

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

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Kubota, S., Hishikawa, T., Makino, M., Ushida, K., Momose, T. and Shida, T., 1997. Novel Intramolecular Hydrogen Abstraction in the Radical Cation of Some Dioxacyclohexanes as Studied by EPR Spectroscopy and Kinetic Analysis. – Acta Chem. Scand. 51: 579–584. © Acta Chemica Scandinavica 1997.

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 carbonium ion. Site selective deuteration of **1** demonstrates that the abstraction occurs predominantly at the methylene groups adjacent to the oxygen atoms of the carbonium ion. The experimental result is analyzed in terms of the Siebrand theory for quantum mechanical tunnelling. By means of the harmonic oscillator approximation efficient recurrence formulae have been developed to calculate analytically the dual integration appearing in the theoretical rate constant.

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



have studied the reaction both experimentally^{1–13} 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 R· in reaction (I) 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 formulae for the dual Franck–Condon factor needed to calculate the theoretical rate constant within the harmonic oscillator approximation.

† Lecture held at the 14th International Conference on Radical Ions, Uppsala, Sweden, July 1–5, 1996.

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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 deuteriated species in frozen CFCl₃ matrices. The solutions were placed in a high-quality quartz tube of outer diameter 2–3 mm and γ -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 10⁻¹ 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 γ -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 deuteriated species, 1-5,5-*d*₂ (**2**) and 1-4,4,6,6-*d*₄ (**3**), were synthesized by condensation of acetaldehyde and protiated or deuteriated 1,3-propanediols according to the

literature.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 γ -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 (\square 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

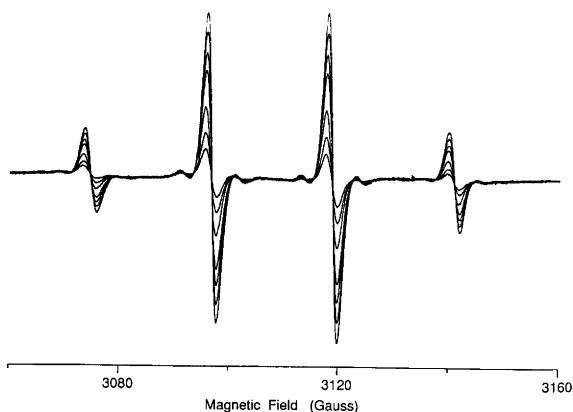


Fig. 1. EPR spectra observed for a γ -irradiated 2-methyl-1,3-dioxacyclohexane in a CFCl_3 matrix at 77 K. The homogeneous decay of methyl radical with no other EPR signal is most remarkable.

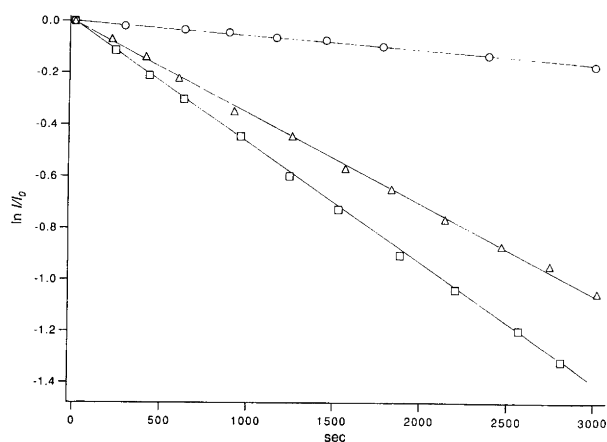


Fig. 2. Decay of the relative intensities for the three isotopomeric systems, 2-methyl-1,3-dioxacyclohexane (**1**) (\square) and its deuteriated species, 1-5,5- d_2 (Δ) and 1-4,4,6,6- d_4 (\circ).

