polarization of the phosphoryl moiety. These effects may be combined to facilitate the breakdown of V, perhaps by complexation with the departing phenoxide and/or carboxylate. Thus, the two transition states leading to and from V would be of lower energy resulting in catalysis.

V

These results imply that divalent metal ions in biological phosphorylation reactions may in some cases be functioning mainly at the pentacoordinate level of the phosphoryl transfer reaction. We are continuing to explore a number of aspects concerning these model systems, including the effects of metal ions on intramolecular catalysis by neutral nucleophiles.

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Internal Return of Caged Geminate Radicals from 9-Azophenyl-2-bromo-9-methylfluorene. Viscosity-Dependent Rotation of Caged Radicals[1]

Sir:

In a previous communication[2] direct evidence was reported for return (k_{-1}, eq 1) of caged geminate

$$R_1N{=}NR_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \overline{R_1{\cdot} + {\cdot}N_2R_2} \overset{k_{diff}}{\underset{k_{decomp}}{\longrightarrow}} \text{products}$$
$$(-) \qquad (-)$$
$$k_r \Big\Vert k_r \qquad\qquad (1)$$
$$R_1N{=}NR_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \overline{R_1{\cdot} + {\cdot}N_2R_2} \overset{k_{diff}}{\underset{k_{decomp}}{\longrightarrow}} \text{products}$$
$$(+) \qquad (+)$$

radicals generated in the one bond thermolysis of an azo compound (I, $R_1 = C_6H_5CHCH_3$; $R_2 = CH_3$). The rate of loss of optical activity of a solution of $(-)$-I is faster than the rate of nitrogen evolution indicating rotation (k_r) of caged α-phenylethyl radical with respect to its azomethyl partner radical. Decomposition of I in hexadecane at 162°[3] is accompanied by a relatively small amount of return which is in harmony with the notion that the predominant fate of the azomethyl radical is carbon–nitrogen bond rupture as suggested by previous kinetic isotope effect studies.[4a,b]

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.
(2) A. Tsolis, S. G. Mylonakis, M. T. Nieh, and S. Seltzer, J. Amer. Chem. Soc., 94, 829 (1972).
(3) The temperature at which kinetics can be easily measured.
(4) (a) S. Seltzer and F. T. Dunn, J. Amer. Chem. Soc., 87, 2628 (1965); (b) S. G. Mylonakis and S. Seltzer, ibid., 90, 5487 (1968); (c) N. A. Porter, L. J. Marnett, C. H. Lochmüller, G. L. Closs, and M. Shobataki, ibid., 94, 3664 (1972), and papers cited therein.

Return in photochemical azo decomposition has also been demonstrated.[4c]

In an attempt to find a higher degree of return during azo compound thermolysis, a new compound, II,

II

expected[5] to lead to a more labile R_1–N bond and a more stable N_2R_2 radical, was synthesized in our laboratory.[6] First-order rate constants ($k_{N=N}$) for the disappearance of the azo chromophore at 410 nm due to $(\pm)$-II in paraffinic hydrocarbons were measured at 80° with a Datex-digitized Cary spectrophotometer.[7] Rate constants (k_α) for the loss of optical activity of reactant $(+)$- or $(-)$-II were also measured under identical conditions with a Datex-digitized Bendix polarimeter, and these are all shown in Table I.

Table I. Spectrophotometric and Polarimetric First-Order Rate Constants for the Disappearance of 9-Azophenyl-2-bromo-9-methylfluorene (II)[a]

Compd	$10^3 \times$ concn, M	Solvent	$10^4 k_{N=N}$, sec^{-1}	$10^4 k_\alpha$, sec^{-1}	$k_{-1}/$ (k_{decomp} $+ k_{diff}$)
$(+)$-II	3.49	n-C$_7$H$_{16}$		3.56	
$(\pm)$-II	9.63	n-C$_7$H$_{16}$	3.40[b]		0.288
$(-)$-II	6.60	n-C$_7$H$_{16}$		3.82	
$(\pm)$-II	6.50	n-C$_8$H$_{18}$	3.24[b]		0.352
$(\pm)$-II	6.50	n-C$_{10}$H$_{22}$	3.05[b]		0.436
$(\pm)$-II	6.50	n-C$_{12}$H$_{26}$	2.91[b]		0.505
$(\pm)$-II	4.9–10.6	n-C$_{16}$H$_{34}$	2.41[b]		0.817
$(+)$-II	4.90	n-C$_{16}$H$_{34}$		2.99	
$(-)$-II	7.45	n-C$_{16}$H$_{34}$		3.18	
$(\pm)$-II	6.25	n-C$_{18}$H$_{38}$	2.27[b]		0.930
$(+)$-II	6.80	n-C$_{18}$H$_{38}$[c]		2.74	
$(+)$-II	6.15	n-C$_{18}$H$_{38}$[c]		2.75	
$(\pm)$-II	8.62	n-C$_{18}$H$_{38}$[d]	2.46		
$(\pm)$-II	6.5	n-C$_{18}$H$_{38}$[c]	2.26		
$(\pm)$-II	7.23	n-C$_{18}$H$_{38}$[e]	2.21		

