ALC-100. Elution was with hexane at a flow rate of 3 ml/min. In order to preserve the activity of the columns, a drying column of activated silica gel was included in the line connecting the solvent reservoir and the pump.

Portions of ca. 50 mg of photovinylcyclopropanes were injected as solutions in ca. 250 μl of hexane and eluted until a total of five to eight cycles had been completed. In each case a partial separation had been effected by this time; the uv scan showed two overlapping peaks, the faster moving of which was later seen to contain the cis isomer. The eluate was collected at this point and fractions were concentrated. In each case all but ca. 50 ml of the solvent was distilled off at reduced pressure through a short column of glass beads; the rest was removed *in vacuo*. Then, after elimination of solvent residue *via* chromatography on a short (1.0 × 25 cm) silica gel column, specific rotations were measured. From the photo-vinylcyclopropanes of quantum yield No. 2 were obtained 25.1 mg of material highly enriched (ca. 90%) in the cis isomer and 32.6 mg similarly enriched in the trans isomer. Both of these fractions were subjected to further recycling hplc, and the material obtained was, in each case, combined with parallel product from quantum yield No. 1 and chromatographed again. The rate at which the separation progressed was indicated by the improvement with repeated chromatography of the $[\alpha]^{27}_{365}$ of the cis- and trans-enriched fractions. In the cis case these values changed as follows: after the first chromatography, 267 ± 6°; after the second, 273 ± 3°; and after the last, 274 ± 1°. In the trans case these rotations were: after the first chromatography, −442 ± 13°; after the second, −460 ± 8°; after the third, −472 ± 5°; and after the last, −470 ± 2°.

The specific rotations (at 27°) of the cis vinylcyclopropane that had been chromatographed to constant rotation were (λ in parentheses): 64.0 ± 0.4° (589), 67.2 ± 0.4° (578), 78.5 ± 0.5° (546), 148.5 ± 1.5° (436), 273 ± 3° (365) (c 0.005, hexane). Those of the similarly purified trans isomer were: −117 ± 1° (589), −123 ± 1° (578), −141 ± 1° (546), −263 ± 2° (436), −472 ± 5° (365) (c

0.005, hexane). The purified cis- and trans-3-ethyl-3-methyl-2-(2'-methylpropenyl)1,1-diphenylcyclopropanes had ir and nmr spectra identical with those of the independently synthesized compounds, and their ORD curves were perfect mirror images of those of the independently synthesized compounds.

Control Experiment. The Effect of Hplc on Optically Active *trans*-3-Ethyl-3-methyl-2-(2'-methylpropenyl)-1,1-diphenylcyclopropane. A 50.5-mg sample of *trans*-3-ethyl-3-methyl-2-(2'-methyl-propenyl)-1,1-diphenylcyclopropane, $[\alpha]^{27}_{365}$ 490 ± 4°, was subjected to hplc under conditions identical with those described above. After five cycles the eluate was collected. Approximately the first 10% of the vinylcyclopropane to elute was removed. The rest amounted to 35 mg of clear colorless oil, $[\alpha]^{27}_{365}$ 494° (c 0.009, hexane), after removal of solvent residue on a short silica gel column. This material was rechromatographed under the same conditions, and this time all the eluate was combined to give 19 mg of clear slightly yellow oil, $[\alpha]^{27}_{365}$ 479 ± 1° (c 0.009, hexane). This oil was subjected to hplc once again, with separation of the first 10% or so of the collected vinylcyclopropane from the rest. The larger fraction amounted to 11.2 mg of clear yellow oil, $[\alpha]^{27}_{365}$ 487 ± 3° (c 0.0056, hexane). Nmr and ir spectral properties of the three-times chromatographed *trans*-vinylcyclopropane were unchanged.

Kinetics of the Electron Transfer Reactions of Azaviolene Radical Ions. I
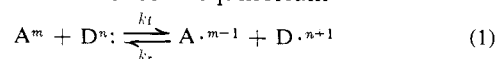
Claude F. Bernasconi,* [1] Robert G. Bergstrom, and William J. Boyle, Jr.

Contribution from the Thimann Laboratories of the University of California, Santa Cruz, California 95064. Received October 9, 1973

Abstract: Azaviolenes are part of a two-step redox system in which three forms can be reversibly interconverted by one-electron transfers, $Ox^{2+} + e^- \rightleftharpoons Sem^+ + e^- \rightleftharpoons Red$. The comproportionation–disproportionation kinetics of two such systems have been studied by the temperature-jump and stopped-flow methods in 50% 2-methoxy-ethanol–water. It is shown that, depending on the pH, there are up to three electron transfer pathways of importance, *viz.*, (1) $Red + Ox^{2+} \rightleftharpoons 2Sem^+$, (2) $RedH^+ + Ox^{2+} \rightleftharpoons Sem^+ + SemH^{2+}$, and (3) $RedH_2^{2+} + Ox^{2+} \rightleftharpoons 2SemH^{2+}$. Furthermore, there is a general acid–base catalyzed pathway, *viz.*, $RedH^+ + Ox^{2+} + B^- \rightleftharpoons 2Sem^+ + BH$. This study focuses on the relationship between rate and equilibrium constants in organic redox systems and in particular on the question of how strongly must an electron transfer reaction be favored thermodynamically for its rate to become diffusion controlled. Our results correlate reasonably well with the Marcus theory of electron transfer reactions.

B ecause of the fundamental importance of electron transfer reactions in organic redox systems, it is desirable to seek a better understanding of the factors determining the rates of these elementary processes. We now focus attention on the relationship between the kinetics and the thermodynamics of systems for which both the equilibrium constant and the rate of equilibration can be determined.

With reference to the redox equilibrium

$$A^m + D^n \underset{k_r}{\overset{k_f}{\rightleftharpoons}} A^{\cdot m-1} + D^{\cdot n+1} \qquad (1)$$

a relevant question is: how large must the equilibrium constant $K_f = k_f/k_r$ be in order for the k_f step to be diffusion controlled?

For another important class of elementary processes, *viz.*, proton transfer reactions, there exists a large body of data correlating rates with equilibrium constants; the data give a satisfactory answer to the same kind of question.[2a] Unfortunately, relatively few such data exist for reversible organic redox reactions.

A class of compounds, known as azaviolenes,[2b] ap-

(1) Alfred P. Sloan Fellow, 1971–1973.

(2) (a) M. Eigen, *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964); (b) S. Hünig, *Pure Appl. Chem.*, **15**, 109 (1967).

pear to be particularly suitable for a systematic approach to answering our question. The azaviolenes occur in three states of oxidation which are reversibly interconverted in a two-step redox system.
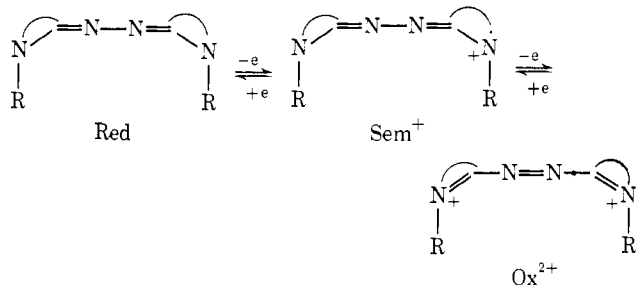
In many cases, the three forms can be independently isolated. Hünig has adopted the nomenclature of Michaelis[3] in designating the three forms reduced (Red), semi-quinone (Sem$^+$), and oxidized (Ox^{2+}). The redox equilibrium can be written as in eq 2 and a semiquinone

$$\text{Red} + \text{Ox}^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\text{Sem}^+ \tag{2}$$
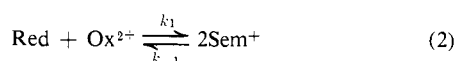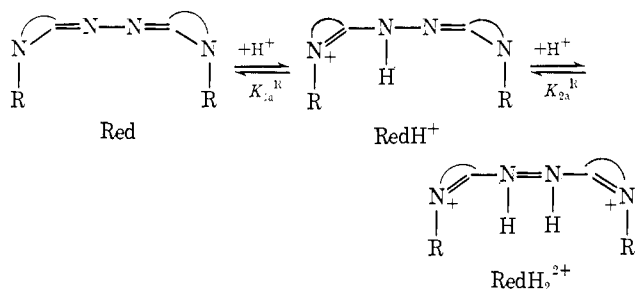
formation constant, K_1, can be defined by eq 3. K_1's for

$$K_1 = \frac{k_1}{k_{-1}} = \frac{[\text{Sem}^+]^2}{[\text{Red}][\text{Ox}^{2+}]} \tag{3}$$

many of the azaviolenes have been determined by polarography[2b,4] and are typically 10^4 to 10^{10}.

