all superimposed on a broad featureless line. Apart from the weak secondary lines which will be discussed momentarily, this spectrum is quite similar to the spectrum observed in the products of the photolysis of oxygen difluoride (OF_2) in a propane/argon matrix and attributed to the isopropyl radical produced by the reaction: $C_3H_8 + F \rightarrow i - C_3H_7 + HF.$[9] Also, the intensities of its eight main lines agree reasonably well with those calculated for an isotropic i-propyl radical with equal α- and β-proton hyperfine splittings (stick spectrum at the bottom of Fig. 2), which they are to well within the widths of the rather broad observed lines. The spectrum of matrix-isolated i-propyl should resemble a broadened isotropic spectrum, even though the radical cannot reorient rapidly enough in the matrix to have a truly isotropic spectrum, because the dominant hyperfine an-

isotropy of the lone α proton has a near maximum axial asymmetry and, therefore, yields a nearly symmetric powder pattern.[8]

There is no significant contribution to this spectrum from the n-propyl radical, if its ESR spectrum in propane is similar to that observed in argon[8,11] and krypton.[13] This n-propyl spectrum has a readily identifiable triplet of strong sharp lines due to splitting of the $M_\alpha=0$ hyperfine line, in which the large hyperfine anisotropies of the two α-protons cancel to zero, by hyperfine interactions with two equivalent β protons.[8,11]

This shows that the tunneling reaction of an H atom with propane preferentially abstracts hydrogen from the secondary carbon atom, probably because this C–H bond is somewhat weaker. In retrospect, it is likely that the reaction between F atoms and propane in an argon matrix at 4.2 K is also a tunneling process involving thermally equilibrated F atoms, as site selectivity in a reaction involving "hot" F atoms is highly unlikely.

A secondary conclusion is that there is very little reaction of propane with "hot" hydrogen atoms, in which the site of hydrogen abstraction should be random yielding a 3:1 ratio of n-propyl to i-propyl. A possible reason for this is that the energetic H atoms are thermally equilibrated even more rapidly by collisions with the relatively complex propane molecules than they are in methane, where a limited reaction with "hot" H atoms is observed.

These conclusions differ from those reached by Iwasaki et al.,[5] who reported no site preference in the abstraction of hydrogen from propane, and also isobutane, in Xe at 4.2 K. They found a preference for the secondary site at higher temperatures around 50 K, however. Our spectra and theirs are quite similar; the different conclusions stem primarily from whether the two β-proton hyperfine splittings of n-propyl in these matrices are the same, as we believe on the basis of its spectrum in argon and krypton, or different, as Iwasaki et al. postulated. In the latter case, the six strongest lines in Fig. 2 can be accounted for by n-propyl as well as by i-propyl.[5] Iwasaki et al. distinguished between the n-propyl and i-propyl contributions to these lines by assuming that in all i-propyl radicals the six equivalent β-proton splittings are further split by methyl tunneling rotations. At low temperatures this causes each methyl proton hyperfine multiplet to be a 1:1:1:2:1:1:1 septet with half the splitting of the usual 1:3:3:1 quartet.[14–16] Our interpretation, on the other hand, which is consistent with the presence in Fig. 2 of only weak hints of the additional "tunneling" lines in the form of inflections between the strong lines, is that the entire spectrum is due to i-propyl, with a fraction of the radicals in matrix sites where the tunneling rotations produce additional splittings.

Additional support for this interpretation comes from the early stages of the HI/propane photolysis. Here, the ESR spectra are somewhat better resolved, and, as shown in Fig. 3 for photolysis times of 5 and 10 min at 12 K, the "tunneling" lines are most prominent in the initial stages of the photolysis and decrease in relative intensity as the photolysis progresses. This indicates, at the very least, a strong initial preference for abstraction of hydrogen from the secondary
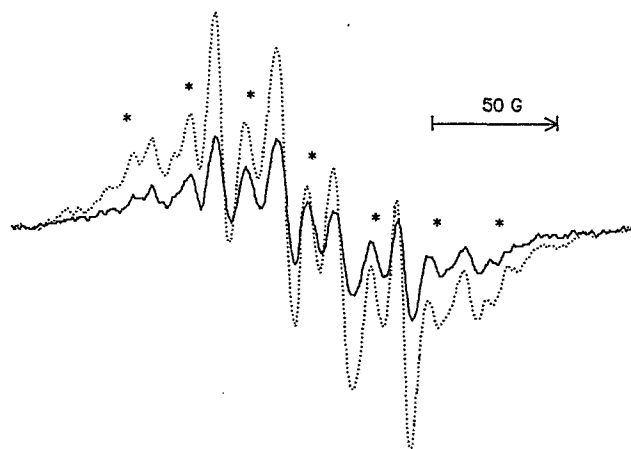

