

Kinetics and mechanism of the oxidation of dimethyl, dipropyl and diphenyl sulfides by benzimidazolium dichromate

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Abstract : The oxidation of dimethyl-, dipropyl- and diphenyl sulfides by benzimidazolium dichromate (BIDC) in dimethyl sulfoxide, to the corresponding sulfoxides, is first order with respect to BIDC. Michaelis-Menten type kinetics were observed with respect to sulfide. The reaction is catalysed by hydrogen ions and the order is less than one. It appears that the BIDC-H⁺ is the active electrophile. An intermediate of composition Sulfide-BIDC-H⁺ has envisaged. An analysis of the solvent effect by Swain's equation indicated that though both the anion- and cation-solvating powers of the solvent contribute to the observed solvent effect, the role of cation-solvation is major. A mechanism involving the rate-determining oxygen atom transfer within complex, formed by a nucleophilic attack of sulfide-sulfur on BIDC-H⁺ in a rapid pre-equilibrium, is suggested to give product via a cyclic transition state.

Keywords : Kinetics, mechanism, sulfides, oxidation, Cr^{VI} complex, benzimidazolium dichromate.

Introduction

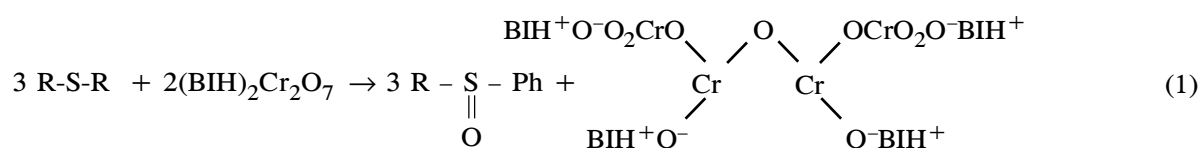
The selective oxidation of organic compounds under non-aqueous conditions is an important transformation in synthetic organic chemistry. For this, a number of different chromium(VI) derivatives have been reported^{1,2}. In 1998, Meng *et al.*³ reported a new Cr^{VI} derivative – benzimidazolium dichromate (BIDC). It is neither hygroscopic nor light sensitive, thus more stable and easily stored as compared to other Cr^{VI} reagents. BIDC is reported to convert benzylic and allylic alcohols to corresponding carbonyl compounds in yield ranging from 75 to 98%. We have been interested in the kinetics and mechanism of the oxidation by newer complex Cr^{VI} derivatives. There seems to be only few reports available on the kinetic and mechanistic aspects of the oxidation by BIDC⁴⁻⁹. These are published from our laboratory. In the continuation of our earlier studies, we report here the

kinetics and mechanism of the oxidation of dimethyl-, dipropyl- and diphenyl sulfides by BIDC in dimethyl sulfoxide (DMSO) as the solvent. The present investigation was undertaken, primarily to discuss the kinetic and mechanistic aspects of the oxidation of sulfides and secondly to compare the results with that of the oxidation of organic sulfides by other dichromate complexes.

Results and discussion

Rates and other experimental data were obtained for all the sulfides. Since the results are similar, only representative data are reproduced here.

The product analysis and stoichiometric determination revealed that the oxidation of sulfide resulted in the formation of the corresponding sulfoxide. The overall reaction may be represented as :



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The oxidation of sulfides by B IDC, in an atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. In blank experiments, with the substrate absent, no noticeable consumption of B IDC was observed. The addition of acrylonitrile had no effect on the rate of oxidation (Table 1). To further confirm the absence of free radicals in the reaction pathway, the reaction was carried

out in the presence of 0.05 M of 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively. It indicates that a one-electron oxidation giving rise to free radicals is not operative in this reaction¹⁰.

The reactions were found to be of first order with respect to B IDC, as evidenced by the linear plots of log [B IDC] versus time. Further, the pseudo-first order rate constants do not depend on the initial concentration of B IDC (Table 2). This also confirms the first-order dependence of rate on the concentration of oxidant. The order with respect to sulfide was less than one (Table 1). A plot of k_{obs} vs [sulfide] is a smooth curve with a downward curvature (Fig. 1). This indicates the existence of a complex. A plot of $1/k_{\text{obs}}$ versus $1/[\text{sulfide}]$ was linear with an intercept on the rate ordinate (Fig. 2). This suggests that the reaction follows the Michaelis-Menten type kinetics. In such a case the slow step is preceded by the reversible formation of a complex between the substrate

Table 1. Rate constants for the oxidation of dimethyl sulfide by B IDC at 288 K

[Sulfide] (mol dm ⁻³)	10 ³ [B IDC] (mol dm ⁻³)	[H ⁺] (mol dm ⁻³)	10 ² k_{obs} (s ⁻¹)
0.01	1.0	0.50	20.5
0.02	1.0	0.50	37.3
0.03	1.0	0.50	52.0
0.04	1.0	0.50	63.8
0.05	1.0	0.50	74.7
0.10	1.0	0.50	110
0.02	0.5	0.50	38.4
0.02	2.0	0.50	35.5
0.02	4.0	0.50	36.0
0.02	6.0	0.50	37.1
0.01	1.0	0.50	20.1 ^a
0.01	1.0	0.50	22.0 ^b

^a & ^b Contained 0.001 and 0.005 mol dm⁻³ acrylonitrile.