An additional feature of the azaviolenes is that Red easily undergoes mono- or even diprotonation in acidic solution.

These additional species provide two additional pathways for the semiquinone formation reaction (Scheme I); the proton in SemH^{2+} presumably sits on one of the

Scheme I
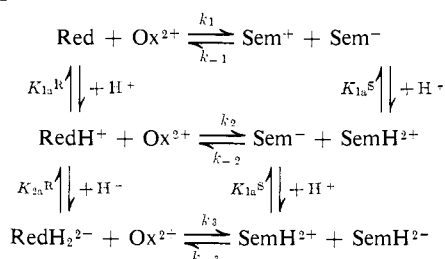
bridge nitrogens, just as in RedH$^+$.

Though these new pathways make a kinetic study rather complicated, they provide additional data (such as k_2 and k_{-2} which relate to $K_2 = k_2/k_{-2}$ and k_3 and k_{-3} which relate to $K_3 = k_3/k_{-3}$) toward answering our

(3) L. Michaelis, Chem. Rev., 16, 243 (1935).

(4) (a) S. Hünig, H. Balli, H. Conrad, and A. Schott, Justus Liebigs Ann. Chem., 676, 52 (1964); (b) S. Hünig, G. Kiesslich, F. Linhart, and H. Schlaf, ibid., 752, 182, 196 (1971).

question. Because upon protonation Sem$^+$ loses part of its ability to delocalize the single electron,[2b] the stability of SemH^{2+} decreases correspondingly. Thus one expects $K_3 \ll K_2 \ll K_1$, as is borne out by our results.

We recently[5] reported preliminary results on a kinetic study of the azaviolene system derived from 1-ethyl-2-quinolone azine (1) in 50% 2-methoxyethanol–water (v/v) at 25°. Data were presented on both the first and second pathways. We now report details of a more extensive study of the behavior of 1 in which all three horizonal pathways in Scheme I are shown to be important. Furthermore, kinetic data on a derivative of a different charge type, the salt of the 6,6'-disulfonic acid 2,[6] have been obtained over a pH range in which the first two pathways are important.
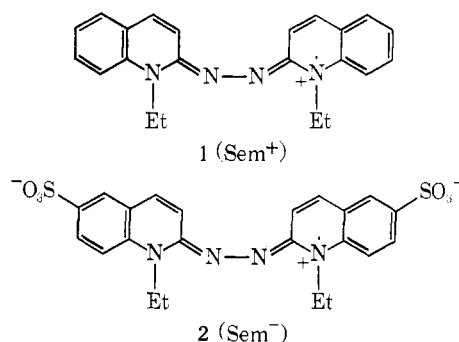
Results

Our results are summarized in Table I.

Table I. Rate and Equilibrium Constants for Azaviolenes in 50% 2-Methoxyethanol–Water (v/v) at 25°

	1		2
	$\mu = 0.50^a$	$\mu = 0.10^b$	$\mu = 0.10^a$
K_1	2.42×10^5	$2.14 \times 10^5\ ^c$	$1.47 \times 10^5\ ^d$
k_1, M^{-1} sec^{-1}	1.56×10^9	1.82×10^9	1.52×10^9
k_{-1}, M^{-1} sec^{-1}	6.45×10^3	8.53×10^3	1.03×10^3
K_2	6.2×10^{-2}	$(6.2 \times 10^{-2})^e$	$(\approx 10^{-2})^h$
k_2, M^{-1} sec^{-1}	1.14×10^6	5.5×10^5	4.0×10^5
k_{-2}, M^{-1} sec^{-1}	1.8×10^7	$(9 \times 10^6)^e$	$(\approx 4 \times 10^7)^h$
K_3	2.5×10^{-4}		$(\approx 8 \times 10^{-6})^h$
k_3, M^{-1} sec^{-1}	2.7×10^3		
k_{-3}, M^{-1} sec^{-1}	1.1×10^7		
K_{1a}^R, M	2.14×10^{-7}	1.12×10^{-7}	3.02×10^{-6}
pK_{1a}^R	6.67	6.95^f	5.52^g
K_{2a}^R, M	3.40×10^{-3}	2.04×10^{-3}	3.55×10^{-2}
pK_{2a}^R	2.47	2.69	1.45
$K_{1a}^S = K_1 K_{1a}^R/K_2$, M	0.84	0.14^e	$(\approx 44)^h$
pK_{1a}^S	0.18	0.85	$(\approx -1.65)^h$

^{a} Added electrolyte was KCl. ^{b} Electrolyte was NaCl. ^{c} Reference 4a. ^{d} 6.61 $\times 10^4$ in ref 4a. ^{e} Using K_2 value for $\mu = 0.5$. ^{f} 6.5 in ref 4a. ^{g} 5.1 in ref 4a. ^{h} Estimated by assuming k_2 to be on the Marcus curve in Figure 2 (see Discussion).

K_1, pK_{1a}^R, and pK_{2a}^R. The uv spectra[4a] of Red, RedH$^+$, and RedH$_2^{2+}$ are sufficiently different for both 1 and 2[6] as to permit a straightforward determination of pK_{1a}^R and pK_{2a}^R by a standard spectrophotometric technique.

Further, from Scheme I it is evident that the equilib-

(5) C. F. Bernasconi, R. G. Bergstrom, and S. Hünig, Chem. Commun., 1495 (1971).

(6) Note that for 2 all species of Scheme I have a net charge reduced by two, e.g., Red^{2-}, RedH$^-$, Sem$^-$, etc.

Table II. pH Dependence of Slopes (A) of Plots of $(1/\tau)(\text{pH})$ vs. $[\text{Sem}^+]_0$ for **1** at $\mu = 0.10$ and 0.50^a

$\mu = 0.10$		$\mu = 0.50$	
pH	$10^{-5}A,^b$ M^{-1} sec^{-1}	pH	$10^{-5}A,^b$ M^{-1} sec^{-1}
4.79	6.80	4.80	7.39
3.86	3.00	4.59	6.27
3.19	2.40	4.30	4.81
2.37	2.89	3.87	3.79
2.02	3.09	3.55	3.54
1.43	3.70	2.90	3.70
1.26	3.91	2.70	4.30
1.11	4.08	2.50	4.55
		1.98	5.15
		1.80	5.35
		1.37	5.60
		1.08	5.60
		0.78	5.42
		0.61	5.23
		0.39	5.00

^{a} Temperature $= 25.0°$. $^b A = \Delta(1/\tau)(\text{pH})/\Delta[\text{Sem}^-]_0$. Range of $[\text{Sem}^+]_0$ concentrations used was 3×10^{-5} to $2 \times 10^{-4} M$. For experiments above pH 3, where buffers were used, each $(1/\tau)(\text{pH})$ value is the intercept of a plot of $1/\tau$ vs. [buffer] for a given $[\text{Sem}^+]_0$

rium concentrations of Sem^- and Ox^{2+} must also be pH dependent. We took advantage of this fact to determine K_1 spectrophotometrically in the visible region where Sem^+ and Ox^{2-} but not Red, RedH$^-$, nor Red-H$_2^{2+}$ have significant absorptions.[7] The procedure is described in the Experimental Section.

