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Correlation analysis of reactivity in the oxidation of organic sulfides by benzyltrimethyl-ammonium dichloroiodate

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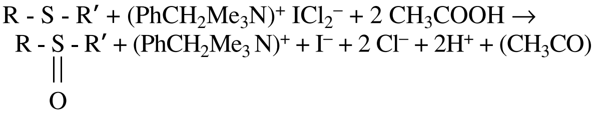
The oxidation of organic sulfides by benzyltrimethylammonium dichloroiodate (BTMACI), in glacial acetic acid in the presence of zinc chloride, involves the formation of a halogenosulfonium cation in the rate-determining step.

Keywords: organic sulfides, benzyltrimethyl-ammonium dichloroidate

Benzyltrimethylammonium polyhalides are widely used as halogenating reagents in synthetic organic chemistry.[1,2] We have recently reported the oxidation of substituted benzyl alcohols,[7] aliphatic aldehydes[8] and diols[9] by benzyltrimethylammonium dichloroiodate (BTMACI). Here, we describe the kinetics of oxidation of 35 organic sulfides by BTMACI, in glacial acetic acid in the presence of zinc chloride. Mechanistic aspects are discussed.

BTMACI was prepared by the reported method[1] and its purity was checked by an iodometric method. BTMACI is only slightly soluble in acetic acid at room temperature. However, addition of zinc chloride renders it readily soluble in acetic acid. The reactions were carried out under pseudo-first-order conditions by maintaining a large excess of the sulfide over BTMACI. The solvent was glacial acetic acid. The reactions were carried out in the presence of zinc chloride (0.003 mol/dm^3) and were followed by monitoring the decrease in [BTMACI] iodometrically for at least three half lives. The pseudo-first-order rate constant, k_{obs}, was evaluated from the linear ($r^2 > 0.995$) plots of log [BTMACI] against time. The experimental third order rate constant, k_3, was determined from the relationship: $k_3 = k_{obs}/[\text{sulfide}]\,[ZnCl_2]$.

The oxidation of organic sulfides by BTMACI resulted in the formation of the corresponding sulfoxides. The overall reaction can be represented as eqn (1).



$$\text{R-S-R}' + (PhCH_2Me_3N)^+ ICl_2^- + 2\,CH_3COOH \rightarrow \text{R-}\underset{\underset{O}{\|}}{S}\text{-R}' + (PhCH_2Me_3N)^+ + I^- + 2\,Cl^- + 2H^+ + (CH_3CO)_2O \tag{1}$$

The reactions were found to be first order with respect to BTMACI, the sulfide and ZnCl$_2$. An addition of benzyltrimethylammonium chloride (BTMAC) enhances the reaction rate slightly. The oxidation of methyl phenyl sulfide, in an atmosphere of nitrogen, failed to induce the polymerisation of acrylonitrile. Further, the addition of acrylonitrile had no effect on the rate of oxidation. Thus a one-electron oxidation, giving rise to free radicals, is unlikely. The rates of oxidation of sulfides were determined at different temperatures and the activation parameters were calculated.

UV–VIS spectra of BTMACI alone and in the presence of different concentrations of ZnCl$_2$ showed that the nature of the spectra is not much different in the presence and absence of zinc chloride. However, there is an initial sharp decrease in the absorbance followed by a regular but gradual decrease in the absorbance of BTMACI on further addition of increasing amounts of ZnCl$_2$. This clearly showed that a strong complex is formed initially which undergoes further complexation, its concentration increases with an increase in the concentration of ZnCl$_2$.

From our data[7] on the solubility of BTMACI in the absence and presence of zinc chloride, the value of the equilibrium constant, K_1, is estimated to be *ca* 2400 mol^{-1} dm^3. This indicates that even at the lowest concentration of zinc chloride used, almost the whole of the BTMACI will be in the form of complex (A) [eqn (2)]. The linear increase in the rate with an increase in the concentration of zinc chloride points to a further complexation [eqn (3)]. This is also supported by the spectral studies.

$$[PhCH_2Me_3N]^+ ICl_2^- + ZnCl_2 \overset{K_1}{\rightleftharpoons} \underset{(A)}{[PhCH_2Me_3N]^+ [IZnCl_4]^-} \tag{2}$$

$$(A) + ZnCl_2 \overset{K_2}{\rightleftharpoons} \underset{(B)}{[PhCH_2Me_3N]^+ [IZn_2Cl_6]^-} \tag{3}$$

Therefore, (B) is the only reactive oxidising species in the oxidation of sulfides.