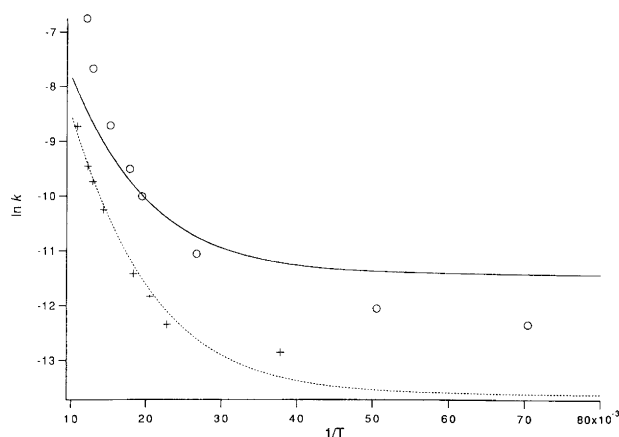


Fig. 3. Temperature dependence of the rate constant of the decay of methyl radical. The curves are theoretical (see the text).

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 γ -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 \circ for **1** and \times 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,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 $-\text{O}-\text{CH}^+-\text{O}-$ and $\cdot\text{CH}_3$ fragments, which is, in fact, observed for 2-methyl-1,3-dioxacyclopentane.²⁹

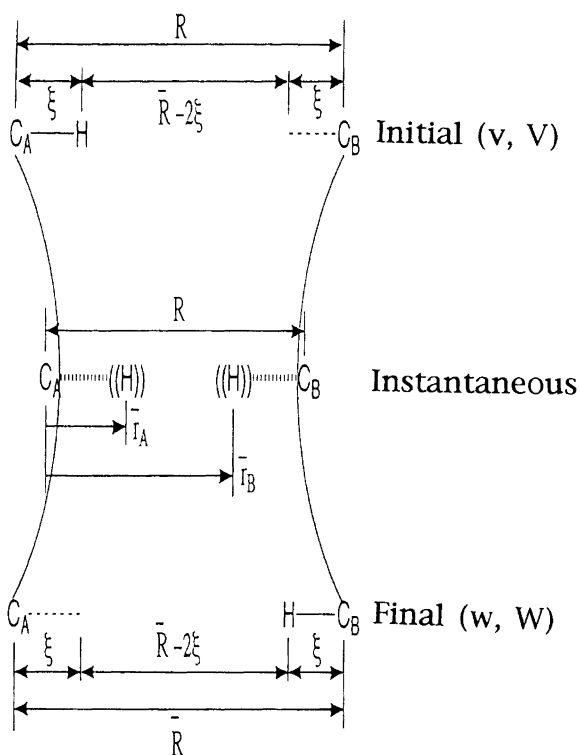


Fig. 4. Notations in Siebrand's model used in the present analysis.

C-H and C-C vibrations, respectively, to the final state with quantum numbers w and W is given by eqn. (4) where Δ is the exothermicity of the reaction and the Franck-Condon integral is given by eqn. (5).

$$k(v, V \rightarrow w, W) = \frac{4\pi^2}{h} \rho(\varepsilon_w + \varepsilon_W - \varepsilon_v - \varepsilon_V + \Delta) \times |\langle \Lambda_w(R - \bar{R}) | J_{AB}(R - \bar{R}) S_{w,v} \rangle|^2 \quad (4)$$

$$S_{w,v}(R - 2\xi) = S_{wV}(\bar{r}_B - \bar{r}_A) = \langle \chi_w^B(r - \bar{r}_B) | \chi_v^A(r - \bar{r}_A) \rangle \quad (5)$$

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 ρ 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.

$$k(T) = \left[\sum_V \sum_v k_{v,V} \exp\left(-\frac{\varepsilon_v + \varepsilon_V}{k_B T}\right) \right] \times \left[\sum_V \sum_v \exp\left(-\frac{\varepsilon_v + \varepsilon_V}{k_B T}\right) \right]^{-1} \quad (6)$$

