Novel Intramolecular Hydrogen Abstraction in the Radical Cation of Some Dioxacyclohexanes as Studied by EPR Spectroscopy and Kinetic Analysis†

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The radical cation of 2-methyl-1,3-dioxacyclohexane (1) in a frozen Freon matrix is found to release spontaneously a methyl radical and abstract intramolecularly a hydrogen atom from the resulting carbocation. Site selective deuteration of 1 demonstrates that the abstraction occurs predominantly at the methylene groups adjacent to the oxygen atoms of the carbocation. The experimental result is analyzed in terms of the Siebrand theory for quantum mechanical tunnelling. By means of the harmonic oscillator approximation efficient recurrence formulæ have been developed to calculate analytically the dual integration appearing in the theoretical rate constant.

Free radical conversion of the type shown in reaction (1) is one of the most thoroughly studied radical reactions in solids at low temperatures. A number of authors

\[
\text{CH}_3 + \text{RH} \rightarrow \text{CH}_4 + \cdot \text{R}
\]

(1)

have studied the reaction both experimentally1-13 and theoretically.14-18 In most of the experimental studies EPR spectral monitoring of the decay of the methyl radical and the growth of radical \( \cdot \text{R} \) in reaction (1) have been carried out. However, the overlap of the EPR signals of the two paramagnetic species as well as the random distribution of the intermolecular distance of the reactant pair hampers precise determination of the decay rate of the methyl radical.

In the present work we report a novel system in which the EPR signal appears solely due to the methyl radical which decays exponentially at various temperatures below 77 K. A reaction mechanism is proposed to account for the apparent lack of any other EPR spectrum. The system is regarded as ideal for the application of the Siebrand theory.9-13,15 We have improved the scope of the theory by providing analytic recurrence formulæ for the dual Franck–Condon factor needed to calculate the theoretical rate constant within the harmonic oscillator approximation.

Experimental

The system studied comprised dilute (10–100 mmol dm\(^{-3}\)) solutions of 2-methyl-1,3-dioxacyclohexane (1) [see reaction (II) for the chemical formula of 1] and its deuterated species in frozen CFCl\(_3\) matrices. The solutions were placed in a high-quality quartz tube of outer diameter 2–3 mm and \( \gamma \)-irradiated at 77 K to such an extent as to convert the parent solute molecules into their radical cations to a concentration of the order of 10\(^{-4}\) mmol dm\(^{-3}\). Details of this technique for producing radical ions are given elsewhere.19-24

The EPR measurement of the irradiated sample was carried out with a JEOL RE-2X spectrometer. An Air Products LTR-3 liquid helium transfer Heli-Tran refrigerator was used for the measurement at temperatures between ca. 90 and 14 K. A calibrated Au–Fe/chromel thermocouple was used for the temperature determination. These procedures are the same as adopted in our previous work.22-24 The EPR signal was processed with an EPSON PC286VG microcomputer for plotting the spectrum. The measurement of the signal intensity was started immediately after the cessation of \( \gamma \)-irradiation. The height of the derivative of the absorption was regarded as approximately proportional to the intensity of the radical.

2-Methyl-1,3-dioxacyclohexane (1) and its deuterated species, 1-5,5-\( \delta \)-1,3-propanediols according to the
literature.\textsuperscript{25} 1,3-Propanediol-2,2-$d_2$ and 1,3-propanediol-1,1,3,3-$d_4$ used for the synthesis of 1-5,5-$d_2$ and 1-4,4,6,6-$d_4$ were obtained by the methods in the literature (Refs. 26 and 27–28, respectively).

Results

Fig. 1 shows the EPR spectra observed at 77 K for \(\gamma\)-irradiated 1 in CFCl\(_3\) solutions at various times. Three different initial concentrations of 1, i.e., 10, 50 and 100 mmol dm\(^{-3}\) gave practically the same spectra and showed the same decay behaviour. The decay is semi-logarithmic as shown in Fig. 2 (□ represents a sample of 50 mmol dm\(^{-3}\) kept at 77 K). From Fig. 1 it is obvious that only the methyl radical is formed and the radical decays uniformly without giving rise to any new EPR spectra. The semi-logarithmic decay and the independence of the initial concentration of 1 indicate, respectively, that the decay is of a unimolecular type and that no reaction of the methyl radical with another molecule of 1 is involved. Almost identical spectra were observed for the two deuteriated isotopomers, 2 and 3. However, the three isotopomers revealed different decays at each temperature studied. Fig. 2 demonstrates representatively, the case of 77 K. The ordinate of the figure is the relative intensity normalized to the ‘initial’ intensity which corresponds to the first recording of the EPR spectrum immediately after \(\gamma\)-irradiation, i.e., about 2 min after cessation of irradiation.

