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Effect of Isotopic Substitution on the Electron Spin Dynamics of the $CH_3\dot{C}(COOH)_2$ Radical in X-Irradiated Methyl Malonic Acid Powder: Intrinsic Potentials and Activation Energies

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The temperature-dependent EPR line shapes from the methyl rotor of the X irradiation-induced $CH_3\dot{C}(COOH)_2$ radical in powder MMA (methyl malonic acid) and the X irradiation-induced radical $CD_3\dot{C}(COOH)_2$ in methyl-specifically deuterated powder MMA are studied experimentally for the temperature range 4.8 K (5 K) to 77 K (65 K). The hydrogenated system is simulated using a quantum inertial dynamical model with a hindering potential and three-site exchange rotation. The deuterated system is simulated using a classical three-site exchange model. The results show that due to the increase in moment of inertia, the tunneling frequency is negligible for the deuterated rotor, resulting in a stopped rotor low-temperature spectrum, while being sufficiently large for the hydrogenated system for this to exhibit tunneling. From the low-temperature deuterated analogue spectrum, the potential twist angle is estimated to $\delta = \pm 50° \pm 2°$ ($+n{\cdot}60°$, $n \in Z$). The site-exchange activation energy of the deuterium rotor is observed to be 387 K, substantially lower than the hindering potential depth of 618 K. The hydrogenated system exchange rotation rate assumes a linear behavior with 754 K activation energy in the classical region of temperatures above 50 K.

Introduction

Throughout the history of EPR, much attention has been paid to the temperature study of radical fragments of the type $\rangle\dot{C}$-CH_3 in solids, where the methyl group is undergoing hindered rotary or vibratory motion with respect to the lone electron orbital.[1] One reason for this is that it forms a very simple model system for the examination of the interplay between on one hand quantum mechanical effects particularly dominant at low temperature, such as mass dependence, the Pauli exclusion principle and tunneling, and on the other hand stochastic reservoir interactions responsible for high-temperature effects.

Contrary to the low-temperature quantum effects, the reservoir interactions are believed to be mass independent.[2] Methyl-specific isotopic substitution is therefore a very important tool in examining the relative influence of these mechanisms.[3,4]

The methyl rotation in the radical $CH_3\dot{C}(COOH)_2$ induced in powder MMA (methyl malonic acid) by x irradiation has previously been studied by Heller,[5] Clough et al.,[6] Clough and Hill,[7] Clough et al.,[8] and by Mottley et al.[9]

The earlier work[5] suffers from the misinterpretation of the composite spectrum of the two radicals present in unannealed x-irradiated MMA caused by the assumption that the E-lines of the $CH_3\dot{C}(COOH)_2$ 1:1:1:2:1:1:1 tunneling septet visible in the spectrum is due to the other radical. In a theoretical benchmark treatise by Freed,[10] the quantum septet EPR spectrum of $\rangle\dot{C}$-CH_3 radicals is later recognized.

In the EPR/ENDOR work by Clough et al.[6] on single-crystal MMA, the low-temperature tunneling 1:1:1:2:1:1:1 EPR septet of the $CH_3\dot{C}(COOH)_2$ radical is appreciated and confirmed by ENDOR measurements. A value for the tunneling frequency is obtained from the low-temperature ENDOR data by using an effective spin Hamiltonian operator including the tunneling splitting in a way inspired by the Heisenberg spin exchange model. In the present study, the potential barrier depth is obtained from the reported tunneling frequency by numerical calculations. Moreover, a model taking into account the full molecular degrees of freedom including all important vibration levels is employed in interpreting the experimental findings of the present work.

In the EPR/ELDOR works on single-crystal MMA by Clough et al.,[8] Mottley et al.,[9] and Clough and Hill,[7] experimental first-order transition sidebands are studied. Stating simplified formulas for the potential *twist angle* dependence of the relative intensities of the sideband transitions, Clough et al.[8] interpret their findings in terms of a value for the this angle. The twist angle (δ in eq 1) is the angle separating the potential minimum and the lone electron 2p orbital. In the present work, the same parameter is accurately determined from the deuterated analogue low-temperature spectrum. It is shown that the intensity ratio of the hydrogenated system sideband is consistent with the twist angle observed by us.

It is observed in the present work that, due to the increased mass, the deuterated analogue radical is stopped at low temperatures, although the hydrogenated system exhibit tunneling effects at similar temperatures. This extreme inertial effect allows the use of a classical three-site exchange model in the deuterated analogue case while a line shape model combining three-site exchange rotation with the quantum-inertial rotor Hamiltonian must be employed in the hydrogenated case.

The work of Clough et al.[6] and in particular the works on sidebands by Clough et al.,[8] Mottley et al.,[9] and Clough and Hill[7] represent very accurate measurements of the tunneling frequency from low-temperature experiments. The experimental

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temperature dependence of the exchange rates for the same radical and its deuterated analogue reported in the present work, therefore allows an investigation of the relationship between the potential barrier depth and the site-exchange activation energy.

Experimental Section

MMA powder with quoted purity of not less than 99% was irradiated at room temperature for 5−7 min with a W-anode X-ray tube operating at 70 kV and 20 mA. First derivative EPR spectra were recorded at X-band with a Varian E9 EPR spectrometer employing 100 kHz field modulation. The temperature dependence of the spectra was obtained by passing helium gas into the sample cavity using an Oxford ESR-9 cryostat.

