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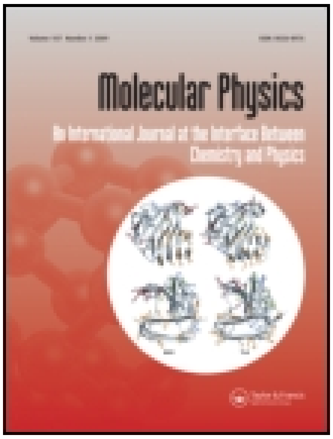

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Electron spin relaxation in polarized secondary radicals

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Electron spin relaxation in polarized secondary radicals
Part II. Some α-diketone radical anions

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The spin–lattice relaxation of some α-diketone radical anions has been studied following their production in a spin-polarized state by reaction of the parent molecule with a polarized primary radical. The latter was the amine radical which results on irradiation of benzophenone in the presence of triethylamine ; the relaxation of the polarized benzophenone ketyl produced simultaneously was also studied.

The relaxation of the radical anion from camphorquinone has been investigated in several solvents over wide ranges of viscosity and temperature and has been analysed in terms of contributions from the spin–rotation and *g*-anisotropy interactions. Different relaxation times were observed at low temperature from optically active *d*-camphorquinone radical anion in solution in the two optical isomers of 2-octanol.

1. INTRODUCTION

When free radicals are produced in solution by flash-photolysis of a sample held within the cavity of an electron spin resonance (ESR) spectrometer they are often formed in a spin-polarized state. The signals, first observed about 1 μs after the flash, decay with time as the radicals attain thermal equilibrium with their surroundings. From this time-dependence the spin–lattice relaxation time of the radicals can be obtained ; relaxation is so fast as to be essentially complete before reaction ensues. The polarization results in our experiments from radical formation by rapid reaction of the spin-polarized triplet state formed via anisotropic inter-system crossing from the excited singlet state of the irradiated molecule [1].

A major advantage of this method for studying relaxation is the wide variety of radicals to which it may be applied, for it is concerned with transient species. Originally [2] it was limited to those polarized radicals which could be produced directly by photolysis of substrate molecules at 347 nm, the wavelength of the nitrogen laser used to provide a flash of short duration as compared with a typical relaxation time. Recently it has been shown [3–5] that this limitation can be removed by forming polarized secondary radicals by reaction with polarized primary ones within their relaxation times.

In Part I of this study [6] it was shown that the relaxation time of a secondary radical can be obtained properly from the decay of its polarization. In this

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paper are reported the results of a study of a series of α-diketone radical anions, all produced as polarized secondary species by reaction of the parent molecules with the polarized $Me\dot{C}HNEt_2$ radical. This is formed on irradiation of benzophenone in the presence of triethylamine in alcoholic solvents :

$$^3Ph_2CO^* + NEt_3 \rightarrow Me\overset{*}{\dot{C}}HNEt_2 + Ph_2\overset{*}{\dot{C}}OH,$$

where the asterisk denotes a polarized species. The amine radical reacts too quickly with added substrate for it to be observed and yields the secondary radical

$$\begin{array}{l} Me\overset{*}{\dot{C}}HNEt_2 + RCOCOR' \rightarrow R\overset{*}{\dot{C}}OHCOR' + CH_2{=}CHNEt_2 \\ \phantom{Me\dot{C}HNEt_2 + RCOCOR' \rightarrow R}\rightleftharpoons \\ \phantom{Me\dot{C}HNEt_2 + RCOCOR' \rightarrow} R\dot{C}\bar{O}COR'^*. \end{array}$$

The detailed chemistry of the solutions was discussed in Part I.

The alcoholic solvents were chosen to allow experimentation over a wide range of viscosities without changing the basic organic functional group. Our solutions contained four constituents, benzophenone, triethylamine, the diketone and the alcohol, and in each solution their relative amounts were adjusted to optimize the light absorbed by the benzophenone, to minimize triplet energy transfer and competing reactions as well as to optimize the polarized signal from the secondary species, which had to be produced within the relaxation time of the primary one. Depending on the precise nature of the molecules used and of their light-absorption and reaction characteristics, it was not always possible to obtain sufficiently strong signals from the secondary radicals to merit analysis.

