groups in other radicals to see if the mechanism we propose here is general for CF_3 groups.

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Peter J. Scheidler, James R. Bolton
Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

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Dependence of Rate Constants of an Electron-Transfer Reaction on the Optical Configuration of the Reactants

Sir:

We have used esr methods for determination of rates of electron-transfer reactions between the radical anion of the optically active hydrocarbon 1-(α-naphthyl)-1-phenylethane[1] and the neutral molecule.[2] Line breadths were measured in mixtures of radical anions and neutral molecules containing only the *d* enantiomer and in racemic mixtures.

Standard methods for preparation of the anions by chemical reduction were used. Rates were determined from broadening of the lines at the low- and high-field extremes of the spectrum. The separation of these lines from their neighbors is large enough to eliminate complications from overlapping lines.

Partial reduction of the *d* enantiomer did not lead to racemization in a time long compared with the time required for each esr experiment. Measurements of the rates were carried out in dimethoxyethane (DME) and tetrahydrofuran (THF) with the sodium and potassium salts. Complications arise in interpretation of the data for the sodium salts because of contributions of ion-association phenomena to the line breadths. We therefore report here only the results for the potassium salts. The measurement of the rate for the pure enantiomer (**1**) leads directly to the rate constant k_{dd} for the reaction

$$[d\text{-}\mathbf{1}]^- + [d\text{-}\mathbf{1}]^0 \overset{k_{dd}}{\rightleftarrows} [d\text{-}\mathbf{1}]^0 + [d\text{-}\mathbf{1}]^-$$

Corresponding measurements for a racemic mixture yield an apparent rate constant k_R, which in turn is related to the rate constant k_{dl}, for the reaction

$$[d\text{-}\mathbf{1}]^- + [l\text{-}\mathbf{1}]^0 \overset{k_{dl}}{\rightleftarrows} [l\text{-}\mathbf{1}]^- + [d\text{-}\mathbf{1}]^0$$

by $k_{dl} = 2k_R - k_{dd}$. Table I lists the rate constants at 25° and apparent activation energies for the reaction of the potassium salts in DME and THF.

Table I. Rate Constants and Energies of Activation for Electron Transfer between Potassium 1-(α-Naphthyl)-1-phenylethanide and 1-(α-Naphthyl)-1-phenylethane (25 ± 1°)[a]

	Solvent	k_{dd} × 10^{-8}, M^{-1} sec^{-1}	k_{dl} × 10^{-8}, M^{-1} sec^{-1} [b]	E_{dd}, kcal mole^{-1}	E_R, kcal mole^{-1} [c]
1	DME	0.68 ± 0.07	1.10 ± 0.34	1.6 ± 0.5	0.6 ± 0.5
2	THF	0.19 ± 0.04	0.20 ± 0.06	2.3 ± 0.06	1.7 ± 0.4

[a] Limits of uncertainty are standard deviations from the mean. [b] Calculated values. [c] E_R is obtained from the temperature dependence of k_R.

Our experiments bear directly on the applicability of the relation proposed by Marcus[3,4] $k_{AB} = (k_{AA}k_{BB}K_{AB}\cdot f)^{1/2}$, where k_{AA} and k_{BB} are the rate constants for the reactions $A^- + A = A + A^-$ and $B^- + B = B + B^-$, respectively; k_{AB} is the rate constant, and K_{AB} is the equilibrium constant for $A^- + B = A + B^-$; f is a function of K_{AB}, k_{AA}, k_{BB}, and the collision number which has the property $f \equiv 1$ when $K_{AB} = 1$. Since $k_{dd} = k_{ll}$ and $k_{dl} = 1$, the relation predicts $k_{dd} = k_{dl}$.

Our data indicate that at 25° in THF k_{dd} and k_{dl} are equal within limits of experimental error but that in DME they differ by almost a factor of 2. In each solvent the energies of activation are different.

The standard statistical criteria indicate that the confidence level for the difference in DME is about 85%. The differences in activation energies are statistically more reliable. Further, errors associated with measurements of concentrations do not appear in the activation energies, because only *ratios* of line broadenings for a given sample at various temperatures are used.

We believe that our results exhibit small, but real, deviations from the Marcus relation. Further work on other optically active systems is under way in order to assess the reasons for the deviations.

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Walter Bruning, S. I. Weissman
Washington University
St. Louis, Missouri 63130

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