Some of our pK_a and K_1 values were obtained under the same conditions (ionic strength) as those determined polarographically;[4a] our pK_{1a}^R values at $\mu = 0.1$ are 6.95 for **1** and 5.52 for **2**, whereas Hünig, et al.,[4a] reported 6.5 for **1** and 5.1 for **2**. There is a discrepancy of about 0.4 pK unit for both compounds for which we have no clear explanation. The discrepancy in K_1 for **2** as measured by Hünig, et al.,[4a] and by us is a factor of about 2.

Kinetic Studies of 1. The equilibration kinetics for **1** were studied by the temperature-jump relaxation technique[10] in the pH range 0.39 to 4.80 in 50% 2-methoxyethanol-water (2-ME-H$_2$O). Experimentally the system was found to be characterized by a single relaxation process.[11] The experiments were carried out by dissolving the Sem$^+$ perchlorate in the solvent at the appropriate pH, maintained by buffering with HCl or a carboxylic acid buffer. Temperature jumps of up to 7.5° were used, but the final reaction temperature was 25° in all cases. The reciprocal relaxation time,

(7) SemH^{2+} never contributes measurably to the absorption. This is because at the pH values where a significant fraction of Sem$^+$ is in the form of SemH^{2-} (pH <1), its equilibrium concentration is negligible compared to that of RedH$^-$, RedH$_2^{2+}$, and Ox^{2-}. Another possible contributor to the visible spectrum is the protonated form of Ox^{2-}. Janata and Williams[8] suggest that Ox^{2-} of a related azaviolene, 2,2'-(3-methylbenzothiazolinone) azine, is protonated in strong acid. Their suggestion was based on observation of a shift of 10 nm in the absorption maximum of Ox^{2+} when the medium was changed from 0.19 M H$_2$SO$_4$ to 1.87 M H$_2$SO$_4$. We observed no such change in the pH range of our study (pH 0.39 to 4.80). Inasmuch as the pK_a of the conjugate acid of azobenzene is -3,[9] no protonation of Ox^{2+} would be expected since the presence of a positive charge β to each nitrogen should reduce the basicity of Ox^{2+} even below that of azobenzene.

(8) J. Janata and M. B. Williams, *J. Phys. Chem.*, **76**, 1178 (1972).

(9) S.-J. Weh and H. H. Jaffe, *J. Amer. Chem. Soc.*, **81**, 3779 (1959).

(10) M. Eigen and L. De Maeyer "Techniques of Organic Chemistry," Vol. VIII, part 2, A. Weissberger, Ed., Interscience, New York, N. Y., 1963, p 895.

(11) The relaxation times associated with proton transfer reactions (vertical equilibria in Scheme I) are too fast to be measured by the temperature-jump method.
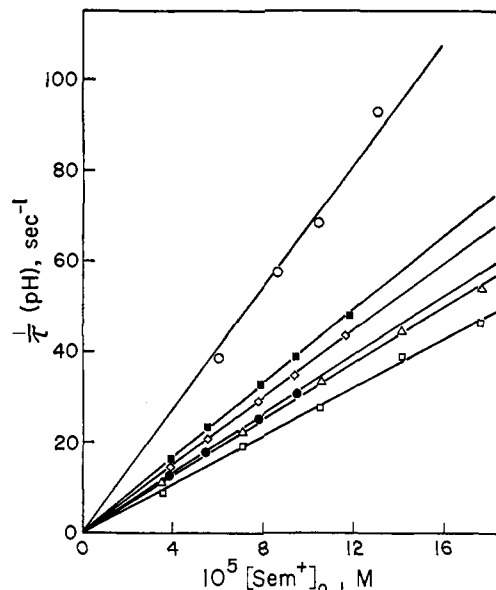
Figure 1. Representative plots of $1/\tau(\text{pH})$ vs. $[\text{Sem}^+]_0$ at 25° in 50% 2-ME-H$_2$O, $\mu = 0.1 M$, compound **1**: (O) pH 4.79; (■) pH 1.11; ($\Diamond$) pH 1.43; (●) pH 3.86; ($\triangle$) pH 2.37; ($\square$) pH 3.19.

$1/\tau$, was found to depend strongly on the stoichiometric semiquinone concentration, the pH, and the buffer concentration. In buffered solutions it was necessary to use several buffer concentrations for each semiquinone concentration and extrapolate to zero buffer concentration in order to obtain buffer-independent relaxation times, $\tau(\text{pH})$. In all cases plots of $(1/\tau)(\text{pH})$ vs. $[\text{Sem}^+]_0$ at each pH were linear with intercepts at the origin; some representative plots are shown in Figure 1; the slopes (A) of all the plots are compiled in Table II.

On the basis of Scheme I and the assumption, to be justified in the Discussion, that all the proton transfers are fast compared to the electron transfers, an expression for $(1/\tau)(\text{pH})$ can be derived using known principles[10] (see Appendix). Expression in terms of the stoichiometric concentration $[\text{Sem}^+]_0$ results in eq 4

$$\frac{1}{\tau}(\text{pH}) =$$

$$\left(k_1 + \frac{k_2[\text{H}^+]}{K_{1a}^R} + \frac{k_3[\text{H}^+]^2}{K_{1a}^R K_{2a}^R}\right)\left(\frac{2}{Q_R(2 + Q_S(K_1/Q_R)^{1/2})} + \frac{4(K_1/Q_R)^{1/2}}{K_1 Q_S(2 + Q_S(K_1/Q_R)^{1/2})}\right)[\text{Sem}^+]_0 \quad (4)$$

where Q_R and Q_S are defined by eq 5 and 6 and $K_2 =$

$$Q_R = 1 + \frac{[\text{H}^+]}{K_{1a}^R} + \frac{[\text{H}^+]^2}{K_{1a}^R K_{2a}^R} \quad (5)$$

$$Q_S = 1 + \frac{[\text{H}^+]}{K_{1a}^S} = 1 + \frac{K_2[\text{H}^+]}{K_1 K_{1a}^R} \quad (6)$$

k_2/k_{-2}. In the presence of buffers an additional term, $(1/\tau)(\text{buffer})$, must be added to account for buffer catalysis (vide infra).

When these results were originally communicated,[5] we thought that only the first two pathways were involved in the reaction at $\mu = 0.10$. On extending the study to lower pH (the last two entries under $\mu = 0.10$ in Table II), however, we saw that the observed $(1/\tau)$

(pH) was beginning to increase at lower pH after having decreased with decreasing pH and approximately leveled off. Since these new results did not fit with relaxation times reckoned from k_1 to k_2 values previously obtained, it appeared that a third pathway might be operative. In order to test this possibility and fully to evaluate the scheme, more data over a wide pH range were required. Consequently the experiments were repeated (Table II) using 0.5 M ionic strength and 15 pH values between 4.8 and 0.39.

The experimental data were fit to eq 4 by a procedure described in the Experimental Section. Table III
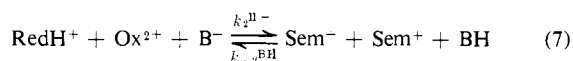
Table III. Calculated[a] and Observed Values of $A = \Delta(1/\tau)(pH)/\Delta[\text{Sem}^+]_0$ with Three Pathways Involved ($\mu = 0.50$)[b]

pH	$10^{-5}A_{obsd}$, M^{-1} sec^{-1}	$10^{-5}A_{calcd}$, M^{-1} sec^{-1}	% diff[c]
4.80	7.39	7.69	+4.2
4.59	6.27	6.24	−0.5
4.30	4.81	4.80	0.0
3.87	3.79	3.61	−4.6
3.55	3.53	3.29	−6.9
2.90	3.70	3.73	+1.0
2.70	4.30	4.06	−5.4
2.50	4.55	4.42	−2.9
1.98	5.15	5.18	+0.6
1.80	5.35	5.35	0.0
1.37	5.60	5.53	−1.1
1.08	5.61	5.52	−1.4
0.78	5.42	5.39	−0.6
0.61	5.24	5.26	+0.4
0.39	5.00	5.03	+0.6

[a] Calculated from eq 4 using the values in Table I. [b] Temperature = 25.0°. [c] $((A_{calcd} - A_{obsd})/A_{obsd})100$.

shows there is in fact an excellent fit between slopes (A) calculated on the basis of the parameters summarized in Table I and the experimental data.

