Conformation and Mobility of Radicals in Heterogeneous Systems
ESR Spectra at 4 K of Methyl, Ethyl, n-Propyl and Allyl Radicals Adsorbed on Silica Gel

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ESR spectra of the methyl, ethyl, n-propyl and allyl radicals adsorbed on silica gel were analysed in terms of g-factor and hyperfine coupling anisotropies. The magnitudes of the anisotropies demonstrate that at 4 K the methyl radical reorients about its threefold axis, and the ethyl radical reorients about the C—C-bond axis. The experimental data for the methyl and ethyl radicals have been combined to yield the dipolar hyperfine coupling for an α-proton. The constants thus derived are $B_x=12.5$ G, $B_y=-13.0$ G and $B_z=0.5$ G. The n-propyl radical has a rigid conformation at 4 K with a spectrum which arises by the hyperfine interactions of two α protons and two β protons. The β protons have $a_{\beta 1}=40$ G and $a_{\beta 2}=22$ G, which is indicative of an asymmetric conformation. The allyl radical at 4 K also gives the rigid limit spectrum. The temperature dependence of the spectra was studied in the range 4 K—183 K.

Introduction

Previous measurement by means of electron spin resonance (ESR) has allowed the anisotropic g-factors and hyperfine couplings to be determined for simple radicals like methyl and ethyl in the adsorbed state[1]. Following analysis of the data it was concluded that at 77 K the methyl radical rotates rapidly about its threefold axis whereas the ethyl radical reorients about the C-C bond.

The present study represents an extension of this work involving the measurement of spectra at 4 K. At this low temperature thermal motion is reduced particularly for species larger than methyl and ethyl. It should therefore be possible to deduce the conformation of the rigid radical. A study was also made of differences in conformation and mobility which exist between different matrices. For this purpose the methyl, ethyl, propyl and allyl radicals were prepared in a silica gel matrix and their ESR spectra were analyzed for comparison with results of a similar analysis of these spectra in an argon matrix[2].

Experimental

Sample preparation and radical production by γ-irradiation of the halides at 77 K were performed using the procedure described in the preceding paper[1]. ESR measurements at 4 K were made in liquid helium employing a field modulation of 270 Hz and a microwave power of 0.02 mW to avoid rapid passage and saturation effects as far as possible. The experimental conditions for ESR measurement at 77 K and higher temperatures were such that no noticeable distortion of the line shape was caused by instrumental factors such as magnetic field modulation or microwave power saturation.

Results

The ESR spectrum of the methyl radical at 4 K, shown in Fig. 1 a, is similar to that measured at 77 K except for the difference in the peak-peak linewidth, ΔH_{pp}, of the first derivative spectrum. The spectrum at 183 K in Fig. 1 d is less asymmetric. The signal from irradiated silica gel is superimposed on the central part of the spectrum. A quantitative measure of the asymmetry of the lines and the deviation from the binominal intensities distribution is given in Table 1. In the present case, the asymmetry of a line was estimated by dividing the amplitude of the positive half of the first derivative line by the total amplitude of the line. Peak intensities at each temperature were normalized to the total amplitude of the first peak at the lowest magnetic field.

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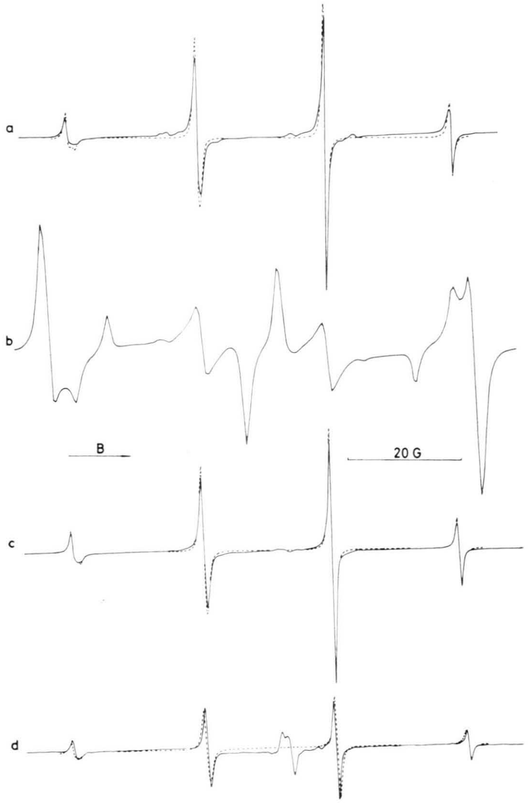

Fig. 1. ESR spectra of the methyl radical adsorbed on silica gel.

