Reduction and Racemization of Sulfoxides by Halide Ions in Aqueous Perchloric Acid

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Abstract: The mechanism of reduction and racemization of sulfoxides with halide ions has been studied in aqueous solutions of perchloric acid 0.5–8.2 *M*. The complex dependence of rates of reaction on a_{H^+} has been analyzed in the light of the recent study on the protonation equilibrium of sulfoxides. The results indicate that the protonated sulfoxide is transformed by the action of the halide ion and a second proton into a halosulfonium ion which is the common intermediate for the reduction and racemization reactions. The formation of this intermediate is rate determining for both reactions but its fate is different depending on the specific halide. The reaction with iodide ion gives reduction to sulfide, whereas with bromide and chloride ions it gives only racemization. The polar effects, measured on a series of substituted phenyl methyl sulfoxides, on the rates of reduction are small and they reflect almost exclusively the polar effects on the preequilibrium protonation of sulfoxides. The steric effects are quite large and of similar magnitude in the two reactions. The study of the above reactions allowed us to evaluate a scale of thiophilicity for iodide, bromide, and chloride ions which was found consistent with a previous report.

The mechanism of reduction of sulfoxides by iodide ion in acid solution has attracted much attention in the last few years.[2–5]

Unitary orders in sulfoxide and iodide ion have been reported except in a series of sulfinylcarboxylic acids,[1] where, in some cases,[6] zero order in iodide ion was observed. This seems to be due to a specific participation of the carboxylic group which also modifies other aspects of the kinetics of the reaction.

The form of the acid catalysis is, on the other hand, an open question. Krueger[3] found a second-order dependence on [H$^+$] in the reduction of DMSO in DMSO–water (from 75 to 98.5% of DMSO) with iodide ion in dilute acid solution. However all the other studies deal with aqueous solutions where fairly high acid concentrations are necessary to obtain measurable rates. In these cases, the experimental data have been analyzed with the aid of the H_0 function. Allenmark[7] found a slope of about 1 for log *k vs.* $-H_0$ plots in the reaction of sulfinylcarboxylic acids, whereas Andersen, *et al.*,[4] reported a slope near two in the case of phenyl alkyl sulfoxides. We[8] have observed, when a wide range of acidity is considered, slopes near two in the low acidity side and near one in the high acidity side. However, these data,[2–8] as well as those of other acid-catalyzed reactions of sulfoxides,[9] should be reconsidered in light of our recent findings[10] that the protonation of the SO group cannot be represented by the H_0 function and that, consequently, the meaning of correlations of reaction rates of sulfoxides with H_0 function is doubtful.

Results

The rates of reduction with iodide ion of some phenyl alkyl sulfoxides and DMSO were measured in aqueous perchloric acid at 25°. Under similar conditions the racemization of (+)-*p*-tolyl methyl sulfoxide catalyzed by chloride and bromide ions was also measured.

The reaction order in sulfoxide concentration has always been found by other authors[2,4] and ourselves[11] to be equal to one. This is confirmed by the present results; with an excess of halide ions and acid the rates of the reactions follow the first-order kinetic equation (eq 1) up to 80% or more conversion

$$\text{rate} = k_{\text{obsd}}[\text{SO}]_{\text{st}} \qquad (1)$$

where k_{obsd} is the experimental rate coefficient and $[\text{SO}]_{\text{st}}$ the stoichiometric concentration of sulfoxide. [SO] and [SOH$^+$] are for the concentration of sulfoxides as free and protonated base, respectively.

The dependence of rates on acid concentration is complex. The first point to consider is that, in the range of acidity used in this work, the sulfoxides are significantly protonated. It implies that the rates must be expressed as a function of the protonated sulfoxide (eq 2), which, in turn, requires the knowledge of the protonation equilibrium.

$$\text{rate} = k_1[\text{SOH}^+] \qquad (2)$$

The protonation ratio ([SOH$^+$]/[SO]) changes with h_0 more slowly than required for a Hammett base, being the slope of plots of log [SOH$^+$]/[SO] *vs.* H_0, about 0.4–0.6.[10,12] With the aid of the Bunnett and Olsen equation[13] the thermodynamic pK_a values were evaluated;[10] they range from −1.8 to −2.9 for the sulfoxides studied.

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Since the protonation equilibrium of sulfoxides follows satisfactorily the H_A acidity function,[10] the H_A value at half-protonation may be assumed as their pK_a.[14] The two sets of pK_a evaluated with the aid of the Bunnett and Olsen equation or with the aid of the H_A function are quite similar. They, indeed, differ consistently by about 0.4 pK unit, the former more positive than the latter. This difference, which may stem from the intrinsic uncertainties of the acidity functions[13] and from the approximation involved in the use of the H_A function (based on amides) for sulfoxides, is small enough to allow the use of such a function to evaluate the amount of protonated sulfoxide.

The fraction of protonated sulfoxide, taking h_A for the activity of the proton, and introducing the pK_a values evaluated with the H_A methods, is

$$K_a = \frac{[\mathrm{SO}][\mathrm{H^+}]}{[\mathrm{SOH^+}]} = \frac{[\mathrm{SO}]h_A}{[\mathrm{SOH^+}]} \tag{3}$$

$$[\mathrm{SO}]_{st} = [\mathrm{SOH^+}] + [\mathrm{SO}] \tag{4}$$

$$[\mathrm{SOH^+}] = \frac{h_A}{h_A + K_a}[\mathrm{SO}]_{st} \tag{5}$$

By rearranging eq 2 and expressing $[\mathrm{SOH^+}]$ as a function of $[\mathrm{SO}]_{st}$ (eq 5) the relation 6 is easily obtained

$$k_1 = \frac{\text{rate}}{[\mathrm{SOH^+}]} = k_{obsd}\frac{h_A + K_A}{h_A} \tag{6}$$

The rate coefficients k_1, although they take into account the protonation of sulfoxides, increase with acid concentration. Experimentally we observed that log k_1 is linear with both $-H_0$ (slopes near one) and $-H_A$ (slopes near 1.5). This is consistent with the findings of Yates and McClelland[15] that many acidity functions are, to a first approximation, linearly correlated.