with

$$k_{v,V} = \sum_W \sum_w k(v, V \rightarrow w, W) \quad (7)$$

For the computation of $k(T)$ in eqn. (6) five parameters must be specified, namely the fundamental wave-numbers in cm^{-1} for C-C and C-H stretching, $\tilde{\nu}_{C-C}$, and $\tilde{\nu}_{C-H}$ along with $\bar{R} - 2\xi$, \bar{J} , and Δ . Except for $\tilde{\nu}_{C-H}$ (and $\tilde{\nu}_{C-D}$ in the case of the deuteriated species) an *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 $\tilde{\nu}_{C-H}$ (and $\tilde{\nu}_{C-D}$ modified by the ratio of the reduced masses) to a typical value of 3000 cm^{-1} (2202 cm^{-1}) and let the remaining four parameters be determined by the least-squares fitting procedure of the computer. The result for **1** turns out to be $\tilde{\nu}_{C-C} = 75.87 \text{ cm}^{-1}$, $\bar{R} - 2\xi$ (net distance of the hydrogen transfer) = 1.13 \AA , $\Delta = 87.36 \text{ cm}^{-1}$, and $\bar{J} = 3.83 \text{ eV}$. Likewise, for **3** we obtain $\tilde{\nu}_{C-C} = 74.17 \text{ cm}^{-1}$, $\bar{R} - 2\xi = 1.00 \text{ \AA}$, $\Delta = 89.73 \text{ cm}^{-1}$, and $\bar{J} = 0.67 \text{ eV}$. From the results we note that the three parameters, $\tilde{\nu}_{C-C}$, $\bar{R} - 2\xi$, and Δ are more or less the same in the two systems **1** and **3** which is physically reasonable. However, as to the electronic term \bar{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 **1** in Fig. 3 is drawn by replacing the above $\bar{J} = 3.83 \text{ eV}$ with the value for **3**, that is, $\bar{J} = 0.67 \text{ eV}$. 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 $\tilde{\nu}_{C-C}$, 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.

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 $\tilde{\nu}_{C-C}$ determined by the fitting may be associated with bending vibrations of the six-membered ring of the carbonium ion.

Acknowledgements. The work was supported by a Grant-in-Aid for Scientific Research on Priority Areas No. 05232105 and Grant (A) No. 07404034 of the Ministry of Education, Science, Culture, and Sports, Japan. T.S. is grateful to The Murata Science Foundation for travel support.

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).

$$S_{w,v}(x) = \int_{-\infty}^{\infty} dr \chi_w^B(r) \chi_v^A(r+x) \quad (\text{A-1})$$

$$S_{w,v}(x) = S_{0,0}(x) \sum_i^{w+v} A_{w,v}(i) x^i \quad (\text{A-2})$$

$$S_{w,v+1}(x) = \sqrt{\frac{1}{2(v+1)}} \alpha_H x S_{w,v}(x) + \sqrt{\frac{w}{v+1}} S_{w-1,v}(x) \quad (\text{A-3})$$

$$S_{w+1,v}(x) = -\sqrt{\frac{1}{2(v+1)}} \alpha_H x S_{w,v}(x) + \sqrt{\frac{v}{w+1}} S_{w,v-1}(x) \quad (\text{A-4})$$

Here, $x = R - \bar{R}$ and $S_{0,0}(x) = \exp(-\alpha_H^2 x^2/4)$ with $\alpha_H = 2\pi \sqrt{m_H c \tilde{\nu}_{C-H}/h}$, c being the velocity of light.

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

$$A_{w,v+1}(i) = \sqrt{\frac{1}{2(v+1)}} \alpha_H A_{w,v}(i-1) + \sqrt{\frac{w}{v+1}} S_{w-1,v}(i) \quad (\text{A-5})$$

$$A_{w+1,v}(i) = -\sqrt{\frac{1}{2(v+1)}} \alpha_H A_{w,v}(i-1) + \sqrt{\frac{v}{w+1}} A_{w,v-1}(i) \quad (\text{A-6})$$

with

$$A_{0,v}(i) = \begin{cases} \frac{\alpha_H^v}{\sqrt{2^v v!}} & \text{for } i = v \\ 0 & \text{for } i < v \end{cases} \quad (\text{A-7})$$

$$A_{v,0}(i) = \begin{cases} \frac{-(\alpha_H)^v}{\sqrt{2^v v!}} & \text{for } i = v \\ 0 & \text{for } i < v \end{cases} \quad (\text{A-8})$$

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 Λ_v (or Λ_w) explicitly given in (A-9) to Λ_w and Λ_v 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 .

$$\Lambda_v(x) = \sqrt{\frac{\alpha_C}{\sqrt{\pi m_C 2^v V!}}} \times \exp\left(-\frac{\alpha_C^2 x^2}{2}\right) H_v(\alpha_C x) \quad (\text{A-9})$$

with $\alpha_C = 2\pi \sqrt{\frac{m_C c \tilde{\nu}_{C-C}}{h}}$

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Received July 1, 1997.