(a) The solid line is the spectrum measured at 4 K. The dotted line represents a computed lineshape with $A_\perp = -22.6$ G, $A_{||} = -21.9$ G, a Lorentzian peak-peak linewidth of $\Delta H_{\mathrm{pp}} = 0.45$ G, and $g_\perp = 2.0027$, $g_{||} = 2.0024$.

(b) Computed line shape for the completely anisotropic spectrum with $A_x = -9.9$ G, $A_y = -35.4$ G, $A_z = -21.9$ G and $\Delta H_{\mathrm{pp}} = 1.0$ G, $g_\perp = 2.0027$ and $g_{||} = 2.0024$.

(c) The solid line is the spectrum measured at 77 K. The dotted line represents a computed lineshape with the same parameters as the dotted line in (a) except that $\Delta H_{\mathrm{pp}} = 0.50$ G.

(d) The solid line is the spectrum measured at 183 K. The dotted line represents a computed lineshape with the same parameters as the dotted line in (a) except that $\Delta H_{\mathrm{pp}} = 0.60$ G.

As shown in Fig. 2 the spectrum of the ethyl radical measured at 4 K differs little from that recorded[1] at 77 K. Some difference appears on the wings of the spectrum. As the sample was further heated from 77 K, the separation between the outer and inner lobes on the wings decreased and at 178 K these peaks changed into isotropic lines[1].

The spectra of the n-propyl radical measured at 4 K, 77 K, 113 K, and 153 K are shown in Figure 3. The signals from irradiated silica gel at $g = 2.008$ and $g = 2.0008$ shown in Fig. 3 are superimposed on the central part of the spectra. The spectrum at 4 K consists of six lines separated by about 21 G (Figure 3 a). The spectrum at 77 K (Fig. 3 b) also

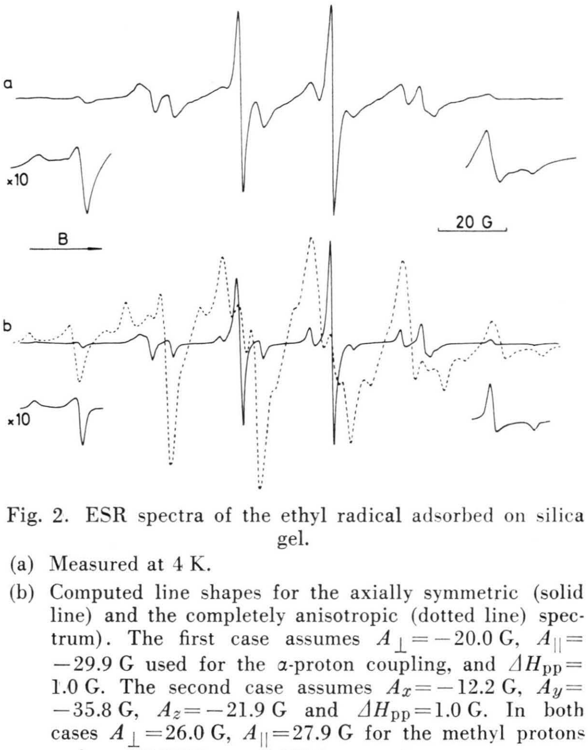

Fig. 2. ESR spectra of the ethyl radical adsorbed on silica gel.

(a) Measured at 4 K.