The linearity of log k_1 *vs.* $-H_0$ (or $-H_A$) is directly observable at constant halide ion concentration. Since the reactions are first order in $[\mathrm{Hal^-}]$ (see below) we also plotted log $k_1/[\mathrm{Hal^-}]$ *vs.* $-H_0$ and $-H_A$ obtaining the same results as above over a much wider range of rates (10^7) and of acidity (up to 5 H_0 units). The data are collected in Tables I–VI.

Table I. Rate Constants for the Racemization of (+)-*p*-Tol-SOMe (0.005 *M*) with Chloride Ion[a]

$[\mathrm{H^+}]$, mol/l.	$[\mathrm{Cl^-}]$, mol/l.	$k_{obsd} \times 10^6$, sec^{-1}	$-H_0$[b]	$-H_A$[b]	6 + log $k_1/[\mathrm{Cl^-}]$,[c] sec^{-1} mol^{-1} l.
1.38	1.0	0.050	0.73	0.67	0.64
2.11	0.9	0.192	1.04	1.00	0.95
2.11	1.0	0.250	1.05	1.01	1.00
2.11	1.2	0.368	1.09	1.04	1.06
2.11	1.5	0.598	1.15	1.08	1.14
2.57	1.0	0.724	1.28	1.23	1.25
6.29	0.3	119.0	3.10	2.46	2.97
6.30	0.3	122.0	3.10	2.47	2.99
6.66	0.2	140.0	3.28	2.60	3.15
6.66	0.3	231.0	3.30	2.61	3.18
6.66	0.4	319.0	3.32	2.63	3.19
6.66	0.5	428.0	3.34	2.64	3.22
6.72	0.3	208.0	3.32	2.64	3.13
7.49	0.3	806.0	3.83	2.94	3.59

[a] In aqueous perchloric acid at 25°. [b] Corrected for salt effect (see Experimental Section). [c] The pK_a value used is in Table VIII.

Table II. Rate Constants for the Racemization of (+)-*p*-Tol-SO-Me (0.005 *M*) with Bromide Ion[a]

$[\mathrm{H^+}]$, mol/l.	$[\mathrm{Br^-}]$, mol/l.	$k_{obsd} \times 10^6$, sec^{-1}	$-H_0$[b]	$-H_A$[b]	6 + log $k_1/[\mathrm{Br^-}]$,[c] sec^{-1} mol^{-1} l.
1.02	1.0	0.0684	0.53	0.45	0.99
1.38	1.0	0.237	0.70	0.67	1.31
2.06	0.9	0.812	1.01	0.99	1.58
2.06	1.2	1.37	1.07	1.03	1.65
2.06	1.5	2.11	1.12	1.07	1.70
2.57	1.0	3.52	1.28	1.23	1.94
4.07	0.8	44.5	1.95	1.75	2.66
5.24	0.8	368.0	2.53	2.14	3.26
5.68	0.8	931.0	2.80	2.31	3.54
5.86	0.4	510.0	2.85	2.33	3.57
5.86	0.6	898.0	2.88	2.35	3.62
5.86	0.8	1390.0	2.92	2.38	3.66

[a] In aqueous perchloric acid at 25°. [b,c] See Table I.

Table III. Rate Constants for the Reduction of *p*-Tol-SO-Me (0.005 *M*) with Iodide Ion[a]

$[\mathrm{H^+}]$, mol/l.	$[\mathrm{I^-}]$, mol/l.	$k_{obsd} \times 10^4$, sec^{-1}	$-H_0$[b]	$-H_A$[b]	4 + log $k_1/[\mathrm{I^-}]$,[c] sec^{-1} mol^{-1} l.
0.51	0.8	0.00230	0.13	0.05	0.01
0.51	1.0	0.00358	0.16	0.08	0.08
0.51	1.2	0.00518	0.20	0.11	0.13
0.51	1.5	0.00793	0.25	0.15	0.18
0.81	1.0	0.0129	0.45	0.31	0.40
1.03	1.0	0.0224	0.55	0.47	0.48
2.29	1.0	0.442	1.13	1.09	1.17
3.05	1.0	2.28	1.53	1.43	1.56
4.13	0.16	0.927	1.85	1.69	1.73
5.16	0.16	6.25	2.38	2.02	2.28
5.64	0.11	10.9	2.67	2.19	2.55
5.64	0.16	18.6	2.68	2.20	2.62
5.64	0.34	52.4	2.71	2.22	2.72
5.64	0.50	90.6	2.74	2.24	2.78
5.64	0.60	120.0	2.77	2.26	2.81
6.10	0.16	48.7	2.93	2.37	2.92
6.81	0.16	153.0	3.37	2.69	3.24

[a] In aqueous perchloric acid at 25°. [b,c] See Table I.

Order in $[\mathrm{Hal^-}]$. The determination of the order in $[\mathrm{Hal^-}]$ is not straightforward because of the complex dependence of rates on acid concentration and the effect of added salts on the values of H_0 and H_A.

The "constant ionic strength" method is not of general applicability since the salt effect on the acidity function is dependent on the anions as well as on the cations.[16] On the other hand it has been shown that the effects of chloride and bromide ions are very similar[16] and it seems safe to assume that iodide ion (for which directs measurements are made uncertain by the easy oxidation to I_2) should behave in the same way.

Therefore we evaluated the acidity functions in the presence of the appropriate amount of sodium chloride, taken as standard salt; the acidity functions values thus obtained were used to evaluate the order in $[\mathrm{Hal^-}]$.

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[14] We thank Professor K. Yates who kindly supplied the H_A values of aqueous solutions of perchloric acid. These data will be published by the cited author elsewhere.

