vermiculine lacked a previously reported[2] multiplet at δ 1.65 but otherwise agreed with the earlier[2] account. The mass spectra obtained by us also showed the expected molecular ion at *m/e* 392 (previously reported[2] to be absent). The infrared spectra of natural and racemic vermiculine in KBr pellet differ markedly.

(13) For a synthesis using differing methodology of a simpler, related cyclic diester (pyrenophorin), see E. W. Colvin, T. A. Purcell, and R. A. Raphael, *J. Chem. Soc., Chem. Commun.*, 1031 (1972).

(14) We are indebted to the National Institutes of Health for a grant in support of this research.

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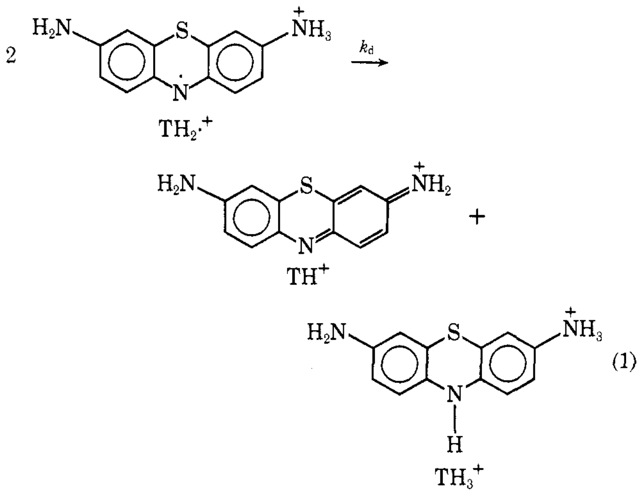
Received January 20, 1974

Solvent Effects on the Electron-Transfer Disproportionation Rate Constant of Semithionine Radical Cation

Sir:

The radical cation semithionine, $TH_2\cdot^+$, undergoes rapid disproportionation to thionine, TH^+, and leucothionine, TH_3^+, in acidic aqueous solution (eq 1).[1-8] In 0.05 *M* aqueous sulfuric acid[4] or 0.01-0.1 *M* aqueous trifluoromethylsulfonic acid (HTFMS) at 25°, $k_d = 2.4 \times 10^9\ M^{-1}\ sec^{-1}$.



(1)

We have found that k_d is dramatically lower, in some cases by as much as a factor of 10^3, in several aqueous organic solvent mixtures. Furthermore, in a wide variety of solvent mixtures, there is a fairly good linear relationship between log k_d and an empirical measure of solvent polarity, Kosower's *Z* parameter[10,11] (Figure 1). Such a quantitative correlation of the specific rate of disproportionation of a charged radical with the *Z* parameter has not been previously reported.[12]

The linear variation of log k_d with solvent *Z* value can reasonably be expected if the rate-determining step in the disproportionation of $TH_2\cdot^+$ is electron transfer followed by a proton transfer (Scheme I) rather than H atom transfer.[13-15] The partial electron-transfer characteristic of the difference between the reactants and the transition state in reaction 2 is analogous to the partial electron transfer which characterizes the difference between the ground and excited states of 4-carbomethoxy-1-ethylpyridinium iodide (CEPI), the transition which defines the solvent *Z* value.[10,16] The linear correlation of log k_d with *Z* value also suggests that there is negligible change in the orientation of the solvent around the reactant molecules in going from the separated ions to the transition state of step 2, a condition which must be true in the transition from the ground to excited state of CEPI.

Scheme I

$$2TH_2^{\cdot+} \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} TH_2^{2+} + TH_2 \qquad (2)$$

$$TH_2^{2+} \underset{H^+}{\overset{-H^+}{\rightleftharpoons}} TH^+ \qquad (3)$$

$$TH_2 \underset{-H^+}{\overset{H^+}{\rightleftharpoons}} TH_3^+ \qquad (4)$$

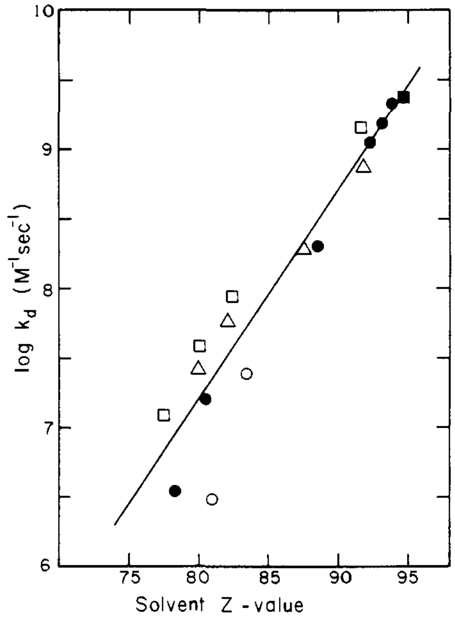


Figure 1. Effect of solvent on the rate constant for disproportionation of semithionine, k_d. (●) Aqueous *N,N*-dimethylacetamide (DMA); % v/v DMA in order of decreasing *Z* value: 10, 18, 25, 50, 75, 84%. (□) Aqueous 1,2-dimethoxyethane (DME); % v/v DME in order of decreasing *Z* value: 25, 50, 75, 95%. (△) Aqueous acetonitrile (AN); % v/v AN in order of decreasing *Z* value: 25, 50, 75, 92%. (○) Aqueous ethanol; % v/v ethanol in order of decreasing *Z* value: 75, 95%. (■) Water.