Buffer Data. We assumed that the buffer dependence is due entirely to the reaction of eq 7; this assumption

$$\text{RedH}^+ + \text{Ox}^{2+} + \text{B}^- \underset{k_{-2}^{BH}}{\overset{k_2^{B-}}{\rightleftharpoons}} \text{Sem}^- + \text{Sem}^+ + \text{BH} \quad (7)$$

will be justified in the Discussion.

Reaction 7 introduces an additional term into eq 4 which is given by eq 8 (see Appendix). Since k_2^B is the only unknown in eq 8 it is readily calculated from

$$\frac{1}{\tau}(\text{Buffer}) = k_2^B \frac{[\text{H}^+]}{K_{1a}^R}\left(\frac{2}{Q_R(2 + Q_S(K_1/Q_R)^{1/2})} + \frac{4(K_1/Q_R)^{1/2}}{K_1Q_S(2 + Q_S(K_1/Q_R)^{1/2})}\right)[\text{Sem}^+]_0[\text{B}^-] \quad (8)$$

the slope of a plot of $1/\tau$ vs. [B$^-$] at constant pH and [Sem$^+$]$_0$. The k_2^{B-} and k_{-2}^{BH} values for three carboxylic acids used in this study are reported in Table IV: the

Table IV. Rate Constants for General Base Catalysis[a] (Compound 1)

Buffer Base	pK_a[b]	k_2^{B-}, M^{-2} sec^{-1}	k_{-2}^{BH}, M^{-2} sec^{-1}[c]
CH$_3$CO$_2^-$	5.50	7.8 × 10^8	4.8 × 10^4
HCO$_2^-$	4.30	2.0 × 10^8	1.9 × 10^5
ClCH$_2$CO$_2^-$	3.55	7.6 × 10^7	4.1 × 10^5

[a] At 25.0° and $\mu = 0.50$ in 50% 2-ME–H$_2$O. [b] Determined by potentiometric titration in 50% 2-ME–H$_2$O, $\mu = 0.5$. [c] Calculated from $k_{-2}^{BH} = k_2^{B-}K_a^{BH}/K_1K_{1a}^R$.

apparent pK_a values of the carboxylic acids were determined by potentiometric titration in 50% 2-ME–H$_2$O.[12] Bronsted plots of these data gave good straight lines of $\beta \approx \alpha \approx 0.5$.

Kinetic Studies of 2. Because solutions of Sem$^-$[6] are unstable at low pH, the kinetics of reactions of 2 could not be studied by the temperature-jump method. Instead, a stopped-flow method was used in which a neutral solution of Sem$^-$ (stable for some hours) was mixed with solutions of HCl of varying concentrations, in effect producing a pH jump. Although the pH jumps used are large perturbations so that the rate equation can no longer be linearized,[10] this problem could be circumvented by monitoring only the last 5 to 10% of the chemical relaxation, where the system is in fact close to equilibrium and the formalism of relaxation kinetics is applicable. Using reactions of 1 as a test system, we could show that the relaxation times obtained by this pH-jump technique were identical with those from the temperature-jump technique.

Relaxation times for reactions of 2 were obtained at 5 pH values from 1.10 to 3.11 at 0.10 ionic strength: above pH 3.1 the relaxation amplitude becomes small and buffering with HCl is no longer adequate. Attempts to use carboxylate buffers were frustrated because these buffers greatly accelerate the decomposition of the reactant solution.

As with 1, plots of $1/\tau$ vs. [Sem$^-$]$_0$ were linear with zero intercepts and the slopes depend on pH: the results are summarized in Table V.

Table V. pH Dependence of Slopes (A) of Plots of $1/\tau$ vs. [Sem$^-$]$_0$ for 2 at $\mu = 0.10$[a]

pH	$10^{-5}A$, M^{-1} sec^{-1}	pH	$10^{-5}A$, M^{-1} sec^{-1}
3.11	5.24	1.65	1.97
2.64	3.31	1.11	1.95
2.11	2.40		

[a] Temperature = 25.0°.

Since the pK_{1a}^R and pK_{2a}^R of 2(RedH$^-$) and 2(RedH$_2$), respectively, are considerably lower than those of 1(RedH$^+$) and 1(RedH$_2^{2+}$), respectively, only the first two pathways contribute significantly to the overall rate of equilibration at the pH values used and only k_1, k_{-1}, and k_2 could be calculated from our data. However, Table I includes estimates on K_2, k_{-2}, K_{1a}^S, and K_3 based on the Marcus theory, obtained as described in the Discussion.

Discussion

Justification of Assumptions. Since all our kinetic data were treated by eq 4 or simplifications thereof, the validity of an assumption underlying it, viz., that all proton transfer equilibria are rapidly established, has to be ascertained. This assumption may not seem justified in view of the fact that rate coefficients for electron transfer processes are frequently of the same

(12) That the dependence of $1/\tau$ on buffer concentration is due to buffer catalysis and not to specific salt effects sometimes observed[13] in mixed aqueous solvents was demonstrated by repeating experiments with one buffer using NaNO$_3$, NaCl, and NaClO$_4$ as the compensating electrolyte. The same results were obtained with all three salts.

(13) P. Salomaa, A. Kamkaamperä, and M. Lahti, J. Amer. Chem. Soc., 93, 2084 (1971).

order of magnitude as those for proton transfers. However, because the substrate concentration was very low in all our experiments and the electron transfer processes are second-order reactions, their *rates* are effectively much slower than those of the proton transfers: the latter are pseudo-first-order processes and the equilibration rate is solely determined by the respective rate constants and the pH. This qualitative argument can be amplified by a mathematical treatment.[14] The fact that all plots of $(1/\tau)(pH)$ *vs.* [Sem+]$_0$ are linear with zero ordinate intercepts (Figure 1), as called for by eq 4, is *experimental* proof for the validity of our assumption. Note that at significantly higher [Sem+]$_0$ one could expect a leveling off because of proton transfer becoming (partially) rate limiting.

Rate *vs.* Equilibrium Constants. Correlation with Marcus Theory. With one exception all our kinetic data refer to electron transfer reactions of the general type represented in eq 1: the exception is the third pathway with substrate **1** where a (presumably concerted) proton transfer accompanies the electron transfer, making it in effect a hydrogen transfer reaction.

In Figure 2 we have plotted the various log k_f ($k_f = k_1, k_2, k_3$) and log k_r ($k_r = k_{-1}, k_{-2}, k_{-3}$) *vs.* log K_f ($K_f = K_1, K_2, K_3$). Literature data on two similar systems are included on the plot. One is the redox equilibrium between benzoquinone and the hydroquinone dianion to form the semiquinone radical anion **3**. The following data, obtained by the temperature-jump technique at 11° in aqueous solution, $\mu = 0.1$ M, have been reported: $k_f = 2.6 \times 10^8 M^{-1} \sec^{-1}$, $k_r = 6.8 \times 10^7 M^{-1} \sec^{-1}$, $K_f = 3.8$.[15] The second system is the equilibrium reaction between the Red and Ox^{2+} forms of the violene 1,1',2,2'-tetramethylvinylene-3,3'-diindolizine, for which the Sem+ form has structure **4**. The data

O·
|
[structure] CH$_3$ CH$_3$ CH$_3$ CH$_3$
|
O_

3 (Sem−)   4 (Sem+)
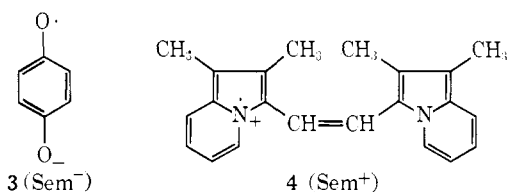
obtained by the stopped-flow method in acetonitrile at 25° are $k_f = 6.5 \times 10^5 M^{-1} \sec^{-1}$, $k_r = 8.1 \times 10^5 M^{-1} \sec^{-1}$, and $K_f = 800$.[16]