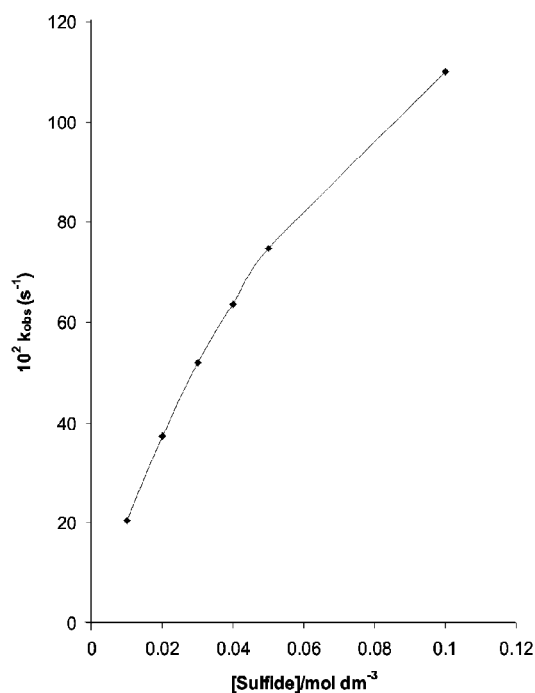


Fig. 1. A plot of k_{obs} vs [Me₂S] : [B IDC] = 0.001 mol dm⁻³; [TsOH] = 0.5 mol dm⁻³; T = 288 K.

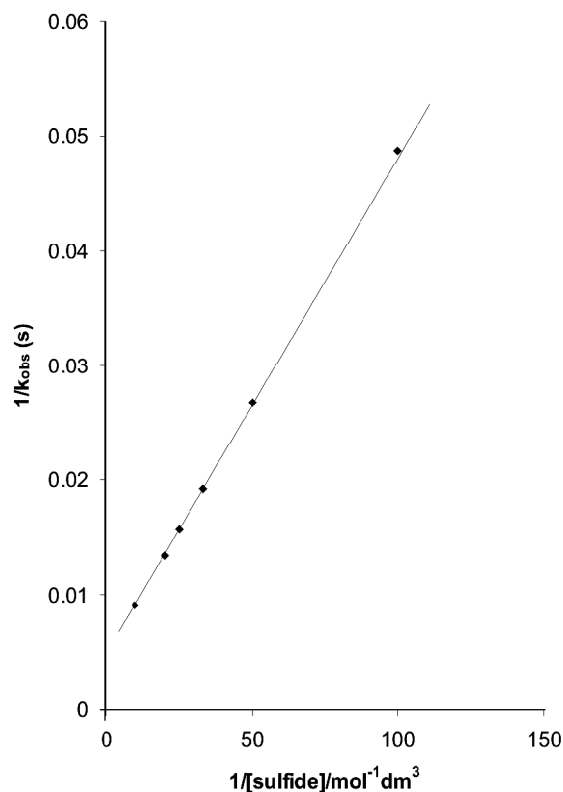


Fig. 2. A double reciprocal plot of $1/k_{\text{obs}}$ vs $1/[\text{Me}_2\text{S}]$: [B IDC] = 0.001 mol dm⁻³; [TsOH] = 0.5 mol dm⁻³; T = 288 K.

and the oxidant. The complex in turn undergoes unimolecular decomposition to give products. The steps and the rate law may be written as below :



$$\text{Rate} = k_2 K [\text{RSR}][\text{BIDC}]_t / (1 + K [\text{RSR}]) \quad (4)$$

or,

$$(\text{Rate}/[\text{BIDC}]_t)^{-1} = 1/k_{\text{obs}} = 1/k_2 K [\text{RSR}] + 1/k_2 \quad (5)$$

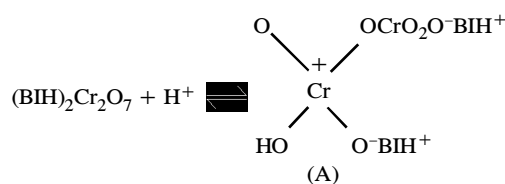
Here,

$$[\text{BIDC}]_t = [\text{BIDC}] + [\text{Complex}] \quad (6)$$

The dependence of k_{obs} on the concentration of sulfides were studied at different temperatures and the values of K and k_2 were evaluated from the double reciprocal plots. The thermodynamic parameters for the complex formation and the activation parameters for decomposition of the complexes were calculated from the values of K and k_2 respectively, at different temperatures (Tables 2 and 3).

ent concentrations of hydrogen-ion i.e. $[\text{H}^+] = 0.2, 0.3$ and 0.5 M (Table 5). It was observed that the value of K increases linearly with the concentration of hydrogen-ion, however, the rate of decomposition of complex, k_2 , does not vary appreciably with the hydrogen-ion concentration.