It should be noted that the variation in k_d is not related to such bulk solvent parameters as dielectric constant or viscosity. For example, in both 98% v/v *N*-methylpropionamide (MPA) (ϵ_{MPA} (30°) = 164, μ_{MPA} (25°) = 4.568 cP)[17] and in 92% v/v acetonitrile (AN) (ϵ_{AN} (25°) = 37.5, μ_{AN} (25°) = 0.304 cP),[14] k_d is much lower than in water (ϵ_{water} (25°) = 78.54, μ_{water} (25°) = 0.89 cP).[14] The measured *Z* value for 98% v/v MPA is ≈78 and $k_d < 2 \times 10^6\ M^{-1}\ sec^{-1}$. Obviously k_d is influenced by specific solvent-solute interactions rather than by bulk solvent characteristics.

In the present experiments, $TH_2\cdot^+$ was generated according to reaction 5 by flash excitation of solutions containing

$$TH^+ \xrightarrow[Fe^{2+},\,H^+]{h\nu} TH_2^{\cdot+} + Fe^{3+} \qquad (5)$$

2×10^{-6} *M* TH^+, 0.03 *M* $Fe(TFMS)_2$, and 0.01 *M* HTFMS. The temperature was maintained at 25 ± 1°. The disappearance of $TH_2\cdot^+$ or the reappearance of TH^+ following flash excitation was followed by monitoring the absorbance at 730 and 580 nm, respectively. Where possible, *Z* values for the solvent mixtures in Figure 1 were determined by measuring the absorption spectrum of CEPI in those solvents. Using CEPI recrystallized twice from cold acetone, we obtained excellent agreement with the published *Z* values for ethanol-water mixtures.[10] Since it has been shown that the presence of ions can markedly increase the *Z* value of some solvents,[18] 0.1 *M* NaTFMS was added to the CEPI solutions to obtain solutions with the same ionic strength as those used for the measurement of k_d. The further addition of 0.1 *M* HTFMS had no measurable effect. It was not possible to directly measure *Z* values for solvent mixtures containing more than 50% v/v water. For such mixtures, *Z* was estimated from extrapolation of a plot of *Z* vs. mole fraction of the organic component.

Factors affecting the rate constants for redox reactions of reduced thionine are of particular interest because of the possibility of using thionine in the construction of a photogalvanic cell.[19-22] Further work will be necessary to determine whether the rate constants for other reactions in the iron–thionine system (e.g., the oxidation of $TH_2\cdot^+$ and TH_3^+ by Fe^{3+}) are also dependent on solvent *Z* values.

Acknowledgment. This research was supported by the National Science Foundation's Research Applied to National Needs program under Grant SE/AER 72-03597.

References and Notes

(1) Indicated structures are arbitrary canonical forms.
(2) V. Balzani and V. Carassite. "Photochemistry of Coordination Compounds", Academic Press, New York, N.Y., 1970, pp 156–158, and references cited therein.
(3) R. Havemann and K. G. Reimer, *Z. Phys. Chem.* (*Leipzig*), **216**, 334 (1961), and earlier papers of this series.
(4) C. G. Hatchard and C. A. Parker, *Trans. Faraday Soc.*, **54**, 1093 (1961).
(5) R. Hardwick, *J. Am. Chem. Soc.*, **80**, 5667 (1958).
(6) S. Ainsworth, *J. Phys. Chem.*, **64**, 715 (1960).
(7) J. Schlag, *Z. Phys. Chem.* (*Frankfurt am Main*), **20**, 53 (1959).
(8) E. Rabinowitch, *J. Chem. Phys.*, **8**, 551 (1940).
(9) Present work.
(10) E. M. Kosower, "An Introduction to Physical Organic Chemistry", Wiley, New York, N.Y., 1968, and references cited therein.
(11) Solvent *Z* values cited in Figure 1 are for 0.1 *M* ionic strength.
(12) The possibility of such a correlation has been suggested by Kosower[13] for *a* similar system.
(13) E. M. Kosower, A. Teuerstein, and A. J. Swallow, *J. Am. Chem. Soc.*, **95**, 6127 (1973).
(14) M. Mohammad and E. M. Kosower, *J. Am. Chem. Soc.*, **93**, 2709 (1971).
(15) M. Mohammad and E. M. Kosower, *J. Am. Chem. Soc.*, **93**, 2713 (1971).
(16) A referee has called attention to the fact that the data of Figure 1 correspond to $\Delta\Delta G^{\ddagger}/0.5\Delta Z \sim 0.5$, a value considerably smaller than the 0.7–0.8 reported[15] for the electron-transfer reaction between 1-ethyl-4-carboxymethylpyridinyl radical ($\dot{Py}$) and 4-nitrobenzyl halides. Reaction 2 is different in charge type from the latter reaction (which is identical with the charge type of the process which defines *Z*) in a way such that the observed smaller sensitivity is to be expected.
(17) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", Butterworths, London, 1959, p 458.
(18) M. Mohammad and E. M. Kosower, *J. Phys. Chem.*, **74**, 1153 (1970).
(19) E. Rabinowitch, *J. Chem. Phys.*, **8**, 360 (1940).
(20) A. E. Potter and L. H. Thaler, *Sol. Energy*, **3**, 1 (1957).
(21) K. G. Mathai and E. Rabinowitch, *J. Phys. Chem.*, **66**, 663 (1962).
(22) L. J. Miller, *U.S. Dep. Commer., Off. Tech. Serv.*, Report AD 282, 878 (1962).