Though the data plotted in Figure 2 are not all strictly comparable because (1) the reactions belong to different charge types, (2) they were not all conducted in the same solvent, at the same ionic strength, and at the same temperatures, and (3) one of them is accompanied by a proton transfer, a qualitative discussion on the basis of the Marcus[17] theory is nevertheless interesting. According to Marcus the bimolecular rate constant for a chemically (in constrast to diffusion) controlled electron transfer is given by eq 9 where $Z \approx 10^{11} M^{-1} \sec^{-1}$

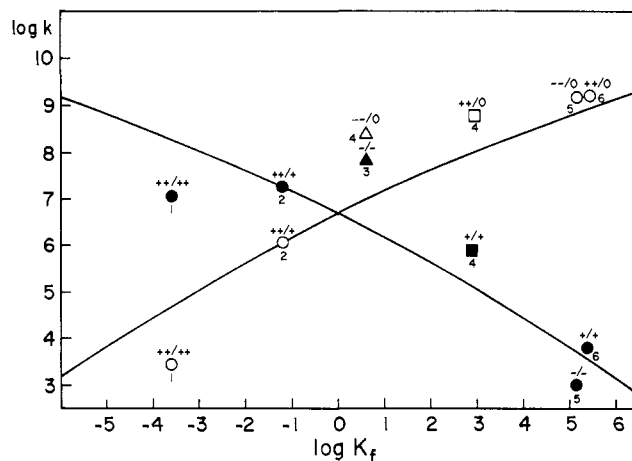$$k_{\text{act}} = Ze^{-\Delta F^*/RT} \qquad (9)$$

and ΔF^* is the free energy of activation. ΔF^* is given

(14) R. G. Bergstrom, Ph.D. Thesis, University of California, Santa Cruz, 1973.

(15) H. Diebler, M. Eigen, and P. Matthies, *Z. Naturforsch. B*, **16**, 629 (1961).

(16) B. C. Bennion, J. J. Auborn, and E. M. Eyring, *J. Phys. Chem.*, **76**, 701 (1972).

(17) (a) R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956); (b) *ibid.*, **43**, 679 (1965); *Discuss. Faraday Soc.*, **29**, 21 (1960).

Figure 2. Log k *vs.* log K_f for various electron transfer reactions. Open symbols are for k_f and filled symbols are for k_r. Charge type of reactants is indicated, *e.g.*, $+/+$ means reaction between two cations bearing one charge each. Circles refer to azaviolenes in 50% 2-ME-H$_2$O: no. 1, k_3 and k_{-3} for **1**; no. 2, k_2 and k_{-2} for **1**; no. 5, k_1 and k_{-1} for **1**; no. 6, k_1 and k_{-1} for **2**; no. 3, k_1 and k_{-1} for **3** (in H$_2$O); no. 4. k_1 and k_{-1} for **4** (in acetonitrile). Curves calculated for k_{act} on the basis of the Marcus theory, see Discussion.

by eq 10; W_r and W_p are the Coulombic work of

$$\Delta F^* = \frac{W_r + W_p}{2} + \frac{\lambda}{4} + \frac{\Delta F^0}{2} + \frac{(\Delta F^0 + W_p - W_r)^2}{4\lambda} \qquad (10)$$

bringing together reactants and products, respectively; ΔF^0 is the standard free energy, equivalent to $-RT \ln K$. The reorganization parameter, λ, is given by eq 11,

$$\lambda = \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right)\left(\frac{1}{D_{\text{op}}} - \frac{1}{D_s}\right)(\Delta ze)^2 \qquad (11)$$

where a_1 and a_2 are the effective radii of the reactants and r is the effective radius of the activated complex, usually taken as $a_1 + a_2$; D_{op} is the optical dielectric constant, equal to the square of the refractive index; D_s is the static dielectric constant; Δz is the number of electrons transferred; and e is the electric charge of an electron.

For reactions approaching the diffusion-controlled limit, the observed rate constant is given by eq 12[18]

$$k_{\text{obsd}} = k_{\text{act}}k_{\text{diff}}/(k_{\text{act}} + k_{\text{diff}}) \qquad (12)$$

where k_{diff} is the diffusion-controlled rate constant, k_{act}, defined by eq 9.

Rather than calculating λ from eq 11 which requires an estimate of a_1, a_2, and r we use the semiempirical approach of calculating ΔF^* corresponding to k_2 of the reaction RedH+ + Ox^{2+} → Sem+ + SemH^{2+} of **1** (point 2 in Figure 2) *via* eq 9 and then obtain $\lambda = 23.6$ kcal from eq 10 by assuming W_r and W_p to be negligible at the high ionic strength (0.5 M) used. With this λ we can then calculate ΔF^* for any ΔF^0 value *via* eq 10, again assuming W_r and W_p to be negligible. After converting ΔF^* into log k_{act} and ΔF^0 into log K we obtain the "theoretical" curves shown in Figure 2.

Incidentally, if we assume $a_1 = a_2$ and $r = a_1 + a_2$,

(18) R. A. Marcus, *J. Chem. Phys.*, **43**, 3477 (1965).

$\lambda = 23.6$ kcal corresponds to $a_1 = 3.87$ Å according to eq 11.[19]

Azaviolenes. If we focus on our own data (circles in Figure 2) the Marcus curve correlates the points 2, 5, and 6 quite well in both directions. On the other hand in no. 1 (k_3 and k_{-3} for **1**) the rate constants are about 20-fold lower than expected from the curves. This is undoubtedly due in part to large charge repulsion which makes W_r and W_p no longer negligible. An additional possible factor is that the electron transfer is accompanied by a proton transfer.

A central question of interest is whether the two k_1 values (no. 5 and 6, open circles) which are associated with equilibrium constants in the order of 10^5 have reached the diffusion-controlled limit. The fact that they have not fallen below the Marcus curve would suggest that the diffusion limit has not nearly been reached yet ($k_{obsd} = k_{diff}$ when $k_{act} \gg k_{diff}$, eq 12).

A different approach to this question is to estimate k_{diff}. According to the combined Smolunchowsky[21] and the Stokes–Einstein[21] equations and assuming equal molecular radii for the reactants, k_{diff} is given by eq 13

$$k_{diff} = \frac{8RT}{3000\eta} M^{-1} sec^{-1} \qquad (13)$$

where η is the viscosity in poise. In 50% 2-ME–H$_2$O, $\eta \approx 0.026^{20}$ P and thus $k_{diff} \approx 2.5 \times 10^9 M^{-1} sec^{-1}$. This line of reasoning suggests that our k_1 values *have* nearly reached the diffusion limit and somewhat contradicts the conclusion reached on the basis of the Marcus curve. More experimental data are needed for definite conclusions.
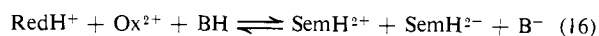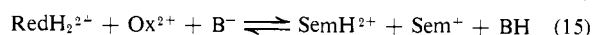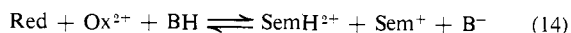
Estimates of K_2, k_{-2}, $K_{1a}{}^S$, and K_3 for 2 Based on Marcus Curves. The good correspondence between theoretical and experimental rate constants for no. 2, 5, and 6 suggests that the k_2 value for **2** will also be close to the theoretical curve.[22] This allows us to estimate K_2 and from it k_{-2}, K_3, and $K_{1a}{}^S$. The estimates included in Table I were calculated assuming k_2 lies exactly on the Marcus curve.