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Table IV. Rate Constants for the Reduction of m-$ClC_6H_4SOCH_3$ (0.005 M) with Iodide Ion[a]

$[H^+]$, mol/l.	$[I^-]$, mol/l.	$k_{obsd} \times 10^4$, sec^{-1}	$-H_0$[b]	$-H_A$[b]	$4 + \log k_1/[I^-]$,[c] sec^{-1} mol^{-1} l.
0.97	1.0	0.00473	0.51	0.43	0.23
2.97	0.5	0.171	1.39	1.34	1.18
2.98	0.7	0.279	1.42	1.37	1.22
2.98	0.8	0.333	1.45	1.38	1.23
2.92	1.0	0.583	1.47	1.39	1.37
2.98	1.2	0.839	1.52	1.44	1.40
3.42	0.5	0.338	1.59	1.48	1.34
3.41	1.0	1.51	1.68	1.55	1.63
4.30	0.5	1.71	2.01	1.77	1.77
4.56	0.5	4.11	2.12	1.86	2.07
4.72	0.16	0.967	2.13	1.89	1.91
4.85	0.75	8.14	2.31	2.00	2.06
5.01	0.16	1.47	2.30	1.97	2.02
5.02	0.5	10.2	2.36	2.01	2.33
5.84	0.16	10.5	2.78	2.28	2.60
6.30	0.5	106.0	3.14	2.49	2.94
6.36	0.16	399.0	3.10	2.47	3.03
6.65	0.098	44.8	3.24	2.58	3.21
6.57	0.3	134.0	3.25	2.57	3.21
6.57	0.5	286.0	3.29	2.59	3.29
6.71	0.16	83.9	3.30	2.62	3.24
6.82	0.5	326.0	3.43	2.70	3.28
7.32	0.16	294.0	3.68	2.86	3.62
8.23	0.16	1770.0	4.38	3.19	4.25

[a] In aqueous perchloric acid at 25°. [b,c] See Table I.

Table V. Rate Constants for Reduction of Dimethyl Sulfoxide (0.01 M) with Iodide Ion[a]

$[H^+]$, mol/l.	$[I^-]$, mol/l.	$k_{obsd} \times 10^5$, sec^{-1}	$-H_0$[b]	$-H_A$[b]	$5 + \log k_1/[I^-]$,[c] sec^{-1} mol^{-1} l.
2.09	0.3	1.67	1.34	1.29	1.61
3.88	0.2	6.60	1.78	1.60	2.15
3.88	0.3	10.3	1.80	1.62	2.14
3.88	0.4	16.0	1.81	1.63	2.20
3.88	0.5	20.8	1.83	1.64	2.22
4.85	0.3	43.2	2.26	1.94	2.55
5.82	0.3	240.0	2.84	2.30	3.12
6.79	0.3	1130.0	3.41	2.66	3.75

[a] In aqueous perchloric acid at 25°. [b] See Table I. [c] The pK_a value used is −2.11.

Table VI. Correlations between Rate Coefficients for the Reactions of $RSOCH_3$ with Halide Ions[a] and Acidity Functions[b]

		log $k_1/[Hal^-]$ vs.			$\log (k_1/[Hal^-]) + H_0$ vs.
R =	Hal^- =	$-H_0$ s (r)	$-H_A$ s (r)	$H_0 + \log [H^+]$ s (ϕ) (r)	$H_0 + \log [H^+]$ s (ϕ)[c]
p-$CH_3C_6H_4$	Cl^-	0.96 (0.9994)	1.34 (0.9994)	−1.23 (0.9978)	+0.06
	Br^-	1.09 (0.9993)	1.42 (0.9977)	−1.51 (0.9942)	−0.12
	I^-	1.01 (0.9987)	1.21 (0.9962)	−1.59 (0.9860)[d]	−0.01
m-ClC_6H_4	I^-	1.05 (0.9969)	1.53 (0.9917)	−1.30 (0.9914)	−0.06
CH_3	I^-	0.99 (0.9976)	1.51 (0.9975)	−1.19 (0.9963)	+0.02

[a] In aqueous perchloric acid at 25°. [b] The slopes (s) and correlation coefficients (r) were evaluated by least-squares analysis. [c] The correlation coefficients have in this case low values as expected for slopes near to zero. They are not listed. [d] A better correlation line (ϕ = 1.22; r = 0.9951) is obtained without the point at low acidity ($[H^+]$ 0.8 M).

Another minor correction must be introduced since the plots of log k_1 vs. $-H_0$ have a slope (α) which differs from unity. Consequently the orders in $[Hal^-]$ of the various reactions were evaluated by plotting log $k_1 + \alpha H_0$ vs. log $[Hal^-]$ with the values of α's calculated by least-squares analysis from a set of data at constant $[Hal^-]$ and variable $[H^+]$ in the range of acidity where the order in $[Hal^-]$ had to be evaluated.

As reported in Table VII, the slopes are always near one, showing that all the reactions studied are first order in $[Hal^-]$.

Structural Effects. The polar effects on the rates of reduction were studied in a series of para- and meta-substituted phenyl methyl sulfoxides at fixed acid ($HClO_4$, 4.85 M) and iodide ion (0.3 M) concentrations at 25°. The results obtained are similar to those obtained by Andersen, *et al.*,[4] at 35°. The overall effect (plot of log k_{obsd} vs. Hammett's σ) is characterized by a ρ = −0.72 (r = 0.98). However, the plot of log k_1, which takes into account the structural effects on pK_a, vs. σ has a slope near zero (see Table VIII).

The steric effects on the reduction and racemization reactions were studied on a series of phenyl alkyl sulfoxides by changing the alkyl moiety from methyl to *tert*-butyl.

The results, reported elsewhere,[5] show that the rates of reduction by iodide ion and those of racemization by bromide and chloride ions are strongly depressed by almost the same amount by α ramification: the phenyl isopropyl sulfoxide reacts about 60 times slower than the methyl derivative.