The rates of the *ortho-*,*meta-* and *para*-compounds failed to exhibit a significant correlation in terms of any single- or dual-substituent substituent parameter equations. The rates of oxidation of *meta-*, *para-* and *ortho-* substituted aryl methyl sulfides were then correlated in terms of Charton's[23] LDR/LDRS equations.

$$\log k_3 = L\,\sigma_l + D\,\sigma_d + R\,\sigma_e + h \tag{9}$$

$$\log k_3 = L\,\sigma_l + D\,\sigma_d + R\,\sigma_e + S\,\upsilon + h \tag{11}$$

The latter two substituent parameters are related by eqn (10),

$$\sigma_D = \eta\sigma_e + \sigma_d \tag{10}$$

where η represents the electronic demand of the reaction site which is given by $\eta = R/D$, and σ_D represents the delocalised electrical parameter of the diparametric LD equation.

The rates of oxidation of the *meta-*,*para-* and *ortho*-substituted phenyl methyl sulfides showed excellent correlations with LDR/LDRS equations. All the three regression coefficients, L, D and R are negative indicating an electron-deficient sulfur center in the transition state of the reaction. The positive value of η adds a negative increment to σ_d thereby increasing the electron-donating power of the substituent and its capacity to stabilise a cationic reaction site. The negative value of S indicates that the reaction is subjected to steric hindrance by the *ortho*-substituent. This may be due to steric hindrance of the *ortho*-substituent to the approach of the oxidising species.

The rates of oxidation of alkyl phenyl sulfides yielded an excellent correlation in terms of Pavelich-Taft's[26] dual substituent-parameter (DSP) eqn (14). The negative polar reaction constant confirms that the electron-donating power of the alkyl group enhances the reaction rate. The steric effect plays an inhibitory role.

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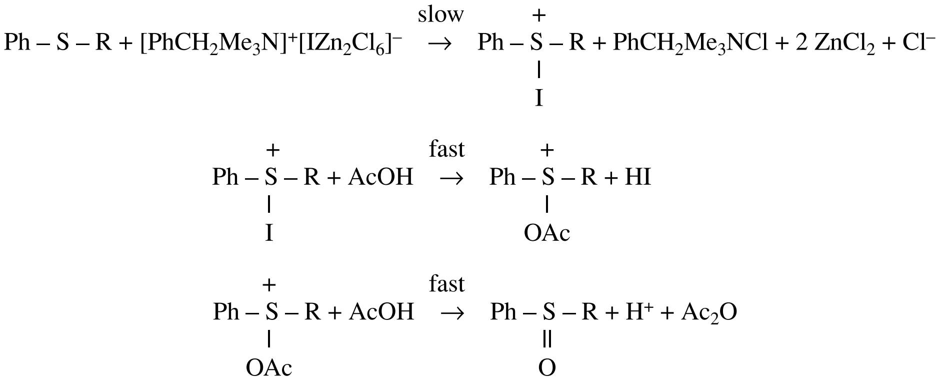
$$\log k_3 = \rho^* \sigma^* + \delta E_s + \log k_0 \qquad (14)$$

The experimental results can be accounted for in terms of rate-determining electrophilic attack of a di-zinc chloride complex (B) [eqn (3)] on the sulfide to yield a halogenosulfonium ion (Scheme 1). A positive value of η, indicating that the substituent is better able to stabilise a cationic or electron-deficient site, supports an electrophilic attack on the sulfide sulfur. We have applied LDR/LDRS equations to the oxidation of sulfides by pyridinium hydrobromide perbromide (PHPB),[34] benzyltrimethylammonium tribromide (BTMAB),[35] bis (2,2′-bipyridyl) copper(II) permanganate (BBCP)[36] and hexamethylenetetramine-bromine (HABR).[37] The polar constants were negative in all the four cases (Table 8). However, the magnitudes of the D and R, in the oxidation of *ortho-* and *para*-benzaldehydes by BBCP, are much smaller when compared with the values obtained in the other studies. The value of η also is lower. The oxidation by BBCP was proposed to involve a direct oxygen transfer. In the oxidation by PHPB, BTMAB and HABR, where the formation of a halogenosulfonium cation has been proposed, the magnitude of the three polar reaction constants and η are comparable to the values obtained in the oxidation by BTMACI. Hence, the formation of a similar transition state leading to the formation of halogenosulfonium cation in the rate-determining step of the present reaction, is indicated. In the oxidation of *meta*-compounds all the reaction constants in these reactions have comparable values. This may be because the delocalisation effect is less important from the *meta* position.

