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Effects of Paramagnetic Lanthanide Shift Reagents on the Proton Magnetic Resonance Spectra of Quinoline and Pyridine

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Abstract: Chemical shifts, line broadenings, and longitudinal relaxation rates are reported for CCl_4 solutions of quinoline and pyridine containing the paramagnetic shift reagents $Eu(DPM)_3$ and $Pr(DPM)_3$. It is found that the induced isotropic shifts are stereospecific and therefore likely to be of dipolar pseudocontact origin. The line broadening is a result of the chemical shift difference between the complexed and uncomplexed states of the substrate, whereas the longitudinal relaxation rate is enhanced due to the electron–nuclear dipolar interaction. Evidence is presented for the existence of chemical-exchange spin decoupling in these systems. The dissociation constant of the $Eu(DPM)_3$–quinoline adduct in CCl_4 is estimated to be 0.07 *M* and its mean lifetime 2×10^{-7} sec. The mean lanthanide–nitrogen distance in the adducts is estimated to be 4.0 Å.

The possibility of utilizing specific electron–nuclear interactions with paramagnetic ions to resolve accidental degeneracies in nmr spectra was realized already in 1960 in an oxygen-17 nmr study of cation hydration.[2] Subsequently proton spin–spin coupling constants have been evaluated from the spectra of the paramagnetic nickelous aminotroponeimineates.[3] It was not until recently, however, that paramagnetic shift reagents had an impact on organic nmr spectroscopy following the report by Hinckley that the dipyridine adduct of europium(III) tris(dipivalomethanate), $Eu(DPM)_3$, produces large and stereospecific chemical shifts in the spectrum of cholesterol.[4] Numerous communications reporting work with lanthanide shift reagents of this type have appeared since.[5] At an early stage it was found that the pyridine-free complex is more effective since pyridine competition with the substrate is avoided.[6] While $Eu(DPM)_3$ usually causes shifts toward lower fields,[4,6] the praseodymium (III) complex, $Pr(DPM)_3$, induces upfield shifts.[7]

Two phenomena caused by paramagnetic ions (or complexes) may generally be observed in the nmr spectra of organic molecules: chemical shifts and enhanced relaxation rates.[8] As a result of enhanced longitudinal relaxation of spin–spin coupled nuclei, chemical-exchange spin-decoupling may also occur.[9] The chemical shift arises from two types of interactions. Direct delocalization and/or spin polarization *via* the molecular orbitals places unpaired electron spin density in an atomic s orbital thereby causing a *contact* shift of the nuclear resonance of that atom.[10] For ions with anisotropic *g* tensors, such as the paramagnetic trivalent lanthanides [except for Gd(III)], the electron–nuclear dipolar interaction gives rise to the so-called pseudocontact shift. For a complex of axial symmetry with a tumbling time, τ, much greater than the electron spin relaxation time, T_{1e}, the pseudocontact shift is given by[11]

$$\delta_p/\nu_0 = -K_pF(r,\theta)G(g_\parallel,g_\perp) \qquad (1)$$

where

$$K_p = \beta^2J(J+1)/45kT$$

$$F(r,\theta) = (3\cos^2\theta - 1)/r^3$$

and

$$G(g_\parallel,g_\perp) = (3g_\parallel + 4g_\perp)(g_\parallel - g_\perp)$$

The symbols in eq 1 are: β = the Bohr magneton, J = the resultant electronic-spin angular momentum (in $\hbar$ units), r = the distance from the metal ion to the nucleus, θ = the angle between the line joining these points and the principal axis of symmetry of the complex, and $g_\parallel$ and $g_\perp$ are the parallel and perpendicular components of the electronic *g* tensor with respect to this axis.

There is no unanimous agreement in the literature regarding the shifts induced by lanthanide shift re-

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agents. Generally the observed shifts are assumed to be mainly of the pseudocontact type although it is clear that protons close to the site of complexation are also influenced by contact interactions.[5] At the same time the variations in the angular factor ($3 \cos^2 \theta - 1$) in the pseudocontact term are often neglected. Neglect of these factors may represent serious obstacles in attempts to derive quantitative structural information from experimental results.