The observed dependence on the concentration of hydrogen-ion indicates the protonation of BIDC to yield a protonated Cr^{VI} species (A), which is a stronger oxidant and active electrophile.



here, BI stands for benzimidazole. Further, the dependence of rate on $[\text{H}^+]$ is of the form :

$$k_{\text{obs}} = a [\text{H}^+]/1 + b [\text{H}^+] \quad (7)$$

Formation of a protonated Cr^{VI} species has earlier been postulated in the reactions of BIDC and other heterocy-

Table 2. Formation constants and thermodynamic parameters for Sulfide-BIDC complexes

Sulfide	K (mol dm ⁻³)				ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	$\Delta G_{\text{at } 298 \text{ K}}$ (kJ mol ⁻¹)
	278 K	288 K	298 K	308 K			
Me ₂ S	12.4	10.4	8.95	7.61	-14.1 ± 0.1	-21 ± 1	-7.91 ± 0.1
Pr ₂ S	11.3	9.61	8.21	7.15	-13.4 ± 0.1	-20 ± 1	-7.72 ± 0.1
Ph ₂ S	13.1	10.9	9.39	7.91	-14.3 ± 0.2	-22 ± 1	-8.02 ± 0.2

Table 3. Rate constants for the decomposition of Sulfide-BIDC complexes and their activation parameters

Sulfide	$k_2 \times 10^2$ (s ⁻¹)				ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (J mol ⁻¹ K ⁻¹)	$\Delta G_{\text{at } 298 \text{ K}}^\ddagger$ (kJ mol ⁻¹)
	278 K	288 K	298 K	308 K			
Me ₂ S	111	217	421	815	44.8 ± 0.6	-83 ± 2	69.4 ± 0.5
Pr ₂ S	208	421	830	1642	46.4 ± 0.5	-72 ± 2	67.7 ± 0.4
Ph ₂ S	7.39	14.1	28.1	55.0	45.2 ± 0.9	-104 ± 1	76.1 ± 0.7

The rate of oxidation increases with an increase in acidity (Table 4). The log-log plot (Fig. 3) of k_{obs} vs $[\text{H}^+]$, for dimethyl sulfide, is linear with a slope = 0.93 ± 0.01 and $r^2 = 0.9996$. This indicates that the order with respect to $[\text{H}^+]$ is less than one. A plot of k_{obs}^{-1} vs $[\text{H}^+]^{-1}$ is found to be linear with a definite intercept (Fig. 4). There was no significant reaction in the absence of TsOH. The dependence of the reaction rate on the concentration of dimethyl sulfide was studied at three differ-

Table 4. Dependence of the reaction rate on hydrogen-ion concentration

[Dimethyl sulfide] = 0.01 mol dm ⁻³ , [BIDC] = 0.001 mol dm ⁻³ , T = 288 K							
$[\text{H}^+]$ (mol dm ⁻³)	0.05	0.1	0.2	0.3	0.4	0.5	
$10^2 k_{\text{obs}}$ (s ⁻¹)	2.41	4.51	8.89	13.0	16.9	20.5	

ent Cr^{VI} species^{5,11}. Quite likely, the protonation of BIDC facilitates the intermolecular coordination from the substrate to the oxidant, resulting in an enhanced reactivity.