The decay was observed not only at 77 K but also at several lower temperatures as shown by ○ for 1 and × for 3 in Fig. 3. The curves in Fig. 3 are theoretical, and will be discussed later.

Reaction mechanism. The appearance of the EPR spectrum of the methyl radical alone for all the three isotopomers is most remarkable in the present work. First, we consider the formation of the methyl radical. The result is consistent with the result of our previous study on the electronic structure of the radical cation of 1,3-dioxalkanes,\textsuperscript{29} where we have shown that the usual order of the highest and the penultimate occupied molecular orbitals consisting mainly of the two ‘out-of-plane’ non-bonding orbitals (n) on the oxygen atoms at sites 1 and 3 is reversed by the interaction of the orbital localized on the C–H or C–CH\(_3\) bond of the carbon atom at site 2. The reversal is represented conveniently as \(n_1 - n_2 < n_1 + n_2\) (higher in orbital energy) where \(n_1 \pm n_2\) stand for the molecular orbitals whose characters are described mainly by the in- and out-of-phase combinations of the two \(n\) orbitals on the oxygen atoms. As a result of this reversal the electron density of the C–H or C–CH\(_3\) bond of the carbon atom at site 2 becomes significant, in contrast to the usual case of \(n_1 + n_2 < n_1 - n_2\), where the electron density at the bond becomes zero on account of the orbital node of \(n_1 - n_2\). Thus, in the radical cation of the 2-methyl derivatives the C–CH\(_3\) bond may be weakened, resulting in breakage into –O–CH\(^{\bullet}\)–O– and CH\(_3\) fragments, which is, in fact, observed for 2-methyl-1,3-dioxacyclopentane.\textsuperscript{29}
Next, we account for the lack of any other EPR signal than that of the methyl radical. Since the decay shown in Fig. 2 is a unimolecular process, one might consider the following pseudo-first order reaction of the radical with the surrounding matrix molecules of CFCl₃, eqn. (III).

\[ ^\cdot \text{CH}_3 + \text{CFCl}_3 \rightarrow \text{CH}_3\text{Cl} + ^\cdot \text{CFCl}_2 \]  

(III)

The \(^\cdot \text{CFCl}_3\) radical is known to exhibit practically no structured EPR spectrum due to the extreme dipolar broadening of the hyperfine splitting, which is compatible with the apparent absence of any new EPR spectrum. However, this consideration contradicts the fact that the decay rates of the three isotopomers are definitely different. The remarkable difference between systems 1 and 3 and the smaller difference between 1 and 2 immediately suggests that the methyl radical abstracts the hydrogen atom mainly from either of the two equivalent methylene groups adjacent to the oxygen atoms of the carboxonium ion in reaction (II). The large difference between 1 and 3 is consistent with a primary isotope effect whereas the smaller one between 1 and 2 is indicative of a secondary isotope effect. Thus, we obtain eqn. (IV) for 1.

\[ ^\cdot \text{CH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_4 + \text{H}_2\text{O} + ^\cdot \text{H} \]  

(IV)

The paramagnetic species in the products of reaction (IV) should exhibit an EPR spectrum even if the proton hyperfine splitting is small due to possible delocalization of the odd \( p \) electron over the conjugative skeleton of \( ^\cdot \text{CH} = \text{O} = \text{C}^+\text{H} = \text{O}^- \). Since there is no sign of such a new spectrum in Fig. 1, we assume two possibilities: (1) the EPR spectrum of the paramagnetic species in the products of reaction (IV) is broadened extremely due to the anisotropy of the hyperfine tensor of the protons in the skeleton, or (2) the paramagnetic product of reaction (IV) is further converted into the radical \(^\cdot \text{CFCl}_3\) which is known to be elusive towards EPR measurement as mentioned above. At the moment we do not have a definite preference for either of the two possibilities. If the second possibility is the case, we have reaction (V).

\[ ^\cdot \text{CH} = \text{O} = \text{C}^+\text{H} = \text{O}^- + \text{CFCl}_3 \rightarrow \text{CH}_3\text{C} = \text{O} + ^\cdot \text{CFCl}_2 \]  

(V)

In this case we presume that the radical centre in the conjugative unit, \(^\cdot \text{CH} = \text{O} - \text{C}^+\text{H} = \text{O}^-\), in the left-hand side of reaction (V) is reactive enough to accept the chlorine atom from a nearby Freon molecule by heavy-atom tunnelling. The assumed reactions (II), (IV), and (V) account for the observation of the uncontaminated spectrum of the methyl radical in Fig. 1.