Reactions of 3 and 4. The data on the reactions of **3** in aqueous solution (no. 3 in Figure 2) and of **4** in acetonitrile (no. 4) do not fall very close to the Marcus curves defined by the azaviolenes in 50% 2-ME–H$_2$O. The deviation is particularly large for **3** with rate constants about 30-fold higher than expected despite the lower temperature (11°). It is unlikely that this is due solely to smaller charge repulsion in reactants and products since the rate-retarding effect of charge repulsion in no. 2 (on which the Marcus curves are based) is expected to be rather small at the high ionic strength used. Hence, granted that the Marcus theory is valid at all, λ would have to be smaller in the reactions of **3**. Since the term $(1/D_{op} - 1/D_s)$ in eq 11 is larger in H$_2$O at 11° (0.550)[23] than in 50% 2-ME–H$_2$O at 25° ($\sim$0.508),[19] the term $(1/2a_1 + 1/2a_2 - (1/r))$ would have to be con-

siderably smaller for the reactions of **3** compared to **1**. It is difficult to assess the physical meaning of this conclusion because the radii a_1, a_2, and r are not very well defined for nonspherical species.
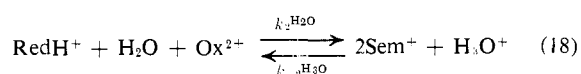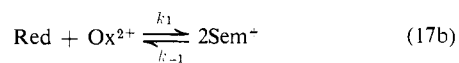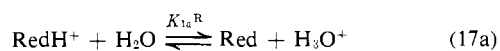
Mechanism of General Acid–Base Catalysis. Buffer Catalysis. Equation 7 is meant to represent general acid–base catalysis by a concerted mechanism.[24] A stepwise mechanism, for example, involving a rate-determining proton transfer between catalyst and substrate, is excluded by the fact that all proton transfers were shown to be very fast compared to the electron transfers, even in the absence of a buffer.

Besides eq 7 there are three other "catalytic pathways" which in principle could account for buffer catalysis. They are eq 14, 15, and 16.

$$Red + Ox^{2+} + BH \rightleftharpoons SemH^{2+} + Sem^+ + B^- \qquad (14)$$

$$RedH_2{}^{2+} + Ox^{2+} + B^- \rightleftharpoons SemH^{2+} + Sem^+ + BH \qquad (15)$$

$$RedH^+ + Ox^{2+} + BH \rightleftharpoons SemH^{2+} + SemH^{2-} + B^- \qquad (16)$$

However, in constrast to eq 7, they all violate the Libido rule[25] according to which concerted general acid–base catalysis of complex reactions only occurs when there is a change in pK at the reaction site which converts an unfavorable into a favorable proton transfer with respect to the catalyst. In eq 14 the opposite holds true; for the process from left to right, the proton transfer from the catalyst (p$K = 3.55, 4.5$, or 5.5) to the reaction site changes from favorable in the reactant (p$K_{1a}{}^R = 6.67$) to unfavorable in the product (p$K_{1a}{}^S = 0.18$). For reaction 15, from left to right, proton transfer from reaction site to base catalyst is favored not only in product but also in reactant (p$K_{2a}{}^R = 2.47$); for the reverse process proton transfer from the acid catalyst to the reaction site is unfavorable in both reactant and product. The same holds true for eq 16, left to right.

General Catalysis by H_3O^+–H_2O? The question arises whether any of the processes in eq 7, 14, 15, or 16, but where BH (B$^-$) is substituted by H_3O^+ (H_2O), could play a significant role. There is no direct way to test this hypothesis experimentally because the stepwise process 17 and the concerted process 18 cannot be

$$RedH^+ + H_2O \underset{}{\overset{K_{1a}{}^R}{\rightleftharpoons}} Red + H_3O^+ \qquad (17a)$$

$$Red + Ox^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Sem^+ \qquad (17b)$$

$$RedH^+ + H_2O + Ox^{2+} \underset{k_{-2}{}^{H_3O}}{\overset{k_2{}^{H_2O}}{\rightleftharpoons}} 2Sem^+ + H_3O^+ \qquad (18)$$

distinguished on the basis of kinetic evidence. However, each one of the four hypothetical concerted pathways violates the Libido rule (pK of H_3O^+ in 50% 2-methoxyethanol assumed to be *ca.* $-\log([H_2O] + [CH_3OCH_2CH_2OH]) = -1.56$) and is thus considered to be insignificant.

Experimental Section

Materials. Water was distilled in an all-glass still and saturated with oxygen-free nitrogen. 2-Methoxyethanol (Mallinckrodt AR reagent) was treated with 1% (v/v) of a solution of FeSO$_4$·7H$_2$O (30 g) and H$_2$SO$_4$ (3 ml) in water (55 ml)[26] and distilled under ni-

(19) $D_s \approx 52;^{20} D_{op} = n_D{}^2$, where $n_D = 1.3804$ as determined by Dr. H.-C. Wang in our laboratory at $\mu = 0.5$ M.

(20) G. J. Janz and R. P. T. Tomkins, "Nonaqueous Electrolyte Handbook," Vol. 1, Academic Press, New York, N. Y., 1972, p 104.

(21) E. F. Caldin, "Fast Reaction in Solution," Wiley, New York, N. Y., 1964, p 10.

(22) W_r and W_p are smaller for **2** than for **1** but the rates for **2** were determined at a lower ionic strength, roughly compensating for the different work terms.

(23) D_{op} and D_s for H$_2$O from "Handbook of Chemistry and Physics," 52nd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1971.

(24) W. P. Jencks, "Catalysis in Chemistry and Enzymology," McGraw-Hill, New York, N. Y., 1969.

(25) W. P. Jencks, *J. Amer. Chem. Soc.*, **94**, 4731 (1972).

(26) J. E. Eastoe, *Chem. Ind.*, 25 (1966).

trogen. The first 10% of the distillate was discarded and the solvent was used within 48 hr of distillation.

Chloroacetic acid (MCB) was recrystallized from hexane. Reagent grade acetic acid, citric acid, formic acid (88%), potassium chloride, sodium chloride, sodium dihydrogen phosphate, and sodium hydroxide were used without further purifications. Standard NaOH and HCl solutions were prepared from Titrisol (Merck) ampoules.

1-Ethyl-2(1H)-quinolone azine (1_{Red}). The reduced form of **1** was generously supplied by Hünig. Additional quantities were prepared from 2-chloroquinoline by the method of Hünig and coworkers.[27] The semiquinone perchlorate (1_{Sem}^+) and oxidized difluoborate ($1_{Ox^{2-}}$) were also supplied by Hünig. The uv–visible spectra of **1** in all three forms have been published.[27]

2,2'-Hydrazobis(1-ethyl-6-sulfoquinolinium hydroxide), Bis(inner salt) (2_{RedH_2}). This compound was prepared according to the method of Hünig and coworkers.[27] The product was purified by dissolving in aqueous alkali and precipitating with concentrated HCl. The precipitate was collected by filtration, then washed with 2 N HCl, acetone, and ether. The pale yellow powder was dried *in vacuo* over P_2O_5 at 110°, gradually becoming dark yellow as water of crystallization was lost, mp >320° (lit.[26] mp >300°). The uv–visible spectrum agreed with the published spectrum.[27]

Anal. Calcd for $C_{22}H_{22}N_4O_6S_2$: C, 52.57; H, 4.41; N, 11.15. Found: C, 51.31; H, 4.36; N, 11.00.

2_{Ox}. Following the procedure of Hünig and coworkers,[27] the reduced form (1.01 g, 2 mmol) was added to 150 ml of 7.5 N HNO$_3$ and heated on a steam bath for 15 min. Some material failed to dissolve, so the hot solution was filtered and the filtrate stored in the refrigerator for 1 day. The fine brown crystals that formed were collected, washed with 50 ml of cold water and with acetone and then air dried; yield: 0.99 g, mp >320°. Analysis after drying *in vacuo* at room temperature gave a correct analysis for a dinitrate salt rather than the bis(inner salt) reported by Hünig, *et al.* The uv–visible spectrum in concentrated H_2SO_4 agreed with the reported[27] spectrum except that we find λ_{max} 388 (ϵ 3.1 × 10^4) whereas Hünig's published spectrum has λ_{max} ~390 (ϵ ~2.8 × 10^4).