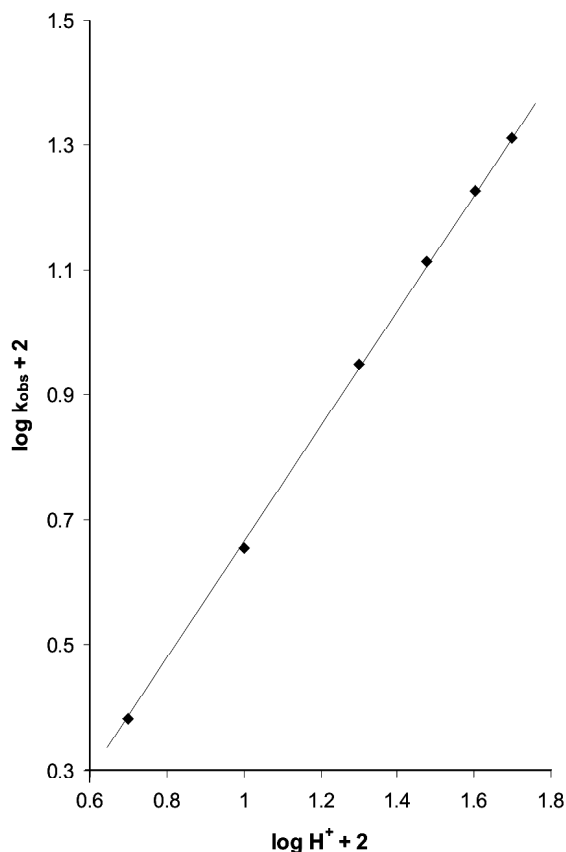


Fig. 3. A plot of $\log k_{\text{obs}}$ vs $\log [\text{H}^+]$: $[\text{BIDC}] = 0.001 \text{ mol dm}^{-3}$, $[\text{Me}_2\text{S}] = 0.01 \text{ mol dm}^{-3}$; $T = 288 \text{ K}$.

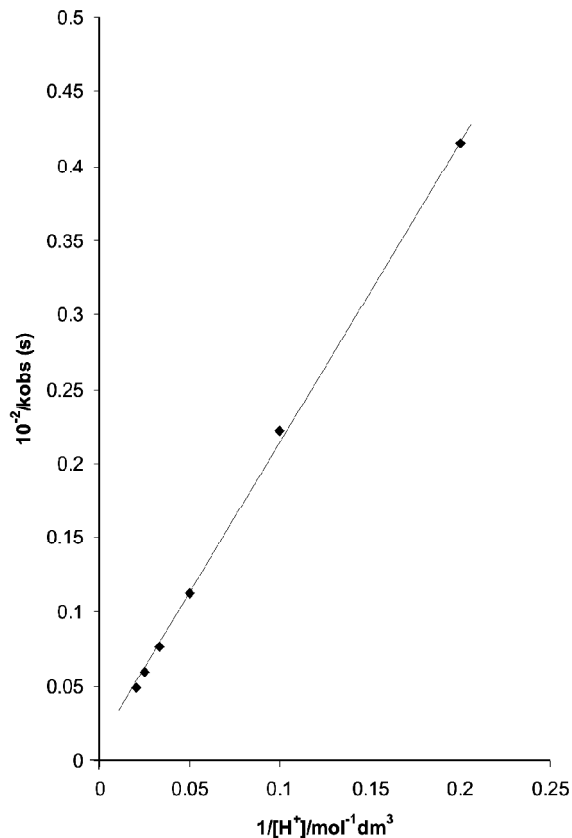


Fig. 4. A plot of $1/k_{\text{obs}}$ vs $1/[\text{H}^+]$: $[\text{BIDC}] = 0.001 \text{ mol dm}^{-3}$, $[\text{Me}_2\text{S}] = 0.01 \text{ mol dm}^{-3}$; $T = 288 \text{ K}$.

Further, the dependence on hydrogen-ion concentration indicates that the equilibrium between BIDC and (A) is rapid, that the equilibrium constant, K_1 , is small and the reaction is not complete even at higher concentrations of hydrogen-ion because no leveling of rate constants took place at higher concentrations of hydrogen-ion. No significant oxidation in the absence of TsOH indicates that only the protonated BIDC (A) acts as oxidizing species.

The oxidation of dimethyl sulfide by BIDC was studied in nineteen organic solvents. The solubility of the reactants and the reaction of BIDC with primary and secondary alcohols limited the choice of solvents. There was no reaction with the chosen solvents. The kinetics were similar in all the solvents. The values of the rate constant, k_2 , are recorded in Table 6.

The data recorded in Table 6 indicate that the equilibrium constant, K , is fairly insensitive to the change in solvent, however, k_2 , varies appreciably. Similar observations were found in the oxidation of sulfides by hexam-

Table 5. Dependence of rate constant on dimethyl sulfide concentration at different hydrogen-ion concentrations

[Sulfide] (mol dm^{-3})	[BIDC] = $0.001 \text{ mol dm}^{-3}$, $T = 288 \text{ K}$		
	$k_{\text{obs}} \times 10^2 \text{ (s}^{-1}\text{)}$		
	[H^+] (mol dm^{-3})		
	0.2	0.3	0.5
0.01	8.75	13.2	20.5
0.02	16.5	25.0	37.3
0.03	24.3	35.4	52.0
0.04	31.3	45.1	63.8
0.05	37.7	53.7	74.7
0.10	64.4	86.2	110
$K \text{ (mol dm}^{-3}\text{)}$	4.24	6.17	10.4
$10^2 k_{\text{obs}} \text{ (s}^{-1}\text{)}$	215	227	217

ethylenetetramine-bromine¹² and of methionine by BIDC⁵. The values of the rate constant of the decomposition of complexes, k_2 , in eighteen solvents (CS_2 was not considered as the complete range of the solvent parameters are not available) were first correlated in terms of linear sol-