Table 8 Reaction constants of the oxidation of sulfides in terms of Charton's LDR/LDRS equations at 298 K

Oxidant	L	D	R	η	S	Ref.
para-substituted						
PHPB	–1.43	–2.11	–2.89	1.37	–	34
BTMAB	–1.40	–2.09	–2.85	1.36	–	35
BBCP	–1.37	–1.53	–1.41	0.92	–	36
HABR	–1.41	–2.09	–3.01	1.44	–	37
BTMACI	–1.62	–2.43	–3.63	1.49	–	This work
meta-substituted						
PHPB	–1.72	–0.99	–0.95	0.96	–	34
BTMAB	–1.68	–1.01	–1.03	1.02	–	35
BBCP	–1.76	–1.35	–1.12	0.83	–	36
HABR	–1.72	–1.05	–1.29	1.23	–	37
BTMACI	–1.97	–1.08	–1.66	1.54	–	This work
ortho-substituted						
PHPB	–1.46	–1.66	–2.25	1.36	–1.13	34
BTMAB	–1.42	–1.72	–2.10	1.22	–1.15	35
BBCP	–1.41	–1.51	–1.45	0.96	–1.12	36
HABR	–1.47	–1.71	–2.67	1.56	–1.14	37
BTMACI	–1.68	–1.80	–2.57	1.43	–1.22	This work



$$\mathrm{Ph-S-R + [PhCH_2Me_3N]^+[IZn_2Cl_6]^-} \xrightarrow{\text{slow}} \mathrm{Ph-}\underset{\substack{|\\ \mathrm{I}}}{\overset{+}{\mathrm{S}}}\mathrm{-R + PhCH_2Me_3NCl + 2\,ZnCl_2 + Cl^-}$$

$$\mathrm{Ph-}\underset{\substack{|\\ \mathrm{I}}}{\overset{+}{\mathrm{S}}}\mathrm{-R + AcOH} \xrightarrow{\text{fast}} \mathrm{Ph-}\underset{\substack{|\\ \mathrm{OAc}}}{\overset{+}{\mathrm{S}}}\mathrm{-R + HI}$$

$$\mathrm{Ph-}\underset{\substack{|\\ \mathrm{OAc}}}{\overset{+}{\mathrm{S}}}\mathrm{-R + AcOH} \xrightarrow{\text{fast}} \mathrm{Ph-}\underset{\substack{\|\\ \mathrm{O}}}{\mathrm{S}}\mathrm{-R + H^+ + Ac_2O}$$

Scheme 1

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Techniques used: Spectrophotometry, correlation analysis

Equations: 14

Figure: 1

References: 37

Table 1. Rate constants for the oxidation of methyl phenyl sulfide by BTMACI at 298 K

Table 2. Rate constants and activation parameters of the oxidation of sulfides by BTMACI

Table 3. Effect of benzyltrimethylammonium chloride on the rate of oxidation of methyl phenyl sulfide by BTMACI

Table 4. Effect of zinc chloride on the rate of oxidation of methyl phenyl sulfide by BTMACI

Table 5. Correlation analysis of the rates of oxidation of *meta-* and *para*-substituted organic sulfides by BTMACI with Taft's dual substituent-parameters at 298 K

Table 6. Temperature dependence of the reaction constants for the oxidation of organic sulfides by BTMACI

Table 7. Correlation of rate of oxidation of alkyl phenyl sulfides by BTMACI in terms of Pavelich–Taft equation[a]

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