Anal. Calcd for $C_{22}H_{22}N_6O_{12}S_{12}$: C, 42.17; H, 3.54; N, 13.41. Found: C, 42.36; H, 3.69; N, 12.98.

2_{Sem}. Although Hünig, *et al.*,[27] reported the uv spectrum of 2_{Sem}^- obtained by the oxidation of 2_{Red}^{2-} in solution, they did not isolate the semiquinone form. We were able to prepare it as follows. A 251-mg (0.5 mmol) sample of the reduced form (2_{RedH_2}) was suspended in 20 ml of DMF and treated with solid lead tetraacetate (140 mg, 1 equiv of 90% Pb(OAc)$_4$). Reaction took place immediately and stirring was continued for 10 min, then a solution of sodium perchlorate (190 mg, 1.5 mmol) in 2 ml of water was added. After stirring for several minutes the solution was filtered to remove a precipitate (which proved to be largely the radical salt), 20 ml of ethyl acetate was added, and the solution was placed in the refrigerator for several hours. Filtration yielded 110 mg of green metallic-looking crystals, mp >320°.

The sample was submitted for analysis, but the analysis did not agree with any of the probable structures and gave a sizable residue on combustion. The material was very soluble in water and gave a uv–visible spectrum identical with the published[27] one with a λ_{max} of 525 nm. Based on the published extinction coefficient of ~2.8 × 10^4, we calculate a molecular weight in the range 500–550. This agrees with the formula of the most probable structure, the monosodium salt of the radical, $C_{22}H_{20}N_4O_6S_2Na$, mol wt 523.5. Consequently, this was assumed to be the correct structure of the material.

Anal. Calcd for $C_{22}H_{20}N_4O_6S_2Na$: C, 50.47; H, 3.85; N, 10.70; S, 12.24; Na, 4.3. Found: C, 49.19; H, 3.86; N, 11.06; S, 10.21; residue, 13.11%.

pH Measurement. The pH's of all solutions were measured on a Corning Model 110 Digital pH meter using a Beckman glass electrode and a Beckman saturated Calomel reference electrode No. 39400 which has a high weep rate especially useful in mixed aqueous solutions. The pH meter was standardized with commercial aqueous buffers and the pH values were not corrected for solvent effects but were used as apparent pH values. Thus, while there may be a small systematic error in the reported equilibrium constants, the relative values are consistent.

pK_a Determinations. The pK_{1a}^R and pK_{2a}^R values were determined from the visible spectrum of the reduced form in buffers of

varying pH recorded on a Cary 14 spectrophotometer. For 1_{Red}, pK_{1a}^R was calculated from the absorbance at 450 nm, pK_{2a}^R from the absorbance at 350 nm, and both at 25.0°. With 2_{Red}, due to instability, the spectra had to be recorded immediately after preparation at room temperature (23 ± 2°); the analytical wavelengths were 450 nm for pK_{1a}^R and 422 nm for pK_{2a}^R. For example, pK_{1a}^R was calculated from the equation

$$pK_{1a}^R = pH + \log \frac{A_{Red} - A}{A - A_{RedH}^+}$$

where A_{red} was obtained at high pH and A_{RedH}^+ at a pH intermediate between pK_{1a}^R and pK_{2a}^R. Since the pK's differ by more than 4 units, it was possible to choose a pH at which RedH$^+$ was essentially the only species present (>99% of initial Red).

K_1 Determinations. The K_1 values for **1** were calculated from the visible spectrum of solutions of 1_{Sem}^- in buffers of various pH at 25.0°; the analytical wavelength was 520 nm, the λ_{max} of 1_{Sem}^-. Solutions of 2_{Sem}^- were too unstable to allow thermostating and recording of the entire spectrum. The following technique was employed.

A stock solution of 2_{Sem}^- in neutral 2-ME–H$_2$O (in which it is reasonably stable) was prepared and HCl buffers were prepared in 50-ml volumetric flask using 45 ml of solution. A 5-ml aliquot of stock 2_{Sem}^- solution was pipetted into the volumetric flask and the volume was adjusted to the mark and quickly mixed and transferred to a uv cuvette. The absorbance at 525 nm (λ_{max} of 2_{Sem}^-) was measured immediately on a Gilford Model 24 spectrophotometer. When this procedure was carried out rapidly it was found that the initial absorbance value was stable for 30–45 sec, then rapidly decreased about 5% before slowing to a more gradual rate of decline. The maximum (initial) value was used in calculating K_1 and was found to give consistent values over a range of pH's. K_1 was calculated from the equation

$$K_1 = Q_R \left(\frac{A_{Ox} - 2A}{A - A_{Sem}} \right)^2$$

where Q_R is defined by eq 5, $A_{Ox} = \epsilon_{Ox}[Sem]_0$, and $A_{Sem} = \epsilon_{Sem}[Sem]_0$.

Kinetic Methods. Temperature-jump experiments were performed on a Messanlagen GmbH temperature-jump transient spectrometer. Temperature jumps of up to 7.5° were used, but the final (reaction) temperature was 25° in all cases. Relaxation times were averaged for three or four oscillograms taken from two independently prepared solutions.

Stopped-flow experiments were carried out on a Durrum stopped-flow spectrophotometer. Relaxation times were averaged from three oscillograms. The pH of reaction was determined by mixing equal volumes of the two reactant solutions and measuring the pH. No attempt was made to measure the pH of the effluent of the stopped-flow instrument.

Evaluation of Kinetic Data. (1/τ)(pH) values were fitted to eq 4 as follows. At pH >3 the third pathway makes a negligible contribution to the observed (1/τ) (pH) values. Also since Sem$^-$ is not significantly protonated at these pH values, the term Q_S (eq 6) reduces to unity. Thus, eq 4 simplifies to eq 19. The data in Table II provide five values of $(\Delta(1/\tau)/\Delta[Sem]_0) = A$ where eq 19 is valid; each pair of A values can then be used with eq 19 to solve simul-

$$\frac{1}{\tau}(pH) = \left(k_1 + k_2 \frac{[H^+]}{K_{1a}^R} \right) \left(\frac{2}{Q_R(2 + (K_1/Q_R)^{1/2})} + \frac{4(K_1/Q_R)^{1/2}}{K_1(2 + (K_1/Q_R)^{1/2})} \right) [Sem^-]_0 \quad (19)$$

taneously for the two unknowns, k_1 and k_2. The ten pairs of simultaneous equations gave average values of $k_1 = (1.50 ± 0.04) × 10^9 \, M^{-1} \, \text{sec}^{-1}$ and $k_2 = (1.39 ± 0.06) × 10^6 \, M^{-1} \, \text{sec}^{-1}$ which were used as "initial guesses" in a computer-fitting procedure.

A computer program written by Wiberg[28] was modified to our purposes.[14] We first let the computer find the best values of k_1 and k_2 fitting the data to eq 19 at pH >3. The fit was excellent with k_1 and k_2, very similar to the ones found by solving the simultaneous equations. However, when data below pH 3 were included, no set of k_1 and k_2 values gave a satisfactory fit with eq 19 over the whole

(27) S. Hünig, H. Balli, H. Conrad, and A. Schott, *Justus Liebigs Ann. Chem.*, **676**, 36 (1964).

(28) K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1966, p 570.

range, indicating that Q_S is no longer unity at pH < 3. Allowing Q_S to vary, i.e., fitting the data to eq 4 minus the k_3 term, gave now an excellent fit down to pH ~ 1 without changing k_1 and k_2; this provided a value for $K_{1a}{}^S$ and with it K_2 since $K_2 = K_1 K_{1a}{}^R / K_{1a}{}^S$.