Two main radicals $CH_3\dot{C}H(COOH)$ and $CH_3\dot{C}(COOH)_2$ were present in the EPR spectrum of MMA after X irradiation, in agreement with previous studies.[5,6] It was possible to obtain clean $CH_3\dot{C}(COOH)_2$ spectra by first heating the irradiated sample for 10−12 h at 80 °C after irradiation. The line shape of $CH_3\dot{C}(COOH)_2$ in the temperature range 77 to 300 K was observed to be the 1:3:3:1 high-temperature quartet. Reversible changes were observed in the line shape when the sample was brought below 77 K.

As will be pointed out in the discussion section, we believe the particular method of preparation of the deuterated sample $CD_3CH(COOH)_2$ is highly important to be secured of the removal of all irrelevant radicals and is therefore given in detail.

The diethyl ester, $CD_3CH(CO_2C_2H_5)_2$, was prepared by reaction of CD_3Br and sodium diethyl malonate.[11] GLC of the distilled product showed it to be >95% pure. The ester (5.3 g, 30 mmol) was hydrolyzed by boiling KOH (86%, 5.9 g, 90 mmol) in water (8 mL) and ethanol (45 mL) for 2h. After evaporation of the ethanol and addition of water (30 mL) the solution was acidified by hydrochloric acid. The diacid was obtained by continuous extraction of this solution by diethyl ether. The ether was evaporated and the $CD_3CH(COOH)_2$ recrystallized from a mixture of ethyl acetate and hexane,[12] mp 127−131 °C (dec). ^{1}H NMR (CD_3CN): δ 3.45 (s, C−H), ∼9.8 (s, very broad, O−H).

The deuterated analogue of the MMA was irradiated and annealed in the same way as the hydrogenated sample. EPR spectra were obtained at X-band with a Bruker ER200D-SRC spectrometer. Two main components were observed in the EPR spectrum of irradiated MMA-d$_3$, $CD_3\dot{C}H{-}COOH$ and $CD_3\dot{C}(COOH)_2$ in agreement with the hydrogenated compound. Only the $CD_3\dot{C}(COOH)_2$ radical remained after annealing of the sample. At 65 K the spectrum showed seven lines which changed reversibly into a pattern of four very broad lines at 5 K.

Reservoir Interaction Models

One of the largest problems of modeling C_3 rotor dynamics in solids is that of including temperature variations in a quantum mechanical dynamic model. The description of the complex thermal interactions between the methyl rotor system and its reservoir has been subjected to a variety of simplified models.

Perhaps the most detailed model proposed is the phonon bath model of Heidemann et al.,[13] in which both system and reservoir are described by Hamiltonians. However, an unreasonably large number of unknown parameters are left to be experimentally determined.

A general approach employing stochastic modeling of the reservoir has been suggested by Freed.[14] A stochastic Liouville operator introduces random transitions between molecular energy levels. However, again, the complexity of the model makes it difficult to use without further simplifications.

Freed[10] has proposed a simplifying assumption that the interaction with the reservoir occurs in random instantaneous events.

Gamble et al.[15] proposed an alternative simplification based on the assumption that the coupling of the spin rotational system to the lattice is sufficiently strong to retain the system at equilibrium in the course of the experiment. This model failed to explain particular experimental observations.[1]

Clough and Poldy[16] assumed a strongly hindered rotor mainly residing in one of the three potential minima. Interactions with the reservoir randomly provide sufficient energy for the rotor to instantaneously pass over the barrier, without affecting spin degrees of freedom. For a rotor with a tunneling frequency sufficiently large to prevent A/E mixing, this stochastic three-site jump model effectively interchanges only the two E-symmetry molecular states for each vibrational level, thus averaging the EPR lines from these states. This model has been successfully applied recently by Matsushita et al..[17] In an attempt to also account for the temperature dependence of sideband positions, Clough and Hill[7] and Allen[18] introduce a model involving only a few vibration levels and a stochastic jumping between the tunneling frequencies of these.

1. The Isolated Quantum Rotor Model. The isolated quantum rotor model assumes the rotors to be initially in thermal equilibrium with the reservoir at temperature *T*. In the course of the experiment, they are assumed not to interact with the reservoir and therefore follow the dynamic law of the quantum mechanical Liouville equation.

$$\frac{\partial\rho(t)}{\partial t} = -iH^{x}\rho(t), \quad H = H_{\mathrm{R}} + H_{\mathrm{SI}}$$

$$H_R = -\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\varphi^2} + \frac{1}{2}V_3(1 - \cos 3(\varphi - \delta)) \qquad (1)$$

$$H_{SI} = \omega_0 S_z - \sum_{n=-1}^{1}\omega_n I_{nz} + \sum_{n=-1}^{1} 2a\cos^2\left(\varphi - \frac{2\pi}{3}n\right)\mathbf{S}\cdot\mathbf{I}_n$$

Here, $\rho(t)$ is the density operator, **S** and $\{\mathbf{I}_n\}$ are electron spin and nuclear spin operators for spin $n = -1, 0, 1$, respectively, V_3 is the potential barrier depth, *I* is the moment of inertia for the rotor, and $H^x = [\mathrm{H}, ...]$. All other symbols have their usual meaning.[2]

The absorption EPR line shape in the linear response approximation is

$$\mathrm{Re}\langle S_+(\omega)\rangle = \mathrm{Re}\int_0^\infty e^{-i\omega t - t/T_2}\,Tr\{S_+\rho(t)\}\mathrm{d}t \qquad (2)$$

$$\rho(t) = e^{-iH^x t}\,(e^{-iS_y\pi/2}e^{-H/kT}e^{iS_y\pi/2})$$

Here, intrinsic broadening of magnitude $1/T_2$ has been added. Inherent in this formalism is the assumption that the initial rotor system condition is equilibrium.