The phenyl *tert*-butyl sulfoxide undergoes decomposition faster than either reduction or racemization[5] in the reaction conditions used in this research. Nevertheless, we could estimate that the rate of reduction by iodide ion must be at least 10^4 times slower than that of the methyl derivative.

Similar steric retardations were observed in other reactions at a sulfur center[17] and in particular our results match, in a qualitative way, those obtained by Mislow, *et al.*,[17c] in the racemization of phenyl alkyl sulfoxides in dioxane–hydrochloric acid.

Discussion

An inspection of the results reported in the previous section shows that the reduction with iodide ion and the racemization with bromide and chloride ions have the same general features and they give the same replies to the various kinetic tests. It indicates that the two reactions follow the same mechanism up to the rate-determining step and that they differentiate at the product-determining step.

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Table VII. Dependence of Rate Constants for the Reactions of $RSOCH_3$ on $[Hal^-]$ at the Indicated Perchloric Acid Concentrations (25°)

R =	Hal =	α[a]	$[H^+]$, mol/l.	Slope[b]	r
p-$CH_3C_6H_4$	Cl^-	0.84	6.66	1.03	0.9996
		1.11	2.11	1.25	0.9943
	Br^-	1.03	5.86	1.06	0.9994
		1.21	2.06	0.92	0.9991
	I^-	1.02	5.64	1.22	0.9996
		1.09	0.51	1.09	0.9982
m-ClC_6H_4	I^-	1.09	6.60	1.05	0.9970
		1.19	2.98	1.16	0.9895
CH_3	I^-	1.01	3.88	1.06	0.9959

[a] α = slope of plots of log k_1 *vs.* $-H_0$ in a limited range of acidity (about 1 H_0 unit) in the vicinity of the acid concentration (column 4) at which the order in $[Hal^-]$ was measured. [b] Slope of the plots of log $k_1 + \alpha H_0$ *vs.* log $[Hal^-]$; *i.e.*, order in $[Hal^-]$.

Table VIII. Structural Effects on the Reduction of $XC_6H_4SOCH_3$ (0.005 M) with Iodide Ion (0.3 M)[a]

X =	pK[b]	log k_{obsd} + 4, sec^{-1}	log k_1 + 3, sec^{-1}
p-OCH_3	−2.29	0.9390	0.45
p-CH_3	−2.61	0.9557	0.71
H	−2.72	0.8370	0.68
p-Cl	−2.89	0.5647	0.56
m-Cl	−2.99	0.4362	0.52
p-NO_2	−3.37	0.2695	0.71

[a] In aqueous perchloric acid (4.85 M) at 25°. [b] Evaluated by the H_A method.

For the sake of simplicity the discussion of the results will be carried out for the reduction reaction but it applies also to the racemization.

The mechanism of loss of chirality and, in general, how the mechanism of the two formally different reactions merge will be discussed in a later section.

The dependence of rates on sulfoxide and on halide ion concentrations has been confirmed to be unitary. This means that the second iodide, required by the stoichiometry of the reduction, intervenes after the rate-determining step.

$$\rangle SO + 2H^+ + 2I^- \longrightarrow \rangle S + H_2O + I_2 \qquad (7)$$

The main problem, as far as the form of the kinetic equation is concerned, is the dependence on acid, on which there is no agreement in the literature.

Because of the well-recognized basic properties of sulfoxides and the clear evidence of acid catalysis the first step in the reaction must be the reversible protonation of sulfoxide.

$$\rangle SO + H^+ \rightleftharpoons \rangle SOH^+ \qquad (8)$$

The recent definition of the properties of this equilibrium[10] allows us to include in the kinetic equation the correct expression for taking into account the pre-equilibrium 8. When this is done, we observed that $k_1 = k_{obsd}(h_A + K_a)/h_A$ is still dependent on the acid concentration.

The problem now arises as to how to analyze this acid dependence and the exact meaning to attach to it. Because of the range of acid concentration used it is beyond doubt that the simple $[H^+]$ concentration cannot be a reasonable parameter.

As reported in the Results, log $k_1/[Hal^-]$ increases linearly with H_0, the plots having a slope near one. Higher slopes were found by plotting *vs.* H_A. This might indicate that a second proton is involved in the reaction, as is also suggested by the stoichiometry.

Another approach, suggested by more recent theoretical treatment of acid-catalyzed reactions in moderately concentrated acids,[18,19] is to analyze the data on the basis of the ϕ parameter.[19] This parameter is the slope of the plots[20] of log k *vs.* H_0 + log $[H^+]$ and it is an indication of the change in solvation from the initial to the transition state. ϕ values >0.58 are found in reactions in which water is involved as the proton transfer agent in the rate-limiting step; ϕ +0.22 to +0.56 in reactions in which water is involved as a nucleophile in the rate-limiting step; $\phi < 0.0$ in reactions in which water is not involved in the rate-limiting step.

By plotting log $k_1/[Hal^-]$ *vs.* H_0 + log $[H^+]$ we found (see Table VI) a good linear correlation in every case with slopes (ϕ values) in the range −1.2 to −1.6. These very high negative values are unusual, particularly for moderately basic substrates. In fact among the data collected by Bunnett and Olsen[18] negative ϕ values, but less negative than those we found, are observed only in typical unimolecular reactions of weakly basic substrates, like hydrolysis of acetals, *tert*-butyl acetate, and methyl mesitoate.

However, recently Buncel and Lawton[21] analyzed with the Bunnett criterium the Wallach rearrangement, which is thought to involve two protons in the rate-determining step, and found ϕ values of the same order of magnitude as ours; however, in this case the plots were not linear.

The largely negative ϕ values found in our case as well as in the Wallach rearrangement match the large increase in rates observed in the first-order rate coefficient after correction for the protonation of the substrate. The most logical way to explain these facts is to consider that two protons are involved in or before the rate-determining step and therefore that the rate expression is second order in $[H^+]$ or better in a_{H^+}.

