methine proton), and 7.3–9.5 ppm (peaks due to phenyl and substituted phenyl protons).

Anal. Calcd for $C_{15}H_{12}SN_2O_5$: C, 54.21; H, 3.64; S, 9.65. Found: C, 54.52; H, 3.99; S, 9.68.

1-Phenyl-*cis*- and -*trans*-2-chloro-1-(2,4-dinitrophenylthio)propene (5 and 6). To a solution of 1.0 g (0.005 mol) of PCl_5 dissolved in 20 ml of CCl_4 was added dropwise a solution of 0.05 g (0.0016 mol) of 1-phenyl-1-(2,4-dinitrophenylthio)propanone in 20 ml of ethylene chloride. The solution was refluxed for 48 hr, cooled, and then washed with 50 ml of water. The organic layer was dried over anhydrous $MgSO_4$, concentrated, and placed onto a 1% $AgNO_3$–alumina column which was eluted with CCl_4. Six fractions were collected, and the solvent was removed by evaporation in a stream of air. The first fraction which contained pure *trans* isomer was recrystallized from methanol, mp 116–117°; $\lambda_{max}^{95\%\ EtOH}$ 340 mμ (ϵ 14,900); nmr 2.67 (3 H, singlet due to methyl protons) and 7.5 ppm (multiplet due to protons of phenyl and substituted phenyl groups).

Anal. Calcd for $C_{15}H_{11}ClSN_2O_4$: C, 51.36; H, 3.11; Cl, 10.01. Found: C, 51.00; H, 3.08; Cl, 10.27.

Repeated chromatography on a 1% $AgNO_3$–alumina column provided a sample of the pure *cis* isomer; $\lambda_{max}^{95\%\ EtOH}$ 341 mμ (ϵ 13,200); nmr 2.42 (singlet due to methyl protons) and 7.3–9.5 ppm (scattering of peaks, due to phenyl and substituted phenyl protons).

Anal. Calcd for $C_{15}H_{11}ClSN_2O_4$: C, 51.36; H, 3.11; Cl, 10.01. Found: C, 50.98; H, 3.31; Cl, 9.99.

Reaction of 2,4-Dinitrobenzenesulfenyl Chloride and 1-Phenylpropyne. To a solution of 0.63 g (0.0026 mol) of 2,4-dinitrobenzenesulfenyl chloride in 10 ml of chloroform was added dropwise 0.27 g (0.0024 mol) of 1-phenylpropyne. The reaction vessel was covered with tin foil and was placed in a constant temperature bath at 50.98°. When the starch test was negative, the reaction vessel was removed from the bath, and the solvent was removed on a rotary evaporator.

A sample of known weight of the reaction mixture was placed on an alumina column and was eluted with CCl_4. A single yellow band was collected. The sample was taken to dryness by evaporation in a stream of air. The solid was weighed and its nmr spectrum was then recorded.

Using mixtures of known composition, it was demonstrated that no significant product fractionation occurs during the isolation process.

No difference in product composition was observed when the reaction was carried out in the presence of added oxygen or in the presence or absence of light.

Product Stability. A 0.0958-g sample of known composition of **3**, **4**, **5**, and **6** (122:8:13:12, respectively) was placed in 10 ml of chloroform containing 0.010 g of 2,4-dinitrobenzenesulfenyl chloride. The solution was allowed to stand for 3 days at 50.98°. Upon removal of the solvent, the nmr spectrum was recorded and showed the original composition.

Kinetic Studies. Solutions of 2,4-dinitrobenzenesulfenyl chloride and 1-phenylpropyne in chloroform were prepared by weight. The reaction solutions were prepared by adding the sulfenyl chloride solutions to the acetylene solution, both being preequilibrated at the bath temperature (50.98 ± 0.02°). Aliquots (0.5 ml) were withdrawn at intervals and were stored at −25° until the reaction was complete. The nmr spectra of all the samples were recorded and integrated in the region 2–3 ppm. The data for one typical run are shown in Table III.

Table III. Reaction of 2,4-Dinitrobenzenesulfenyl Chloride with 1-Phenylpropyne in Chloroform at 50.98 ± 0.02°

Time × 10^4, sec	Concn of acetylene[a] (a_T), mol/l.	$1/a_T$, l./mol	$(1/a_T) - (1/a_0)$, l./mol	$k \times 10^4$, l. mol^{-1} sec^{-1}
0	0.181	4.98	0	
0.36	0.179	5.59	0.61	(1.69)[b]
1.62	0.141	7.09	2.11	1.30
2.16	0.131	7.65	2.67	1.23
3.24	0.119	8.42	3.44	1.06
3.78	0.111	9.04	4.06	1.07
8.64	0.0683	14.62	9.64	1.11
9.90	0.0644	15.54	10.56	1.07
10.80	0.0603	16.58	11.60	1.07
17.28	0.0402	24.87	19.89	1.15
			Mean *k*	1.13

[a] Both reactants were at equal initial concentrations. [b] Values in parentheses were neglected in calculating the mean value of *k*.