(b) Computed line shapes for the axially symmetric (solid line) and the completely anisotropic (dotted line) spectrum). The first case assumes $A_\perp = -20.0$ G, $A_{||} = -29.9$ G used for the α-proton coupling, and $\Delta H_{\mathrm{pp}} = 1.0$ G. The second case assumes $A_x = -12.2$ G, $A_y = -35.8$ G, $A_z = -21.9$ G and $\Delta H_{\mathrm{pp}} = 1.0$ G. In both cases $A_\perp = 26.0$ G, $A_{||} = 27.9$ G for the methyl protons and $g_\perp = 2.0032$, $g_{||} = 2.0026$ are used.

Peak		1st	2nd	3rd	4th
ΔH_{pp} (G)	4 K	1.69 ± 0.1	1.06 ± 0.05	0.43 ± 0.05	0.63 ± 0.05
	77 K	1.24 ± 0.1	0.92 ± 0.05	0.59 ± 0.05	0.63 ± 0.05
	183 K	1.06 ± 0.1	0.77 ± 0.05	0.66 ± 0.05	0.53 ± 0.05
asymmetry of lines	4 K	0.26	0.42	0.57	0.62
	77 K	0.32	0.44	0.56	0.62
	183 K	0.42	0.47	0.53	0.53
relative peak intensity	4 K	1.0	5.1	10.0	2.4
	77 K	1.0	4.5	8.3	2.2
	183 K	1.0	4.2	5.3	1.6

Table 1. The linewidth ΔH_{pp}, asymmetry and relative peak intensity of each hyperfine line of the methyl radical at 4, 77 and 183 K.

consists of six lines but the linewidth of the 2nd and 6th peaks was narrower than the corresponding lines at 4 K. When the temperature was further increased, the resolution gradually increased as illustrated by the spectrum at 113 K (Figure 3 c). At 153 K (Fig. 3 d) the isotropic coupling constants were estimated to be $a_\alpha = 21.5$ G, $a_\beta = 30.6$ G.

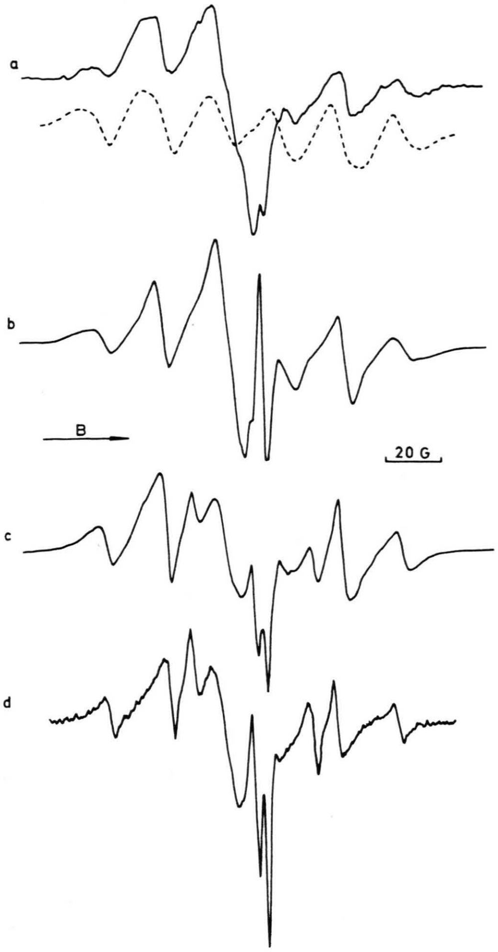

Fig. 3. ESR spectra of the n-propyl radical adsorbed on silica gel.

(a) The solid line corresponds to the spectrum measured at 4 K. The dotted line represents a computed lineshape assuming principal values of the g-factor of $g_\perp = 2.0032$, $g_\| = 2.0026$, principal values of the hyperfine coupling for the α protons of $A_x = -12.2$ G, $A_y = -35.8$ G, $A_z = -21.9$ G, isotropic couplings $a_{\beta 1} = 40$ G, $a_{\beta 2} = 22$ G for the β protons and $\Delta H_{\mathrm{pp}} = 4.0$ G.
(b) The spectrum measured at 77 K.
(c) The spectrum measured at 113 K.
(d) The spectrum measured at 153 K.