In many cases line broadening of protons close to the site of coordination has been observed. It has been found that different $Ln(DPM)_3$ complexes cause different relative broadenings.[12] Unexpected broadening as well as "washing-out" of some spin–spin splittings have been observed in the spectrum of quinoline in the presence of $Eu(DPM)_3$.[13]

In order to gain a better insight into these problems, we have examined the nmr spectra of quinoline and pyridine as influenced by $Eu(DPM)_3$ and $Pr(DPM)_3$. We present here the results of chemical shift, line broadening, and longitudinal relaxation time measurements as well as some observations of chemical-exchange spin-decoupling.

Experimental Section

Nmr spectra were recorded at 220 MHz with a Varian HR-220 spectrometer equipped with Varian Fourier Transform accessories. Measurements were made at the ambient probe temperature (*ca.* 20°). The magnetic field homogeneity was readjusted before each recording. Spectral assignments were easily done on the basis of the observed splitting patterns. Chemical shifts were referred to internal tetramethylsilane (TMS). Transverse relaxation rates were obtained directly from the full line width at half-height, Δ, using the relation for Lorentzian lines $1/T_2 = \pi\Delta$. Longitudinal relaxation times, T_1, were obtained from the signal intensities, M, observed after a 180–90° pulse sequence with different intervals, τ, between the pulses.[14]

The materials (quinoline, pyridine, and CCl_4) were highest purity reagents obtained from K & K Laboratories and were used without treatment. As judged from the nmr spectra no detectable impurities were present. The shift reagents $Eu(DPM)_3$ and $Pr(DPM)_3$ were supplied by Thompson-Packard Inc.

All solutions were made up in CCl_4 containing 0.5 vol % TMS and were between 0.1 and 0.2 M in substrate (quinoline or pyridine). The amount of shift reagent was continuously varied up to a reagent substrate molar ratio of *ca.* 0.6 for the shift and line-width measurements and *ca.* 0.2 for the T_1 measurements.

Results and Discussion

Chemical Shifts. In all previous work with lanthanide shift reagents the observed shifts increase monotonically with increasing reagent concentration. This indicates the existence of fast chemical exchange between the complexed and uncomplexed substrate, *i.e.*, $1/\tau_M \gg 2\pi\delta_M$, τ_M being the mean lifetime of the reagent–substrate adduct and δ_M, the chemical shift between the complexed and uncomplexed states. The isotropic shift in this case is given by

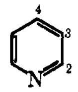
$$\delta = \delta_M \sigma \qquad (2)$$

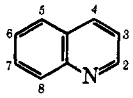
where $\sigma = S_b/S_t$, S_t being the total substrate concentration and S_b that of bound substrate, and $\delta_M = \delta_c + \delta_p$, where δ_c and δ_p are respectively the contact and pseudocontact contributions. It has become customary (see, *e.g.*, ref 13 and references therein) to plot δ *vs.* R_t/S_t (hereafter denoted by ρ), R_t being the total reagent concentration. It is usually observed that the plot is linear at sufficiently low values of ρ. We also find apparent linearity[15,16] with the systems investigated in this work. The measured shifts were plotted in this manner and the values extrapolated to $\rho = 1.0$ are summarized in Table I. For comparison also given in Table I are the reported shifts obtained with $Yb(DPM)_3$.[17]

Table I. Isotropic Proton Shifts[a] of Quinoline and Pyridine with Lanthanide Shift Reagents

Proton	$Pr(DPM)_3$	$Eu(DPM)_3$	$Yb(DPM)_3$[b]
		Quinoline	
2	59.4	−25.1	−85.2
3	17.0	−7.95	−31.5
4	13.6	−7.63	−27.6
5	10.2	−5.18	−22.0
6	7.46	−4.27	−14.2
7	8.34	−3.18	−13.3
8	49.0	−20.6	−78.6
		Pyridine	
2	72.7	−25.9	−90.0
3	25.9	−9.0	−35.1
4	20.7	−8.2	−28.0

[a] In ppm, linearly extrapolated to a reagent/substrate ratio of 1.0, negative sign designates shifts toward lower field. [b] From ref 17.





