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Electron Spin Relaxation by Spin-Rotation Interaction in Benzoyl and other Acyl Type Radicals

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Abstract. In various studies of the spin dynamics in radical pairs, benzoyl-type radicals have been one of the two paramagnetic pair species. Their electron spin relaxation has been assumed to be slow enough to be neglected in the data analysis. This assumption is checked by measuring the electron spin relaxation in a sequence of three acyl radicals (benzoyl, 2,4,6-trimethylbenzoyl and hexahydrobenzoyl) by time-resolved electron paramagnetic resonance spectroscopy. In contrast to the assumed slow relaxation, rather short spin-lattice relaxation times (100–400 ns) are found for benzoyl and 2,4,6-trimethylbenzoyl radicals from the decay of the integral initial electron polarization to thermal equilibrium at different temperatures and viscosities. The relaxation is induced by a spin-rotation coupling arising from two different types of radical movements: overall rotation of the whole radical and hindered internal rotation of the CO group. The predominant second contribution depends on the barrier of the internal rotation. The obtained results are well explained in the frame of Bull's theory when using a modified rotational correlation time τ_r. The size of the spin-rotation coupling due to the internal CO group rotation in benzoyl radicals is estimated to be $|C_\alpha| = 1510$ MHz.

1 Introduction

The electron spin relaxation rate is one of the major parameters which determine mechanism and size of magnetic spin effects in photochemically initiated radical reactions, especially in viscous and micelle solutions [1, 2]. The theoretical analysis of magnetic, isotope as well as CIDNP magnetic field dependences requires knowledge of the mechanism of electron spin relaxation for the radicals under study. The solvent viscosity and temperature dependences of the various possible relaxation mechanisms (due to modulation of hyperfine interaction [hfi] and g-tensor anisotropy, spin-rotation interaction, dipole-dipole interaction, etc.) are substantially different. For example, the dependence of the electron spin relaxation rate due to the modulation of the hfi anisotropy is proportional to the solvent viscosity, whereas it is inversely proportional to the viscosity in the case of relaxation due to spin-rotation interaction [3]. Recently, it has been shown that in going to very low magnetic fields the electron spin relaxation due to the modulation of the hfi anisotropy should go to zero [4], whereas electron spin relaxation due to spin-rotation interaction should increase twice [5, 6]. Thus, knowledge of the dominating electron spin relaxation mechanism is of great importance in the data analysis. The information can be obtained only on the basis of experimental studies of the temperature and viscosity dependence of electron relaxation times.

Magnetic and spin effects for radical pairs (RPs) in micelles involving benzoyl or 2,4,6-trimethylbenzoyl radicals have been investigated in a variety of studies [7–11]. In most of the papers the calculation of the relaxation rate in the RPs was carried through under neglect of the electron spin relaxation of the benzoyl species, taking into account only the contribution of the electron spin relaxation induced by the modulation of the hfi anisotropy of the corresponding alkyl or phosphonyl radical. However, later work has shown [12] that the electron spin relaxation of small acyl radicals is actually rather fast and is determined by spin-rotation interaction, and recently, the fast electron spin relaxation observed in acyl-containing biradicals was attributed to a spin-rotational mechanism as well [13, 14]. Thus, the neglect of the contribution of the electron spin relaxation of the benzoyl radical in the micelle work might have led to wrong predictions of the viscosity and magnetic field dependences of chemically induced dynamic nuclear polarization (CIDNP), isotope effect and magnetic-field modulation of reaction yields, as well as to errors in the different resulting parameters of escape rate and electron exchange interaction.

In this paper we have studied the electron spin relaxation in a sequence of three acyl radicals (benzoyl, 2,4,6-trimethylbenzoyl and hexahydrobenzoyl) by time-resolved electron paramagnetic resonance (TREPR) measurements at different temperatures and viscosities. On the basis of the obtained results the role of hindered rotation of the CO group for the spin-rotational relaxation in acyl type radicals is carefully analysed in the frame of the theoretical model of Bull [15], developed for nuclear spin relaxation in nuclear magnetic resonance (NMR) spectroscopy.