[a] Rate constants measured in degassed systems at 80.22 ± 0.05°. Two separate thermostats were used but both were adjusted with the same thermocouple. [b] Average of three runs. Average deviations for these range between ±0.2 and ±1.9%. [c] Contained 0.50 M 1-octadecene. [d] Benzoyl peroxide (BPO) was present. Initial [BPO]/[II] = 0.13. [e] Contained same concentration of BPO as in d and 0.50 M 1-octadecene.

That these are true rate constants for unimolecular decomposition are shown by the last few entries of Table I. Addition of benzoyl peroxide (BPO) causes a 10% increase in azo decomposition rate presumably due to induced decomposition resulting from additional phenyl and benzoyl radicals. Addition of 0.50 M 1-octadecene to this solution brings the rate constant back to about the value observed in the absence of BPO. 1-Octadecene appears to be an efficient scavenger.[8] Moreover, in the absence of BPO, the

(5) S. G. Cohen, F. Cohen, and C. H. Wang, J. Org. Chem., 28, 1479 (1963).
(6) J. S. Fowler, ibid., 37, 510 (1972).
(7) C. Santiago and S. Seltzer, J. Amer. Chem. Soc., 93, 4546 (1971).
(8) 1-Olefins have a 5–10% lower absolute viscosity than n-alkanes of the same chain length.[9] Assuming ideal behavior, a n-alkane containing 0.50 M of the corresponding 1-olefin might be expected to have its viscosity lowered by 1% or less than the pure alkane. The rate effect due solely to this change in viscosity is in most cases within experimental error of the rate measurements.

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 $k_{diff} > k_{decomp}$. If the rate data $(k_{N=N})$ are correlated with viscosity according to the equation given by Pryor,[10a] $1/k_{obsd} = 1/k_1 + (k_{-1}/k_1A_D)(\eta/A_V)^\alpha$, k_1 and thus $(k_{diff} + k_{decomp})/k_{-1}$ 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 $k_{N=N} = k_1(k_{diff} + k_{decomp})/(k_{-1} + k_{diff} + k_{decomp})$,[2] values of $k_{-1}/(k_{diff} + k_{decomp})$ 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 $r = k_r/k_{-1}$, $b = k_{-1}/(k_{diff} + k_{decomp})$, and $\Delta = (k_\alpha/k_{N=N}) - 1$. 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]

Epimerization or isomerization in these latter three examples could be realized: (1) by internal rotation

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

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.

(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.

(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 × 10^2 were used: n-C$_7$H$_{16}$, 1.5257; n-C$_8$H$_{18}$, 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 $k_{N=N}$ 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 $k_{N=N}$ is 2.5%.

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

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(16) L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **86**, 622 (1964).
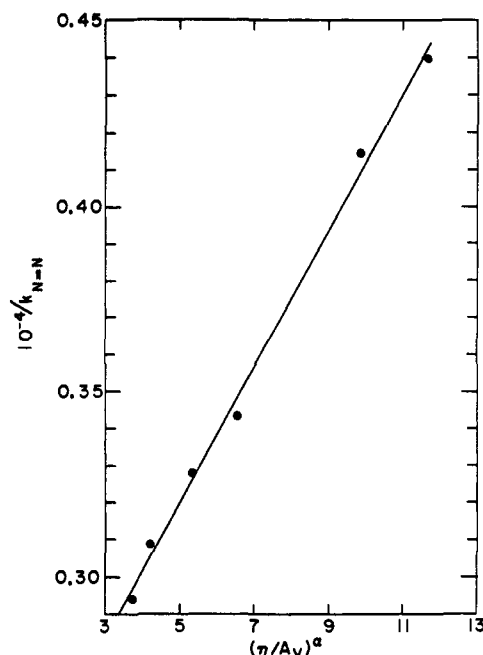
(1) D. F. Evans and M. Wyatt, *J. Chem. Soc., Chem. Commun.*, 312 (1972).

(2) K. Roth, M. Grosse, and D. Rewicki, *Tetrahedron Lett.*, 435 (1972).

(3) B. L. Shapiro and M. D. Johnston, Jr., *J. Amer. Chem. Soc.*, **94**, 8185 (1972).

(4) J. K. M. Sanders, S. W. Hanson, and D. H. Williams, *ibid.*, **94**, 5325 (1972).

Communications to the Editor