A comparison among the shift values themselves with the three shift reagents is complicated by differences in the dissociation constants. Moreover, among the lanthanide series the function $G(g_{\parallel}, g_{\perp})$ greatly differs both in sign and magnitude. The intramolecular ratios of the shifts are, however, to a first approximation, independent of these complicating factors and in the case of pseudocontact shifts should reveal the stereochemcial arrangement of the protons with respect to the central ion and the principal axis of symmetry of the complex.[18–20] For convenience (*vide*

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(14) R. L. Vold, J. S. Waugh, M. P. Klein, and D. E. Phelps, *J. Chem. Phys.*, **48**, 3831 (1968); H. Y. Carr and E. M. Purcell, *Phys. Rev.*, **94**, 630 (1954).

(15) In principle, because of the finite dissociation constant of the reagent–substrate adduct, the plot of δ *vs.* ρ is nonlinear. The asymptotic value of δ for large ρ is δ_M. With δ_M and the values of δ the stoichiometry and the dissociation constant of the adduct can be determined. For the lanthanide shift reagents it has been found that 1:1 adduct is formed and the central ion is heptacoordinated.[16]

(16) K. Norlén, J. S. Leigh, and J. Reuben, submitted for publication.

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(18) Equation 1 has explicitly been derived for complexes of axial symmetry, *i.e.*, complexes for which $g_x = g_y \neq g_z$.[11] An equation for the general case of $g_x \neq g_y \neq g_z$ has also been given,[19] but owing to its greater complexity cannot be used intuitively. The assumption of axial symmetry for the $Ln(DMP)_3$-substrate adducts has some circumstantial justifications although it still needs definite proof. It has been found that in the adduct the central ion is heptacoordinated[16] while at the same time the *tert*-butyl protons of the complex are magnetically equivalent.[20] The equivalence of the side-chain protons may be a result of their equal distance and angle in a complex of axial symmetry or it may be due to fast fluxional isomerization. The third possibility of accidental degeneracy may be discarded since this equivalence is found for the complete series of $Ln(DPM)_3$ complexes.[20]

(19) G. N. La Mar, W. De W. Horrocks, Jr., and L. C. Allen, *J. Chem. Phys.*, **41**, 2126 (1964).

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Table II. Internal Shift Ratios of Quinoline and Pyridine

Proton	$Pr(DPM)_3$	$Eu(DPM)_3$	$Yb(DPM)_3$	Mean	Calcd[a]
		Quinoline			
2	4.37	3.29	3.09	3.58	3.27
3	1.25	1.04	1.13	1.14	1.23
4	[1]	[1]	[1]	[1]	[1]
5	0.75	0.68	0.80	0.74	0.775
6	0.55	0.56	0.51	0.54	0.47
7	0.61	0.42	0.48	0.50	0.344
8	3.61	2.70	2.85	3.05	3.33
		Pyridine			
2	3.52	3.16	3.22	3.30	3.27
3	1.25	1.10	1.255	1.20	1.23
4	[1]	[1]	[1]	[1]	[1]

[a] See text.

infra) we chose the shift of H_4 as reference for both quinoline and pyridine and calculated the ratios $R_i = \delta_i/\delta_4$ (see Table II). Also given in Table II are the mean values of the shift ratios for the three individual $Ln(DPM)_3$ complexes and the values calculated from molecular models (*vide infra*). For pyridine the differences are relatively small, less than 10%. Larger differences are observed for quinoline. Thus the difference from the mean of R_2 with $Pr(DPM)_3$ is 22% and the same for R_7. The differences may arise from two concurrent sources: (1) contact shifts may have different relative contributions for different lanthanides as is found, *e.g.*, for the aquolanthanides;[21] and (2) the adduct geometry may vary slightly along the lanthanide series due to variations of the ionic radii of the central ion. In this case the shift of protons with small r and wide angle θ (see eq 1) will be more sensitive to small configurational changes. In addition, one may intuitively expect that for quinoline, steric interference with the side chain of the complex will be more pronounced and protons H_2, H_7, and H_8 will be most sensitive to small configurational differences. The observation that the differences for pyridine are small suggests that contact contributions to the shifts are small.