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Kinetics of the Reaction of *p*-Benzoquinone with Sodium Thiosulfate

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Abstract: The reaction of *p*-benzoquinone with sodium thiosulfate has been kinetically studied in aqueous and aquoethanolic solutions. The reaction at pH 1–5 gives a quantitative yield of hydroquinonethiosulfuric acid, while the reaction at pH above 5.6 accompanies hydroquinone and other products together with it. The reaction follows second-order kinetics in the range of pH 2–5, E_a and $\Delta S^{\ddagger}$ being 4.0 kcal/mol and −39 eu, respectively. The rate is affected by the acidity of the media, showing general acid catalysis. The rate is considerably accelerated by increasing the content of ethanol in the solvent. These results are discussed in terms of nucleophilic addition of thiosulfate ion.

The reactions of quinones with thiol compounds have been the subjects of many investigators who have shown the reaction products to be hydroquinones and/or their addition compounds with thiols.[1–6] However, the mechanism of the addition is still obscure, although

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(1) W. A. Pryor, "Mechanism of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 71.

(2) J. M. Snell and A. Weissberger, *J. Am. Chem. Soc.*, **61**, 450 (1939).

(3) R. H. Thomson, *J. Org. Chem.*, **16**, 1082 (1951).

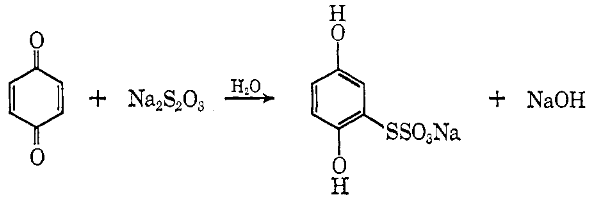
(4) A. Blackhall and R. H. Thomson, *J. Chem. Soc.*, 1138 (1953).

(5) L. F. Fieser and R. B. Turner, *J. Am. Chem. Soc.*, **69**, 2335 (1947).

(6) W. Alcolay, *Helv. Chim. Acta*, **30**, 578 (1947).

various thiols, *e.g.*, thioglycolic acid, thiophenol, alkyl mercaptan, and thiosulfate, have been found to give the addition products of analogous type.

In connection with the dehydrogenation by quinones[7] and also with the inhibition of autoxidation by sulfur compounds, it is of interest to study the nature of the reactions of quinones with thiols. The present study was undertaken to obtain some information on the reaction of *p*-benzoquinone with thiosulfate, one of the water-soluble thiols, to give hydroquinonethiosulfate in aqueous solutions.



(1)

This irreversible reaction has been utilized to obtain mercaptohydroquinones by the reduction of addition products.[6]

Experimental Section

Materials. Commercial reagents of guaranteed grade were used without further purification.

Kinetics. Aqueous solutions of *p*-benzoquinone and of sodium thiosulfate containing acetate buffer in separate flasks were thermostated at a definite temperature. The reaction was started by mixing the two solutions followed by a nimble transfer into a thermostated quartz cell for the ultraviolet spectrophotometry. The unreacted quinone was estimated directly from the optical density at 246 mμ, where molecular extinction coefficients of *p*-benzoquinone, hydroquinone thiosulfate, and thiosulfate are 22,000, 2700, and 488, respectively. The concentration of the quinone was determined by the difference method, since absorbances at 246 mμ are proportional to their concentrations.

The kinetic reactions were conducted in the presence of excess thiosulfate. The obtained pseudo-first-order rate constant holds good constancy over 90% conversion. Since the rate constants thus obtained were found to be porportional to the initial concentration of sodium thiosulfate, the present reaction was observed to follow second-order kinetics with respect to both reactants (Table I).