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Received October 19, 1974

Interpretation of Electron Spin Resonance Copper(II) Isotropic Hyperfine Splittings

Sir:

In a recent communication Zink and Drago[1] proposed that the predominant mechanism affecting the ESR nuclear isotropic hyperfine splitting in Cu^{2+} systems is a change in the energy separation between the ligand and the copper atomic orbitals. They offered this mechanism as an alternative to my earlier one[2] which consisted of a covalent and 4s dependence for the isotropic *A* values.

To review the problem briefly, the experimental isotropic ESR *A* values[3] predict a covalency dependence which is the direct opposite of the dependence obtained from the anisotropic ESR *A* values.[2] Since the trend predicted from the anisotropic ESR *A* values was consistent with other experimental data concerning covalency,[3] the anisotropic ESR results were accepted by me as correct, and the isotropic ESR theory was assumed to be incorrect.

Table I. Theoretical Molecular Orbital Data for $Cu(O-CR_1-CH-CR_2-O)_2$

R_1	R_2	R_1[a]	R_2[a]	Energy[d] of $d_{x^2-y^2}$ MO	α[e]	α[f]
F	F	F	F	−75.5881	0.9408	0.0704
H	F	F	F	−75.3716	0.9293	0.0685
H	F	H[b]	F[b]	−75.1629	0.9186	0.0673
H	F	H[c]	F[c]	−75.1622	0.9185	0.0666
H	H	F	F	−75.0699	0.9124	0.0676
H	H	H	F	−74.8640	0.9026	0.0662
H	H	H	H	−74.5814	0.8880	0.0655

[a] R_1 and R_2 of the second ligand. [b] The fluorines are trans to each other. [c] The fluorines are cis to each other. [d] In units of 1000 cm^{-1}. [e] The coefficient of the $d_{x^2-y^2}$ atomic orbital in the singly occupied molecular orbital. [f] The coefficient of the 4s atomic orbital in the molecular orbital which is predominantly d_{z^2} in character.

Zink and Drago[1] make the opposite assumption. They assume that the trend predicted by the isotropic ESR *A* values is correct, and, therefore, the anisotropic theory must be incorrect (although they do not make the second part of this statement it is implicit from their paper).

The basis of their mechanism is that electron withdrawing groups should decrease the energy difference between the metal $d_{x^2-y^2}$ atomic orbital and the ligand σ orbital. The decrease would then result in a greater covalency for this particular molecular orbital. Since the overall accepted effect of electron withdrawing groups is to decrease the covalency, they postulate that the above increase is more than offset by changes in the other occupied molecular orbitals.

The basic question is the following. What is the effect of electron withdrawing groups on the singly (electron) occupied molecular orbital? To determine this behavior I have extended the molecular orbital calculations of Cotton, Harris, and Wise[4] for $Cu(O-CR_1-CH-CR_2-O)_2$ to cases where R_1 and/or R_2 are fluorines. The pertinent results are given in Table 1. They are completely consistent with my earlier conclusions and, also, in agreement with the trend in substituent effects on energy levels as determined from ionization potential data.[5,6]

One does not have to rely on theoretical calculations to test these two alternate models. Ligand hyperfine splitting data can be used to give a more direct indication of unpaired electron delocalization. The limited data of this type that were available to Zink and Drago were considered by them to be inconclusive on this point due to the possibility of hybridization changes. Fortunately, a very complete single-crystal ESR study of the influences of different host lattices upon the ESR parameters of a Cu(II) complex has been published.[7] The anisotropic metal hyperfine splittings and the ligand nitrogen splittings gave a covalency trend which is in the opposite direction of the trend given by the isotropic metal hyperfine values. In addition the isotropic term *did correlate with the amount of orthorhombic distortion* (expected if 4s mixing is the predominant reason for changes in the isotropic hyperfine term).

If the above arguments concerning the incorrectness of Zink and Drago's model are accepted, one is still left with the question of what assumption or part of their model is not applicable. This question appears to be answered by the X-ray structure analysis of copper bisacetylacetonate–