By expanding eq 2 into the real eigenbasis of H, the following further simplification is achieved (summation over *m* and *n* is implicit):

$$\mathrm{Re}\langle S_+(\omega)\rangle = \frac{1}{2}\langle m|S_+|n\rangle[(\langle n|S_+|m\rangle - \langle m|S_+|n\rangle)(e^{-E_n/kT} - e^{-E_m/kT}) - \sum_k(\langle n|S_+|k\rangle\langle k|S_+|m\rangle + \langle k|S_+|n\rangle\langle m|S_+|k\rangle - \langle n|S_+|k\rangle\langle m|S_+|k\rangle - \langle k|S_+|n\rangle\langle k|S_+|m\rangle)e^{-E_k/kT}] \times \frac{1/T_2}{(\omega - (E_m - E_n))^2 + 1/T_2^{\,2}} \quad (3)$$

Performing the calculations in the Hilbert and not in the Liouville space shortens the calculation time dramatically. Each of the remaining matrix elements calculations reduce to a single loop over all basis vectors since eigenvectors for S_z are employed, and the principal numerical problem is thus the diagonalization of the Hamiltonian.

To minimize calculation time and numerical instability, a representation in which the Hamiltonian is real symmetric is chosen, specifically the real Fourier series basis[2] functions $\{\cos k\varphi/\sqrt{\pi},\ k\in\mathrm{N}\}\cup\{\sin k\varphi/\sqrt{\pi},\ k\in\mathrm{N}\}\cup 1/\sqrt{2\pi}$. A starting point for further refinement is therefore the product of these functions with the nuclear spin basis functions $|m_{-1}m_0m_1\rangle$ where $|m_n\rangle$ is the eigenfunction of the $\mathbf{I}_{nz}$ operator in eq 1.

For three identical nuclei, the Pauli principle requires overall wave functions that are unchanged under two two-nuclei interchanges. This renders the totally symmetric C_3 representation the only acceptable. By projection operator methods, functions possessing this symmetry are extracted from the above-assumed basis.[19] They are

$$\Phi_k = \Psi_k\left(|1\rangle + \cos\frac{2\pi k}{3}[|2\rangle + |3\rangle]\right) - \Psi_{-k}\left(\sin\frac{2\pi k}{3}[|2\rangle - |3\rangle]\right)$$

$$\Psi_k = \begin{cases} \frac{1}{\sqrt{\pi}}\sin|k|\varphi,\ k < 0 & |1\rangle = |m_{-1}m_0m_1\rangle \\ \frac{1}{\sqrt{2\pi}},\ k = 0 & |2\rangle = |m_1m_{-1}m_0\rangle \\ \frac{1}{\sqrt{\pi}}\cos|k|\varphi,\ k > 0 & |3\rangle = |m_1m_0m_{-1}\rangle \end{cases} \quad (4)$$

The spin functions $\{|i\rangle\}$ are interrelated by C_3 rotations or cyclic permutation of indices. If all combinations of spin labels (m_1,m_2,m_3) *not* inter-relateable by cyclic permutations are employed *once*, the joint set of corresponding $\{\Phi_k\}$ forms a complete orthonormal totally symmetric basis for the problem. In the case of all three nuclei in the same spin state, only basis vectors with ($k = 3n$, $n\in\mathrm{Z}$) exist.

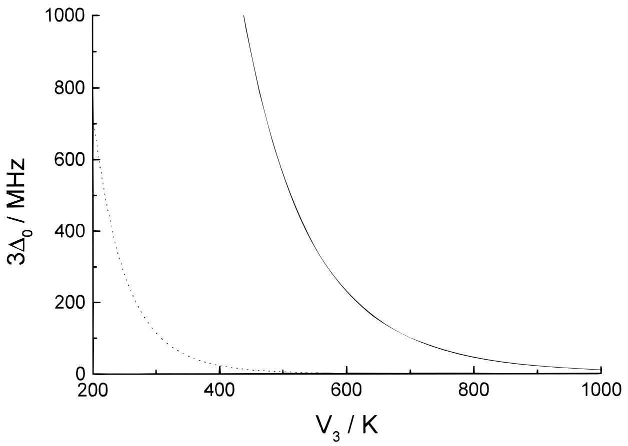

Figure 1. The tunneling frequency $3\Delta_0$ in MHz calculated from the numerical diagonalization of the molecular Hamiltonian and plotted against the hindering potential depth, V_3, in K for the rotor $-CH_3$ (solid line) and the rotor $-CD_3$ (dotted line).

The fundamental assumption of the model is that the temperature is fairly low, so that the rotor system is isolated from the reservoir during the experiment. Unlike many previous quantum mechanical theories,[15,16] the complete molecular Hamiltonian (cf. eq 1) is included, and the initial Boltzmann distribution is taken into account and is allowed to be affected by the electron spin dynamics through the hyperfine interaction. For the low-temperature limit, the model should therefore in itself be adequate, while it fails to account for the increasing degree of reservoir interactions as the temperature increases. A characteristic property of the model is therefore that it fails to give an averaged high-temperature spectrum for reasonable temperatures and potentials of the order of magnitude most frequently reported in the literature, a problem common to such models.[1] To make the model valid in the entire temperature range, a stochastic three-site exchange rotation model is included, as is discussed below.