At 4 K the spectrum of the allyl radical consists of a main quintet of lines split by about 14.5 G. Each line has some degree of structure (Figure 4 a). The central part of the spectrum is distorted by the signal which emanates from silica gel. The resolution improves and the total linewidth of the spectrum decreases with increasing temperature. At 173 K the spectrum changes into a quintet of doublets with $a_1 = 13.9$ G and $a_2 = 3.9$ G having first exhibited an intermediate line profile at 128 K, shown in Figure 4 d.

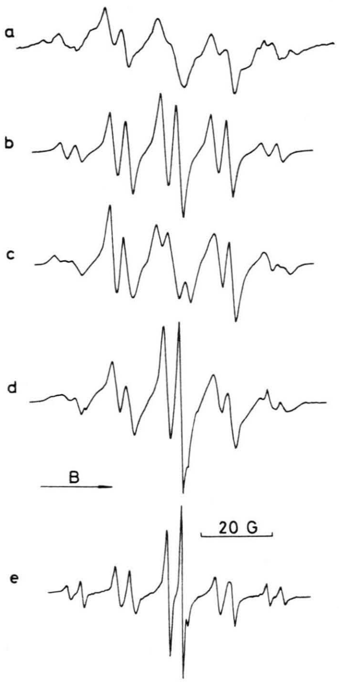

Fig. 4. ESR spectrum of the allyl radical adsorbed on silica gel.

(a) The spectrum measured at 4 K.
(b) Computed lineshape assuming parameters of $g_\perp = 2.0036$, $g_\| = 2.0021$, $A_\perp = -13.8$ G, $A_\| = -14.0$ G for the four protons attached to carbon 1 and 3, $A_\perp = 4.7$ G, $A_\| = 2.3$ G for the proton attached to carbon 2 and $\Delta H_{\mathrm{pp}} = 1.5$ G.
(c) Computed lineshape assuming parameters of $g_\perp = 2.0029$, $\mathrm{g}_\| = 2.0036$, $A_\perp = -12.2$ G, $A_\| = -17.3$ G for three protons two attached to carbon 1 and one to carbon 3, $A_\perp = 17.4$ G, $A_\| = -7.0$ G for the other proton attached to carbon 3, $A_\perp = 3.3$ G, $A_\| = 5.1$ G for the proton (1H) attached to carbon 2 and a Lorentzian linewidth of 1.5 G.
(d) The spectrum measured at 128 K.
(e) The spectrum measured at 173 K.

Line Shape Analysis

In a previous paper the axially symmetric hyperfine couplings for methyl and ethyl radicals adsorbed on silica gel were reported[1]. It was concluded that the axial symmetry was produced by a rapid reorientation which occurs preferably about the threefold axis of the methyl radical and about the $C_\alpha - C_\beta$ bond axis of the ethyl radical. From these data values for the dipolar couplings B_x, B_y and B_z can be calculated by employing the equations

$$B_\perp(\cdot C_2H_5) = \tfrac{1}{2}[B_x \cos^2 30 + B_y \cos^2 60 + B_z]\,,$$
$$B_\parallel(\cdot C_2H_5) = B_x \cos^2 60 + B_y \cos^2 30\,,$$
$$B_\parallel(\cdot CH_3) = B_z\,.$$

The assumptions were made that the value of B_z is the same for ethyl and methyl and that the radicals are planar with an $H - C_\alpha - H$ angle of 120°. Experimental values for the ethyl radical are $B_\perp = 3.3$ G, $B_\parallel = -6.6$ G while for methyl $B_\parallel = 0.5$ G. This gives for the inplane components $B_x = 12.5$ G along the $C_\alpha - H$ bond and $B_y = -13.0$ G perpendicular to the $C_\alpha - H$ bond, while $B_z = 0.5$ G is the component perpendicular to the plane. By comparison, the hyperfine couplings for $\cdot CH(COOH)_2$ are of a slightly smaller magnitude[3], namely $B_x = 10.8$ G, $B_y = -11.3$ G and $B_z = 0.5$ G. Multiplying by the ratio 23.3/21.2, which represents the isotropic coupling constant for ethyl divided by the coupling constant for $\cdot CH(COOH)_2$, the following values are obtained: $B_x = 11.9$ G, $B_y = -12.4$ G and $B_z = 0.5$ G. They are in good agreement with the values deduced above.

