addition of 0.50 M 1-octadecene produces no change in the rate constant suggesting that the normal paraffins can efficiently scavenge the radicals produced in the thermolysis of II.

The data clearly show a retardation of rate with increasing viscosity of the medium and is consistent with the mechanism shown in eq 1 where $k_{\text{diff}} > k_{\text{decomp}}$. If the rate data ($k_{\text{N=N}}$) are correlated with viscosity according to the equation given by Pryor,[10a] $1/k_{\text{obsd}} = 1/k_1 + (k_{-1}/k_1A_{\text{D}})(\eta/A_{\text{V}})^{\alpha}$, k_1 and thus $(k_{\text{diff}} + k_{\text{decomp}})/k_{-1}$ can be obtained.[11] In early studies[10a] α was set at 0.5, but more recently a better fit of viscosity-dependent rate constants for thermal decomposition of peresters and peroxides was obtained when $\alpha = 0.72$.[12] A least-squares computed fit of our data yields $\alpha = 0.472$ and $k_1 = 4.38 \times 10^{-4}$ sec^{-1} and is illustrated in Figure 1.[13] Since $k_{\text{N=N}} = k_1(k_{\text{diff}} + k_{\text{decomp}})/(k_{-1} + k_{\text{diff}} + k_{\text{decomp}})$,[2] values of $k_{-1}/(k_{\text{diff}} + k_{\text{decomp}})$ can be calculated for each solvent, and these are shown in Table I.

In our previous report[2] the equation

$$r = \frac{1}{2b}\left[\frac{1 + 1/b}{1/\Delta - 1/b}\right]$$

was derived where $r = k_r/k_{-1}$, $b = k_{-1}/(k_{\text{diff}} + k_{\text{decomp}})$, and $\Delta = (k_{\alpha}/k_{\text{N=N}}) - 1$. The present data now allow calculation of r, the ratio of the rate of rotation of caged 2-bromo-9-methylfluorenyl radical with respect to azophenyl radical to the rate of recombination. Rotation is relatively slow and is solvent dependent. In heptane $k_r/k_{-1} = 0.94$ while in octadecane the ratio equals 0.30.

Values of r have been determined in a few other studies. Greene, *et al.*,[14] found $r \cong 14$ in the combination of caged α-phenylethyl radicals generated in the two bond thermal cleavage of azobis-α-phenylethane, and Kopecky, *et al.*,[15] found a similar value for caged benzyl and α-phenylethyl radicals generated in a similar manner. The nitrogen molecule formed between the radical pair might be expected to retard combination but cannot be primarily responsible for the higher r in these two studies since the diradical intermediate from the two step cycloaddition of substituted olefins exhibits an $r \cong 10$.[16]

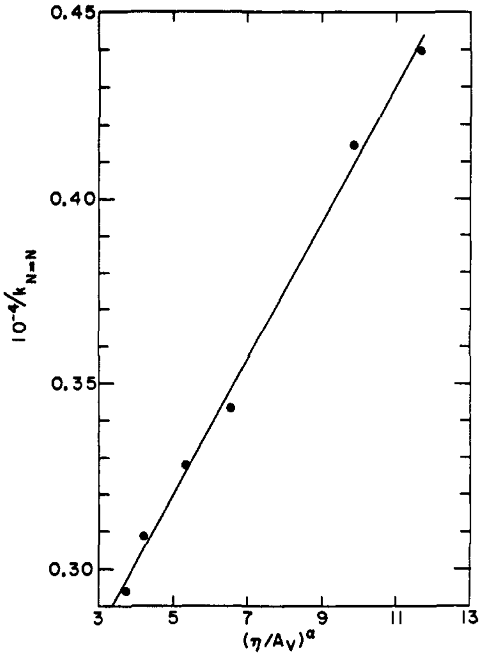

Figure 1. Plot of $1/k_{\text{N=N}}$ *vs.* $(\eta/A_{\text{V}})^{\alpha}$ where $\alpha = 0.472$. The drawn line represents the least-squares solution.