Table I. Second-Order Rate Constants for the Reaction of *p*-Benzoquinone with Sodium Thiosulfate in an Aqueous Solution

pH	Temp, °C	Initial concn, $M \times 10^5$ [Quinone]	Initial concn, $M \times 10^5$ [Thiosulfate]	Second-order rate constant, k, M^{-1} sec^{-1}
3.19[a]	9.5	3.49	15.0	33.5
		3.49	30.0	31.3
		3.49	40.0	31.5
		3.49	50.0	33.2
		1.49	50.0	30.0
		4.39	50.0	29.6
Ca. 7[b]	19.5	2.50	15.0	0.53
		2.50	30.0	0.57
		2.50	45.0	0.52

[a] Buffered with 0.0181 *M* acetate buffer. Salt effect was not appreciable on addition of 0.05 *M* sodium sulfate or potassium chloride. [b] The reaction in pure water.

Reaction Products. *p*-Benzoquinone (2.2 g, 0.02 mol) in 240 ml of water and sodium thiosulfate (5.0 g, 0.02 mol) in 100 ml of water were mixed in the presence of acetate buffer at pH 3.2. The yellow color of the quinone faded out soon after the mixing and then the color of the reaction mixture changed to light brown The solution was condensed by evaporation under reduced pressure up to *ca.* 15 ml, and salting out by addition of KCl (3 g) resulted in the precipitation of potassium hydroquinone thiosulfate. Triplicate recrystallizations from water gave *ca.* 0.8 g (15% yield) of fine crystals, mp 225–250° dec.

Anal. Calcd for $C_6H_5O_5S_2K$: C, 27.68; H, 1.94. Found: C, 27.57; H, 2.01.

The infrared spectrum of the salt, determined by Nujol paste method, shows peaks at 635, 832, 870, 1035, 1245, and 1660–2000 cm^{-1} characteristic of SO, two adjacent ring H, one isolated ring H, SO_2, phenolic OH, and 1,2,4-trisubstituted ring H, respectively. The ultraviolet spectrum in water shows a peak at 313.5 mμ (ϵ 4190).

The yield of hydroquinone thiosulfate at pH 2–5, however, is quantitative on the basis of direct spectrophotometry in uv cell instead of isolation of the product. The yield was significantly reduced at pH above 5, *e.g.*, *ca.* 60% at pH 5.6. The main by-product, isolated from the ether extract, was found to be hydroquinone on the basis of ir and uv spectra, but the analysis for all other products was not carried out because of the complexity of products due to the further reaction of hydroquinone and benzoquinone.

Results

The reaction of *p*-benzoquinone with sodium thiosulfate was found to give nearly quantitative yield of the addition product, sodium hydroquinone thiosulfate, at pH 1–5 in an aqueous solution (eq 1), the rate being expressed as follows (see Table I).

$$v = k[\text{quinone}][\text{thiosulfate}] \qquad (2)$$

Rate data at various pH's are summarized in Table II. The rate measurement at pH above 7 was unsuccessful because of the deep coloration of the reaction mixture. The salt effect was negligible under these conditions of low concentration of alkali acetate or chloride, since no appreciable difference in the rate was observed when a comparable amount of sodium sulfate was added.

Table II. Effect of pH on the Reaction of *p*-Benzoquinone with Sodium Thiosulfate at 19.5 ± 0.3° [a]

pH	Buffer (molar ratio)	f[b]	k', M^{-1} sec^{-1} [c]	k'/f[d]
1.2	HCl–KCl (65:50)	0.232	109	470
1.6	HCl–KCl (26:50)	0.430	98	228
2.2	HCl–KCl (6.7:50)	0.751	74	99
3.2	AcOH–AcONa (32:1)	0.970	20.2	20.8
3.8	AcOH–AcONa (8:1)	0.99	12.3	12.4
4.7	AcOH–AcONa (1:1)	1.00	5.5	5.5
5.3	AcOH–AcONa (1:4)	1.00	2.5	2.5
6.2	AcOH–AcONa (1:32)	1.00	0.9	0.9
Ca. 7	None	1.00	0.5	0.5

[a] Initial concentrations: [quinone] = 2.5×10^{-5} *M;* [thiosulfate] = 15.0×10^{-5} *M.* [b] Molar fraction of thiosulfate ion ($[S_2O_3^{2-}]/([S_2O_3^{2-}] + [HS_2O_3^-])$) estimated from K_2 value of 0.019.[8] [c] Second-order rate constant at zero buffer concentration. [d] The ratio (k'/f) is the rate constant corrected for the dissociation of $H_2S_2O_3$ to $S_2O_3^{2-}$.