Analysis of the decay rate. In this section we analyse the observed decay rates of the methyl radical originating from the radical cations of 1 and 3 shown, respectively, by \( \circ \) and \( \times \) in Fig. 3. The system is ideal to test the Siebrand theory for quantum mechanical tunneling, where the hydrogen atom transfer from \( ^\cdot \text{C}_\text{A} = \text{H} + \text{C}_\text{B} \) to \( ^\cdot \text{C}_\text{A} + \text{C}_\text{B} = \text{H} \) is treated in terms of the golden rule by regarding the C–H vibration as perturbed by a low frequency vibration between the two carbon atoms. In the present system \( \text{C}_\text{A} \) and \( \text{C}_\text{B} \) correspond, respectively, to the carbon atom of either of the two equivalent methylene groups adjacent to the oxygen atoms of the carboxonium ion and the carbon atom of the methyl radical in reaction (IV). Although the precise location of the methyl radical detached from the radical cation of 1 or its deuterated isotopomers in reaction (II) is not known, we conjecture that the radical finds an energy minimum after detachment and faces the methylene unit of the resulting carboxonium ion in preparation for the hydrogen abstraction.

In the Siebrand theory the hydrogen atom transfer is regarded as being promoted by a high frequency C–H stretching modulated with a low frequency C–C vibration under the electronic interaction operator \( J_{\text{AB}}(R) \) with \( R \) denoting the instantaneous distance of the two carbon atoms shown schematically in Fig. 4. The rate constant of the transition from the initial state with the quantum numbers \( \nu \) and \( V \) for the C–H and C–C vibrations, respectively, to the final state with quantum numbers \( w \) and \( W \), is determined by means of the transition matrix \( U_{\nu,v} \). The arrangement of \( \text{C}_\text{A}, \text{H}, \) and \( \text{C}_\text{B} \) is assumed to be collinear.

\[ U_{\nu,v} = A_\nu(R - \bar{R}) |\chi_\nu|^2 |\chi_v|^2 (r - \bar{r}_A) A_\nu(R - \bar{R}) \]  

(1)

The symbols \( \lambda \) and \( \chi \) represent, respectively, the wavefunctions for the C–C and C–H vibrations, and the electronic interaction term \( J_{\text{AB}} \) is assumed to be given by eqn. (2) where \( \zeta \) is an orbital exponent (\( \pm 1.625 \)) for carbon and \( a_0 \) is the Bohr radius.

\[ J_{\text{AB}} = \bar{J} \exp(-\zeta(R - \bar{R})/a_0) \]  

(2)

If one notes that the instantaneous distance \( R \) is related to the hydrogen atom coordinates at equilibrium \( \bar{r}_A \) and \( \bar{r}_B \) and the sum of the two C–H bond lengths \( 2\bar{z} \) as in eqn. (3), the Franck–Condon integral for the C–H vibration appearing in eqn. (1) becomes an operator for the wavefunctions of the C–C vibration.

\[ R = \bar{r}_A - \bar{r}_B + 2\bar{z} \]  

(3)

Thus, the rate constant of the transition from the initial state with the quantum numbers \( \nu \) and \( V \) for the
C–H and C–C vibrations, respectively, to the final state with quantum numbers \( w \) and \( W \) is given by eqn. (4) where \( \Delta \) is the exothermicity of the reaction and the Franck–Condon integral is given by eqn. (5).

\[
k(v, V \rightarrow w, W) = \frac{4\pi^2}{\hbar} \rho(\epsilon_w + \epsilon_w - \epsilon_v - \epsilon_v + \Delta) \\
\times |\langle \Lambda_w(R - \bar{R})|J_{AB}(R - \bar{R})S_{w,v} \rangle|^2 \\
S_{w,v}(R - 2\xi) = \langle \chi_w^b(r - \bar{r}_b) || \chi_v^a(r - \bar{r}_A) \rangle
\]  