2 Experimental

2.1 TREPR Experiments

Our experimental setup for TREPR measurements after laser flash photolytic radical generation has been described previously [16]. It comprises a Compex 102 excimer (308 nm, 20 ns pulse width) or Nd-YAG (355 nm, 6 ns pulse width) laser and an X-band continuous-wave (cw)-EPR detection system without field modulation (response time $\tau_R = 90$ ns). Sample solutions were deoxygenated by purging with helium (30–40 min) and then exposed to laser irradiation (0.3–2 mJ per pulse on sample surface, 10 Hz repetition rate) while slowly flowing (50–100 laser shots per irradiation volume) through a quartz cell (1 mm optical path length) inside a TE_{103} EPR cavity. TREPR experiments were carried out with toluene solutions at temperatures varying from -95 to $+60$°C, with isopropanol solutions in the temperature range of $-35°C \leq T \leq 40°C$, and with a variety of other polar and unpolar solvents of different viscosities at room temperature. Alkanes were used as unpolar solvents to reproduce the internal media of micelles: heptane (0.41 cP), nonane (0.71 cP), dodecane (1.50 cP), hexadecane (3.32 cP), squalane (32.4 cP), a 4:1 mixture of squalane and heptane (8.32 cP) and paraffin oil (106.7 cP). Viscosities of the solvents were taken from ref. 17 or measured by capillary viscosimetry. 2-Hydroxy-2-methyl propiophenone (HMPP) and *tert*-butyl-cyclohexyl ketone (*t*-BCHK) were excited with the excimer laser; diphenyl-2,4,6-trimethylbenzoyl phosphine oxide (DTPO) solutions were excited with the Nd-YAG laser. The initial concentrations of the reagents were chosen so that the optical densities of the solutions were kept within 0.2–0.5. Spectra and time profiles were recorded at microwave powers of 0.3–10 mW, sufficiently low to keep saturation small ($\omega_1^2 T_1 T_2 \leq 0.1$).

2.2 Synthesis of tert-Butyl-Cyclohexyl Ketone

100 ml of a 2 M solution of cyclohexyl magnesium chloride in diethylether (Aldrich) were slowly added during 2 h to a solution of 60 ml pivalic anhydride (Fluka) in 250 ml of THF at −35°C with intensive stirring under argon atmosphere. Afterwards the reaction mixture was stirred at −20°C during 4 h and then at room temperature during night. The usual workup gave a mixture of the targeted product and pivalic anhydride. The mixture was dissolved in 50 ml of ethanol and the anhydride was hydrolyzed at 80°C for 3.5 h with a water solution of NaOH. After dilution with 30 ml of water, the organic layer was separated from the mixture and the water layer extracted by ether. The combined organic layers were washed by 5% NaOH, water, and 20% NH_4Cl. After drying over $MgSO_4$ and evaporation of the ether, the product was distilled twice, which gave 27 g (80%) of pure *tert*-butyl-cyclohexyl ketone [18].

All others chemicals were purchased from Fluka or Aldrich in their purest commercially available forms and used as supplied.

3 Results

After laser flash irradiation of HMPP in toluene solution the EPR spectrum depicted in Fig. 1 is observed. The photolysis of HMPP yields strongly TM polarized benzoyl and 2-hydroxy-2-propyl radicals via Norrish type I cleavage from a short-lived (~1 ns) excited triplet state, formed from the photoexcited singlet state of HMPP via intersystem crossing [19]. Figure 2a shows in more detail the benzoyl radical spectrum obtained during photolysis of HMPP in toluene at room temperature. Obviously, the lines are very broad, and the time profile of the EPR signal intensity (Fig. 2b) decays on a time scale of 0.5–1 μs due to short relaxation times T_1 and T_2.

For the analysis of the broad and unresolved EPR spectrum of benzoyl radicals the commonly applied solution of the Bloch equations cannot be used since

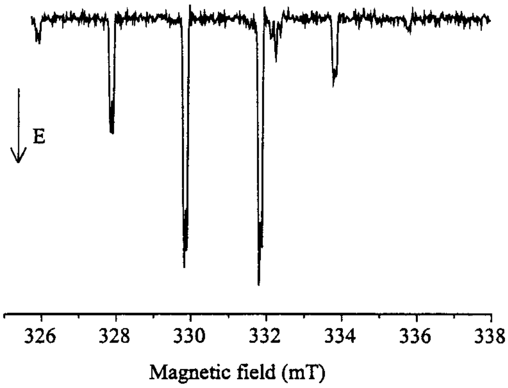

Fig. 1. EPR spectrum of benzoyl and 2-hydroxy-2-propyl radicals recorded 0.5 μs after laser excitation of HMPP in toluene at room temperature.

it is valid only for a single EPR transition. Therefore, to find out the electron spin relaxation times T_1 of the radicals we have used an approach which is described in detail elsewhere [20, 21]. The method involves the integration of the solution of the Bloch equations over the frequency range, in order to find out the time dependence of the integral magnetization instead of that of a single EPR transition. The analysis of the integral magnetization is especially easy if the rates of radical termination and creation of F-pair polarization remain well below the relaxation rate ($T_1^{-1} \sim 2-5 \cdot 10^6\ \mathrm{s}^{-1}$). Therefore, we have performed all TREPR measurements at low laser pulse energies (i.e., low concentrations of initiated radicals) to meet this condition. Then, the EPR-time profiles of the benzoyl type radicals, integrated over the magnetic field, should follow the solution obtained in ref. 20 in the fast-relaxation limit, which reads under the conditions $\omega_1^2 T_1 T_2 \ll 1$ and $T_1 \neq \tau_R$:

$$S(t) = \frac{C\pi\omega_1}{1-\tau_R/T_1}(M_z^0 - P_{eq}R_0)\left(\exp\left(-\frac{t}{T_1}\right) - \exp\left(-\frac{t}{\tau_R}\right)\right) + C\pi\omega_1 P_{eq}R_0\left(1-\exp\left(-\frac{t}{\tau_R}\right)\right), \qquad (1)$$

where M_z^0 is the initial z-magnetization of the radicals, R_0 the initial radical concentration, and $P_{eq}R_0$ its equilibrium z-magnetization. ω_1 is the microwave field amplitude, and τ_R and C are the response time and sensitivity, respectively, of the spectrometer. Equation (1) can be parameterized as

$$S(t) = \frac{A-B}{1-\tau_R/T_1}\left(\exp\left(-\frac{t}{T_1}\right) - \exp\left(-\frac{t}{\tau_R}\right)\right) + B\left(1-\exp\left(-\frac{t}{\tau_R}\right)\right). \qquad (2)$$

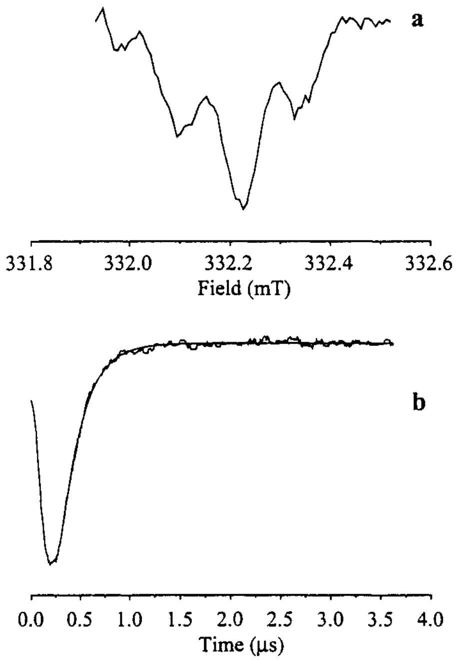

Fig. 2. EPR spectrum (**a**) and integrated EPR time profile (**b**) of benzoyl radicals in toluene at room temperature after laser excitation of HMPP and least-squares fit with Eq. (2).

Thus, keeping the condition $\omega_1^2 T_1 T_2 \ll 1$ satisfied (low microwave field amplitude), one can obtain the value of T_1 by least-squares fitting of Eq. (2) with only three parameters A, B and T_1 to the experimental EPR time profiles integrated over the magnetic field.

A typical example for the quality of the fits is plotted in Fig. 2b. Only the part of the time profile representing the decay of the initial magnetization to its equilibrium level was fitted. The initial (negative) rise of the integrated EPR profiles turned out to be contaminated by several effects resulting from the large line widths on the early time scale (e.g., cutting of line wings and heavy overlap with the neighboring line of the 2-hydroxy-2-propyl radicals [Figs. 1 and 2a]. The statistical error in T_1 was about ±(5–10)%. The absolute error is believed to be within ±(15–20)%, depending mainly on the accuracy of the τ_R determination and partial violation of the condition for the fast-relaxation limit [20].

In order to examine the dependence of T_1 of benzoyl radicals on viscosity (η) and temperature (T), the TREPR spectra of that radical were recorded in a variety of unpolar solvents at different temperatures. The experimental data were fitted by the procedure described above.

A series of alkanes (see Sect. 2) with different viscosities (ranging from 0.41 to 106.7 cP) were used to get viscosity-dependent TREPR spectra at room temperature. In Fig. 3 the resulting viscosity dependence of T_1^{-1} is plotted (open squares) over T/η. Obviously, the relaxation rate T_1^{-1} decreases with increasing viscosity. A linear increase of the relaxation rate with T/η is characteristic for a spin-rotation relaxation mechanism [22, 23]. A linear fit of the data with

$$T_1^{-1} = AT/\eta + B \tag{3}$$

leads to a slope $A = 2860\ \mathrm{s^{-1}K^{-1}cP}$ and an intercept $B = 4.25 \cdot 10^6\ \mathrm{s^{-1}}$. In simple cases, a stochastically modulated spin-rotation interaction should result in a relaxation rate given by [22]

$$\begin{aligned} T_1^{-1} &= (12\pi r_0^3)^{-1}(\Delta g_{\parallel}^2 + 2\Delta g_{\perp}^2)(k_B T/\eta), \qquad (4)\\ \Delta g_{\parallel} &= g_{zz} - 2.0023, \\ \Delta g_{\perp} &= (g_{xx} + g_{yy})/2 - 2.0023, \end{aligned}$$

where $r_0 = 0.28$ nm is the radical radius in spherical approximation [24], $g_{xx} = 2.0040$, $g_{yy} = 2.0024$, $g_{zz} = 1.9961$ [25] are the principal values of the g-tensor of the benzoyl radical, and k_B is the Boltzmann constant. This dependence of T_1^{-1} in Eq. (4) on the parameter T/η is plotted in Fig. 3 as dotted line. Its slope agrees with the experimental finding, but the actually observed relaxation rate in alkanes is much faster than the one estimated from Eq. (4). Obviously, the relaxation is dominated by an additional contribution contained in the parameter B in Eq. (3).