Particularly in our case simple chemical considerations suggest that the displacement of the oxygen from sulfur must require two protons. Apart from the charge, the protonated sulfoxide formally resembles an alcohol and its reaction with halide ion resembles the nucleophilic substitution of OH with Hal. As in the case of alcohol, a simple displacement is not likely, since OH^- is a poor leaving group and the reaction should occur only if a second proton transforms OH^- to H_2O.

If we consider the reactions as the acid-catalyzed transformation of the protonated sulfoxide into products the expression for testing the Bunnett criterium becomes log $(k_1/[Hal^-]) + H_0$. The plot of this quantity *vs.* H_0 + log $[H^+]$ is linear with slopes slightly different from zero. In other terms such treatment gives ϕ values within the range −0.12 to +0.06 which are quite reasonable values for the parameter.

Finally the hypothesis of the intervention of two pro-

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(18) J. F. Bunnett, *J. Amer. Chem. Soc.*, **83**, 4956, 4968, 4973, 4978 (1961).

(19) J. F. Bunnett and F. P. Olsen, *Can. J. Chem.*, **44**, 1917 (1966).

(20) Log k = log $k_{obsd} + H_0$ (for the reaction of weakly basic substrates) or log k_{obsd} − log $[SH^+]/[S]_{st}$ (for moderately basic substrates) or log k_{obsd} (for strongly basic substrates).

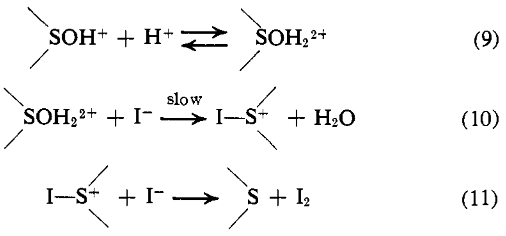
(21) E. Buncel and B. T. Lawton, *Can. J. Chem.*, 43, 862 (1965).

tons in the rate expression is supported by Krueger's results[3] for the acid-catalyzed reduction of DMSO by iodide ion in DMSO–H_2O. The system is quite different from ours but he found definite evidence of a second-order dependence of rates on $[H^+]$.

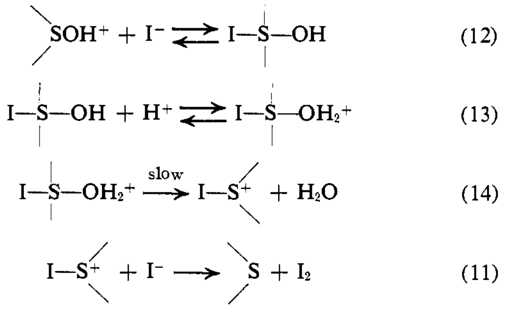
To sum up, the kinetic study shows that the rate of the reaction depends on the first power of protonated sulfoxide, halide ion, and acid activity.

On these bases two alternative schemes (I and II) for the reduction of sulfoxides by iodide ion may be proposed (in both cases the first step is the protonation equilibrium of the sulfoxide, eq 8).

Scheme I

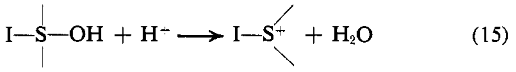


Scheme II



The two schemes have the common fast step 11 after the rate-determining formation of the iodosulfonium ion. Evidence in favor of this hypothesis stems from studies on the oxidation of sulfides[22,23] with halogens. Independently, the absence of any evidence of a second order in $[Hal^-]$ forces the postulate that reaction 11 is fast.

In Scheme II eq 13 and 14 may be unified as in eq 15

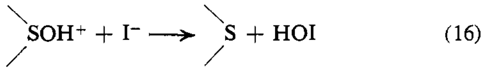


(15)

which would represent the general acid catalyzed removal of the water molecule from the tetracovalent sulfur intermediate formed in reaction 12.

Schemes I and II have many points in common and the possibility to distinguish between them will be discussed below. Another radically different alternative must be taken into consideration; that is, the attack of iodide ion at oxygen and not at sulfur.[6,24]

Such a possibility in our system seems unlikely. A mechanism of this kind, which may be simply represented as in eq 16 and 17, should not require a second order in $[H^+]$. Reaction 17 is known to be very fast and, in any case, a second order in $[H^+]$ should be accompanied by a second order in iodide ion. Independently of that, the large steric requirement of the reaction supports the hypothesis of an attack at sulfur more than an attack at oxygen.



(16)

$$HOI + H^+I^- \longrightarrow H_2O + I_2 \qquad (17)$$

More difficult is the distinction between the alternative Schemes I and II. Indeed they require the same kinetic equation and also the steric requirements should be similar since both involve attack of iodide ion at sulfur.

Scheme I is simpler but the intervention of a diprotonated sulfoxide seems unlikely. Independently of the fact that no direct evidence of such species has ever been found[10] even in 100% sulfuric acid,[25,26] *e.g.*, at acidity levels 4 to 6 powers of ten higher on the h_0 scale than those used in this study, some difficulties arise in considering the reverse reaction. Equation 10 from right to left would be the slow step in the oxidation of sulfides by iodine. It implies that a water molecule displaces iodide ion from sulfur forming a dication before the removal of a proton.

On the other hand, Scheme II requires the intervention as intermediate of a "pentacoordinate" tetracovalent[27] sulfur species and a complex series of equilibria. However, recently in a number of cases, intermediates of this kind have been suggested[28] and also physical and chemical evidences of its presence offered.[29,30]

The analysis of the substituent effect is of little help. In fact it reflects only the changes of the position of the preequilibrium protonation, *i.e.*, of the concentration of $[SOH^+]$, the active species.