This was a considerable limitation in an initial attempt, reported below, to study relaxation in a closely related series of diketone radicals. During this work some interference was experienced from underlying resonances from the polarized primary benzophenone ketyl radical whose relaxation was also studied before applying the corrections discussed in Part I. It was usually possible however to choose magnetic field settings at which no line overlap occurred.

Much more success was obtained from studies on the radical anion of camphorquinone which was studied in a range of alcohols and also over a range of temperature in 2-octanol.

2. EXPERIMENTAL

Except where stated, measurements were made at 293 K, using the fast-response electron spin resonance spectrometer, which employs 2 MHz modulation described previously [1, 7]. The light source was a nitrogen laser emitting 1 mJ/pulse at 337·1 nm and signal averaging was necessary ; under the conditions used this implied radical concentrations of about 10^{-6} mol dm^{-3}/flash, which is sufficiently low to eliminate exchange contributions to relaxation. Observations were made on the absorption signals.

The viscosities of the solutions were depressed strongly by the addition of triethylamine to the alcohols and had to be measured. At 273–293 K this was by means of Ostwald viscometers and below 273 K a falling-ball viscometer was used ; in both cases calibration was against standard liquids of known viscosity. The errors in viscosity are difficult to assess but are thought to be proportionately greater than those in the relaxation times.

All chemicals used were the purest available commercially and were used without further purification. Depending upon the precise reaction system, benzophenone concentrations were generally in the range 0·25–0·50 mol dm^{-3}, triethylamine was about 2 mol dm^{-3} and the concentration of the diketone was 0·075–0·10 mol dm^{-3}. When experiments were performed on 1-phenyl-propane-1,2-dione the comparatively high extinction coefficient of this compound at the laser frequency necessitated use of 0·045–0·10 mol dm^{-3} solutions with 0·60 mol dm^{-3} benzophenone. For benzophenone itself triethylamine was added at 0·1 mol dm^{-3}.

3. RESULTS

Initial observations were made of the primary ketyl radical produced from benzophenone. The relaxation times observed in four alcohols are given in table 1 ; all are comparatively long and longer than those of the α-diketone radicals studied subsequently. This implies that at worst only small corrections were needed to the observed relaxation of the latter when there was possible line overlap (see [6]). All the values in this table were extrapolated to zero microwave power, at low viscosities by an empirical procedure and at high viscosity by plotting the relaxation rate against the microwave power [2]. The relaxation time in cyclohexanol is shorter than would have been expected from the other measurements and the relaxation exhibits a similar behaviour with viscosity in all these solvents to that of the camphorquinone anion reported and discussed subsequently.

Table 1. Observations on the benzophenone ketyl radical.

Solvent	Viscosity/cP	Relaxation time/μs
Isopropanol	1·89	21·7 ± 0·7
1-pentanol	3·00	28·9 ± 0·5
2-octanol	5·23	33·6 ± 0·5
Cyclohexanol	29·30	47·0 ± 1·0

There appears to be no information in the literature on the variation of T_1 with radical structure along a homologous series of compounds. An attempt was therefore made to study the radical anions of the series MeCOCOR, with R = Me, Et, *n*-Pr and Ph, all of which can be produced in the spin-polarized state by secondary polarization techniques. The results are given for a series of alcohols in table 2, which also lists the solution viscosities. For each radical there exists a broad correlation between the relaxation time and the viscosity of the solution. The apparent sole exception is the biacetyl radical anion (R = Me) but it exists in two isomeric forms and the hyperfine structure shows that in isopropanol the *trans*-radical is present whilst in 2-octanol and cyclohexanol the *cis*-isomer is. The relaxation time of the 1-phenyl-propane-1,2-dione (R = Ph) radical anion in 2-octanol appears anomalously large. All values were extrapolated to zero microwave power.

Table 2. Relaxation times in a homologous series (μs).