(4)

In order to compare the theoretical rate constant with the observed one at a temperature \( T \), summation over all the final as well as the initial states is necessary. Also, the energy conservation condition imposed by the delta function \( \rho \) must be taken into account.\(^{10}\) After all these factors have been taken care of, one has the expression of the theoretical rate constant at a temperature \( T \) as in eqn. (6), which can be compared with the experimental value.

\[
k(T) = \left[ \sum_v \sum_v k_{v,v} \exp\left( -\frac{\epsilon_v + \epsilon_v}{k_BT} \right) \right] \\
\times \left[ \sum_v \sum_v \exp\left( -\frac{\epsilon_v + \epsilon_v}{k_BT} \right) \right]^{-1}
\]  

(6)

with

\[
k_{v,w} = \sum_w \sum_w k(v, V \rightarrow w, W)
\]

(7)

For the computation of \( k(T) \) in eqn. (6) five parameters must be specified, namely the fundamental wave numbers in \( \text{cm}^{-1} \) for C–C and C–H stretching, \( \tilde{\nu}_{\text{C-C}} \), and \( \tilde{\nu}_{\text{C-H}} \) along with \( R - 2\xi, J, \) and \( \Delta \). Except for \( \tilde{\nu}_{\text{C-H}} \) (and \( \tilde{\nu}_{\text{C-D}} \) in the case of the deuterated species) an \textit{a priori} estimation of reasonable values for the rest of the parameters is not straightforward.

Although we deem that the experimental spectra and kinetic data are most valuable in this work, it is also interesting to see whether the experimental rate constant is reproduced by the Siebrand theory with reasonable values of these parameters. To determine the parameters we adopted the harmonic oscillator model for both C–C and C–H vibrations. This spoils the reality of the system. However, the drawback is partially compensated by the fact that the dual integration necessary for the calculation of eqn. (4), can be analytically expressed with the use of recurrent formulae, as detailed in the Appendix, so that non-linear least-squares fittings for the multi-parametric systems can be applied to determine the parameters automatically. After a number of trials of the set of the initial values for the parameters we have compromised by fixing \( \tilde{\nu}_{\text{C-H}} \) (and \( \tilde{\nu}_{\text{C-D}} \) modified by the ratio of the reduced masses) to a typical value of 3000 \( \text{cm}^{-1} \) (2202 \( \text{cm}^{-1} \) ) and let the remaining four parameters be determined by the least-squares fitting procedure of the computer. The result for \textit{I} turns out to be \( \tilde{\nu}_{\text{C-C}} = 75.87 \text{ cm}^{-1}, R - 2\xi \) (net distance of the hydrogen transfer) = 1.13 \( \text{Å} \), \( \Delta = 87.36 \text{ cm}^{-1} \), and \( J = 3.83 \text{ eV} \). Likewise, for \textit{3} we obtain \( \tilde{\nu}_{\text{C-C}} = 74.17 \text{ cm}^{-1}, R - 2\xi = 1.00 \text{ Å}, \Delta = 89.73 \text{ cm}^{-1} \), and \( J = 0.67 \text{ eV} \). From the results we note that the three parameters, \( \tilde{\nu}_{\text{C-C}}, R - 2\xi, \) and \( \Delta \) are more or less the same in the two systems \textit{I} and \textit{3} which is physically reasonable. However, as to the electronic term \( J \) the difference between the two is conspicuously large which cannot be physically justified. However, we found that manipulating this parameter independently of the other parameters over a wide range does not affect seriously the overall fitting of the experimental plots to the theoretical curve. For example, the curve for \textit{I} in Fig. 3 is drawn by replacing the above \( J = 3.83 \text{ eV} \) with the value for \textit{3}, that is, \( J = 0.67 \text{ eV} \). Thus, by sweeping this parameter under the carpet we may say that the Siebrand model, emphasizing the importance of the modulation by the low frequency C–C vibration, is compatible with the present experiment. A positive aspect of the above results is that the frequencies \( \tilde{\nu}_{\text{C-C}} \), considered to be crucial in the model, are comparable with typical frequencies of puckering of small ringed hydrocarbons.\(^{31}\) Thus, we may visualize the hydrogen atom transfer in reaction (IV) as assisted by the intramolecular ring puckering of the carbonium ion.