Table 6. Effect of solvent on the oxidation of dimethyl sulfide by B IDC at 288 K

Solvent	K (mol dm ⁻³)	$k_{\text{obs}} \times 10^2$ (s ⁻¹)
Chloroform	8.97	61.2
1,2-Dichloroethane	10.1	71.0
Dichloromethane	7.91	68.8
DMSO	10.4	217
Acetone	10.0	58.2
Dimethylformamide	10.3	110
Butanone	9.36	43.1
Nitrobenzene	8.62	81.9
Benzene	10.4	20.0
Cyclohexane	8.82	1.86
Toluene	11.5	16.2
Acetophenone	10.3	86.1
Tetrahydrofurane	7.93	28.9
Tetra-Butyl alcohol	9.65	25.3
Dioxane	9.59	30.1
1,2-Dimethoxyethane	8.96	16.4
Acetic acid	11.4	13.1
Ethyl acetate	10.3	23.5
Carbon disulfide	9.97	7.80

Table 7. Stoichiometry of the oxidation of dimethyl sulphide by B IDC

10 ³ [B IDC] (mol dm ⁻³)	10 ³ [Sulfide] (mol dm ⁻³)	10 ³ [Residual B IDC] (mol dm ⁻³)	[Sulfide]/ [Consumed B IDC]
5.0	1.0	4.37	1.59
5.0	2.0	3.66	1.49
5.0	3.0	3.07	1.55
Mean = 1.54 ± 0.05			

vation energy relationship (LSER) of Kamlet *et al.*¹³. But the correlations were insignificant.

The data on solvent effect were then analysed in terms of Swain's eq. (8), where A represents the anion-solvating power of the solvent and B the cation-solvating power; C is the intercept term, and $(A + B)$ is postulated to represent the solvent polarity¹⁴.

$$\log k = aA + bB + C \quad (8)$$

The results of the correlation analyses in terms of eq. (8), individually with A and B , and with $(A + B)$ are given below.

$$\log k_2 = 0.81 \pm 0.01 A + 1.78 \pm 0.01 B - 2.14 \quad (9)$$

$$R^2 = 0.9996, \text{ sd} = 0.01, n = 19, \psi = 0.02$$

$$\log k_2 = 0.56 \pm 0.59 A - 0.64 \quad (10)$$

$$r^2 = 0.0501, \text{ sd} = 0.47, n = 19, \psi = 1.0$$

$$\log k_2 = 1.72 \pm 0.14 B - 1.60 \quad (11)$$

$$r^2 = 0.8945, \text{ sd} = 0.16, n = 19, \psi = 0.33$$

$$\log k_2 = 1.46 \pm 0.12 (A + B) - 1.83 \quad (12)$$

$$r^2 = 0.8900, \text{ sd} = 0.17, n = 19, \psi = 0.34$$

The data on solvent effect showed an excellent correlation in terms of Swain's eq. (9) with both anion- and cation-solvating powers contributing to the observed solvent effect. However, the role of cation-solvation is major, it alone accounts for *ca.* 89% of the data. There is no significant collinearity between A and B for the nineteen solvents ($r^2 = 0.0108$; $\text{sd} = 0.27$). The solvent polarity, represented by $(A + B)$ accounted for *ca.* 89% of the data. In view of the fact that *ca.* 89% of the data is accounted by $(A + B)$, an attempt was made to correlate the data with the relative permittivity of the solvents. A plot of $\log k_2$ against the inverse of relative permittivity, however, is not linear ($r^2 = 0.5533$).

The solvent effect leads to the conclusion that the transition state is more polar than the reactants. The increased polarity of the transition state is facilitated by an increase in the ionizing power of the solvent. Further, the fact that both cation- and anion-solvating powers of the solvents play important roles, suggests that a moderate degree of charge separation takes place during the rate-determining step. Thus, a nucleophilic attack of sulfur on electrophilic B IDC, resulting in the development of partial positive charge on sulfur atom and partial negative on oxygen atom, in the transition state of rate-determining step, is postulated.