Epimerization or isomerization in these latter three examples could be realized: (1) by internal rotation about C–C bonds of the radical and (2), in the case of the α-phenylethyl radical, by tumbling with respect to its caged partner.[17] In the present study, racemization of the cage can only be accomplished by rotation of the 2-bromo-9-methylfluorenyl radical about an axis which is approximately coplanar with the ring or by translation of the azophenyl radical to the opposite face of the fluorenyl radical. The lower r observed in this system is expected to be mainly a result of the larger moment of inertia of the fluorenyl radical.

(9) F. D. Rossini, Ed., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Materials," API Research Project No. 44, Carnegie Press, Pittsburgh, Pa., 1952, Tables 20c and 24c.

(10) (a) W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 5403 (1970). Earlier studies of similar nature are (b) W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962); (c) H. Kiefer and T. G. Traylor, *J. Amer. Chem. Soc.*, **89**, 6667 (1967); (d) T. Koenig, J. Huntington, and R. Cruthoff, *ibid.*, **92**, 5413 (1970).

(11) η is taken as the absolute viscosity of the solvent at 80° listed in ref 9. A_{V} values were recalculated by a least-squares fitting of viscosity–temperature data given in the above table and differ from A_{V} values previously reported.[10a] The following A_{V} values in cP $\times 10^2$ were used: n-C_7H_{16}, 1.5257; n-C_8H_{18}, 1.4608; n-$C_{10}H_{22}$, 1.2874; n-$C_{12}H_{26}$, 1.1935; n-$C_{16}H_{34}$, 0.9180; n-$C_{18}H_{38}$, 0.8323.

(12) W. A. Pryor, E. H. Morkved, and H. T. Bickley, *J. Org. Chem.*, 37, 1999 (1972).

(13) Standard deviation between experimental and calculated $k_{\text{N=N}}$ is 1.5%. If α is set at 0.50, however, $k_1 = 4.09 \times 10^{-4}$ sec^{-1} and the standard deviation in $k_{\text{N=N}}$ is 2.5%.

(14) F. D. Greene, M. A. Berwick, and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 867 (1970).

(15) K. R. Kopecky and T. Gillan, *Can. J. Chem.*, **47**, 2371 (1969).

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(17) A referee has suggested that tumbling is probably more important than internal rotation as a path for racemization in the α-phenylethyl case.

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On the Stoichiometry of Lanthanide Shift Reagent–Substrate Complexes

Sir:

While there is an extensive bibliography on the use of lanthanide shift reagents in structure elucidation work, little has been published on the details of the interaction between shift reagent and substrate. It has usually been assumed that only complexes of 1:1 stoichiometry are formed, but there is recent evidence for the formation of LS_2 and possibly larger complexes.[1–4] In this case the induced shifts may be weighted averages of several sets of bound shifts, for each of the different complexes.

(1) D. F. Evans and M. Wyatt, *J. Chem. Soc., Chem. Commun.*, 312 (1972).

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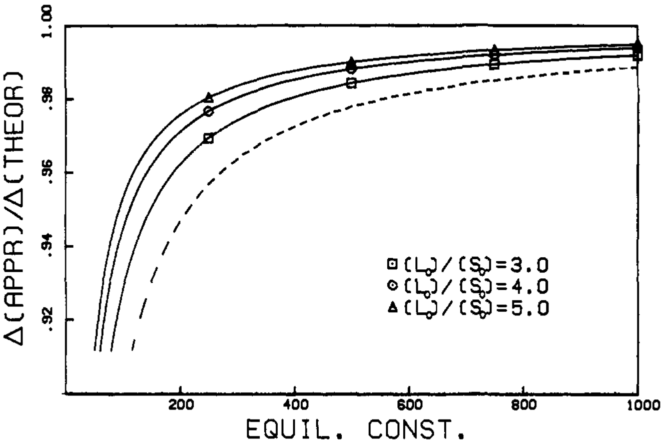


Figure 1. Plot of ratios of approximate to theoretical bound shifts *vs.* equilibrium constants for the equilibrium $L + S \rightleftharpoons LS_1$. The substrate concentration is 0.1 mol/l. Solid lines: the Δ(appr) are the theoretical induced shifts for the $[L_0]/[S_0]$ ratios indicated in the insert. Dashed line: the Δ(appr) are the theoretical initial slopes.

$$\delta_{ij} = ([LS_1]/[S_0])_j\Delta_{1i} + 2([LS_2]/[S_0])_j\Delta_{2i} + \ldots \quad (1)$$

In this communication a simple test for the presence of shift reagent complexes containing more than one substrate molecule is described, and some of the implications of changes in stoichiometry for the determination of the bound shifts are examined. Only LS_1 and LS_2 complexes will be considered in the following.