2. Thermally Activated Three-Site Exchange Rotations. It has been shown that the three-site jump model rotating motional wave functions 0°, ±120° can be reduced to an effective two-site jump process interchanging the molecular eigenstates E_+ and E_-.[16,17] Following Clough and Poldy,[16] the Anderson theory[20] for calculating resultant spectra from a two-site jump process is employed. Each pair of E-lines obtained in the resultant spectrum from the quantum Liouvillean calculations is replaced by the calculated two-site jump process resultant spectrum before they are added to the total output spectrum, taking into account the original intrinsic broadening. Following Abragam,[21] given an intrinsic broadening of $1/\tau$, a jump rate of Ω, and taking the average and the interval between the E doublet to be μ and δ, respectively, the resultant line shape is calculated:

$$v \propto \begin{bmatrix}1\\1\\1\end{bmatrix},\quad A = \begin{bmatrix} i(-(\omega-\mu)+\delta/2) - \Omega - 1/\tau & \Omega \\ \Omega & i(-(\omega-\mu)-\delta/2) - \Omega - 1/\tau \end{bmatrix} \quad (5)$$

$$I(\omega) \propto \mathrm{Re}\{\langle v|A^{-1}|v\rangle\} \quad (6)$$

$$I(\omega) \propto \frac{-32\tau^3(\omega-\mu)^2 - 16\tau^4\delta^2\Omega - 128\tau^3\Omega^2 - 128\tau^2\Omega - 8\tau^3\delta^2 + 32\tau}{16\tau^4(\omega-\mu)^4 + (64\tau^4\Omega^2 - 8\tau^4\delta^2 + 64\tau^3\Omega + 32\tau^2)(\omega-\mu)^2 + \tau^4\delta^4 + 16\tau^3\delta^2\Omega + 8\tau^2\delta^2 + 64\tau^2\Omega^2 + 64\tau\Omega + 16} \quad (7)$$

The above model is valid under the assumption that A/E level mixing is negligible, which is guaranteed if the tunneling frequency $3\Delta_0$ exceeds the hyperfine coupling constant.[19] To be able to test that A/E mixing really is absent, a secular Hamiltonian with one A-level and two E-levels is employed in a stochastic Liouvillean rotating all states by three-site exchange rotations. This model is accurate in describing the effect of stochastic rotation on mixed states, but does not take into account the exact Hamiltonian with all vibration levels initially Boltzmann-distributed. A general model not subjected to any of the limitations of these models is in preparation.

Results

The EPR/ENDOR investigations of Clough et al.[6] on the $CH_3\dot{C}(COOH)_2$ radical of MMA conclude with an estimate of $3\Delta_0 = 160 \pm 30$ MHz for the tunneling frequency. The observations by Clough et al.[8] Mottley et al.[9] and Clough and Hill[7] on first-order transition EPR sidebands, offer a refinement of the tunneling frequency to 196 MHz using methods that secure high accuracy of the result. These results are therefore not questioned in the present work.

Figure 1 shows numerical calculations of the ground-state-vibration-level tunneling frequency $3\Delta_0$ for various potential barrier depths for $-CD_3$ and $-CH_3$ rotors obtained by diagonalizing the rotor Hamiltonian H_R of eq 1. The value of $3\Delta_0 = 196$ MHz for a $-CH_3$ rotor is observed to correspond to a potential barrier depth of about 618 K. For this potential barrier depth, Figure 1 gives a deuterium tunneling frequency of about 1.13 MHz. A value this much smaller than the hyperfine coupling results in an effective stopped rotor spectrum. The reason for the considerable reduction in tunneling frequency is the reduced deuterium amplitude of zero-point torsional oscillation[22] related to the mass increase.

The reports[7-9] on low temperature first order transition sidebands exterior to the central 1:1:1:2:1:1:1 spectrum provide useful information about a structural parameter that can be discussed in the light of the findings reported here. Assuming only zero vibration level contribution, secular approximation and validity of first-order perturbation theory, the relative intensities of the four lines present in each of the two sidebands give useful indication of the hindering potential twist angle δ of eq 1. It can be shown that with these approximations, the intensities of the inner and the outer transitions in the quartet sideband on each side of the central spectrum are given by eq 8, (scaled so that the central spectrum transitions have intensity unity to zero order in the states).[19]

$$\frac{a^2 \cos^2 3\delta}{18\Delta_0^2\left(1 + \frac{a^2}{72\Delta_0^2}\right)\left(1 + \frac{a^2}{72\Delta_0^2}\cos^2 3\delta\right)}, \qquad \omega = \omega_0 \pm 3\Delta_0 \pm \frac{a}{4} \text{ (inner pair)}$$

$$\frac{a^2 \sin^2 3\delta}{18\Delta_0^2\left(1 + \frac{a^2}{72\Delta_0^2}\right)\left(1 + \frac{a^2}{72\Delta_0^2}\sin^2 3\delta\right)}, \qquad \omega = \omega_0 \pm 3\Delta_0 \pm \frac{3a}{4} \text{ (outer pair)} \quad (8)$$

A version of this relationship is given in the original work by Mottley et al.[9] From the experimental observations of Mottley et al.,[9] a ratio of approximately 2:1 between inner and outer pair of lines in the sideband quartets may be estimated. By employing eq 8 (the denominator may be neglected), this ratio is related to a twist angle of $\delta = \pm 50° \pm 2° + n \cdot 60°$, $n \in Z$. Clough et al.[8] assume the same relationship and report a twist angle of $\delta = 12° + n \cdot 120°$, not observing the full ambiguiety in this result. The experimental results on the deuterium analogue radical presented in the present work offer an estimate of this parameter consistent with the choice $\delta = \pm 50° \pm 2° + n \cdot 60°$, $n \in Z$.