B IDC seems to be an ionic compound as a result of proton transfer. To find out the state of B IDC in our reaction conditions, conductivity measurements have been carried out at 308 K. It was observed that the conductance values for DMSO, 0.001 mol dm⁻³ and 0.01 mol dm⁻³ solutions of B IDC in DMSO are found to be 3.4 ± 0.1 , 3.4 ± 0.1 and 3.5 ± 0.1 μmho respectively. This indicates that the addition of B IDC in DMSO shows negligible change in the conductivity value. Therefore, B IDC can be considered to be remained as non-ionised under our reaction conditions and does not dissociate as dichromate and benzimidazolium ions⁵. Further, the parent compound benzimidazole was added which is supposed to be present as benzimidazolium ion in the presence of pro-

tons. It is observed that there is no effect of added benzimidazole on the rate of oxidation. This also supports the postulation that B IDC remains as non-ionised⁵. The crystal structure study of B IDC, reported by Meng *et al.*¹⁵ supports the non-ionic nature of the oxidant in the reaction system. The dichromate ion connects two benzimidazolium rings via hydrogen bonds. With the effective hydrogen donor (N-H) and hydrogen acceptor (O) in the molecule, B IDC forms a number of hydrogen bonds. Furthermore, an intermolecular hydrogen bridge is remarkably formed between two neighboured dichromate ions. The molecules are then linked into infinite chains by these hydrogen bridges which controlled the releasing process of dichromate ions in the reaction system and thus the compound is considered to behave as non-ionic in our reaction system¹⁵.

Mechanism : The acid-catalysis is accounted in terms of prior-protonation of B IDC to give B IDC-H⁺. The formation of a cation is supported by the major role of the cation-solvating power of the solvent. The Michaelis-Menten type kinetics with respect to sulfide leads us to suggest the formation of a 1 : 1 complex by a nucleophilic attack of sulfide-sulfur on B IDC-H⁺ in a rapid pre-equilibrium. The complex then undergoes a rate-determining oxygen atom transfer from oxidant to sulfide to give corresponding sulfoxide (Scheme 1). Thus, the reaction scheme involves the formation of a complex (B) by the coordination of sulfur to electron-deficient chromium in a rapid equilibrium. It is then followed by unimolecular decomposition of the ion-pair to give the products due to the transfer of the second electron to the oxidant via transition state shown in the Scheme 1. The similar type of mechanism involving oxygen atom transfer in the rate-determining step is also suggested for the oxidation of sulfides by pyridinium chlorochromate¹² and of methionine by B IDC⁵. The solvent effect supports an S_N2-like transition state. The observed high negative entropy of activation further supports a cyclic transition state⁵. As the ΔS[‡] value is not exactly associated with the rate-determining step, no definite conclusions can be drawn from it.

Applying the equilibrium treatment, Cr^{VI} can be determined :

$$\begin{aligned} -d[\text{Cr}^{\text{VI}}]/dt &= k_2 [\text{B}] \\ &= k_2 K_1 K_2 [\text{R}_2\text{S}] [\text{Cr}^{\text{VI}}] [\text{H}^+] \end{aligned} \quad (13)$$

or,

$$-d[\text{Cr}^{\text{VI}}]/dt = \frac{k_2 K_1 K_2 [\text{R}_2\text{S}] [\text{Cr}^{\text{VI}}]_t [\text{H}^+]}{1 + K_1 [\text{H}^+] + K_1 K_2 [\text{R}_2\text{S}] [\text{H}^+]}$$

or,

$$k_{\text{obs}} = \frac{k_2 K_1 K_2 [\text{R}_2\text{S}] [\text{H}^+]}{1 + K_1 [\text{H}^+] + K_1 K_2 [\text{R}_2\text{S}] [\text{H}^+]}$$

Here, $[\text{Cr}^{\text{VI}}]_t = [\text{Cr}^{\text{VI}}] + [\text{A}] + [\text{B}]$

Since, K_1 is supposed to be small, therefore neglecting K_1 , we get

$$k_{\text{obs}} = \frac{k_2 K_1 K_2 [\text{R}_2\text{S}] [\text{H}^+]}{1 + K_1 K_2 [\text{R}_2\text{S}] [\text{H}^+]} \quad (14)$$

or,

$$k_{\text{obs}}^{-1} = 1/k_2 K_1 K_2 [\text{R}_2\text{S}] [\text{H}^+] + 1/k_2 \quad (15)$$