The results of the next series of experiments are plotted with full circles in Fig. 3. They stem from measurements in toluene solution at different tempera-

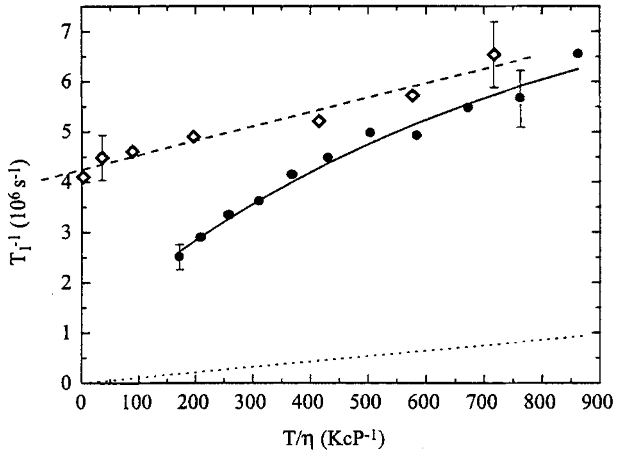

Fig. 3. Dependence of the relaxation rate T_1^{-1} of benzoyl radicals on the parameter T/η in a series of alkanes (◇) at room temperature ($T = 20°$C) and in toluene (●) at temperatures ranging from −35 to +60°C. Dotted line is a plot of the spin-rotational contribution as estimated from Eq. (4). Dashed and solid lines are the least-squares fits to the experimental data with linear regression and Eq. (12), respectively.

tures ranging from −35 to +60°C. The dependence of the toluene viscosity on temperature was taken from ref. 17. In this second series of experiments the relaxation rate T_1^{-1} depends on the parameter T/η in a slightly different way. Variation of the temperature obviously leads to changes in the value of B, which remained unchanged in the first series of experiments at room temperature. Thus, B is a function of temperature, which has to be explained.

The temperature and viscosity dependence of T_1 for the smallest acyl radical, the formyl radical (HCO), has been well described by the spin-rotational mechanism [12]. No additional relaxation mechanism was found. This is reasonable, because the formyl radical possesses a rather strong spin-rotation coupling [26] (Table 1) and a small radius r_0 (note that $T_1^{-1} \propto 1/r_0^3$ in Eq. (4)). The principal values of the g-tensor are almost the same for formyl and benzoyl radicals (Table 1), but the larger radius of the latter species is expected to slow down the spin-rotational relaxation considerably. Nevertheless, it should still be dominant, because estimated values for the relaxation due to the modulation of the g- and hfi-tensor anisotropies turn out to be more than one order of magnitude smaller than the spin-rotation contribution given in Eq. (4). However, Eq. (4) describes only the relaxation arising from the stochastically modulated rotation of the whole molecule. In the benzoyl radical there can be in addition a rotation of the CO group around the C-CO bond. This internal rotation should also lead to relaxation of the electron spin. To check on that qualitatively, we have compared two acyl radicals of about the same size but with different barriers for the rotation of the acyl group. For this purpose we synthesized *tert*-butyl-cyclohexyl ketone (see Sect. 2) to generate photochemically hexahydrobenzoyl radicals. Hexahydrobenzoyl and benzoyl radicals have about the same molecular size, structure and moment of inertia. Hence, relaxation due to coupling of the spin with the overall rotation of the whole molecule should be about the same. But the internal rotation of the CO group should be less hindered in hexahydrobenzoyl than it is in benzoyl radicals because of π-conjugation in the latter. This is well illustrated by comparing the barriers of the corresponding internal rotations around the C-CHO bond in benzaldehyde (4.7–8 kcal/mol, determined by several techniques [27]) and, e.g., isobutyraldehyde (≈1.5 kcal/mol [28]).

The EPR spectrum of the hexahydrobenzoyl radical turned out to consist of one broad line, which could be well measured only at low temperatures. After laser flash irradiation of *tert*-butyl-cyclohexyl ketone in toluene solution at −95°C the EPR spectrum shown in Fig. 4a is observed. For comparison, Fig. 4b gives the spectrum of benzoyl and 2-hydroxy-2-propyl radicals observed after laser flash

Table 1. Spectroscopic constants of formyl [26] and benzoyl radicals [25].