Effect of pH. The present reaction is shown to undergo general acid catalysis but not base catalysis (Figure 1). Hence, the rate may be expressed as follows.

$$v = \{k_0[H_2O] + k_{H^+}[H^+] + k_{AH}[AH]\}[\text{quinone}][S_2O_3^{2-}]$$

The catalytic constant (k_{AH}) for acetic acid, k_{AcOH}, is *ca.* 1600 M^{-2} sec^{-1}, and the constant for hydrogen chloride, k_{HCl}, is *ca.* 1700 M^{-2} sec^{-1} at 19.5°. The uncatalyzed

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[7] L. M. Jackman in "Advances in Organic Chemistry, Method and Results," Vol. II, P. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 329.

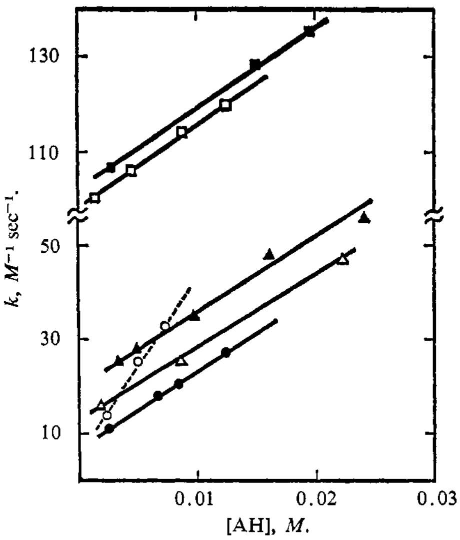

Figure 1. Plots of second-order rate constant, *k*, *vs.* [acid] for the reaction of *p*-benzoquinone with sodium thiosulfate at 19.5 ± 0.3°: HCl-KCl buffer: ■, pH 1.2; □, pH 1.6; AcOH-AcONa buffer: ▲, pH 3.2; △, pH 3.8; ●, pH 4.7; ---○---, pH 4.7 in 20% EtOH.

or solvent-catalyzed reaction is considerably slower, the catalytic constant, k_0, being *ca.* 0.010 M^{-2} sec^{-1} at 19.5°.

The first dissociation constant of thiosulfuric acid, K_1, is 0.21 and the second dissociation constant, K_2, is 0.019 at zero ionic strength.[8] Hence, the second dissociation must be considered. The rate constants extrapolated to zero buffer concentration, k', are corrected to express the value with respect to the concentration of ionized species, $[S_2O_3{}^{2-}]$, and are shown as k'/f in the last column in Table II. The values of k'/f increase with increasing pH of the media, but the plot of log (k'/f) *vs.* pH gives a bended line with a slope of −0.4 to −0.6.

Effects of Solvent and Reaction Temperature. Table III contains the kinetic data obtained at various temperatures at pH 3.19. The plot of log *k vs.* 1/*T* gives a straight line, which affords the values of Arrhenius energy and entropy of activation of 4.0 kcal/mol and −39.2 eu (30°), respectively.

Table III. Effect of Temperature and Solvent on the Reaction of *p*-Benzoquinone with Sodium Thiosulfate

Solvent, % in vol	Temp, °C	k, M^{-1} sec^{-1}
A. Effect of Temperature at pH 3.19[a]		
100% H_2O	10.0	34.3
	20.0	45.5
	30.0	56.0
	40.0	70.5
	50.0	83.5
B. Effect of Solvent Composition at pH 4.7[b]		
100% H_2O	19.5	16.7
10% EtOH	19.5	24.6
20% EtOH	19.5	33.0
30% EtOH	19.5	38.5

[a] Buffered by 0.0181 *M* acetate buffer. [b] Buffered by 0.0150 *M* acetate buffer.

The rate data in Table III also show the pronounced effect of solvent, indicating a remarkable acceleration of rate by increasing the content of ethanol. The value of k_{AcOH} increases from 1600 M^{-2} sec^{-1} in 100% water up to 3600 M^{-2} sec^{-1} in 20% ethanol, while the rate constant at zero buffer concentration, k', is nearly identical in both solvents at pH 4.7.

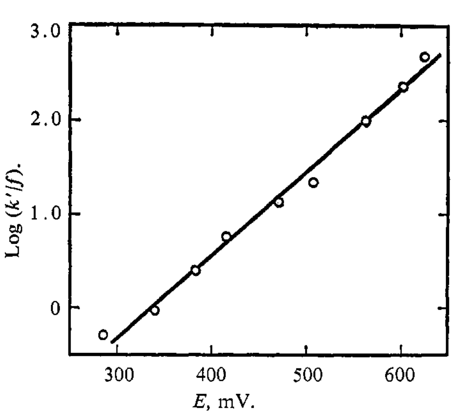

Figure 2. Plot of log (k'/f) *vs.* the redox potential, *E*, at various pH's for the reaction of *p*-benzoquinone with sodium thiosulfate at 19.5 ± 0.3°. The potentials, *E* (in millivolts at 19.5°), were calculated from the equation: $E = 695 - 59\text{pH}$.