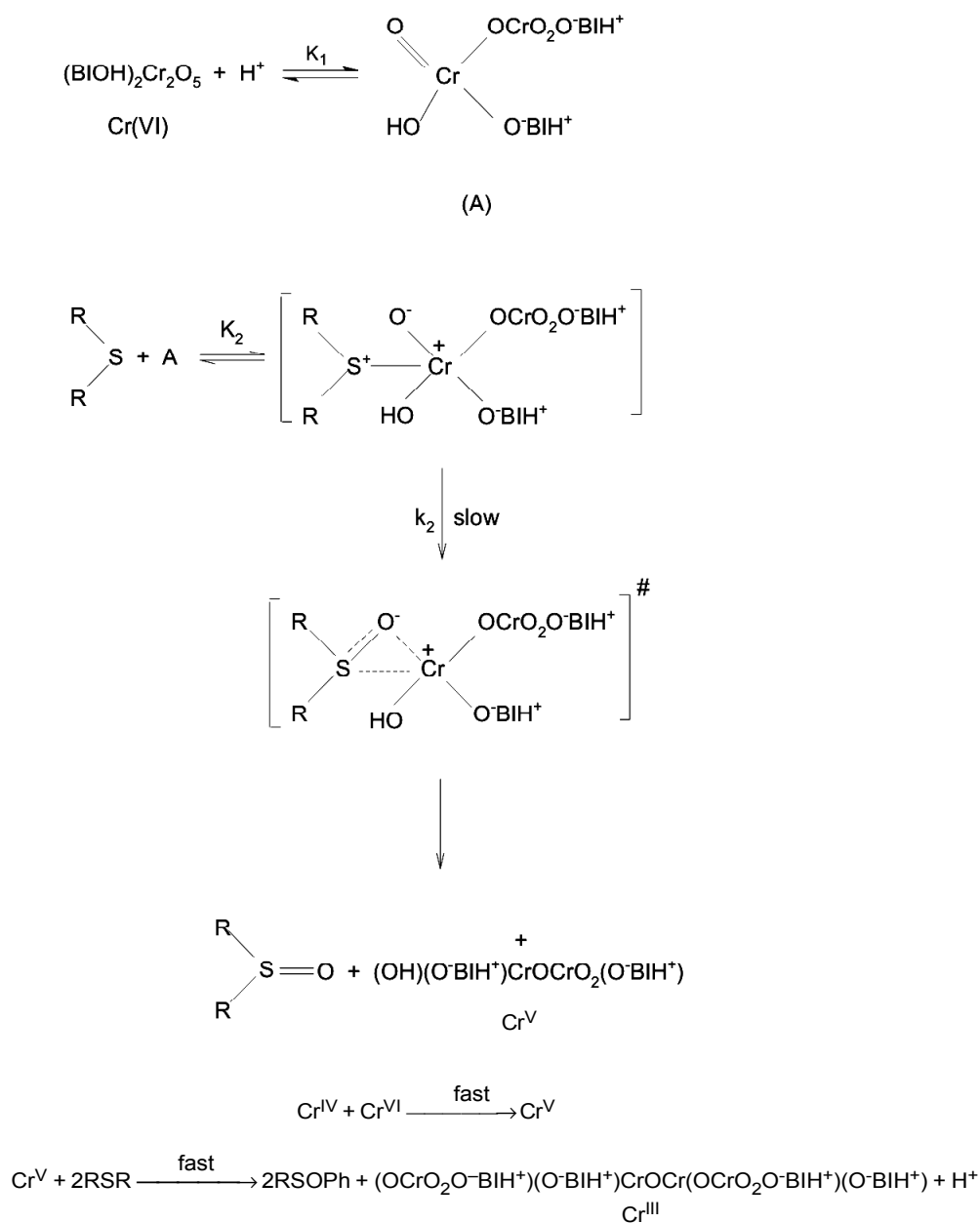
The eqs. (14) or (15) characterise the reaction system well.

Comparing eqs. (4) and (14), we get $K = K_1 K_2 [\text{H}^+]$.

Initially Cr^{VI} is reduced to Cr^{IV}. It is likely to react with another Cr^{VI} to generate Cr^V which is then reduced in a fast step to the ultimate product Cr^{III}. Such a sequence of reactions in Cr^{VI} oxidations is well known¹⁶.

It is of interest here to compare the kinetics of the oxidation of organic sulfides by other dichromate complexes. It is observed that the oxidation of sulfides by butyltriphenylphosphonium dichromate (BTPPD)¹⁷ reported a different kinetics i.e. the reactions are of first order with respect to the oxidant, however, the order with respect to each the sulfide and hydrogen ion is two. Further, the mechanism involved is the rate-determining electrophilic attack of BTPPD-oxygen to electron-rich sulfur to produce the corresponding sulfoxide via an S_N2 type transition state. The doubly protonated BTPPD is the active electrophile. The kinetics of the oxidation of diethyl sulfide by pyridinium dichromate (PDC)¹⁸ in acetonitrile, exhibited first order kinetics with respect to each PDC and sulfide and of second order dependence on TsOH. In case of aryl methyl sulfides, the order with respect to TsOH is greater than 1 and smaller than 2, while Michaelis-Menten type kinetics were observed with respect to the sulfide. A non-linear Hammett plot was obtained with both electron-donating and electron-with-

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Scheme 1. Mechanism of oxidation of sulfides by BDC.

drawing groups slowing down the rate of reaction. The reaction was retarded by acrylonitrile, thereby indicating a one-electron oxidation giving rise to free radicals. The nicotinium dichromate (NDC) oxidation¹⁹ of sulfides, in acetonitrile, brought about by TsOH, is first order in NDC and TsOH, and is zero order with respect to sulfide in the concentration range investigated. A mechanism involving TsOH catalysed rate-limiting decomposition of the NDC-sulfide complex is postulated. The zero order

dependence on sulfide concentration is accounted in terms of high formation constant of NDC-sulfide complex. Karunakaran *et al.*²⁰ reported the kinetics of oxidation of diphenyl sulfide by imidazolium dichromate (IDC) in acetonitrile, in the presence of TsOH. The product formed is corresponding sulfoxide. The reactions are of first order with respect to each the oxidant and reductant. Rate dependence on TsOH is of Michaelis-Menten type. The oxidizing species is suggested to be IDC-TsOH complex.