Radical	Spin-rotational coupling (MHz) C_1	C_2	C_3	Electronic g-value g_1	g_2	g_3
Formyl	−207.5	17.1	8120	2.0037	2.0023	1.9948
Benzoyl	–	–	–	2.0040	2.0024	1.9961

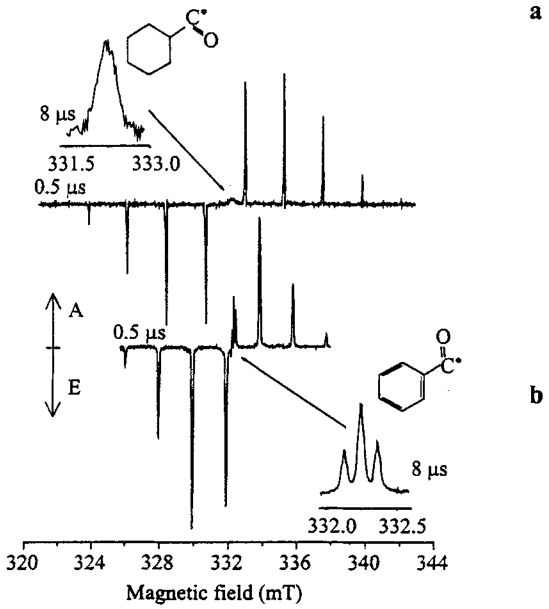

Fig. 4. **a** EPR spectrum of hexahydrobenzoyl and *tert*-butyl radicals recorded 0.5 µs after laser excitation of *tert*-butyl-cyclohexyl-ketone in toluene at −95°C. **b** EPR spectrum of benzoyl and 2-hydroxy-2-propyl radicals recorded 0.5 µs after laser excitation of HMPP in toluene at −86°C. Lines of the corresponding acyl radicals, measured 8 µs after laser excitation, are given enlarged.

photolysis of HMPP in toluene at −86°C. As expected, the line width of the hexahydrobenzoyl radicals is considerably larger than that of the benzoyl radicals, meaning that T_2 is clearly shorter for the former species (note that $T_1 = T_2$ for spin-rotational relaxation).

In addition we have also measured the relaxation time T_1 of 2,4,6-trimethylbenzoyl radicals by photolyzing DTPO in benzene and methanol at room temperature. The T_1 of these species turned out to be more than two times shorter than that of the unsubstituted benzoyl radical. Again, the rotational barrier of the CO group rotation in 2,4,6-trimethylbenzoyl radical is smaller than it is in the benzoyl species, according to the data for the corresponding aldehydes [27]. In Table 2 we have summarized the literature and our data on line widths and electron spin-lattice relaxation times T_1 of a series of acyl radicals. We also give the rotational barriers around the C-CHO bond in the corresponding aldehydes, in order to illustrate the barrier dependence of the relaxation rate. The barriers of the CO group rotation in radicals are usually unknown.

Table 2. Line widths $\Delta H_{1/2}$ and spin-lattice relaxation times T_1 of acyl radicals in dependence on the barrier V_a of the CHO group rotation in the corresponding aldehydes.

Radical	Solvent	T (°C)	$\Delta H_{1/2}$ (mT) [31]	T_1 (ns), this work	V_a (kcal/mol)
HCO	MTHF	−103	0.33(4)		0
CH_3CO	MTHF	−103	0.25(4)		1.2^a
C_2H_5CO	MTHF	−83	0.23(5)		1.25^b
$(CH_3)_2CHCO$	MTHF	−95	0.23(5)		1.5^a
$(CH_3)_3CCO$	MTHF	−95	0.32(5)		0.96^c
$(C_6H_{11})CO$	MTHF	−95	$>0.20^d$		1.5^e
	Toluene	−95	$>0.20^d$		
$(C_6H_5)CO$	THF	−90	0.012(2)		
	Toluene			200	
	Benzene			200	7.6^f
	Methanol	+20		155	4.6^g
	Isopropanol			185	
	Acetonitrile			215	
2,4,6-trimethyl-$(C_6H_5)CO$	Benzene	+20		<100	2.0^g
	Methanol	+20		<80	

[a] From microwave and infrared measurements [28].
[b] From microwave and infrared measurements [29].
[c] From microwave and infrared measurements [30].
[d] This work.
[e] Assumed to be the same as for isobutyraldehyde.
[f] From NMR methods [27].
[g] Calculated (MMP1) [27].

4 Discussion

EPR spectra of saturated acyl radicals have been reported to exhibit rather broad lines [12, 31]. On the other hand, Davies et al. [32] reported narrow well-resolved spectra of acyl radicals with the CO group attached to an unsaturated moiety. This is in line with our results for the benzoyl and hexahydrobenzoyl. Obviously, the internal CO group rotation in acyl radicals induces an effective electron spin relaxation, which becomes the faster the lower the rotational barrier is (Table 2).

The common model for the spin-rotational mechanism of electron spin relaxation considers only the effect of the overall rotation of a radical on the electron relaxation [22, 23]. The contribution of internal rotations to the spin-rotational mechanism of electron relaxation has not been described in literature. However, spin-rotational relaxation due to internal rotations has been found to play a significant role in nuclear spin relaxation observed by NMR [33–36].