1. Hydrogenated Radical Spectrum Temperature Dependence. The line shape simulation method outlined above, employs a full quantum mechanical treatment of the rotary degrees of freedom. It includes a form of three-site exchange stochastic rotations of the motional wave function that is valid for high potential (with respect to the kinetic constant $\hbar^2/2I$) and sufficiently large tunneling splitting (with respect to the isotropic coupling constant a) to prevent A/E-state mixing. It is assumed that the magnitude $3\Delta_0 = 196$ MHz observed in this system is sufficient for this condition to be valid. Judging from the low intensity ratio between satellite lines and central spectrum,[7-9] it is concluded that A/E-mixing is negligible for our purposes.

The experimental spectra obtained from X irradiation induced $CH_3\dot{C}(COOH)_2$ radicals (possibly with other radicals present in minor concentrations) in MMA powder at 4.8−77 K are shown in Figure 2a. Spectra calculated using the stochastic quantum dynamical model outlined in the present work were fitted to the experimental observations of Figure 2a by variation of the exchange rotation rate $1/\tau$. The parameters $a = 25.28$ G, $V_3 = 618$ K, $\delta = 50°$, and the experimental temperatures were used as input. The calculated spectra showing an optimal fit with the experiments are shown in Figure 2b.

Three remarks should be made concerning the interpretation of the experimental spectra. First, it is observed that the outermost lines of the low-temperature experimental septet spectrum are more broadened than other parts. This is probably due to the effect of hyperfine anisotropy in the powder sample, since the transitions where all nuclei have identical spin quantum numbers are more affected by the anisotropy than other transitions, and since this broadening is absent in single-crystal samples.[6] Second, there is a small peak between the central pair of transitions in the high temperature 1:3:3:1 spectrum not seen in the calculated spectra. The presence of such a peak is not compatible with a 1:3:3:1 intensity ratio with our models. Furthermore, focusing on fitting 50−77 K spectra to the shape of this peak alone is not consistent with fitting to the remaining features of these spectra. For these reasons, this particular peak is believed to result from other radicals or effects otherwise not inherent in our models and it is not paid attention to in the temperature range indicated, when fitting spectra. Clough et al.[6] report the ENDOR observation of a second radical with tunneling frequency of about 600 MHz. The observed peak may originate from such a radical, or from radicals of entirely different chemical structure. Third, it should be noted that the line shape model used does not let the stochastic exchange influence the sidebands. Thus, the sidebands barely observed in the calculated spectra of Figure 2b do not show correct temperature dependence.

The rotation exchange rates of the calculated spectra giving an optimal fit to the experiments for the given temperatures are plotted against inverse temperature in Figure 3. The plot reveals a kink at about 50 K. For temperatures above this kink, an Arrhenius type exchange rate expression of activation energy 754 K (±127 K) may be fitted to the observations. At temperatures below this point, a similar expression with 275 K (±55 K) activation energy may be fitted to the points. The

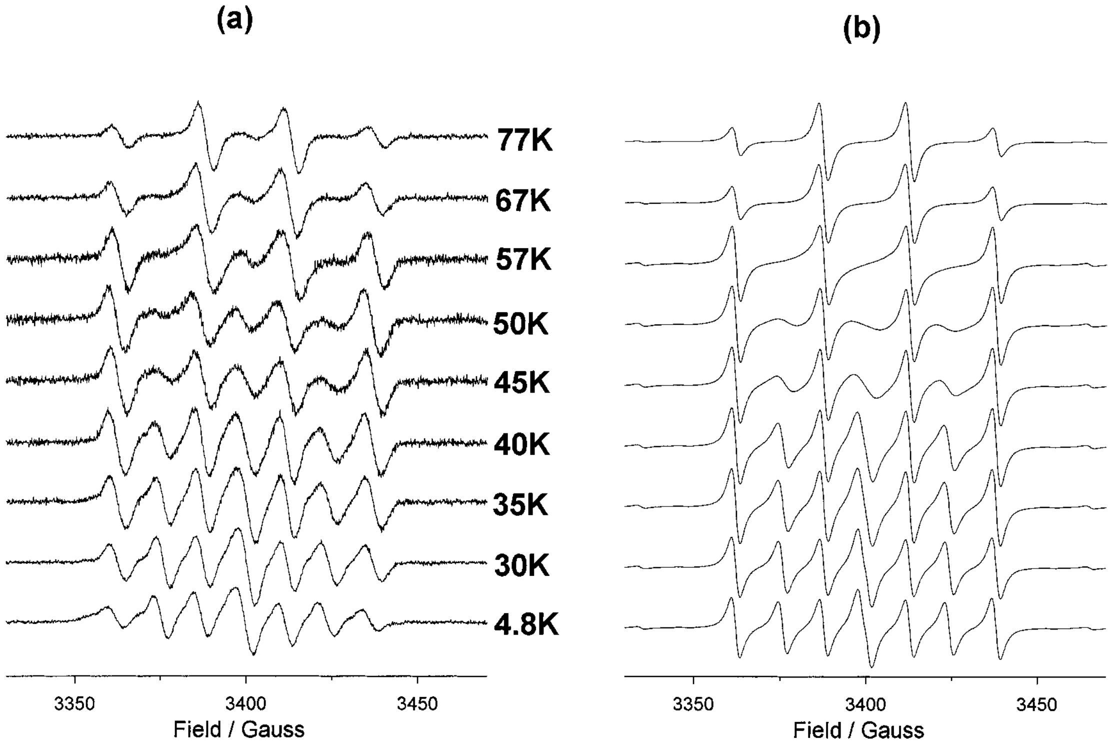

Figure 2. (a) Experimental EPR spectra from the $CH_3\dot{C}(COOH)_2$ radical in X-irradiated powder MMA in the temperature range 4.8−77 K. (b) Calculated spectra using a full molecular Hamiltonian model with hindering potential depth $V_3 = 618$ K, hyperfine coupling constant $a = 25.28$ G, potential twist angle $\delta = 50°$, temperatures as indicated in Figure 2a and stochastic exchange rotation rates as indicated in Figure 3.