Solvent	R = Me	Et	*i*–Pr	Ph
Isopropanol	3·4 ± 0·4	—	8·0 ± 1·5	7·5 ± 1·0
Viscosity/cP	1·6		1·3	1·6
1-pentanol	—	7·0 ± 1·0	—	—
Viscosity/cP		2·0		
2-octanol	2·5 ± 0·5	—	—	15·0 ± 0·5
Viscosity/cP	3·7			3·7
Cyclohexanol	7·2 ± 0·8	9·7 ± 0·5	13·5 ± 2·0	16·3 ± 0·8
Viscosity/cP	13·9	9·6	9·6	13·9

When making comparisons within the homologous series it was unfortunate that optimizing the polarization observed by varying the composition of the solution led to wide changes in viscosity which made comparison difficult. Only one measurement (for R = Et) was attempted in 1-pentanol but the other vacancies in table 2 reflect our inability to produce sufficiently good polarized spectra from the compounds in these solutions. However, the two quite complete series in isopropanol and cyclohexanol do show that T_1 increased with increasing chain length, as expected, and that there was little difference between the compounds containing *n*-Pr and Ph groups.

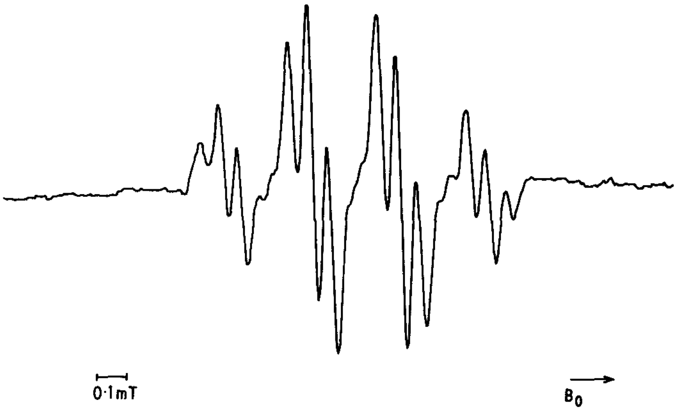

Figure 1. The spectrum of the camphorquinone radical anion produced by irradiation at 100 p.p.s. Relaxation time measurements were recorded on the most intense peak to high field of centre.

A much fuller study was possible when camphorquinone was used as substrate for this gave strong polarized signals in a variety of solvents ; the spectrum observed in 2-octanol is shown in figure 1. Previous studies of this spectrum in other solvents [8–10] have suggested that the radical concerned is the neutral species with the one hydroxyl proton produced by hydrogen abstraction from the solvent exchanging too rapidly between the carbonyl oxygens for its coupling to be observed. Simulation of the spectrum using the literature values for the coupling constants yields a close but not precise fit to our (or the literature) spectrum and the identity of the radical remains in some doubt. However, in the experiments reported it was always the radical anion of the 1,2-diketone that was formed under our conditions, and our belief that this is the identity of our camphorquinone species is reinforced by its lifetime in solution. In 2-octanol this was about 300 ms, much longer than that usually associated with neutral radicals ; for example benzophenone ketyl exists for only about 70 ms under the same conditions.

Camphorquinone absorbs only weakly at 337·1 nm and the quantum yield for its disappearance is low [8], suggesting that it is a poor abstracter of hydrogen from alcohols. However, it undergoes triplet energy transfer from benzophenone readily [8] : we estimate a rate constant of $2{\cdot}4\times10^9$ dm^3 mol^{-1} s^{-1} for this process in our solutions and this is approximately equal to the rate constant for the reaction of benzophenone with triethylamine [11]. Thus, to minimize triplet energy transfer the amine concentration was kept at least 20 times that of the quinone (typically 2 mol dm^{-3} and 0·09 mol dm^{-3} respectively). The proton transfer reaction between benzophenone ketyl and camphorquinone is so slow [8] that it cannot influence the polarized signal observed.

The relaxation times observed for the radical, extrapolated to zero microwave power, in several alcoholic solvents, and ethyl lactate, are given in table 3

Table 3. Relaxation times of camphorquinone radical anion in various solvents.