Consider the δ_{ij} *vs.* $[L_0]/[S_0]$ plot for a substrate forming only LS_1 species. For small $[L_0]/[S_0]$ ratios $[LS_1] \approx [L_0]$, and the slopes Δ_{1i}' of the curves in the linear part of the plot are approximately equal to the bound shifts Δ_{1i}. For large $[L_0]/[S_0]$ ratios $[LS_1] \approx [S_0]$ and the observed shifts Δ_{1i}'' approach the Δ_{1i} asymptotically. Both the Δ_{1i}' and the Δ_{1i}'' are only approximations of the true bound shifts Δ_{1i} but, as Figure 1 shows, the Δ_{1i}'' are the better approximations. This means that the experimental points for small $[L_0]/[S_0]$ must lie below lines with slopes equal to the induced shifts for high $[L_0]/[S_0]$ ratios.

The appearance of the δ_{ij} *vs.* $[L_0]/[S_0]$ plot changes as LS_2 adducts are formed. The same amount of shift reagent binds twice as much substrate in LS_2 complexes, and therefore the fraction of bound substrate can be up to twice as high as in the case of LS_1 adducts. Since the induced shifts are proportional to the fractions of bound substrate, the experimental initial slopes can be up to twice as large as the maximum slopes in the 1:1 model.

Thus there is a simple test for the presence of LS_2 species. Straight lines through the origin are constructed with slopes equal to the induced shifts observed for high $[L_0]/[S_0]$ ratios. If the experimental points lie below these lines, only LS_1 complexes have been formed. If the experimental points lie above these lines, LS_2 adducts have been formed, most likely in addition to LS_1 complexes.

Figure 2 shows a plot of induced shifts *vs.* shift reagent–substrate ratios for the borneol-Pr(fod)$_3$ system. Also indicated are the dividing lines between 1:1 and 1:2 stoichiometries. The fact that the gradients of the lines through the initial points are nearly 50% larger than the maximum observed induced shifts (Table I) clearly indicates the formation of LS_2 adducts. The method is very sensitive because the necessary parameters, the chemical shifts and the initial slopes in the shifts reagent plots, can be measured quite accurately. The test is also attractive because the standard shift reagent experiment, the measurement of induced shifts after successive addition of shift reagent, yields practically all the necessary information. At most one additional spectrum at high shift reagent concentration is required.

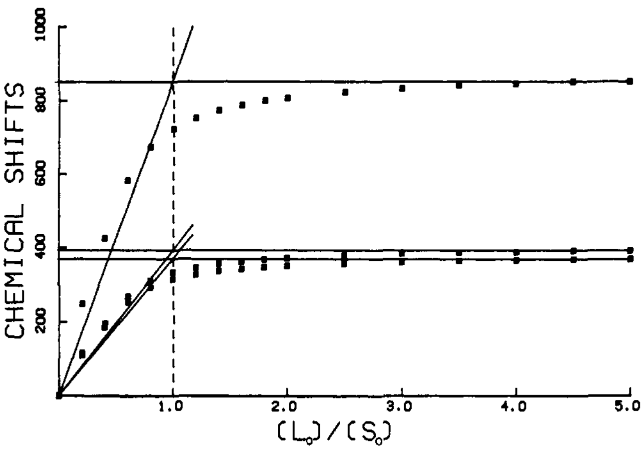
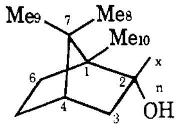


Figure 2. Plots of induced shifts *vs.* shift reagent/substrate ratios for the methyl protons of borneol in the presence of Pr(fod)$_3$.