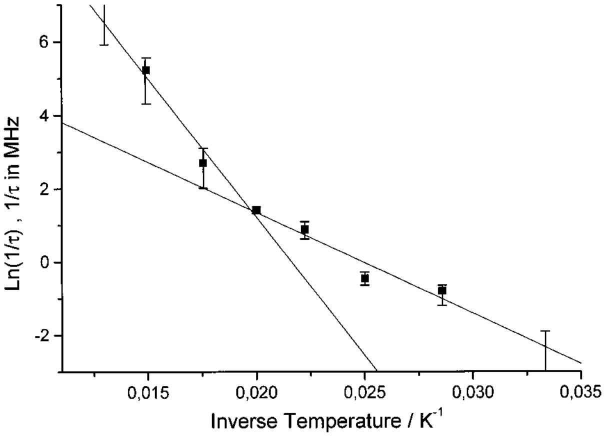

Figure 3. Stochastic three-site exchange rotation rates $1/\tau$, employed for calculating the spectra shown in Figure 2b showing the optimal correspondence to the experiments of Figure 2a of $CH_3\dot{C}(COOH)_2$ radicals in X-irradiated MMA. $\ln(1/\tau)$ in units of ln(MHz) is plotted logaritmically against inverse temperature in K^{-1}. The lines represent the optimal linear fits to the 4.8−50 K temperature region (Activation energy 754 K (±127 K)) and the 50−77 K region (Activation energy 275 K (±55 K)). The lowest (and highest) temperature data point is represented only with "error" bar, as the spectrum is unchanged for temperatures below (and above) the indicated temperature. This is the low (and high) temperature limit.

diverse behaviors in the classical and tunneling regions have been EPR-observed by other authors[17,23] using similar models. These observations conform with the theory of tunneling in chemical kinetics. As has been pointed out by Bell,[24] the effect of tunneling is to lower the activation energy. Thus, at temperatures where tunneling is dominant, a lower activation energy is expected, resulting in a kink in the reaction-rate vs temperature plot.

The analysis results obtained with the above presented line shape model were supported by similar findings using a quantum mechanical model with random three-site exchange rotation allowing A/E mixing, but assuming only zero vibration level contributions and secular Hamiltonian.

2. Deuterated Radical Spectrum Temperature Dependence. The experimental spectra obtained from X irradiation induced $CD_3\dot{C}(COOH)_2$ radicals in methyl-specific deuterated MMA powder at 5−65 K are shown in Figure 4a.

A stopped rotor spectrum is expected of the deuterated analogue radical, due to the small tunneling frequency. Indeed, employing the quantum mechanical line shape calculation program outlined above with a $V_3 = 618$ K potential, a temperature of 5 K, an isotropic hyperfine coupling constant of $a = 4.0$ G and a $\delta = 50°$ twist angle gives a spectrum identical with that of a classical deuterated methyl rotor stopped at 50°. To have a good fit with the experimental spectrum, twist angles of absolute value between ±48° and ±52° ($+n\cdot 60°$) must be employed. The optimal fit is achieved for $\delta = \pm 50° + n\cdot 60°$, $n \in Z$. From the study of the hydrogenated system sidebands or the deuterated analogue low-temperature spectrum alone, it is not possible to exclude the possibility of a 6-fold potential. However, as argued by Clough et al.,[8] a 6-fold potential symmetry requires an environment containing a plane of symmetry. This, in turn, would suggest a symmetric equilibrium orientation of the rotor with respect to the lone electron 2p orbital, which is not the case for this system.

Based on the above observations, it is assumed that a purely classical three-site exchange model mixing the three hyperfine couplings corresponding to 50°, 170°, and 290° rotor orientations will be adequate for representing the experimental observations.

A program developed earlier[4] is employed for these calculations, using the parameters $a = 4.0$ G and $\delta = 50°$ and varying the exchange rate $1/\tau$ to fit the calculations to the experimental observations. The calculated spectra showing optimal correspondence with the observations are shown in Figure 4b. The exchange rates obtained in this fashion are plotted against inverse temperature in Figure 5. An Arrhenius type exchange-rate temperature-dependence seems compatible with these data.