In order to compute the spectra for radicals trapped in a rigid matrix values are required for the anisotropic coupling constants. For the methyl, ethyl and propyl radicals these sets of data were calculated from the derived values of the dipolar coupling constants and the measured values of the isotropic coupling constants. The simulations were made employing the computer programme MARU which is an extended version of the programme described in Reference[4]. When anisotropy prevails an accurate simulation requires that account be taken of the effect of the nuclear Zeeman interaction. In this case each proton will give rise to four transitions. Among the radicals considered here spectra of rigidly trapped allyl type radicals[5] have already been computed. For a rigid methyl radical no simulation including the effect of the nuclear Zeeman term has hitherto been reported and this calculation was therefore performed. For ethyl and propyl, however, approximate simulations, in which the nuclear Zeeman term was neglected, proved sufficient to differentiate between spectra of rigid and reorientating radicals.

The computed spectrum of a rigid methyl radical, calculated on the basis of the anisotropic couplings $A_x = -9.9$ G, $A_y = 35.4$ G and $A_z = -21.9$ G, is shown in Figure 1 b. By contrast spectra for a reorienting radical have been computed by using the couplings $A_\perp = -22.6$ G, $A_\parallel = -21.9$ G for three different values of the line width parameter ΔH_{pp}, namely 0.45 G, 0.50 G and 0.60 G. These spectra are represented by dotted lines in Fig. 1 a, 1 c and 1 d respectively.

Spectra to be expected for a rigid and a reorienting ethyl radical are similarly compared in Figure 2 b. The parameters for the methyl proton couplings, the *g*-factor and the line width are identical in the two cases.

The simulation shown by the dotted line in Fig. 3 a was obtained on the basis of a rigid structure for the propyl radical in which the two β protons interact unequally to give $a_{\beta_1} = 40$ G, $a_{\beta_2} = 22$ G. The small anisotropy of the protons is simply regarded to be a line broadening factor which gives $\Delta H_{pp} = 4$ G.

Three different models were tested to fit the spectra of the allyl radical. In the first model the radical is assumed to be rigid. This gives the type of spectrum containing five lines which was reported by Chachaty and Maruani[5] but not reproduced here. In the second model the radical is assumed to rotate about an axis perpendicular to the radical plane. The principal in-plane values of each coupling are then averaged to yield a perpendicular component, while the component parallel to the rotation axis remains unchanged. The resulting spectrum is shown in Figure 4 b. In the third model the radical is assumed to rotate about the $C_1 - C_2$ bond, which results in the spectrum of Figure 4 c.

Discussion

A noteworthy feature of the spectra is the reversible change of line shape with temperature. Such changes are associated with the degree of molecular motion at different temperatures; analysis of the ESR spectra should accordingly provide some information on this subject. For simple radicals such as methyl and ethyl the experimental spectra can be interpreted on the assumption of rapid reorientation about a fixed axis at 77 K[1]. With the simulation programme employed[4] line shapes can also be analyzed on the assumption of a rigid structure. This would be the case at a sufficiently low temperature and the spectra at 4 K is therefore given detailed consideration.

The analysis of the methyl radical spectra shown in Fig. 1 indicates that the anisotropic parameters do not vary with temperature although the line width changes slightly. This implies that even at 4 K the methyl radical reorients rapidly about its threefold axis to retain axial symmetry. This indication is further supported by the poor agreement between the experimental spectrum and the simulation using the parameters derived for a rigid structure.

The similarity of the ethyl spectra recorded at 4 and 77 K suggests that reorientation is rapid enough to give a spectrum with axially symmetric couplings even at 4 K. The simulations confirm that the resonance parameters are the same as at 4 K which is taken to imply that rapid rotation occurs about the C – C bond axis.