FIG. 3. ESR spectrum of the products of the ultraviolet photolysis of the HI/C_3H_8=2/98 matrix for shorter times at 10 K. (—) 5 min, (···) 10 min. *: Lines due to tunneling rotations in the methyl groups of i-propyl.

site in propane because any possible contribution of n-propyl to the spectrum in Fig. 3(a) must be much smaller than the i-propyl contribution indicated by the intensities of the "tunneling" lines, which can only be due to i-propyl. For the same number of radicals the intensities of the strongest n-propyl ESR lines will be much greater than the corresponding i-propyl intensities because the n-propyl intensity is shared among only two β protons vs six in i-propyl. Furthermore, the strongest n-propyl lines correspond to $M_\alpha=0$ hyperfine levels where the α-proton hyperfine anisotropy vanishes,[8,11] whereas all i-propyl lines are broadened and thus weakened by the anisotropic hyperfine splitting of one α-proton.

The relative intensities of the "normal" and "tunneling" lines of the i-propyl spectrum do not change appreciably with increasing temperature up to 35 K, although the estimates of the intensity ratios become increasingly imprecise due to line broadening. Above 35 K the "normal" spectrum, similar to that of Fig. 2, begins to predominate. The persistence of the tunneling spectrum up to 35 K indicates that the methyl reorientations in this system are more strongly hindered than in many others where tunneling effects are only observed at significantly lower temperatures.

C. Effects of tunneling rotations in ethyl

The changes in the 30 K ethyl spectrum, shown in Fig. 1(a), on cooling to 10 K, as shown in Fig. 1(c), are consistent with a decrease in the relative intensities of the inner lines ($M_\beta=\pm\frac{1}{2}$) of the CH_3 hyperfine quartet, but without significant changes in the line widths. At intermediate temperatures the spectra are less well resolved due to line broadening and overlap, however, it can be estimated that the transition between the low and high temperature spectra occurs between 20 and 30 K.

One possible explanation of these changes is that at the lower temperatures there is significant population only of the ground internal rotation state of the radical, for which the intensity ratios of the β-CH_3 hyperfine multiplet can be

1:1:1:1 instead of the usual 1:3:3:1 quartet.[13-16] This is deemed unlikely, however, because the low-temperature spectrum persists to 20 K where there should be significant population of higher internal rotation states. Furthermore, the lowest internal rotation state of ethyl should also exhibit intensity anomalies in the α-CH$_2$ hyperfine triplet, but none are observed. Finally, any model based on equilibrium population of internal rotation states should yield a more gradual transition between the 10 and 30 K spectra than is observed, and without the line broadening observed at the intermediate temperatures.

We believe the correct explanation is a dynamic model, proposed some time ago by Clough et al.[16] According to this model, thermally activated transitions between different orientations of the CH$_3$ group relative to the CH$_2$ group can selectively broaden some lines of the proton hyperfine multiplet of the tunneling methyl group. This broadening occurs at temperatures where the rate of these thermally stimulated transitions is comparable to the resulting changes in the hyperfine frequencies of the individual β-protons, that is $\omega_R \cong \delta\omega_{hfs}$. The broadening is selective because the methyl reorientations have no effect on symmetric methyl hyperfine states (those belonging to the symmetric representation of the C$_3$ rotation group), but do affect a doubly degenerate pair of hyperfine states of lower symmetry. Clough et al. show by calculation and experimental results that, if this reorientation rate goes from slow $(\omega_R \ll \delta\omega_{hfs})$ at the lowest temperatures (ca. 4.2 K) to rapid $(\omega_R \gg \delta\omega_{hfs})$ at higher temperatures, then the CH$_3$ hyperfine multiplet goes from the 1:1:1:2:1:1:1 septet discussed in connection with the i-propyl radical to the characteristic 1:3:3:1 methyl quartet, with a 1:1:1:1 quartet due to the unbroadened symmetric CH$_3$ hyperfine states at intermediate temperatures. This model can account for the observed changes in the $M_\beta = \pm\frac{1}{2}$ lines of the ethyl radical if the methyl reorientation rate between 10 and 20 K corresponds to this intermediate region. Unfortunately, our present apparatus does not permit observations down to 4.2 K, where it might be possible to completely resolve the problem by observation of the complete 1:1:1:2:1:1:1 CH$_3$-tunneling spectrum.

In summary, there is still much to be learned from ESR observations of solid state reactions in cryogenic matrices. The ability of modern cryogenic equipment to deposit various matrices under controlled conditions of temperature and deposition rate, and then to monitor the progress of the reactions by ESR during and after reaction should facilitate these investigations.

ACKNOWLEDGMENTS

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