Relaxation Rates. Longitudinal relaxation times, T_1, were measured for all the protons of pyridine with $Pr(DPM)_3$ and all the protons of quinoline with $Eu(DPM)_3$ and $Pr(DPM)_3$, except for H_7 and $Pr(DPM)_3$ where overlap with the *tert*-butyl protons of the reagent precluded accurate determination. The results expressed as the increment in the relaxation rate ($1/T_{1p}$) due to the presence of the reagent are given in Table III. Also given are the increments in the transverse relaxation rates ($1/T_{2p}$) of H_2 and H_8 of quinoline with $Eu(DPM)_3$. Note that $1/T_{2p} > 1/T_{1p}$.

The longitudinal relaxation rate under conditions of fast exchange is given by[22]

$$1/T_1 = 1/T_1^0 + \sigma/T_{1M} \qquad (3)$$

where T_1^0 is the relaxation rate in absence of reagent, T_{1M} is that of the reagent–substrate adduct, and fast exchange is defined by $\tau_M \ll T_{1M}$. Equation 3 holds only for $\sigma \ll 1$, the corresponding relation for large values of σ being more complicated.[23] For the transverse relaxation fast exchange is defined by $1/\tau_M \gg 1/T_{2M}, 2\pi\delta_M$, and the relaxation rate is given by[24]

Table III. Proton Relaxation Rates[a] of Quinoline and Pyridine

	$1/T_{1p}$			$1/T_{2p}$
Proton	Q + Pr	Py + Pr	Q + Eu	Q + Eu
2	(4.57)[b]	(6.30)[b]	2.97	22 ± 3
3	0.67	0.49	0.12	*c*
4	0.15	0.10	0.08	*c*
5	0.17		0.07	*c*
6	(0.34)[b]		(0.09)[b]	*c*
7	*c*		(0.20)[b]	*c*
8	(6.40)[b]		3.46	18 ± 3

[a] In sec^{-1}, linearly interpolated to a reagent/substrate ratio of 0.1; estimated accuracy for $1/T_{1p}$, ±10%. [b] Obtained from measurement at one reagent concentration. [c] Not measured.

$$1/T_2 = (1 - \sigma)/T_2^0 + \sigma/T_{2M} + \sigma(1 - \sigma)^2\tau_M(2\pi\delta_M)^2 \qquad (4)$$

For a complex of axial symmetry and anisotropic g tensor with tumbling time longer than the electron spin relaxation time, the nuclear relaxation rates are given by[25]

$$1/T_{1M} = 1/T_{2M} = \mathrm{DD} + \mathrm{CR} + \mathrm{HF} \qquad (5)$$

where

$$\mathrm{DD} = \frac{2}{3}\gamma_n{}^2\beta^2 S(S + 1)r^{-6} \times \left[\frac{1}{3}(g_\parallel{}^2 - 2g_\perp{}^2) + g_\parallel{}^2 \cos^2\theta + g_\perp{}^2 \sin^2\theta\right]T_{1e}$$

$$\mathrm{CR} = \frac{4}{9}\gamma_n\beta S(S + 1)\frac{A}{2\pi}r^{-3}(g_\parallel - g_\perp)(3\cos^2\theta - 1)T_{1e}$$

$$\mathrm{HF} = \frac{2}{3}S(S + 1)\left(\frac{A}{2\pi}\right)^2 T_{1e}$$

DD being the dipolar term, CR = the cross term, and HF = the hyperfine term. In the present case the hyperfine coupling constant, A, is small compared with $\gamma_n g_{av}\beta$, and the dipolar term dominates. Note the inverse sixth power dependence on the distance in the dipolar term.