In particular, for several methyl-containing compounds with hindered rotation of the CH_3 group Ellis et al. [37] found a nearly linear relationship between $T_{1,SR}$ and the potential barrier V_0 of the rotation from ^{13}C relaxation measurements at fixed temperature (38°C):

$$T_{1,\mathrm{SR}} = 25.61\,(1 + 0.382\,V_0), \tag{5}$$

where $T_{1,\mathrm{SR}}$ is given in seconds and V_0 is the barrier height in kilocalories per mole, determined by microwave spectroscopic methods. The relation is remarkable in view of the variety of compounds involved, with reported barriers as high as 5.4 kcal/mol. Those results show the same qualitative dependence of the relaxation time on the rotational barrier as observed in this work (see Table 2): the relaxation is the faster the lower the rotational barrier is.

A comprehensive theoretical study of the rotational movement of a symmetric-top molecule with internal rotation was carried out by Bull [15, 38, 39]. In ref. 15 he employed the extended rotational J,M-diffusion (EDJ,M) models for both the rotation of the whole molecule and the internal hindered rotation with a cosinusoidal barrier. In his later treatments he applied a Fokker-Planck-Langevin model [38] for the molecular movement and finally carried through quantum analogues of his two previous treatments [39]. In the treatments he used the assumption that both the overall and internal movements are randomized by collisions and have the same correlation times τ_J, the average time between collisions. The spin-rotation relaxation rate was shown to be the same in the classical and quantum treatments of the ED model if $\Lambda = \hbar^2(I_\alpha k_\mathrm{B}T)^{-1} \ll 1$ [39], where I_α is the moment of inertia of the internal rotor along the axis of rotation. The moment of inertia of the acyl group along the C-CO bond estimated from the molecular structure is $I_\alpha = 2.66 \cdot 10^{-46}$ kgm^2 and, hence, $\Lambda = 0.01$ at room temperature. Since $\Lambda \ll 1$, we used the classical formulation of the general EDJ model. Neglecting interference terms between overall and internal rotation as has been done by Bull, the spin-rotational relaxation rate induced by the internal rotation of the molecular rotor is (eq. (61) in ref. 15)

$$T^{-1}_{1,\mathrm{int}} = \left(\frac{2}{3\hbar^2}\right) I_\alpha \left(1 - \frac{I_\alpha}{I_Z}\right) k_\mathrm{B} T C_\alpha^2 \tau_J \sum_{k=-1}^{1} F(k) (d^{(1)}_{k0}(\theta))^2, \tag{6}$$

where

$$F(k) = I_\alpha \frac{1 - I_\alpha / I_Z}{\tau_J k_\mathrm{B} T} \int_0^\infty \exp(-t/\tau_J) f_k(t) \langle \dot\alpha(0) \dot\alpha(t) \rangle \mathrm{d}t,$$

$$f_k(t) = (1+\xi)^{1/2} \int_0^\pi \left(\sum_a (d^{(1)}_{ka}(\beta))^2 (1 + \xi\cos^2\beta)^{-3/2} (1 - 2C_{ka}) \exp(-C_{ka}) \sin\beta \right) \mathrm{d}\beta,$$

and

$$C_{ka} = \frac{k_\mathrm{B}T}{I_X} t^2 \frac{(a + k\xi\cos\beta)^2}{2(1 + \xi\cos^2\beta)},$$

with θ being the angle between the internal rotation axis and the molecular symmetry axis, i.e., the z-axis. β is the angle between the direction of the angular momentum J and the z-axis, $\xi = (I_X - I_Y)/I_Z$ the asymmetry parameter, $d^{(1)}_{ka}(\theta)$ the first-rank Wigner rotation matrix, C_α the coupling constant between spin and internal rotation, and $\langle\dot{\alpha}(0)\dot{\alpha}(t)\rangle$ is the angular velocity correlation function of the internal rotor.

The dependence of the relaxation rate on the rotational barrier arises from the angular velocity correlation function $\langle\dot{\alpha}(0)\dot{\alpha}(t)\rangle$ of the internal rotation. The time dependence of the angle $\alpha(t)$ of the internal rotor relative to the molecular frame is described by [15]

$$\frac{I_\alpha}{2}\left(1-\frac{I_\alpha}{I_Z}\right)\dot{\alpha}^2+V(\alpha)=E, \tag{7}$$

where the cosinusoidal shape barrier with N-fold symmetry $V_0(1-\cos(N\alpha))/2$ was approximated by the function $V(\alpha) = V\tanh^2(NK\alpha)$, $-\pi \le N\alpha \le \pi$, to get an analytical solution. Here, $V = V_0/0.805946$ is a constant and $K = 0.464884$ was determined from a least squares fit of the $\tanh^2$ function to the cosine function. An analytical solution for $\alpha(t)$ was derived in ref. 15, which was used to calculate the time dependence of the angular velocity and then, numerically, the correlation function $\langle\dot{\alpha}(0)\dot{\alpha}(t)\rangle$.