The oxidation of some alkyl phenyl sulfides by cetyltrimethyl dichromate (CTADC) in dichloromethane-AcOH (80 : 20 v/v) was reported by Stayanarayana *et al.*²¹. The reaction exhibited overall second order kinetics, first order in both the sulfide and CTADC. The oxidizing species is suggested to be diprotonated CTADC. The rate increases with an increase in donating power of substituent and the reaction exhibited steric hindrance. The mechanism involves a bimolecular reaction of sulfide and protonated oxidant to give the corresponding sulfoxide, as a slow step. Thus, it is observed that the kinetics and mode of oxidation depends on the nature of the oxidant.

Experimental

Materials : B IDC was prepared by the reported method³ and its purity was checked iodometrically and melting point determination. The extra pure methyl sulfide, phenyl sulfide and propyl sulfide (Acros Organics/Aldrich) were used as such after their physical constants have been checked. The solvents were purified by the reported methods²². *p*-Toluenesulphonic acid (TsOH) was used as a source of hydrogen ions. The solutions of TsOH prepared were standardized before use by titrating them against standard alkali.

Product analysis : Diphenyl sulfide (0.01 mol) and B IDC (0.01 mol) were dissolved in DMSO (50 ml) and the mixture was allowed to stand for approximately 24 h in the presence of 0.5 M TsOH. Most of the solvent was removed under reduced pressure. The residue was diluted with water and extracted with chloroform (3 × 50 ml). The chloroform layer was dried over anhydrous MgSO₄ and the solvent was removed by evaporation and the residue was analysed by IR and ¹H NMR spectroscopy. The spectra were identical with those of PhSOPh. Peaks characteristic of PhSPh and PhSO₂Ph could not be detected. Similar experiments were performed with other sulfides also. In all cases, the products were the corresponding sulfoxide only.

Stoichiometry : The excess of B IDC was allowed to react with dimethyl sulfide in DMSO in the presence of 0.5 mol dm⁻³ TsOH. The reaction was allowed to stand for 24 h to ensure the completion of the reaction. An analysis of the residual B IDC showed that the reaction exhibited 2 : 3 stoichiometry i.e. two moles of oxidant

reacts with 3 moles of the sulfide (Table 7). The experiment was repeated with other sulfides also and the results were same. The 2 : 3 stoichiometry was also observed in the oxidation of methionine by B IDC⁵.

Kinetic measurements : Pseudo-first order conditions were attained by keeping a large excess (×10 or greater) of sulfides over the oxidant. The reactions were carried out in the temperature range of 278–308 K. All the solutions were kept in a thermostat at a constant temperature with an accuracy of ±0.1 K. Lower than the ambient temperature was obtained with the refrigerated bath circulator. The solvent was DMSO, unless stated otherwise. The Beer's law is valid for B IDC within the concentration range used in our experiments. The reactions were followed by monitoring the decrease in the concentration of B IDC at 364 nm. The pseudo-first order rate constant, *k*_{obs}, was evaluated from the linear (*r*² > 0.995) plots of log [B IDC] versus time. Duplicate kinetic runs showed that the rate constants were reproducible to within ±3%. In correlation analyses, we have used coefficient of determination (*R*² or *r*²), standard deviation (*sd*) and Exner's parameter²³, *ψ*, as the measures of the goodness of fit. The correlation coefficient *r*², representing a degree of fitness of the correlation, gives the fraction of the variation of log *k*, which is explained by the regression equation²⁴.

Conclusion

The oxidation of dimethyl-, dipropyl- and diphenyl sulfides by benzimidazolium dichromate (B IDC) in dimethyl sulfoxide, to the corresponding sulfoxides, is first order with respect to B IDC. Michaelis-Menten type kinetics were observed with respect to sulfide. The reaction is catalysed by hydrogen ions and the order is less than one. It appears that the B IDC-H⁺ is the active electrophile. An intermediate of composition Sulfide-B IDC-H⁺ has envisaged. The oxidation of sulfides, in an atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. The rate of oxidation of sulfide was determined in 19 organic solvents. An analysis of the solvent effect by Swain's equation indicated that though both the anion- and cation-solvating powers of the solvent contribute to the observed solvent effect, the role of cation-solvation is major. A mechanism involving a rate-determining oxygen atom transfer from oxidant to sulfide to give corresponding sulfoxide is postulated.

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