The finding that $1/T_{2p} > 1/T_{1p}$ suggests that the term in eq 4 containing the chemical shift makes a much larger contribution than the term in $1/T_{2M}$. The chemical shift term is a nonlinear function of σ with a maximum at $\sigma = {}^1/_3$. Results of $1/T_{2p}$ measurements as a function of ρ for H_2 and H_8 of quinoline with $Eu(DPM)_3$ are graphically presented in Figure 1. The expected nonlinearity is clearly evident. A maximum occurs at $\rho \simeq 0.5$ at which point $\sigma = {}^1/_3$. From the known concentrations and assuming that a 1:1 complex is formed,[16] the dissociation of the $Eu(DPM)_3$–quinoline adduct in CCl_4 is calculated to be 0.07 *M*. Assuming according to eq 5 that $1/T_{1M} = 1/T_{2M}$, the contribution of the last term of eq 4 was evaluated and with the measured chemical shifts and the above estimated dissociation constant the values of τ_M were calculated. For H_2 we obtain $\tau_M = 2.2 \times 10^{-7}$ sec and for H_8, $\tau_M = 2.0 \times 10^{-7}$ sec. The good agreement between the two values supports the model adopted for the analysis of the results. Transverse relaxation

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(22) See, *e.g.*, Z. Luz and S. Meiboom, *ibid.*, **40**, 2686 (1964).
(23) J. S. Leigh, Jr., *J. Magn. Resonance*, **4**, 308 (1971).
(24) J. Reuben and D. Fiat, *J. Chem. Phys.*, **51**, 4918 (1969).
(25) H. Sternlicht, *ibid.*, **42**, 2250 (1966).

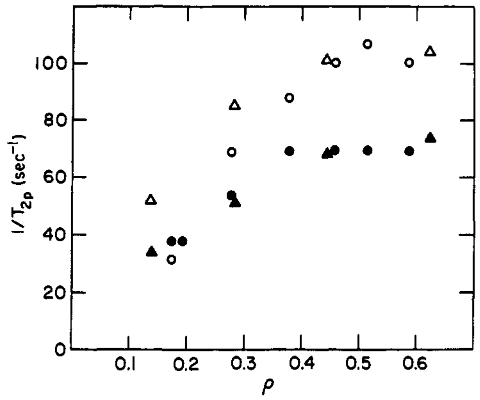

Figure 1. The broadening (expressed at $1/T_{2p}$) of the H_2 (open symbols) and H_8 (filled symbols) protons of quinoline as a function of the $Eu(DPM)_3$/quinoline ratio (ρ): circles, experimental; triangles, calculated (see text).

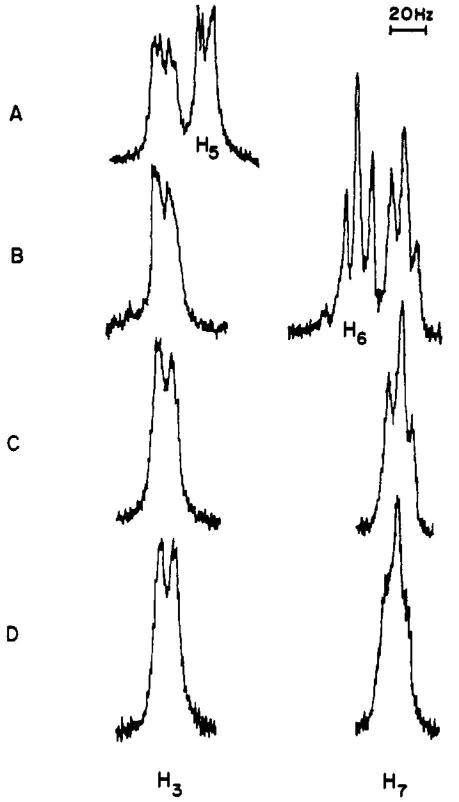

Figure 2. The metamorphosis of the H_3 and H_7 resonances of quinoline with increasing the $Eu(DPM)_3$/quinoline ratio: (A) 0.193, (B) 0.276, (C) 0.378, (D) 0.588.

rates calculated with the above constants at different values of ρ are also presented in Figure 1. The overall agreement is satisfactory.