Table I. Ratios of Induced Shifts and Approximate Bound Shifts of the Methyl Group Protons of Borneol Complexed to Pr(fod)$_3$[a]



$[L_0]/[S_0]$	8[b]	9[b]	10
	Ratios of induced shifts		
0.1	4.63	4.34	10.00
0.2	4.59	4.35	10.00
0.4	4.58	4.34	10.00
0.6	4.59	4.35	10.00
0.8	4.59	4.35	10.00
1.0	4.60	4.35	10.00
2.0	4.61	4.35	10.00
3.0	4.62	4.34	10.00
4.0	4.61	4.34	10.00
5.0	4.61	4.34	10.00
	Approximate bound shifts		
Δ_i'[c]	593.9	563.3	1302.8
Δ_i''[d]	393.0	369.5	852.0

[a] To a 0.1 *M* solution of borneol in CDCl$_3$ aliquots of a 0.5 *M* stock solution of Pr(fod)$_3$ were added. The chemical shifts were obtained on an XL100 nmr spectrometer operating at 32.5°. [b] The assignments may have to be reversed. [c] Initial slopes of the curves in Figure 2. [d] Observed induced shifts for $[L_0]/[S_0] = 5$.

Since the bound shifts are the shift reagent parameters of principal interest, it is necessary to investigate the consequences of diadduct formation for their determination. If both LS_1 and LS_2 species are possible the ratios of the induced shifts δ_{ij}/δ_{nj} will in the most general case be functions of the fractions of bound substrate, *i.e.*, functions of the shift reagent concentrations.

$$\frac{\delta_{ij}}{\delta_{nj}} = \frac{([LS_1]/[S_0])_j\Delta_{1i} + 2([LS_2]/[S_0])_j\Delta_{2i}}{([LS_1]/[S_0])_j\Delta_{1n} + 2([LS_2]/[S_0])_j\Delta_{2n}} \quad (2)$$

Interestingly, the δ_{ij}/δ_{nj} for the borneol–Pr(fod)$_3$ case are found to be independent of the shift reagent concentration in the range $0 \leqslant [L_0]/[S_0] \leqslant 5$ for which there are three possible explanations.

1. No LS$_1$ complexes are formed at all

$$\frac{\delta_{ij}}{\delta_{nj}} = \frac{2([LS_2]/[S_0])_j\Delta_{2i}}{2([LS_2]/[S_0])_j\Delta_{2n}} = \frac{\Delta_{2i}}{\Delta_{2n}} \tag{2a}$$

2. The bound shifts in the 1:1 and 1:2 adducts are equal, $\Delta_{1i} = \Delta_{2i}$

$$\frac{\delta_{ij}}{\delta_{nj}} = \frac{([LS_1]/[S_0] + 2[LS_2]/[S_0])_j\Delta_{1i}}{([LS_1]/[S_0] + 2[LS_2]/[S_0])_j\Delta_{1n}} = \frac{\Delta_{1i}}{\Delta_{1n}} \tag{2b}$$

3. The bound shifts in the 1:1 and 1:2 adducts differ, but are proportional to each other, $\Delta_{2i} = C\Delta_{1i}$

$$\frac{\delta_{ij}}{\delta_{nj}} = \frac{([LS_1]/[S_0] + 2C[LS_2]/[S_0])_j\Delta_{1i}}{([LS_1]/[S_0] + 2C[LS_2]/[S_0])_j\Delta_{1n}} = \frac{\Delta_{1i}}{\Delta_{1n}} \tag{2c}$$

There is no compelling reason why no LS$_1$ adducts should be formed. It also seems unlikely that the Δ_{1i} and Δ_{2i} should be exactly equal. One might expect the metal–oxygen distance to be somewhat larger in 2:1 adducts and consequently the Δ_{2i} to be smaller than the Δ_{1i}. It is conceivable that a small stretching of the metal–oxygen distance can give a new set Δ_{2i} of bound shifts, somewhat smaller than the Δ_{1i}, which remain correlated well enough with the Δ_{1i} for eq 2c to be a good approximation. A definite answer requires a multiparameter fit to the experimental data (3). The important result for structure elucidation purposes, however, is the fact that in each of the three cases mentioned above there is a direct correlation between induced and bound shifts.