Solvent	Viscosity/cP	$(\eta/T)\times10^3$	T_1/μs
Methanol	0·67	2·3	5·8 ± 0·4
Ethanol	0·97	3·3	7·5 ± 0·3
Isopropanol	1·32	4·5	7·7 ± 0·3
1-pentanol	2·03	6·9	9·8 ± 0·2
Ethyl lactate	1·99	6·8	10·8 ± 0·3
2-octanol	2·68	9·1	11·9 ± 0·2
Cyclopentanol	4·39	15·0	12·6 ± 0·2
Cyclohexanol	9·64	32·9	17·2 ± 0·4

Table 4. Relaxation times in 2-octanol as a function of temperature.

Temperature/K	Viscosity/cP	$(\eta/T)\times10^3$	T_1/μs
242	13·5	56·0	43·7 ± 1·5
248	10·7	43·2	37·2 ± 1·5
255	9·65	37·8	26·7 ± 1·0
265	8·85	33·4	22·8 ± 0·8
273	5·33	19·4	16·4 ± 0·4
279	4·54	16·3	16·2 ± 0·3
293	2·87	9·8	12·0 ± 0·2
304	2·02	6·7	10·6 ± 0·2
315	1·49	4·7	9·5 ± 0·2

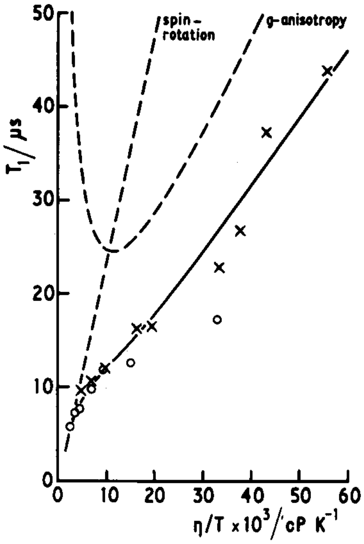

Figure 2. Experimental and calculated relaxation times. Points, ○, were obtained by varying the solvent and × by varying the temperature in 2-octanol. The solidus curve represents the best theoretical fit to the experiments whilst the hatched curves show the relaxation contribution from spin–rotation and from *g*-anisotropy.

together with the measured viscosities (η) of the solutions, and the behaviour is plotted as points in figure 2 as a function of (η/T). These measurements are augmented in that figure with some made in 2-octanol as a function of temperature ; these are listed in table 4.

4. Discussion

The viscosity dependence of relaxation for both the benzophenone ketyl and camphorquinone anion radicals at room temperature is similar to those reported for 2,5-di-*t*-butyl-*p*-benzosemiquinone in methanol and ethanol throughout a similar range of (η/T) values [12]. This was expressed by an empirical relationship

$$\frac{1}{T_1}=A\frac{T}{\eta}+B\exp\left(-\frac{\Delta E}{RT}\right), \tag{1}$$

where A and B are constants and ΔE was interpreted as the energy barrier to rotation, with a value of about 4 kJ mol^{-1}. Our results at room temperature can also be fitted to this relationship with a similar value for the activation energy. However, the results from the camphorquinone anion in 2-octanol extend the range of the measurements and the behaviour departs considerably from this form. Neither these results nor the results obtained for the same ion in all the different solutions, including the 2-octanol results at various temperatures, can be fitted to the expression given in equation (1).

It is more instructive to consider the fundamental contributions to relaxation which may occur. Over the viscosity and temperature ranges studied there are likely to be contributions to relaxation from modulation of the spin-rotation interaction and from the *g*-anisotropy of the radical. We neglect any possible contributions from modulation of the hyperfine interaction for three reasons. Firstly in proton-coupled radicals a hyperfine dependence of the relaxation time is not usually observed. Secondly, no linewidth variations are apparent in figure 1, suggesting that hyperfine contributions to T_2 are small in this radical and the same is probably true for T_1. Thirdly, even with only the spin–rotation and g-anisotropy contributions the system has many variable parameters. However, in an attempt to minimize variations from possible hyperfine contributions all measurements were performed on a single hyperfine line, the strongest peak to high field of the centre of the spectrum.