When the axis of internal rotation coincides with the molecular z-axis ($\theta = 0$), which is quite correct for the benzoyl radical, then $d^{(1)}_{k0}(0) = 0$ for $k = \pm 1$ and $d^{(1)}_{00}(0) = 1$. Thus, the sum in Eq. (6) has only one term with $F(0)$. $F(0)$ is given in Fig. 5 as a function of $\tau_J^* = \tau_J\sqrt{k_B T/I_X}$ for various values of the internal rotation barrier. For calculation of $F(0)$ a two-fold symmetry of the rotational barrier, $N = 2$, was used and the moments of inertia of the benzoyl radical were taken the same as for benzaldehyde [40]: $I_X = 6.96 \cdot 10^{-45}$ kgm^2, $I_Y = 5.25 \cdot 10^{-45}$ kgm^2,

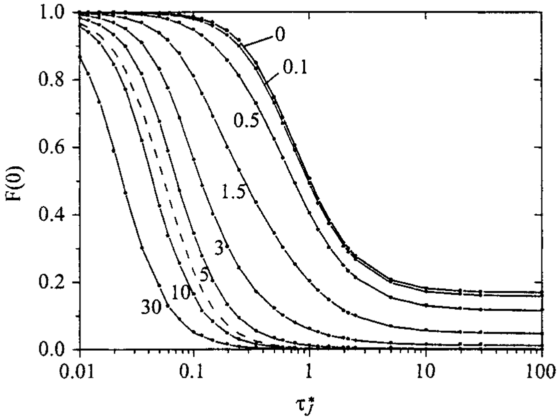

Fig. 5. Correlation factor $F(0)$ of the coupling between spin and internal rotation as function of τ_J^*. The values of V_0/k_BT are indicated for each curve. Dashed line is the plot of the function H^{-1} with $V_0 = 2.8$ kcal/mol ($V_0/k_B\mathrm{T} \approx 5$).

$I_Z = 1.71 \cdot 10^{-45}$ kgm^2. Figure 5 shows that in a wide range of values of τ_J^* the spin-rotation correlation factor $F(0)$ and, therefore, the relaxation rate is sensitive to the barrier. The trend of the $F(0)$ dependence on the barrier is in a good agreement with the trend in the electron spin relaxation rates of acyl radicals and the observations made previously for the ^{13}C nuclear spin relaxation in methyl substituents [37].

For a symmetric top molecule with coinciding molecular symmetry and internal rotation axes ($\theta = 0$) there is in the diffusion limit ($\tau_J^* \ll 1$) an analytic solution of Bull's theory for the total relaxation rate $T_{1,\mathrm{SR}}^{-1}$ induced by both the internal rotation and the overall rotation of the whole radical. Under the condition $k_B T \tau_J^2 / I_\alpha \ll 1$ it reads (eq. (82) in ref. 15):

$$T_{1,\mathrm{SR}}^{-1} = \left(\frac{2}{3\hbar^2}\right) k_B T \tau_J \left(\frac{(C_Z')^2}{I_Z} + \frac{(C_X')^2 + (C_Y')^2}{I_X} + \frac{(C_Z')^2}{I_\alpha}\left(1 - \frac{I_\alpha}{I_Z}\right) H^{-1} \right), \qquad (8)$$

where

$$H = 1 + \frac{2N^2 K^2 V_0 \tau_J^2}{I_\alpha (1 - I_\alpha / I_Z)} \qquad (9)$$

and C_j' are the diagonal elements of the spin-rotation coupling tensor per unit overall angular momentum (note that $C_\alpha = C_Z'/I_\alpha$). In Eq. (8), $F(0)$ has been replaced by H^{-1} which can be calculated from (9). $F(0) = H^{-1}$ is quantitatively correct only for large and small barriers of rotation. According to ref. 41 the barrier of the acyl group rotation in the benzoyl radical is $V_0 \approx 2.8$ kcal/mol. This is an intermediate barrier ($V_0/k_B T \approx 5$ at room temperature) and, therefore, Eq. (8) can be used only for a semiquantitative description. The approximation H^{-1} for $F(0)$ is plotted in Fig. 5 as dashed curve to compare it with the exact numerically calculated curve for $V_0/k_B T = 5$. At $\tau_J^* \leq 0.05$ the values of H^{-1} differ less than 20% from the exact values for $F(0)$.