From this point onward, the apparent ρ value of the reaction is practically equal to zero. As far as the ρ value reflects the change in electron density of the reaction center, in going from reagents to the transition state, it cannot distinguish between Scheme I and Scheme II since the transition state of reaction 10 contains the same species with the same overall charge as the transition state of reaction 14. In effect the two postulated transition states are not identical but they differ only in degree of bonding and therefore it is very difficult to make an *a priori* analysis.

Finally we must discuss the possibility outlined in eq 15. Also for Scheme I a similar modification of the reaction sequence could be envisaged, *i.e.*, that the attack of iodide ion on the protonated sulfoxide occurs contemporarily with the transfer of a second proton.

Such possibilities could be tested in principle by the measurement of a solvent isotope effect, but in this particular case the reply is not straightforward since the isotopic composition of the solvent also affects the equilibrium 8 and therefore it must be independently studied. However, the ϕ values very near to zero would exclude this possibility since it requires the intervention

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(22) H. K. Gensch, I. H. Pitman, and T. Higuchi, *J. Amer. Chem. Soc.*, 90, 2096 (1968), and previous papers of the series.

(23) (a) M. Cinquini, S. Colonna, and D. Landini, *Boll. Sci. Fac. Chim. Ind. Bologna*, 27, 211 (1969); (b) G. Modena, U. Miotti, and L. Sedea, *J. Chem. Soc. B*, 802 (1970).

(24) H. J. Shine and C. F. Dais, *J. Org. Chem.*, 30, 2145 (1965).

(25) R. J. Gillespie and J. A. Leisten, *Quart. Rev., Chem. Soc.*, 8, 40 (1954).

(26) R. J. Gillespie and R. C. Passerini, *J. Chem. Soc.*, 3850 (1956).

(27) M. A. Sabol and K. K. Andersen, *J. Amer. Chem. Soc.*, 91, 3603 (1969); T. Tang and K. Mislow, *ibid.*, 91, 5644 (1969).

(28) (a) B. M. Trost, R. La Rochelle, and R. C. Atkins, *ibid.*, 91, 2175 (1969), and references cited therein; (b) H. Hogeveen, G. Maccagnani, and F. Montanari, *J. Chem. Soc. C*, 1585 (1966); (c) E. L. Muetterties and B. A. Schuun, *Quart. Rev., Chem. Soc.*, 20, 245 (1966).

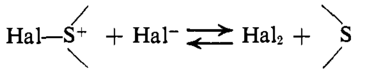
(29) D. C. Owsley, G. K. Helmkamp, and M. F. Rettig, *J. Amer. Chem. Soc.*, 91, 5239 (1969).

(30) C. R. Johnson and J. J. Rigau, *ibid.*, 91, 5398 (1969).

of a water molecule in the transition state for the hydrogen ion transfer and in such cases $\phi > +0.58$ would be expected. However the lack of enough data for reaction involving two protons does not allow a definite reply.

Racemization. As anticipated, the kinetics of the reduction and of the racemization of sulfoxides suggest that the two reactions occur by the same route. It implies that the different stoichiometric course is only reflected by the fate of the iodosulfonium ion and the corresponding bromo- and chlorosulfonium ions formed in reactions equivalent to those reported above for the iodide ion.

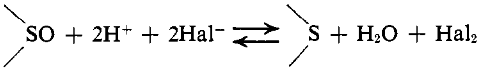
Allowing that reaction 11′ (eq 11 for the iodide ion



$$\text{Hal—S}^+ + \text{Hal}^- \rightleftharpoons \text{Hal}_2 + \text{S} \tag{11'}$$

reaction) is reversible with the position of the equilibrium shifted to the left in the case of bromine and chlorine, the mechanism of the racemization becomes identical with that of the reduction. In fact, as the sulfide is not chiral it is obvious that step 11′ occurs with loss of optical activity.

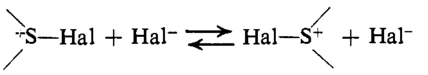
The assumption made above on the position of equilibrium 11′ is supported by the knowledge that the overall equilibrium 7′ is largely shifted to the left for



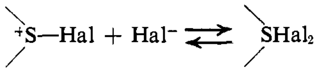
$$\text{SO} + 2\text{H}^+ + 2\text{Hal}^- \rightleftharpoons \text{S} + \text{H}_2\text{O} + \text{Hal}_2 \tag{7'}$$

bromine and chlorine and to the right for iodine.

However, this is not the only way in which the racemization may be explained. Either a fast halogen exchange of the halosulfonium ion (eq 18) or the intermediate formation of a dihalo sulfide (eq 19) followed by a fast hydrolysis could explain the results as well.[17]



$$^{+}\text{S—Hal} + \text{Hal}^- \rightleftharpoons \text{Hal—S}^+ + \text{Hal}^- \tag{18}$$



$$^{+}\text{S—Hal} + \text{Hal}^- \rightleftharpoons \text{SHal}_2 \tag{19}$$

Since all these processes (eq 11′, 18, and 19) occur after the rate-determining step, no kinetic evidence can be found.

Thiophilicity of Halide Ions. Under the hypothesis formulated above that the reduction by iodide ion and the racemization by bromide and chloride ions follows the same mechanism, the difference in rates between them, under otherwise equal conditions, should depend on the thiophilicity of the halide ions. We found that the reactivity ratio evaluated by extrapolation of the data reported in Tables I-III at $H_0 = 0$ is $\text{Cl}^-:\text{Br}^-:\text{I}^- = 1:3:87$. These values match very well with those reported by Kice, *et al.*,[31] for the nucleophilic assisted solvolysis of ArSO-SO$_2$-Ar in 60% dioxane-water.