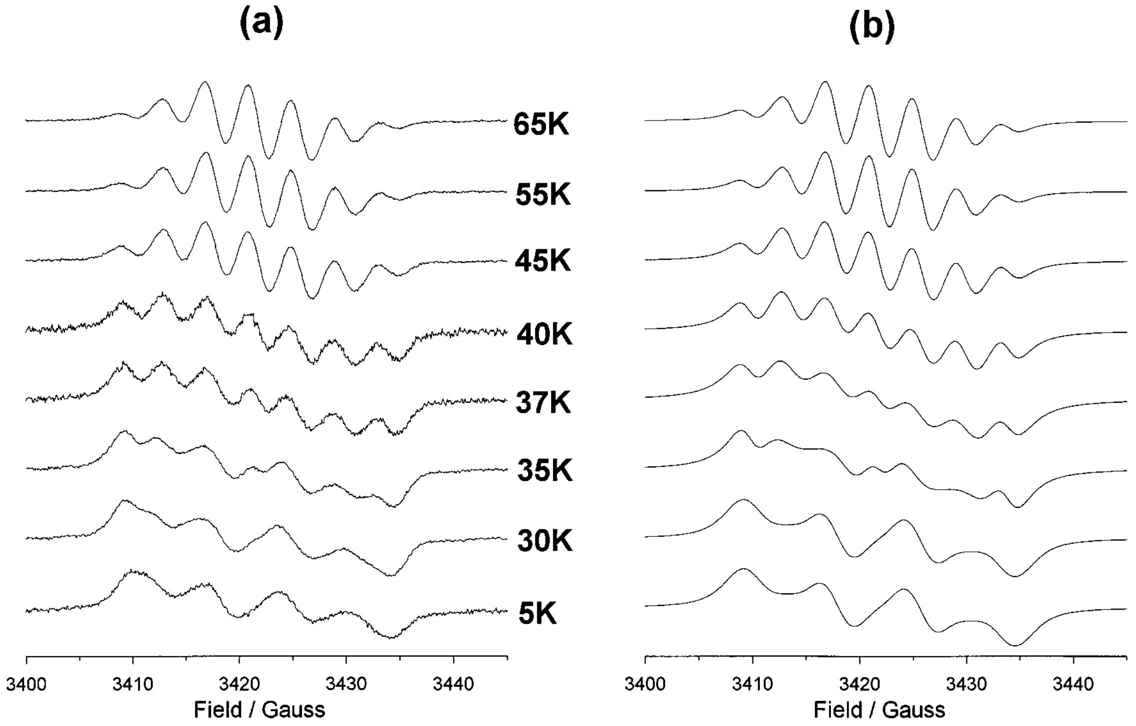

Figure 4. (a) Experimental EPR spectra from the $CD_3\dot{C}(COOH)_2$ radical in X-irradiated powder of methyl-specific deuterated MMA in the temperature range 5−65 K. (b) Calculated spectra using a classical three-site exchange model with a hyperfine coupling constant $a = 4.0$ G, a potential twist angle $\delta = 50°$, temperatures as indicated in Figure 4a and exchange rates as indicated in Figure 5.

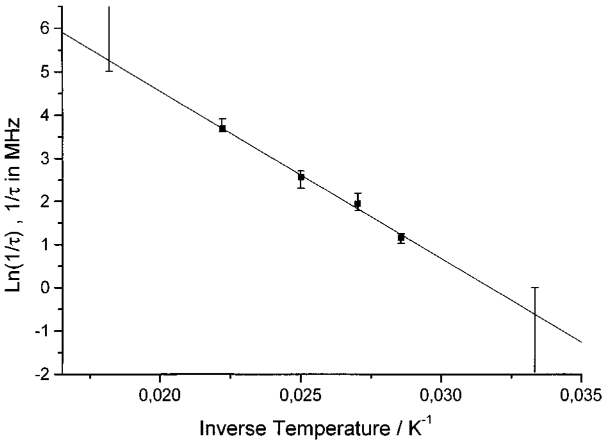

Figure 5. Stochastic three-site exchange rates $1/\tau$, employed for calculating the spectra shown in Figure 4b showing the optimal correspondence to the experiments of Figure 4a of $CD_3\dot{C}(COOH)_2$ radicals in X-irradiated methyl-specific deuterated powder MMA. $\ln(1/\tau)$ in units of ln(MHz) is plotted logaritmically against inverse temperature in K^{-1}. The solid line represents the best linear fit with an activation energy of $E_{a,D} = 387$ K (±21 K) and a preexponential factor of $A_D = 0.22 \times 10^6$ MHz. The lowest (and highest) temperature data point is represented only with "error" bar, as the spectrum is unchanged for temperatures below (and above) the indicated temperature. This is the low (and high) temperature limit.

The best fit of simulations to experiments assuming the Arrhenius exchange rate $1/\tau = A_D \exp(-E_{a,D}/kT)$ is obtained using $A_D = 0.22 \times 10^6$ MHz and $E_{a,D} = 387$ K (±21 K).

The deuterated analogue analysis results obtained with the classical three-site exchanged model were supported by very similar findings using a quantum mechanical model with random three-site exchange rotation allowing A/E mixing, but assuming only zero vibration level contributions and secular Hamiltonian.

Discussion

The tunneling frequency $3\Delta_0 = 196$ MHz reported by Mottley et al.,[9] Clough et al.,[8] and Clough and Hill[7] for the $CH_3\dot{C}(COOH)_2$ radical in MMA is supported by the new experimental investigations in the present work and the interpretation of the low-temperature hydrogenated system tunneling spectrum and the deuterated analogue radical stopped rotor spectrum. The accuracy with which the tunneling frequency can be estimated from the sideband detection[7−9] should be very high and it is interpreted in the present work in terms of a 618 K hindering potential barrier depth.

Furthermore, the present experimental EPR observations of the deuterated analogue radical suggests a twist angle $\delta = \pm 50° \pm 2°$ ($+n\cdot 60°$, $n \in Z$). This value is consistent with the sideband intensity ratio observed[7−9] for the hydrogenated radical.

In an EPR/ENDOR study on radicals in deuterated MMA by Clough and Poldy,[22] a low-temperature EPR spectrum of entirely different appearance than what is presented here, is associated with the $CD_3\dot{C}(COOH)_2$ radical. The authors of that work are not able to match their observations consistently with theory for any choice of spectral parameters without introducing ad hoc assumptions of quadrupole-related selective broadening in parts of the EPR and the ENDOR spectrum. The observations are finally interpreted as that of a rotor tunneling at a frequency in excess of 10 MHz. The experimental findings in the present work may be consistently interpreted as those of a stopped rotor, in accordance with quantum-inertial line shape calculations for hindering potential depth and twist angle identical with that of the hydrogenated radical. We therefore assume that the experimental spectra of Clough and Poldy[22] cannot be assigned to the isolated $CD_3\dot{C}(COOH)_2$ radical. It is possible that their findings may be assigned to a radical of very similar chemical structure, but with different potential barrier. The presence of several radical species may even be suggested. The reason for these problems may lie in the method of obtaining the deuterated sample (cf. Experimental Section).