The rate of relaxation due to the spin–rotation interaction is [13]

$$\frac{1}{T_1^{\mathrm{SR}}}=\frac{6kT}{9I}\sum_i (g_{ii}-g_e)^2\,\tau_J, \tag{2}$$

where I is the moment of inertia of the radical, g_{ii} are the principal values of the g-tensor, g_e is the g-factor of the free electron and τ_J is the correlation time for fluctuations in rotational angular momentum. If τ_{R} is the rotational correlation time we may write for $\tau_{\mathrm{R}} \gg \tau_J$,

$$\tau_{\mathrm{R}}\tau_J=I/6kT\xi, \tag{3}$$

where ξ is an empirical correction factor ; when $\xi=1$ this is the Hubbard [14] relationship. The relaxation rate due to the g-anisotropy is [13]

$$\frac{1}{T_1^{g}}=\tfrac{1}{5}\sum_i (g_{ii}-g_s)^2\,\frac{\omega_0^2}{g_s^2}\,\frac{\tau_{\mathrm{R}}}{(1+\omega_0^2\,\tau_{\mathrm{R}}^2)}, \tag{4}$$

where g_s is the isotropic g-factor and ω_0 is the Larmor frequency. Equations (2) and (4) hold when $\omega_0^2\,\tau_J^2 \ll 1$ and $\tau_J < \tau_{\mathrm{R}}$. In general,

$$\sum_i (g_{ii}-g_e)^2=\sum_i (g_{ii}-g_s)^2+3(g_s-g_e)^2 \tag{5}$$

and combining equations (2), (3) and (5) :

$$\frac{1}{T_1^{\mathrm{SR}}}=\frac{\sum\limits_i (g_i-g_s)^2}{9\xi\tau_{\mathrm{R}}}+\tfrac{1}{3}\,\frac{(g_s-g_e)^2}{\xi\tau_{\mathrm{R}}}. \tag{6}$$

The overall rate of relaxation is given by

$$\frac{1}{T_1}=\frac{1}{T_1^{\mathrm{SR}}}+\frac{1}{T_1^{g}} \tag{7}$$

and we attempt to fit our results to an expression of this form. There are three unknowns, $\sum\limits_i (g_i-g_s)^2$, ξ and τ_{R}.

The rotational correlation time of many molecules even in hydrogen-bonded solvents may often be expressed as a function of viscosity, η [15] :

$$\tau_{\mathrm{R}}=C(\eta/T)+\tau_{\mathrm{R}}^{0}, \tag{8}$$

where τ_{R}^{0} is essentially the free rotation value. Camphor itself is so spherical a molecule that in the absence of hydrogen-bonding the observed correlation time is viscosity independent [16] but our results show that this is not the case for camphorquinone anion in alcohols. The constant C can be expressed as

$$C=\alpha\tfrac{4}{3}\frac{\pi r^3}{k}, \tag{9}$$

where α is a correction factor to the Stokes–Einstein relationship. Empirically, its value is often in the range 0·25–1, even for anions in water [15]. Since the radius of the radical anion is not known exactly (we take it as 0·3 nm from measurements on molecular models), in our theory α includes a correction term to the true radius.

Considerable simplification would occur in the relaxation equations if we could assume either that $\omega_0^2\,\tau_R^2 \gg 1$ or its converse : the former might be expected to apply at high viscosities and the latter at low. However, use of equations (8) and (9) shows that our results encompass the $\omega_0\tau_R=1$ region and no overall simplification is possible. It is tempting nonetheless to speculate that the g-anisotropy dominates the relaxation at high (η/T) values and that spin-rotation does at low. In either extreme the relaxation time becomes directly proportional to the rotational correlation time and a plot of T_1 versus (η/T) should be linear with a non-zero intercept due to the τ_R^0 term in (8). We have performed these plots and used least-squares fitting procedures to them.

At high (η/T), using the 2-octanol results above $16{\cdot}3\times10^{-5}$ PK^{-1}, the fit to a straight line is not very good, as can be seen from figure 2. The reason lies probably in the error in the viscosity measurements. We obtain for the slope

$$\frac{5g_s^2\,C}{\sum_i (g_{ii}-g_s)^2}=0{\cdot}0795 \text{ s P}^{-1}\text{ K}. \tag{10}$$

Unfortunately the intercept has a small negative value $(-8{\cdot}0\times10^{-7}$ s), which suggests either that the assumption of one relaxation mechanism is wrong or that the experimental error is large.