Experimental Section

Materials and Solvents. DMSO, sodium halides, and perchloric acid were Analar grade commercial products, purified, when necessary, by standard methods. All the sulfoxides used in this work were known compounds. They were synthetized by oxidation with iodobenzene dichloride[32] of the corresponding sulfides and carefully purified by column chromatography and by repeated crystallizations. They had the following melting points and/or boiling points: phenyl methyl sulfoxide, bp 148–150° (17 mm), lit.[32] bp 148–150° (17 mm); *p*-anisyl methyl sulfoxide, mp 45–46°, lit.[33] mp 43°; *p*-tolyl methyl sulfoxide, mp 42–43°, lit.[33] mp 42–43°; *p*-chlorophenyl methyl sulfoxide, mp 46–47°, lit.[33] mp 47–48°; *m*-chlorophenyl methyl sulfoxide, mp 43–44°, bp 126–127° (1.5 mm), lit.[34] bp 125–126° (1.3 mm); *p*-nitrophenyl methyl sulfoxide, mp 151–152°, lit.[32] mp 151–152°. (*R*)-(+)-*p*-tolyl methyl sulfoxide was prepared as described in the literature,[35] by the Andersen method,[36] from diastereomerically pure (−)-menthyl (−)-*p*-toluenesulfinate. It had mp 74–76°, $[\alpha]_D$ +145° (*c* 1, acetone), lit.[35] mp 73.5–74°, $[\alpha]_D$ +145.5° (*c* 1, acetone).

Reaction Products. Reduction. A solution (0.005 *M*) of sulfoxide in aqueous perchloric acid (4.85 *M*), containing sodium iodide (0.3 *M*), was kept under nitrogen at 25° until the stoichiometric amount of iodine (see eq 7) was evolved (2–6 hr). The solution was diluted with water, neutralized with sodium carbonate, and extracted with ether containing a known amount of *n*-tetradecane as internal standard (0.005 *M* solution). Vpc analysis on a 3-m SE 30 10% on Chromosorb W column showed, as expected,[2-4] quantitative conversion of sulfoxides to the corresponding sulfides.

Racemization. In a typical experiment 100 mg of (+)-*p*-Tol-SO-Me in 50 ml of 5.8 *M* HClO$_4$ containing sodium bromide (0.8 *M*) was allowed to stand at 25° for 60 min. The loss of optical activity was complete in about 30 min. The acid solution did not show the presence of bromine (iodide starch test); it was neutralized with sodium carbonate and the sulfoxide was extracted with chloroform. Vpc analysis on a 3-m SE 30 10% on Chromosorb W column showed no evidence of sulfide. Removal under reduced pressure of the solvent left 100 mg of the racemic *p*-Tol-SO-Me, infrared spectrum identical with that of starting material.

Measurements of Acidity Functions. The perchloric acid solutions were made up by dilution and titrated with standard NaOH. The H_0 values were obtained by interpolation of published data.[37] The H_A values were kindly provided by Professor K. Yates.[14]

The effect of sodium chloride, in the range 0–1.2 *M*, on H_0 function was evaluated by measuring spectrophotometrically the ionization ratios of suitable indicators at various perchloric acid concentrations.

Following Yates, *et al.*,[37] stock solutions of each indicator were prepared by dissolving a weighed sample of the indicator in reagent grade chloroform. Suitable aliquots were transferred to 50-ml volumetric flasks. The chloroform was evaporated under vacuum and the sample dissolved in perchloric acid of the desired strength, added to known amounts of sodium chloride, and filled to the mark with the acid solution.

Spectra of these solutions were registered with a Cary 15 or Zeiss M4PQII spectrophotometer using 1-cm silica cells and a thermostatically controlled cell block at 25 ± 0.1°.

Ionization ratios were obtained from the expression $I = [\text{BH}^+]/[\text{B}] = (\epsilon_\text{B} - \epsilon)/(\epsilon - \epsilon_{\text{BH}^+})$ where ϵ_{BH^+} and ϵ_B are the extinction coefficients of the fully protonated and unprotonated base, respectively, and ϵ is the extinction coefficient of a solution where the two forms are both present.

The pK_{BH^+} values of amines, used for the calculation of the H_0 function ($H_0 = \text{p}K_{\text{BH}^+} - \log [\text{BH}^+]/[\text{B}]$), are those of the literature.[16,37]

The following commercially available amines were used at the indicated acid concentration: 2-nitroaniline (HClO$_4$ 0.51 *M*), 2-nitro-4-chloroaniline (3.05 *M*), 2,5-dichloro-4-nitroaniline (3.88 *M*), 2,4-dichloro-6-nitroaniline (5.99 *M*), 2,6-dichloro-4-nitroaniline (7.02 *M*).

Linear graphs of $-\Delta H_0$, the difference between H_0 values with and without salt, *vs.* sodium chloride concentration were obtained. The average slope is 0.18.

A typical example is reported in Table IX.

In a similar way, following Yates, *et al.*,[38] salt effect was evaluated on the H_A function by using 4-methoxybenzamide and 3-nitrobenzamide. The plot $-\Delta H_A$ *vs.* [NaCl] has a slope of 0.15.

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[31] J. L. Kice and G. Guaraldi, *Tetrahedron Lett.*, 6135 (1967); see also J. L. Kice, *Accounts Chem. Res.*, 1, 58 (1968).

[32] G. Barbieri, M. Cinquini, S. Colonna, and F. Montanari, *J. Chem. Soc.*, 659 (1968).

(33) A. Cerniani and G. Modena, *Gazz. Chim. Ital.*, **89**, 843 (1959).

(34) K. K. Andersen, W. H. Edmonds, J. B. Biasotti, and R. A. Strecker *J. Org. Chem.*, **31**, 2859 (1966).

(35) K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, *J. Amer. Chem. Soc.*, **87**, 1958 (1965).

(36) K. K. Andersen, W. Goffield, N. E. Papanikolau, J. W. Foley, and R. I. Perkins, *ibid.*, **86**, 5637 (1964).

(37) K. Yates and H. Wai, *ibid.*, **86**, 5408 (1964).

(38) K. Yates, J. B. Stevens, and A. R. Katritzky, *Can. J. Chem.*, **42**, 1957 (1964).