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Conclusions

The features of the present work are summarized as follows. (1) The apparent absence of the EPR signal which overlaps that of the methyl radical confers little ambiguity to the spectral data. (2) The semi-logarithmic decay of the methyl radical can be attributed to an intramolecular reaction with a relatively constant intermolecular distance. The analysis of systems such as the methyl radical in glassy alcohols involves the convolution of the kinetics at various intermolecular distances.\(^1\)\(^-\)\(^3\)\(^-\)\(^8\)\(^-\)\(^16\) (3) The dual integration in the Siebrand theory was expressed analytically by adopting the harmonic oscillator approximation and by developing relevant recurrence formulae. This allows us quick computation of the integration and the automatic determination of the theoretical parameters involved by non-linear least-squares fitting. (4) The low frequency of \(\bar{v}_{C-C}\) determined by the fitting may be associated with bending vibrations of the six-membered ring of the carbonium ion.

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Appendix

The Franck–Condon overlap with regard to the C–H vibration in eqns. (4) and (5) of the text, reproduced as (A-1) below, can be expanded to the polynomial in (A-2) by virtue of the recursive relationships of (A-3) and (A-4).

\[
S_{w,\nu}(x) = \int_{-\infty}^{\infty} dr \alpha^{\nu}(r) \chi^{A}(r + x) \quad (A-1)
\]

\[
S_{w,\nu}(x) = S_{0,\nu}(x) \sum_{i} A_{w,\nu}(i) x^i \quad (A-2)
\]

\[
S_{w,\nu+1}(x) = \sqrt{\frac{1}{2(v+1)}} \alpha^{\nu}x S_{w,\nu}(x) + \sqrt{\frac{w}{v+1}} S_{w-1,\nu}(x) \quad (A-3)
\]

\[
S_{w+1,\nu}(x) = -\sqrt{\frac{1}{2(v+1)}} \alpha^{\nu}x S_{w,\nu}(x) + \sqrt{\frac{v}{w+1}} S_{w,\nu-1}(x) \quad (A-4)
\]

Here, \(x = R - \bar{R}\) and \(S_{0,\nu}(x) = \exp(-\alpha^{\nu} x^2/2)\) with \(\alpha^{\nu} = 2\pi \sqrt{m_{C} c^{2} \nu_{C-H}}/h\), \(c\) being the velocity of light.

Substituting (A-2) into (A-3) and (A-4), we obtain (A-5) and (A-6).

\[
A_{w,\nu}(i) = \sqrt{\frac{1}{2(v+1)}} \alpha^{\nu} A_{w,\nu}(i - 1) + \sqrt{\frac{w}{v+1}} S_{w-1,\nu}(i) \quad (A-5)
\]

\[
A_{w+1,\nu}(i) = -\sqrt{\frac{1}{2(v+1)}} \alpha^{\nu} A_{w,\nu}(i - 1) + \sqrt{\frac{v}{w+1}} A_{w,\nu-1}(i) \quad (A-6)
\]

with

\[
A_{0,\nu}(i) = \begin{cases} \frac{\alpha^{\nu}}{\sqrt{2^i i!}} & \text{for } i = \nu \\ 0 & \text{for } i < \nu \end{cases} \quad (A-7)
\]

\[
A_{\nu,0}(i) = \begin{cases} \frac{-(\alpha^{\nu})^i}{\sqrt{2^i i!}} & \text{for } i = \nu \\ 0 & \text{for } i < \nu \end{cases} \quad (A-8)
\]

From (A-5)–(A-7) the coefficients are obtained for all \(w\), \(v\), and \(i\). Thus, eqn. (5) in the text is now fixed. Substituting the harmonic oscillator wavefunctions \(\Lambda_{\nu}\) (or \(\Lambda_{w}\)) explicitly given in (A-9) to \(\Lambda_{\nu}\) and \(\Lambda_{w}\) in eqn. (1) and referring to eqn. (2) in the text, we obtain the rate constant in eqn. (4) as a sum of the integrals of polynomials in terms of \(R\).

\[
\Lambda_{\nu}(x) = \sqrt{\frac{\alpha_{C}}{\pi m_{C} 2^\nu V!}} \exp(-\frac{\alpha_{C}^2 x^2}{2}) H_{\nu}(\alpha_{C} x) \quad (A-9)
\]

with \(\alpha_{C} = 2\pi \sqrt{m_{C} c^{2} \nu_{C-C}}/h\)

References


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