The spectrum of the n-propyl radical at 4 K (Fig. 3 a) is in reasonable accord with the line profile expected for a rigid limit shown in Fig. 3 a (dotted line). To obtain this fit the two β protons are assumed to be non-equivalent as would be the case when the protons are asymmetrically disposed about the direction of the π-electron orbital containing the unpaired electron. The coupling can be computed from the relationship[6] $a_\beta = B \cos^2 \theta$ where θ is the angle between the direction of the orbital axis and the projection of the $C_\beta - H$ bond on the plane perpendicular to the $C_\alpha - C_\beta$ axis. In the liquid[7] $a_{\beta_1} = a_{\beta_2} = 33.2$ G which is assumed to correspond to $\theta_1 = \theta_2 = 30°$. This gives $B = 44$ G from which $\theta_1 = 17°$, $\theta_2 = 45°$ for the n-propyl radical in the adsorbed state at 4 K. Recently similar values were deduced for the β-couplings from an analysis of the spectrum of hexyl radicals in the adsorbed state[8]. It therefore seems reasonable to postulate that the non-equivalence is produced by a distortion peculiar to the adsorbed state. The non-equivalence of the β protons is consistent with the assumption that the ethyl group does not reorient at 4 K.

The total width of the allyl radical spectrum in Fig. 4 a as well as the positions of the main peaks agrees with that expected[5] for a rigid structure. The total width is greater than that computed for the case with reorienting radicals as exemplified by Fig. 4 b and c. That the additional structure is better resolved for the second and fourth main peaks is consistent with the observation made in an argon matrix[2]. The fine detail of the spectrum is reproduced less clearly by the simulation of the powder spectrum performed by Chachaty and Maruani[5]. An obvious reason for the disagreement is the difference in line width. The calculation assumed $\Delta H_{pp} = 3$ G, whereas a value of $\Delta H_{pp} = 1 - 1.5$ G is more appropriate. A further possibility is that some of the additional structure arises from a weak interaction with the protons of the matrix. In fact spin-flip transitions, indicative of such interactions, have been reported for the methyl radical adsorbed on silica gel[9] and weak satellite lines where observed in the present study both for the methyl (Fig. 1 a) and the ethyl radicals.

Temperature effects: According to the previous analysis[1] the methyl radical rotates preferentially about its symmetry axis at 77 K and it seems probable that this also occurs at 183 K. The axially symmetric hyperfine couplings and the g-factors are the same at the different temperatures. As indicated by the simulations shown in Fig. 1 the difference between the spectra can be accounted for by assuming a temperature dependent line width namely ΔH_{pp} (4 K) = 0.45 G, ΔH_{pp} (77 K) = 0.50 G and ΔH_{pp} (183 K) = 0.60 G, the shape being Lorentzian in each instance.

A different approach to the analysis of the spectrum of methyl radicals on a silica gel surface is based upon the theory of spin relaxation in liquids[10, 11]. Using this theory Gardner and Casey[12] attributed the departure from a binomial intensity distribution as being due to spin relaxation which gives line widths that depend upon the nuclear spin quantum number. A quantitative application of the theory indicated a value of $2 \cdot 10^7$ Hz for the tumbling frequency at 77 K. This interpretation is not supported, however, by the results obtained here. The difference in the measured line widths of the different hyperfine lines can be explained in a simpler fashion by assuming that the methyl radical rotates about its symmetry axis at all temperatures between 4 – 183 K.

It was previously concluded that at 77 K ethyl rotates about the $C_\alpha - C_\beta$ axis and clearly this also occurs at 4 K. The implication is that the barrier for rotation is low, which agrees with the results of an ab initio calculation of the electronic structure of simple alkyl radicals now in progress[13]. It should be noted that the $\cdot CH_2$ group must rotate relative to the laboratory frame of reference in order that the averaged components of the α-coupling tensor should produce an axially symmetric coupling. This will be the case if the $\cdot CH_2$ group rotates about the $C_\alpha - C_\beta$ bond on the silica gel surface. It would not be the case if the $\cdot CH_2$ group were fixed while the methyl group rotated. If finally the whole radical rotated rigidly about the $C_\alpha - C_\beta$ bond the methyl couplings would become non-equivalent which does not accord with observation.