At low viscosity, using those points from all the solutions for which $(\eta/T)<9\times10^{-5}$ PK^{-1} so as to satisfy the condition $\omega_0\tau_R<1$, the fit is much better and yields for the slope

$$\frac{9\xi C}{\sum_i (g_i-g_e)^2}=0{\cdot}094 \text{ s P}^{-1}\text{ K}, \tag{11}$$

whilst the intercept/slope ratio gives

$$\tau_R^0/\alpha=3{\cdot}5\times10^{-11}\text{ s}. \tag{12}$$

Equations (10), (11) and (12) interconnect the unknowns, so that only one need be assumed. By comparison with the literature [16] τ_R^0 is probably 10^{-11} s or less. If it is 10^{-11} s, $\alpha=0{\cdot}28$ (which is of the order expected), and this implies $\sum_i (g_{ii}-g_e)^2=7{\cdot}05\times10^{-5}$, $\sum_i (g_{ii}-g_s)^2=5{\cdot}79\times10^{-5}$ and $\xi=3{\cdot}21$. A value of τ_R^0 of 4 ps implies $\alpha=0{\cdot}1$ (which is rather small), $\sum_i (g_i-g_e)^2=3{\cdot}32\times10^{-5}$, $\sum_i (g_i-g_s)^2=2{\cdot}07\times10^{-5}$ and $\xi=4{\cdot}23$. It is most unlikely that τ_R^0 falls outside of this range. Unfortunately using either of these extreme sets of values to predict the relaxation times observed over the whole range of (η/T) studied yields poor agreement with experiment. It appears that either or both of the original assumptions of dominance by one relaxation mechanism at either end of the (η/T) scale were wrong, or that the information is not sufficiently accurate for this analysis.

The realization that the condition $\omega_0\tau_R=1$ is met within our experimental range is useful for here the relaxation time due to the g-anisotropy passes through a minimum. Since τ_R is greater than τ_J the corresponding minimum in the spin-rotation relaxation time curve falls at a lower (η/T) value. It is likely therefore that an experimental curve obtained in our region of experimentation should show a point of inflexion due to the effect of the g-anisotropy minimum in an essentially linear region of spin-rotation contribution. We attempt an analysis on this basis. It is unlikely that it produces a unique fit to the observed data, for there are too many assumptions which have to be made, but we hope to show that an analysis of our results in terms of the two basic relaxation contributions is possible. We note that our basic model is inconsistent with the Hubbard relationship with $\xi=1$, which predicts $T_1^{\mathrm{SR}} \ll T_1^{g}$ throughout our (η/T) region.

The position of the minimum in the T_1^{g} versus (η/T) curve depends directly on the parameter α and from figure 2 it appears that the point of inflexion which reflects this minimum occurs at $(\eta/T) \sim 10\text{–}12\times10^{-3}$ cP K^{-1}. Assuming that $\tau_R{}^0$ is negligible we take $\alpha=0{\cdot}19$ so as to satisfy the condition $\omega_0\tau_R=1$ in this region. This value is a little lower than expected (*vide supra*), possibly because the radius has been overestimated (a reasonable decrease to 0·275 nm increases α to 0·24). The minimum occurs when

$$\sum_i (g_{ii}-g_s)^2 = 10 g_s{}^2/\omega_0 T_1{}^{\min}. \qquad (13)$$

From figure 2 it is apparent that $T_1{}^{\min} > 12\ \mu$s, which implies that

$$\sum_i (g_{ii}-g_s)^2 < 5{\cdot}9\times10^{-5},$$

a useful guide in the absence of information from the solid state.