In the diffusion limit the angular momentum correlation time τ_J is usually described by a modified Stokes-Einstein relation [23, 42]:

$$\tau_J = \frac{I}{8\pi r_0^3 k \eta}, \qquad (10)$$

where r_0 is as defined above, I is the mean moment of inertia of the solute molecule, and $0 < k \leq 1$ is a parameter which should depend on solute and solvent but not on temperature and viscosity. According to Eq. (8) the relaxation rate $T_{1,\mathrm{SR}}^{-1}$ is proportional to τ_J. Thus, the relaxation rate $T^{-1}{}_{1,\mathrm{SR}}$ goes to zero for $\eta^{-1} \to 0$ and, therefore, cannot describe our experimental data for alkane solvents, where a significant intercept was observed for $T/\eta \to 0$ (see Fig. 3). For the formyl radical a slightly different dependence of τ_J on viscosity has been found [12], namely,

$$\tau_J = \frac{I}{8\pi r_0^3 k\eta} + \tau_c, \tag{11}$$

where τ_c is a solvent-dependent parameter. A similar expression has also been obtained theoretically [43]. To describe the dependence on viscosity and temperature of the electron spin relaxation rate of the benzoyl radical the first two terms in Eq. (8) can be neglected because $I_X, I_Y, I_Z \gg I_\alpha$. Thus, Eq. (8) can be parameterized with Eq. (11) into

$$T_{1,\mathrm{SR}}^{-1} = AT\left(\frac{I}{8\pi r_0^3 k\eta} + \tau_c\right)H^{-1}, \tag{12}$$

where

$$A = \left(\frac{2}{3\hbar^2}\right)k_\mathrm{B}\frac{(C_Z')^2}{I_\alpha}.$$

Equation (12) has been applied to fit the three parameters A, τ_c and k to the relaxation data obtained in toluene. The result is plotted in Fig. 3 as solid line, which reproduces the experimental data quite well with the parameters $A = 4.94\cdot10^{17}\,\mathrm{K}^{-1}\mathrm{s}^{-2}$, $\tau_c = 1.17\cdot10^{-14}\,\mathrm{s}^{-1}$ and $k = 0.49$. Simultaneous analysis of the data obtained in the alkane solvents with Eq. (12) does not make sense, because the parameters τ_c and k can vary from solvent to solvent. Nevertheless, Eq. (12) explains qualitatively the intercept observed at $\eta^{-1} \to 0$.

To check the model additionally, the electron spin relaxation rate of benzoyl radical has been measured also in isopropanol solution at five different temperatures ranging from –35 to 40°C. Figure 6 gives the experimental results and their fit with Eq. (12), yielding $A = 5.09\cdot10^{17}\,\mathrm{K}^{-1}\mathrm{s}^{-2}$, $\tau_c = 1.58\cdot10^{-14}\,\mathrm{s}^{-1}$ and $k = 0.11$. It is quite satisfactory that the relaxation data for both isopropanol and toluene

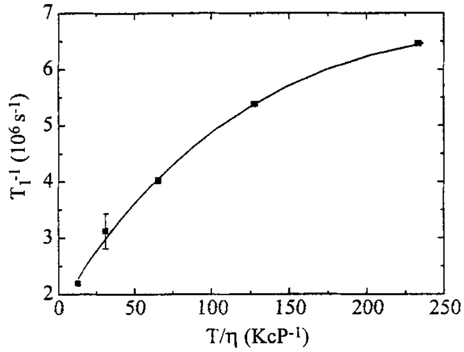

Fig. 6. Dependence of the relaxation rate T_1^{-1} of benzoyl radicals on T/η in isopropanol. Solid line is the fit of Eq. (12) to the experimental data with three variable parameters: A, τ_c and k.

solutions are described with nearly the same value for A, as this parameter should be independent of the solvent.

From the value of A the coupling $C_\alpha = C'_Z/I_\alpha$ between spin and internal rotation of the CO group around the C-CO bond can be calculated. The result is $|C_\alpha| \approx 1510\,\mathrm{MHz}$, a reasonable value which lies in between the principal coupling constants of the formyl radical (see Table 1). This has to be expected for a rotation around an axis which does not coincide with one of the principal axes of the spin-rotation coupling tensor of the formyl radical.

5 Conclusion

The electron spin-lattice relaxation times T_1 of benzoyl and 2,4,6-trimethylbenzoyl radicals are rather short, being about 200 ns and less than 100 ns, respectively, in unpolar solvents at room temperature. The relaxation is induced by spin-rotation interaction of the electron spin with two different types of radical movements: overall rotation of the whole radical and internal rotation of the acyl group around the C-CO bond. The predominant second contribution is sensitive to the barrier of rotation and explains well the fact that saturated acyl radicals, for example, hexahydrobenzoyl radicals, relax faster than those with the CO group attached to an unsaturated moiety. When using a modified rotational correlation time $\tau_J = \tau_c + I/8\pi r_0^3 k\eta$, with τ_c being independent of solution viscosity, then all our relaxation data obtained at various viscosities and temperatures are well explained in the frame of Bull's theory describing the rotational barrier dependence of the relaxation rates as well as their dependences on temperature and viscosity. The value of the spin-rotation coupling for the internal rotation of the CO group in the benzoyl radical is $|C_\alpha| \approx 1510\,\mathrm{MHz}$.

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