Returning to the present work, the observed activation energy of 754 K (±126 K) for the thermally induced methyl rotation of the hydrogenated radical in the high-temperature region is larger than the 618 K intrinsic potential barrier. The deuterated

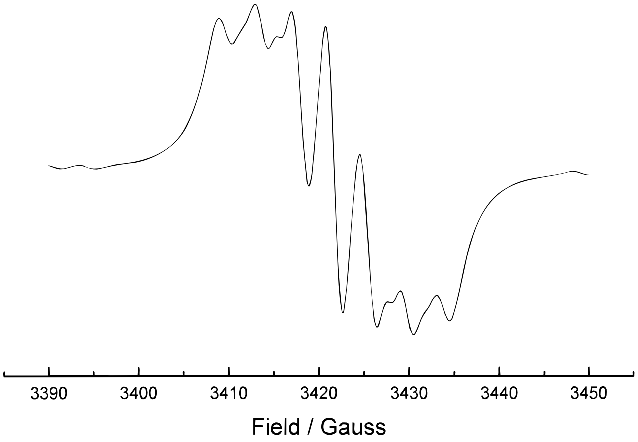

Figure 6. Calculated low-temperature spectrum (no exchange) of the $CD_3\dot{C}(COOH)_2$ radical with hyperfine coupling constant $a = 4.0$ G, potential twist angle $\delta = 50°$, potential barrier depth $V_3 = 387$ K and similar broadening as for the calculations in the 5K spectrum of Figure 4b.

analogue radical exhibits an exchange activation energy of 387 K (±21 K), considerably lower than the intrinsic potential barrier.

The results reported in the present work are surprising in two ways: First, that the hydrogenated and deuterated radical do not exhibit similar activation energies in the high-temperature region; second, that in particular the deuterated system has an activation energy very different from the intrinsic potential barrier depth.

As stated in the Introduction, it has previously been argued that $\rangle\dot{C}\text{-}CH_3$ radicals and methyl-deuterated analogue radicals should exhibit the same exchange rates, both on theoretical[2] and experimental[3] grounds. The experimental observations of Erickson et al.[3] do indicate small discrepancies between such systems, but they are believed to be insignificant. It should be noted that those experiments are conducted at much higher temperatures than the experiments reported in the present work. The results of Erickson et al.[3] indicate a higher activation energy for the deuterated analogue radical, i.e., in contrast to our findings.

The hydrogenated radical spectrum shows subsidiary peaks not reproducible by our theory which are believed to originate from other radicals, and the ENDOR observations of Clough et al.[6] indicate the presence of a radical of 600 MHz tunneling frequency, which is equivalent to a 230 K potential barrier depth. An alternative hypothesis could therefore be to assume that the deuterated spectra are influenced greatly by such a radical. This assumption may be rejected for two reasons. First, the quality of the fit of the single radical model to the experiments is rather good. Second, a potential barrier depth equal to the activation energy of 387 K would give a tunneling frequency of about 27 MHz. This may be observed from the calculations of Figure 6 to give a severely distorted low-temperature spectrum. It is therefore definite from our results alone that the observed activation energy cannot be interpreted as an intrinsic potential barrier. Thus, the parameters V_3 and $E_{a,D}$ both correspond to the same single radical, which is the methyl-deuterated analogue of the $CH_3\dot{C}(COOH)_2$ radical discussed in the literature[6−9] and in the present work.

Although believed to be subjected to numerous intermolecular perturbations, the thermal activation energy of site-exchange processes of $\rangle\dot{C}\text{-}CH_3$ radicals are observed by some authors to reflect intrinsic potential barrier depths.[17] There exist works that seem to contradict this; In the work of Geoffroy et al.[23] on a tunneling methyl rotor radical in X-irradiated 2,2,5-trimethyl-1,3-dioxane-4,6-dione crystals, an intrinsic potential barrier depth estimated from the tunneling frequency is twice the size of the activation energy of obtained from the linear high-temperature region of the exchange rotation rate plot.

In liquids, two mechanisms of activation energy modification have been suggested. Rakhimov et al.[25] discuss the *indirect cage effect* which they assume can give up to 50% reduction in the free activation energy of intramolecular chemical exchange due to the solvent. Additionally, the exchange rate[2,25] is inversely proportional to the friction parameter, which in liquids has an exponential temperature dependence thus affecting the effective overall activation energy. In the case of one-dimensional rotation in crystals, the interpretation of this parameter, beyond that it represents a simplified representation of the dissipative interaction with the reservoir, is not very lucid. We can, however, see no reason for it not to be exponentially temperature-dependent.

It has been pointed out to us that the reason deuterium has a lower activation energy may be related to the fact that the zero-point vibrational amplitude is smaller, making the deuterium atom in a molecule "smaller" than hydrogen.

An alternative theory involving the observed inertial dependence is the spin-rotation interaction discussed by Gutowsky et al.,[26] Brown et al.,[27] and Hubbard.[28] This interaction is shown to have a temperature-dependent effect on nuclear relaxation in liquids[28] that is also dependent on the nuclear species.[26] It may be, however, that the rotational correlation time is too short for the coupling.

Whatever the mechanism may be, it seems apparent that the relationship between activation energies and hindering potentials for the methyl rotor is rather complex and not yet fully understood.

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