Thus, the longitudinal relaxation rate of substrate protons is enhanced in presence of paramagnetic shift reagents due to the electron–nuclear dipolar interaction. On the other hand, the enhancement of the transverse relaxation rate, giving rise to line broadening, is mainly due to the chemical shift difference between the complexed and uncomplexed states. Therefore, one would expect protons experiencing larger shifts to exhibit greater broadening. Also, reagents causing larger shifts will cause larger broadenings, which, if τ_M does not vary, will be proportional to the square of the shift (see eq 4). Such trends are indeed observed.[12]

Chemical-Exchange Spin-Decoupling. "Washing out" of the splitting due to $J_{2,4}$ in the H_4 resonance and due to $J_{2,3}$ in the H_3 resonance of quinoline has already been reported[13] and was observed in the spectra obtained in the present work. Broadening of the H_7 resonance was also observed.[13] The metamorphosis of the H_3 and H_7 resonances of quinoline upon addition of $Eu(DPM)_3$ is shown in Figure 2. It is known that contact shifts *do not* markedly affect the nuclear spin–spin coupling constants as has been demonstrated for a series of nickelous aminotroponeimineates.[3] The plausible origin of the observed effects is the so-called chemical-exchange spin-decoupling, a phenomenon recently described, illustrated, and discussed by Frankel.[9] As a result of the enhancement in the proton longitudinal relaxation rate nuclei are effectively decoupled from other nuclei for which $1/T_1 > 2\pi J/\sqrt{2}$.[9] The initial effect is broadening, which is followed, with increasing reagent concentration, by collapse of the multiplet structure and then by narrowing. These effects are superimposed on the concomitant line broadening due to enhancement of the transverse relaxation rate. As already noted the enhancement in the transverse relaxation rate is relatively large, and therefore collapse of multiplet structure occurs before the condition $1/T_1 > 2\pi J/\sqrt{2}$ is actually fulfilled.

Relation of Nmr Parameters to Structure. The chemical shifts are related to the structure of the complex by eq 1. Attempts were made to relate the observed shifts to the molecular structure. It was assumed that the g tensor of the metal ion in the Ln-$(DMP)_3$-quinoline adduct has axial symmetry with the principal axis of symmetry along the line joining Ln–N–H_4. Thus $R_i = (3\cos^2\theta_i - 1)r_4^3/2r_i^3$. From the T_1 values and neglecting the angular variation of the dipolar term in eq 5 the ratio of distances was calculated. The average value of r_2^6/r_8^6 thus obtained for the $Eu(DPM)_3$ adduct is 1.16. A molecular model of quinoline was used with the internuclear distances C–C, C–N, C–H being 1.40, 1.40, and 1.08 Å, respectively, and internal angles of 120°. In this model the distance d_i of a proton from the axis can directly be measured. Thus $d_2 = 2.15$ Å and $d_8 = 2.43$ Å. Now we have the following relations: $\sin\theta_2 = d_2/r_2$, $\sin\theta_8 = d_8/r_8$, and $\delta_8/\delta_2 = (3\cos^2\theta_8 - 1)r_2^3/r_8^3(3\cos^2\theta_2 - 1)$, and we can calculate the distances, r_i, and angles, θ_i. We find $r_2 = 4.25$ Å, $\theta_2 = 30° 24'$ and $r_8 = 4.14$ Å, $\theta_8 = 35° 57'$. With these values the average Eu–N distance is found (*in the model*) to be 4.0 ± 0.4 Å. We measured (in the model) the r_i and θ_i values of all protons and calculated the corresponding pseudocontact shift ratios R_i. The results are given in the last column of Table II. Except for H_7, for which θ is the largest, the agreement is good.

The structure of the $Ln(DPM)_3$-pyridine adduct was analyzed in a similar manner using the T_1 values of H_2 and H_4 obtained in presence of $Pr(DPM)_3$. Essentially the same results were obtained with the differences (see Table II) being much smaller.