From our first attempts at analysis it appears that both relaxation mechanisms contribute noticeably throughout our observations. We now neglect $\tau_R{}^0$ entirely (which, although usual in relaxation studies, may lead to appreciable underestimation of τ_R at low (η/T) values ; exigency requires that it is neglected here, for we have no firm evidence for its existence). Having chosen a value for α, there remain two fitting parameters, the g-anisotropy function and ξ. The former affects the g-tensor contribution to relaxation, whilst both affect the spin-rotation one. Trial and error produced the fit shown in figure 2 which corresponds to $\sum_i (g_{ii}-g_s)^2=2{\cdot}82\times10^{-5}$ and $\xi=6{\cdot}9$. Moreover, fits could be obtained only in the parameter ranges $\sum_i (g_{ii}-g_s)^2=2{\cdot}2\text{–}3{\cdot}4\times10^{-5}$, $\alpha=0{\cdot}17\text{–}0{\cdot}22$ and $\xi=6{\cdot}3\text{–}7{\cdot}3$. The two points not well fitted are those of the cyclic alcohol solvents for which a different value of α is probably required.

The high value of ξ is worrying and contrasts with a value of 1·23 found by Huang and Kivelson [17] in their study of $(n\text{-C}_4\text{H}_9)_4\text{N NiS}_4\text{C}_4(\text{CN})_4$ in n-butanol (our $\xi=(1-\lambda_2)/\epsilon_0{}^2$ in their nomenclature). The Hubbard relationship seems poor in hydrogen-bonded solvents and our very high figure may reflect our working with a charged species : the rotational diffusion might well be more anisotropic than with a neutral species. This could be consistent with a reasonably normal α-value.

Any attempt to search for other fits to the observations using higher values of the g-anisotropy function produces less good agreement with experiment and implies even higher values for ξ although α increases, too. On the other hand, no fit could be obtained at the other extreme of taking $\xi = 1$.

It is interesting to note that the parameters obtained for the best fit are not so dissimilar from those obtained in our first attempt at analysis and it may well be that that was limited more by the accuracy of the data than by the assumptions made. If this is the case it appears that $\tau_R{}^0 \sim 6 \times 10^{-12}$ s and is not negligible at low (η/T) values. It is equally apparent that our data are insufficiently precise to investigate this point.

We hope to have shown that the relaxation behaviour observed is consistent with the occurrence of two relaxation mechanisms. This interpretation, despite the lack of uniqueness in its fit, appears to be more satisfactory over a wider range of (η/T) values than that suggested in equation (1).

Table 5. Relaxation times of *d*-camphorquinone radical anion in optically active 2-octanol (μs)

Temperature/K	238	242	248	255	264	265
(−)-2-octanol	37·9 ± 1·5	—	32·2 ± 1·5	—	21·6 ± 0·8	—
(+)-2-octanol	—	43·7 ± 1·5	37·2 ± 1·5	26·7 ± 1·0	—	22·8 ± 0·8
Temperature/K	273	276	279	293	304	315
(−)-2-octanol	—	15·9 ± 0·3	—	11·4 ± 0·2	—	—
(+)-2-octanol	16·4 ± 0·4	—	16·2 ± 0·3	12·0 ± 0·2	10·6 ± 0·2	9·5 ± 0·2

Camphorquinone can be obtained as the optically active *d*-isomer, and to investigate a possible subtle solvation effect it was decided to study its relaxation in an optically active solvent, 2-octanol ($\alpha_D = 11 \pm 1°$) in its pure optically active forms. Measurements were made down to 238 K at identical concentrations of solutes so that the only variable was the (+) or (−) character of the solvent. The results are given in table 5. Above 260 K the differences in T_1 lie within experimental error but at lower temperatures the T_1 values diverge significantly until at 240 K there is approximately 5 μs difference in the two solvents. This is all the more surprising when one remembers that the solvent is diluted by triethylamine, which is not optically active and whose effect on the viscosities of alcohol solutions is dramatic. The differences occur in a region where there are significant contributions from both relaxation mechanisms and since the contribution each makes is linear, or nearly linear, in τ_R in this region, it is this quantity which changes. They reflect either a change in the effective hydrodynamic radius between the two solvents or any change in the isotropy of the rotational diffusion. In either case, explanation would lie in different solvent binding between the two isomers.

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