Discussion

Acid Catalysis. It is well known that most addition reactions to carbonyl compounds are subject to both general acid and general base catalysis.[9] Among the general acid catalysis, the catalysis by hydronium ion is important in the addition of amines to carbonyls,[10] and also in the addition of aniline to the C=C double bond of methyl vinyl ketone.[11] A line of unit slope is often obtained for the plot of the logarithm of the rate constant *vs.* pH in these carbonyl additions.

In contrast, the present reaction does not give a line of unit slope but a curve for the plot of log (k'/f) *vs.* pH. The curve becomes a straight line when log (k'/f) is plotted against the redox potential (*E*) of *p*-benzoquinone (Figure 2). This interesting relationship suggests that the redox potential is the main driving force for the addition reaction. Similar relations have been observed for the Pd–$BaSO_4$-catalyzed hydrogenation of 1,4-quinones.[12]

Another driving force is probably the strong nucleophilicity of thiosulfate ion.[13,14] For example, the attempted reaction of acetate ion with *p*-benzoquinone was unsuccessful under these conditions, implying that the reactivity of acetate ion is lower than that of thiosulfate by a factor of over 10^6. This is contrasted with the S_N2 reaction, for example, of *p*-nitrophenyl acetate, the relative rate constant of acetate ion being *ca.* 0.5 compared to that of thiosulfate ion.[15]

The Mechanism. The present addition satisfies second-order kinetics: $v = k[\text{benzoquinone}][S_2O_3{}^{2-}]$, and is subject to general acid catalysis. The product obtained at pH 1–5 is hydroquinonethiosulfuric acid alone, but hydroquinone is formed in addition to it at

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[8] F. M. Page, *J. Chem. Soc.*, 1719 (1953); R. H. Dinegar, R. H. Swellie, and V. K. L. Mer, *J. Am. Chem. Soc.*, **73**, 2050 (1951).

[9] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Company, Inc., New York, N. Y., 1959, p 539.

[10] For example, Y. Ogata and A. Kawasaki, *Tetrahedron*, **20**, 855 (1964).

[11] Y. Ogata, A. Kawasaki, and I. Kishi, *J. Chem. Soc., B*, in press.

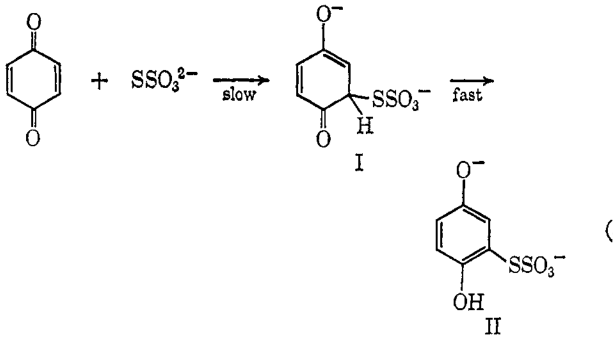
[12] H. Musso, K. Figge, and D. J. Becker, *Chem. Ber.*, **94**, 1107 (1961).

[13] C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, **75**, 141 (1953).

[14] J. O. Edwards, *ibid.*, **76**, 1540 (1954).

[15] W. P. Jencks and J. Carriuolo, *ibid.*, **82**, 1778 (1960).

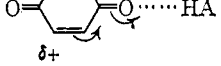
pH above 5.6. The reaction at pH below 5 probably has a mechanism involving a nucleophilic addition of thiosulfate ion.



(3)

The adduct I, a derivative of cyclohexadienone, should rapidly be stabilized by prototropy to form the hydroquinone derivative II. The similar scheme has been proposed for the reaction of *p*-benzoquinone with hydroxide ion to form hydroxyhydroquinone.[16] This mechanism of β addition is characteristic for the additions of nucleophiles to α,β-unsaturated carbonyl compounds.[1,11,12,17] The observed linearity of a plot of log (k'/f) *vs.* redox potential is rational, since the similarity is expected between the present addition and the two-electron reduction of the quinone.