Below pH 1 the fit again becomes unsatisfactory, indicating that the third pathway becomes important. Fixing K_1 and K_2 and allowing $K_{1a}{}^S$ and k_3 to vary gave now an excellent fit to eq 4 with the data at all 15 pH values (Table III) without significantly changing $K_{1a}{}^S$ from its value found at pH > 1. Via the relationships $K_3 = K_2 K_{2a}{}^R / K_{1a}{}^S$ and $k_{-3} = k_3 / K_3$ values for K_3 and k_{-3} were finally calculated.

Our data for **1** at 0.1 M ionic strength indicate that the third pathway is also necessary to get a good fit. However, because of the limited data at low pH, several sets of $K_{1a}{}^S$ and k_3 values gave a good fit and thus the true $K_{1a}{}^S$ and k_3 values remain unknown.

In system **2** k_1 and k_2 were obtained as the average from solving three pairs of simultaneous equations (eq 19) for the data at the three highest pH values. Because of the limited number of runs and because the kinetics are not as precise as with **1**, it was not possible to obtain a value of K_2 (and hence k_{-2}). By arbitrarily assigning values to K_2 and trying to fit the data to eq 4 minus the k_3 term, it was found that the fit starts deteriorating when $K_2 > 1$, thus setting an upper limit for K_2. Further, because $k_2 = 4 \times 10^5$ M^{-1} sec^{-1} and k_{-2} is probably no larger than 5×10^8 M^{-1} sec^{-1}, we obtain a lower limit of $\geq 0.8 \times 10^{-3}$ for K_2. The value estimated from the Marcus curve (Discussion) is well within these limits.

Appendix

Derivation of Equations 4 and 8. The rate law for Scheme I plus reaction 7 is given by eq 20 where O = Ox^{2+}, R = Red, S = Sem$^+$, etc.

$$\frac{d[O]}{dt} = -k_1[R][O] - k_2[RH][O] - k_3[RH_2][O] -$$
$$k_2{}^B[RH][O][B^-] + k_{-1}[S]^2 + k_{-2}[S][SH] +$$
$$k_{-3}[SH]^2 + k_{-2}{}^{BH}[S]^2[BH] \quad (20)$$

For small perturbations we obtain the linearized eq 21.

$$\frac{d\Delta[O]}{dt} = -k_1[R]\Delta[O] - k_1[O]\Delta[R] - k_2[RH]\Delta[O] -$$
$$k_2[O]\Delta[RH] - k_3[RH_2]\Delta[O] - k_3[O]\Delta[RH_2] -$$
$$k_2{}^B[RH][B^-]\Delta[O] - k_2{}^B[O][B^-]\Delta[RH] +$$
$$2k_{-1}[S]\Delta[S] + k_{-2}[S]\Delta[SH] + k_{-2}[SH]\Delta[S] +$$
$$2k_{-3}[SH]\Delta[SH] + 2k_{-2}{}^{BH}[S][BH]\Delta[S] \quad (21)$$

The following equilibrium relationships hold true.

$$[R] = (1/Q^R)[R]_{tot} \quad (22)$$

$$[RH] = \frac{[H^-]/K_{1a}{}^R}{Q_R}[R]_{tot} \quad (23)$$

$$[RH_2] = \frac{[H^-]^2/K_{1a}{}^R K_{2a}{}^R}{Q_R}[R]_{tot} \quad (24)$$

$$[S] = (1/Q_S)[S]_{tot} \quad (25)$$

$$[SH] = \frac{[H^-]/K_{1a}{}^S}{Q_S}[S]_{tot} \quad (26)$$

with $[R]_{tot} = [R] + [RH] + [RH_2]$, $[S]_{tot} = [S] + [SH]$, and Q_R and Q_S given by eq 5 and 6, respectively. Furthermore, since O and R (in its various protonated states) are only produced by disproportionation of S, we also have

$$[R]_{tot} = [O] \quad (27)$$

Mass balance and equilibrium considerations provide the additional relationships 28 through 34.

$$\Delta[O] + \Delta[R] + \Delta[RH] + \Delta[RH_2] + \Delta[S] +$$
$$\Delta[SH] = 0 \quad (28)$$

$$\Delta[O] = \Delta[R] + \Delta[RH] + \Delta[RH_2] =$$
$$-\tfrac{1}{2}(\Delta[S] + \Delta[SH]) \quad (29)$$

$$\Delta[R] = (1/Q_R)\Delta[O] \quad (30)$$

$$\Delta[RH] = \frac{[H^+]/K_{1a}{}^R}{Q_R}\Delta[O] \quad (31)$$

$$\Delta[RH_2] = \frac{[H^-]^2/K_{1a}{}^R K_{2a}{}^R}{Q_R}\Delta[O] \quad (32)$$

$$\Delta[S] = -\frac{2}{Q_S}\Delta O \quad (33)$$

$$\Delta[SH] = -\frac{2[H^-]/K_{1a}{}^S}{Q_S}\Delta[O] \quad (34)$$

Equation 21 can now be expressed as

$$d\Delta O/dt = -(1/\tau)\Delta O \quad (35)$$

with

$$\frac{1}{\tau} = \frac{2}{Q_R} \times$$
$$\left(k_1 + k_2\frac{[H^+]}{K_{1a}} + k_3\frac{[H^+]^2}{K_{1a}{}^R K_{2a}{}^R} + k_2{}^B\frac{[H^+][B^-]}{K_{1a}{}^R}\right)[O] +$$
$$\frac{4}{(Q_S)^2}\left(k_{-1} + k_{-2}\frac{[H^+]}{K_{1a}{}^S} + k_{-3}\frac{[H^+]^2}{(K_{1a}{}^S)^2} +$$
$$k_{-2}{}^{BH}[BH]\right)[S]_{tot} \quad (36)$$

Substituting k_1/K_1 for k_{-1}, k_2/K_2 for k_{-2}, k_3/K_3 for k_{-3}; defining $K_2{}^{B^-} = k_2{}^{B^-}/k_{-2}{}^{BH}$ and substituting $k_2{}^{B^-}/K_2{}^{B^-}$ for $k_{-2}{}^{BH}$; and making use of the relationships $K_2 = K_{1a}{}^R K_1/K_{1a}{}^S$, $K_3 = K_{2a}{}^R K_2/K_{1a}{}^S = K_{1a}{}^R K_{2a}{}^R K_1/(K_{1a}{}^S)^2$, $K_2{}^{B^-} = K_{1a}{}^R K_1/K_a{}^{BH}$ where $K_a{}^{BH}$ is the acid dissociation constant of BH allow us to write eq 36 as eq 37.

$$\frac{1}{\tau} = \left(k_1 + k_2\frac{[H^+]}{k_{1a}{}^R} + k_3\frac{[H^+]^2}{K_{1a}{}^R K_{2a}{}^R} + k_2{}^B\frac{[H^+][B^-]}{K_{1a}{}^R}\right) \times$$
$$\left(\frac{2}{Q_R}[O] + \frac{4}{K_1(Q_S)^2}[S]_{tot}\right) \quad (37)$$

Finally, taking advantage of relations 38, 39, and 25 [O]

$$[S] = (K_1[R][O])^{1/2} = (K_1/Q_R)^{1/2}[O] \quad (38)$$

$$[S]_{tot} + [O] + [R]_{tot} = [S]_{tot} + 2[O] = [S]_0 \quad (39)$$

and $[S]_{tot}$ can be expressed in terms of $[S]_0$ as follows

$$[O] = \frac{1}{2 + Q_S(K_1/Q_R)^{1/2}}[S]_0 \quad (40)$$

$$[S]_{tot} = \frac{Q_S(K_1/Q_R)^{1/2}}{2 + Q_S(K_1/Q_R)^{1/2}} \quad (41)$$

Substituting into eq 37 affords

$$\frac{1}{\tau} = \frac{1}{\tau}(pH) + \frac{1}{\tau}(buffer) \quad (42)$$

with $(1/\tau)(pH)$ given by eq 4 and $(1/\tau)(buffer)$ given by eq 8.