The change in the spectrum of the propyl radical with increasing temperature indicates that thermal motion affects the line shape at 77 K and higher temperatures. By analogy with the case presented for ethyl it might be expected that the $\cdot CH_2$ group would rotate preferentially about the $C_\alpha - C_\beta$ bond axis. In this event strong, narrow lines should be visible in the spectrum when the α protons have antiparallel spins, $M_\alpha = 0$, but this is not observed. Sharp lines which correspond to this condition have been observed in an argon matrix[2] at 4 K, but a similar simple analysis is not applicable in the present instance. As is illustrated in Fig. 3 the spectra change continuously with temperature and at 153 K the positions of the peaks can be accounted for on the basis of the isotropic couplings $a_\alpha = 21.5$ G, $a_\beta = 30.6$ G. In the intermediate temperature region 77 – 113 K no quantitative assignment could be made, possibly because of complications produced by a slow rate of reorientation[14]. It is concluded that the n-propyl radical which, initially at 4 K, is in a rigidly distorted configuration, begins to tumble as the temperature is increased. It would be seen, however, that a quantitative analysis of this effect is not possible using the method of spectrum simulation employed here.

The spectrum of the allyl radical at 77 K is similar to that at 4 K which implies that no motional averaging occurs at this temperature. Motional averaging appears to be responsible, however, for the increased resolution of the spectra recorded at 128 and 173 K as shown in Fig. 4 d and 4 e. The simulation shown in Fig. 4 b indicates that a rapid reorientation about an axis perpendicular to the radical plane would give rise to a spectrum with a doublet structure on each of the five main lines. This agrees with observation except that the outermost components are imperfectly reproduced. Preferential reorientation about a unique axis directed perpendicular to the molecular frame occurs for the adsorbed benzene cation[15] at 203 K and, by analogy, this rotation might take place in other conjugated π-electron radicals as well. However, the assignment might not be unique. Thus, reorientation about one of the conjugated C – C-bonds would also provide the observed doublet splitting of all but the central line but with the additional feature that the outermost lines would not be well resolved (as shown in Figure 4 c). The spectrum of Fig. 4 e corresponds to a case with nearly isotropic couplings, indicative of fast tumbling at 173 K.

Other matrices: Comparison of the results of the present investigation with those of previous studies demonstrates that in certain cases the nature of the matrix significantly affects the conformation and mobility of radicals. Simple alkyl radicals have been prepared by irradiating the pure hydrocarbons[16]. The spectral resolution is, however, better in an argon matrix[2, 17] at 4 K and this permits matrix effects to be elucidated.

The spectrum of methyl in an argon matrix[17] is a quartet with intensities of 1.0 : 2.2 : 2.2 : 1.0 with $\Delta H_{pp} = 2.5$ G. The deviation from a binomial intensity distribution was explained in terms of power saturation while it is also possible that anisotropic tumbling was not taken into account.

The ethyl radical has been found to reorient about the $C_\alpha - C_\beta$ bond axis in an argon matrix[18] at 4 K. The couplings are similar to those observed in the silica gel matrix and the linewidth is about 1.5 G. The spectrum of the n-propyl radical has also been observed in an argon matrix[2]. The lineshape of the double-peaked lobe of each wing of the spectrum could not be accounted for, and the outermost peaks were regarded as being unidentified lines. However, the lineshape and the separation of the lines of the double-peaked lobe are in good agreement with those of the simulated spectrum of ethyl in an argon matrix. This indicates that the $\cdot CH_2$ group reorients about the $C_\alpha - C_\beta$ bond as in ethyl[19]. In contrast to this the n-propyl radical adsorbed on silica gel has a rigid conformation at 4 K. Furthermore the β-proton couplings are different in the silica gel matrix which indicates an asymmetric conformation whereas the protons are equivalent in the argon matrix the value of the coupling constant being $a_\beta = 34.8$ G.

The spectrum reported for the allyl radical[2] in an argon matrix was observed under rapid passage conditions which prevents making a detailed comparison. A qualitative analysis indicated, however, that the allyl radical has a rigid conformation in agreement with the observation made for the adsorbed radical at 4 K.

Acknowledgments

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