The observed general acid catalysis is ascribed to the increased reactivity toward the nucleophilic attack at β-carbon atom by hydrogen bonding to carbonyl oxygen (III). The absence of base catalysis by acetate ion



III

is convincing because thiosulfate has no proton which may be abstracted by base.[18]

The reaction mixture becomes blue and then brown at pH above 5.6 as the reaction proceeds, probably because of the further reaction of hydroquinone derivatives. By increasing the pH above 5.6 the yield of hydroquinonethiosulfate is reduced, while the yield of hydroquinone increases, as observed by uv spectrophotometry. The blue color and the formation of hydroquinone seem to suggest one-electron transfer from thiosulfate giving an intermediary benzosemiquinone which is stable in alkaline media (pK_a of *p*-benzosemiquinone is 4.25).[19] However, another course for the formation of hydroquinone may be possible at higher pH. In fact, the oxidation of hydroquinonethiosulfate by benzoquinone to product hydroquinone becomes apparent at this higher pH. The higher dissociation of hydroquinone thiosulfate may result in a decrease of its redox potential and favors the formation of hydroquinone. On the other hand, the redox potential of benzoquinonethiosulfate having the electron-withdrawing group, $-SSO_3^-$, is found to be higher than that of benzoquinone at pH below 5.[20] The formation of hydroquinone from benzoquinone in an alkaline medium[5] is negligible in this pH range.

Temperature and Solvent Effect. Energy and entropy of activation at pH 3.19 are 4.0 kcal/mol and −39 eu, respectively. These values resemble those of other reactions of α,β-unsaturated compounds, *e.g.*, the reactions of methyl vinyl ketone with aniline (E_a = 5–6 kcal/mol; $\Delta S^{\neq} = -50$ eu)[11] and of $ArSO_2CH{=}CH_2$ with amines (E_a = 6.6 kcal/mol; $\Delta S^{\neq} = -40$ eu).[21] These reactions seem to possess a highly negative entropy of activation, reflecting a crowded transition state with hindered motion of the reactants.

The reaction of the quinone with thiosulfate is accelerated by increasing content of ethanol. The net increase of the rate is the enhancement of k_{AcOH} for acetic acid catalysis. This increase of k_{AcOH} seems to be natural because of the increase of hydrogen bonding to form III with decreasing polarity of solvent. These features are different from the reverse solvent effect for the S$_\text{N}$2 reaction of ethyl bromomalonate with thiosulfate.[22]

Acknowledgment. The authors wish to thank the referees for their helpful suggestions.

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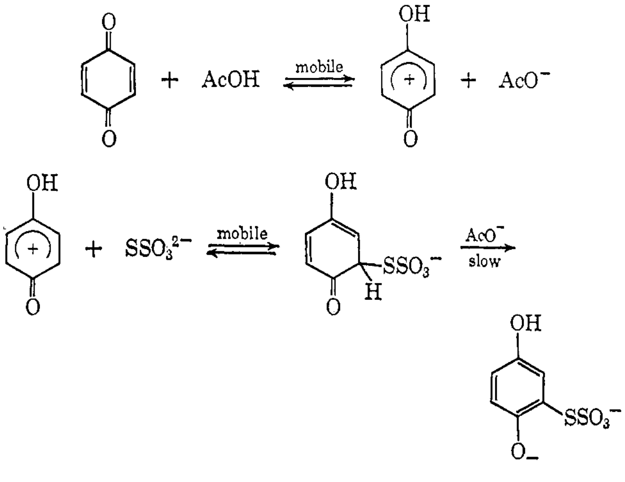
[16] M. Eigen and P. Matties, *Chem. Ber.*, **94**, 3309 (1961).

[17] M. Hauser, *Chem. Rev.*, **63**, 311 (1963).

[18] Another scheme for the specific acid–base catalysis



does not fit the kinetic data which indicate that the rate is approximately independent of the presence of acetate ion (Table II) and that the slope for the plot of log (k'/f) *vs.* pH is not unity. These facts, together with the observation of no increase of k by increasing [$S_2O_3^{2-}$], rule out the above scheme.

[19] I. Yamazaki and L. H. Piette, *J. Am. Chem. Soc.*, **87**, 986 (1965).

[20] See, for example, L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, Chapter 26.

[21] S. T. McDowell and C. J. M. Stiring, *J. Chem. Soc.*, *B*, 343, 348 (1967).

[22] E. S. Amis, "Solvent Effects on Reaction Rates and Mechanisms," Academic Press Inc., New York, N. Y., 1966, p 41; W. J. Broach and E. S. Amis, *J. Chem. Phys.*, **22**, 39 (1954).