The outcome of the above analysis strongly supports the adopted model and suggests that the observed shifts are essentially pseudocontact. Relatively large contact shifts have been observed for neodymium(III) and praseodymium(III) complexes of some substituted pyridines.[26] However, there the Ln-N distance of closest approach is much shorter. A more detailed computer analysis, by continuous variation of parameters until best fit to the experimental results is obtained, is of course possible and has been performed for the $\mathrm{Pr(DPM)_3}$–borneol system[27] and more recently for lanthanide complexes of some mononucleotides.[28]

Conclusions

The study of the effects of paramagnetic lanthanide shift reagents on the proton magnetic resonance spectra of quinoline and pyridine led to the following conclusions.

(a) The induced isotropic chemical shifts are to a great extent stereospecific and therefore of dipolar pseudocontact origin.

(b) The enhancement of the transverse relaxation rates is mainly a result of chemical shift differences between the complexed and free states of the substrate.

(c) The longitudinal relaxation rate is enhanced due to the electron–nuclear dipolar interaction in the complexed state.

(d) Enhancement of the longitudinal relaxation rate of a nucleus leads to chemical-exchange spin-decoupling in the resonance of other nuceli coupled to it, and as a result broadening and collapse of multiplet structures are observed.

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Radical Attack on Propylene as Studied by Electron Spin Resonance

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Abstract: The reactions of propylene with hydroxyl, phenyl, and *tert*-butoxyl radicals have been studied in liquid propylene or mixtures of propylene with ethyl ether. Hydroxyl radicals add to either side of the olefinic linkage, phenyl radicals add predominantly to the terminal carbon atom to give alkyl radicals, and *tert*-butoxyl radicals abstract hydrogen to form allyl radicals. The different behavior of these and other radicals reported in the literature toward propylene is discussed in terms of their electron affinities, and some consequences regarding the formation of aerosols in polluted air are presented.

Propylene, released into the air in auto exhaust, plays an important role in the formation of photochemical smog, and is typical of many of the reactive hydrocarbons present in polluted air.[1] While the initial products of the bimolecular reactions between oxygen atoms (produced by the photodissociation of NO_2 in sunlight) and olefins have been determined,[2] the reactions between hydroxyl and other free radicals present in polluted atmospheres are still far from being understood in complete detail. Three routes for the radical–propylene reactions appear possible: addition to either side of the olefinic linkage or abstraction of a hydrogen atom, leading to alkyl radicals in the first two cases or to allyl radicals in the third case. Recently,

$$\mathrm{R\cdot + CH_2{=}CH{-}CH_3 \longrightarrow R{-}CH_2{-}\dot{C}H{-}CH_3} \quad (1)$$

$$\mathrm{R\cdot + CH_2{=}CH{-}CH_3 \longrightarrow \cdot CH_2{-}CH(R){-}CH_3} \quad (2)$$

$$\mathrm{R\cdot + CH_2{=}CH{-}CH_3 \longrightarrow RH + CH_2{\cdots}\dot{C}H{\cdots}CH_2} \quad (3)$$

it was reported that triethylsilyl radicals, methylthiyl radicals, and *tert*-butylthiyl radicals add to propylene according to reaction 1 in the liquid phase at low temperatures.[3] Under the same conditions, however, *tert*-butoxyl radicals abstract hydrogen from propylene according to reaction 3[4] while no reactions with alkyl radicals were observed.[3] Of particular importance for the formation of smog products are reactions with hydroxyl radicals, whose most likely sources in the atmosphere are hydrogen abstraction from hydrocarbons by oxygen atoms

$$\mathrm{O + RH \longrightarrow R\cdot + \cdot OH} \quad (4)$$

photolysis of nitrous acid

$$\begin{aligned} &\mathrm{NO + NO_2 + H_2O \longrightarrow 2HONO} \\ &\mathrm{HONO \xrightarrow{h\nu} \cdot OH + NO\cdot} \end{aligned} \quad (5)$$

and reactions between hydroperoxy radicals and nitrous oxide

$$\mathrm{HO_2\cdot + NO\cdot \longrightarrow \cdot OH + NO_2} \quad (6)$$

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