Table IX. Ionization Ratios of 2-Nitro-4-chloroaniline ($pK_{BH^+} = -1.07$) and H_0 Values Evaluated in Perchloric Acid (3.05 *M*) Containing Various Amounts of Sodium Chloride

[NaCl], mol/l.	log I	$-H_0$	$-\Delta H_0$
	0.23	1.30	
0.2	0.26	1.33	0.03
0.4	0.29	1.36	0.06
0.6	0.34	1.41	0.11
0.8	0.35	1.42	0.12
1.0	0.41	1.48	0.18
1.2	0.46	1.53	0.23

From the graphs described above the influence of sodium iodide and sodium bromide on the acidity functions was evaluated, assuming the effect of bromide and iodide ions is equal to that of chloride ion.[16]

Kinetic Procedures. Sulfoxide solutions were prepared by weighing out the sulfoxide in a 50-ml volumetric flask which was filled to the mark with perchloric acid stock solution.

The perchloric acid solutions were prepared by dilution of concentrated perchloric acid with distilled water, previously refluxed while passing a stream of nitrogen. They were titrated with standard NaOH.

Sodium halide solutions were prepared by dissolving the desired amount of salt with deoxygenated distilled water in a volumetric flask. The solutions were kept under nitrogen and thermostated at 25 ± 0.05°.

At zero time 10 ml of the salt solution was added to the sulfoxide solution. Aliquots were withdrawn under nitrogen at various time and analyzed as follow.

Reduction. The aliquots were poured in an ice-cold aqueous solution containing a known amount of sodium thiosulfate, to destroy the iodine formed. The residual sodium thiosulfate was back titrated with standard iodine. From the analytical data and the stoichiometric equation (eq 7) the concentration of the sulfoxide at any time was calculated.

The pseudo-first-order rate constants (all the experiments were run with large excess of acid and halide ion) were obtained by plotting log [R_2SO] *vs.* time and determining the slope of the line from the graphs and from a least-squares analysis. An Olivetti Programma 101 desk computer was used.

A typical example is in Table X.

Table X. Reduction of *m*-Chlorophenyl Methyl Sulfoxide (0.005 *M*) with Sodium Iodide (0.5 *M*)[a]

t, sec		30	159	305	503	730	1009	1385	1792	2275
[R_2SO] × 10^3 *M*	5.00	4.90	4.65	4.38	4.04	3.72	3.44	2.85	2.41	1.87

[a] In aqueous perchloric acid (4.56 *M*) at 25°; $k_{obsd} = -2.303 \times \text{slope} = 4.11 \times 10^{-4}\ \text{sec}^{-1}$.

Since the H_A of the solution is −2.12 and the pK_a of *m*-chlorophenyl methyl sulfoxide is −2.99 on the H_A scale (see Table VIII), the ratio $h_A/(h_A + K_a) = 0.0711$, and therefore the values of k_1 ($5.78 \times 10^{-3}\ \text{sec}^{-1}$) and of k_1/[NaI] ($1.15 \times 10^{-2}\ \text{sec}^{-1}\ \text{mol}^{-1}$ l.) can be easily evaluated.

Racemization. The aliquots, withdrawn from the reaction of the optical active sulfoxide with sodium chloride or sodium bromide, were transferred in a thermostated cell of a Perkin-Elmer P22 spectropolarimeter. The optical activity was measured in the range 280–300 nm. From plots of log [α] *vs.* time, the pseudo-first-order constants were evaluated. The calculation has been described in detail in the previous paragraph.

Acknowledgments. We wish to thank Professors J. F. Bunnett and K. Yates for helpful discussions and the Consiglio Nazionale delle Ricerche, Rome, for financial support.

Organic Oxalates. IV. Pyrolysis of Diallyl, Disubstituted-Allyl, and Related Oxalates[1]

Walter S. Trahanovsky[1e] **and Ching Ching Ong**

Contribution from the Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa 50010. *Received May 12, 1970*

Abstract: Products from the low-pressure gas-phase pyrolysis of diallyl, dicrotyl, dicinnamyl, and related oxalates are reported. The results indicate that these oxalates are a convenient source of substituted allyl radicals. The main products from allyl and crotyl radicals are coupling products, but no coupling products are observed from cinnamyl radicals. The main product from the pyrolysis of di-*trans*-cinnamyl oxalate is indene which must result from an intramolecular cyclization of the cinnamyl radical. An isotope effect, k_H/k_D, of 2.92 is reported for the cyclization of *o*-deuteriocinnamyl radical to indene which suggests that formation of the intermediate cyclic radical from the cinnamyl radical is a reversible step. Several radicals generated from the appropriate oxalates that are similar to cinnamyl radicals also undergo cyclizations giving rise to cyclic products.

In part II[2] of this series we reported that the low-pressure gas-phase pyrolysis of ring-substituted dibenzyl oxalates produces benzyl radicals which couple to form bibenzyls in good yield. In part I[3] of this

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(1) (a) Part III: W. S. Trahanovsky and C. C. Ong, *Tetrahedron Lett.*, 3627 (1968). (b) This work was partially supported by Public Health Service Grant No. GM 13799 from the National Institute of General Medical Sciences and Grant No. 3219-A from the Petroleum Research Fund, administered by the American Chemical Society. The mass spectrometer was purchased with funds from National Science Foundation Grant No. GP 1715 and a grant from the Iowa State Alumni Research Fund. We thank these organizations for their support. (c) Based on work by C. C. O. in partial fulfillment of the requirements for the Ph.D. Degree at Iowa State University. (d) Preliminary communications: ref 1a and footnote 10 of ref 2. (e) Alfred P. Sloan Research Fellow, 1970–1972.

(2) W. S. Trahanovsky, C. C. Ong, and J. A. Lawson, *J. Amer. Chem. Soc.*, **90**, 2839 (1968).

(3) W. S. Trahanovsky, J. A. Lawson, and D. E. Zabel, *J. Org. Chem.*, **32**, 2287 (1967).