Thus the following tentative conclusion may be reached: if the ratios of the induced shifts are found to be independent of the shift reagent concentration, there is a direct correlation between induced and bound shifts; *i.e.*, no multiparameter fit is required in this case. Whether it is generally the case that the ratios of the induced shifts are independent of the shift reagent concentration whenever LS$_2$ complexes are formed is presently under investigation.

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Chemically Induced Dynamic Nuclear Polarization in the Presence of Paramagnetic Shift Reagents

Sir:

Nmr spectra showing the chemically induced dynamic nuclear polarization[1] (CIDNP) phenomenon are often difficult to analyze, because many different reaction products can occur, and their resonance lines overlap frequently. The usual measures taken in nmr spectroscopy to separate overlapping resonances, like changing the solvent or increasing the magnetic field strength, do not qualify for most CIDNP studies. They fail because the chemistry of the reactions often changes with the solvent, and the CIDNP enhancement factors decrease with increasing magnetic fields.[1,2]

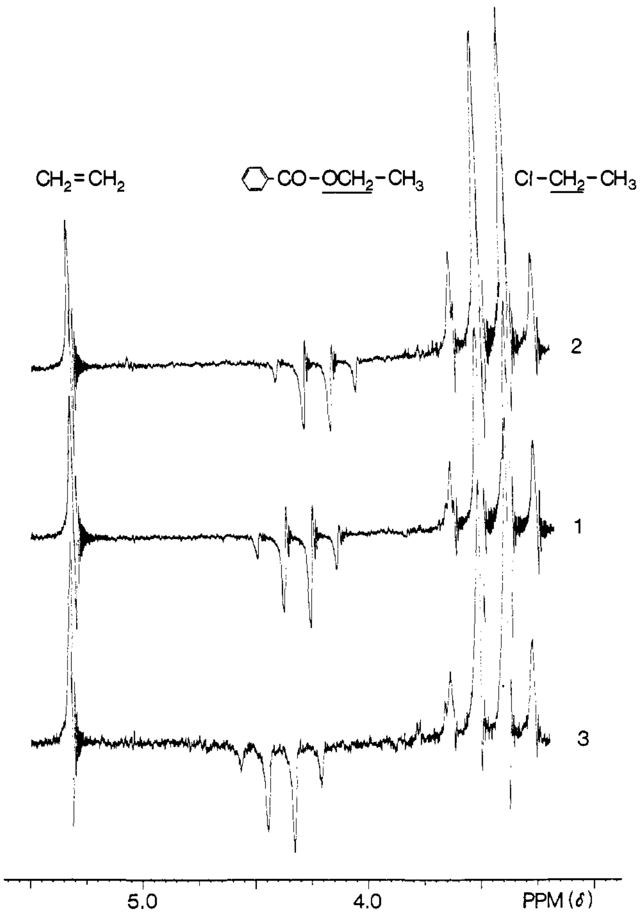

Figure 1. CH$_2$ resonances during the decomposition of BPPO in CCl$_4$ at 60 MHz without shift reagent (1), with Pr(fod)$_3$ (2), and with Eu(fod)$_3$ (3).

We have investigated the possibility of simplifying the analysis of CIDNP spectra with paramagnetic shift reagents and found the following important result. In spite of the fact that increasing concentrations of paramagnetic additives decrease the CIDNP intensities rapidly,[1] paramagnetic shift reagents, for example the lanthanides Eu(fod)$_3$ and Pr(fod)$_3$,[3] can successfully be used to selectively shift the resonance lines of CIDNP—showing products with atoms containing lone-pair electrons like O, N, S, and P.

As a characteristic example we have chosen the thermal decomposition of benzoyl propionyl peroxide (BPPO) in CCl$_4$ as the solvent. The details of this decomposition have been described elsewhere.[4] Figure 1.1 shows the CH$_2$ resonances of the main products ethylene, ethyl benzoate (I), and ethyl chloride. In the presence of Eu(fod)$_3$ the CH$_2$ quartet of I is shifted downfield, whereas the other product lines remain unchanged (Figure 1.2). Similarly in the presence of Pr(fod)$_3$ only the quartet of I is shifted upfield (Figure 1.3). The lanthanide-induced shifts of the ester quartet

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