

Kinetics and mechanism of oxidation of dimethyl sulphoxide by sodium bromate–sodium bisulphite reagent in aqueous medium

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Abstract. Rates of oxidation of dimethyl sulphoxide (DMSO) by HOBr produced *in situ* from sodium bromate-sodium bisulphite reagent have been studied iodometrically in aqueous medium. The order in [DMSO] is one when [DMSO] < 0.01 mol dm⁻³, fractional when [DMSO] is between 0.01 and 0.5 mol dm⁻³ and zero when (DMSO) > 0.5 mol dm⁻³. Different rate laws are operative under these three conditions though HOBr is the effective oxidizing species in all the cases. A mechanism involving an intermediate four-membered cyclic transition state between DMSO and HOBr (formation constant *K*), which decomposes in a slow step with a rate constant (*k*) has been proposed. Thermodynamic parameters for the adduct formation step and activation parameters for the first-order decomposition of the adduct step have been evaluated in the temperature range 308–323 K. Activation parameters have also been determined while the orders in [DMSO] are unity and zero. The reaction product has been identified as dimethyl sulphone (DMSO₂).

Keywords. Oxidation of DMSO; sodium bromate–sodium bisulphite reagent.

1. Introduction

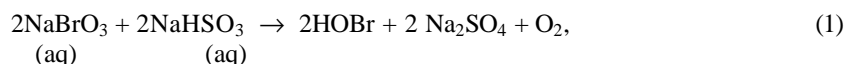
Kinetic studies on the oxidation of DMSO by a number of N-halo compounds like bromamine-T¹, bromamine-B², chloramine-T³, chloramine-B⁴, N-bromosuccinamide⁵, N-chlorosuccinamide⁶, and N-bromoacetamide^{6–8} have already been reported. Oxidation of DMSO in aqueous medium also has been reported from our laboratory in which HOBr was established as effective oxidizing species⁸. Oxidation of DMSO by sodium bromate–sodium bisulphite reagent in aqueous medium has not reported in literature so far. HOBr was found to be easily generated *in situ* from NaBrO₃ in the presence of appropriate reducing agent like NaHSO₃ in aqueous medium⁹. Hence we thought it worthwhile to undertake the title investigation with focus on the elucidation of the mechanism of its reaction.

2. Materials and methods

All the chemicals used were of AR grade. NaBrO₃ and NaHSO₃ used in this study were BDH. DMSO (E Merck) was distilled and used. All the aqueous solutions were prepared in double-distilled water. The reaction between DMSO and sodium bromate–sodium bisulphite reagent was studied in aqueous medium. In the kinetic study, aqueous solutions

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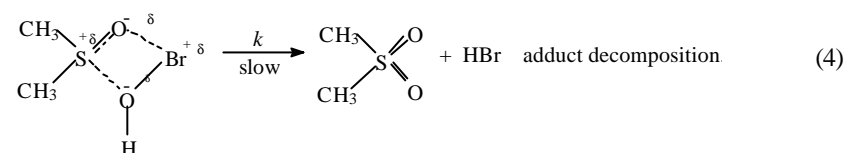
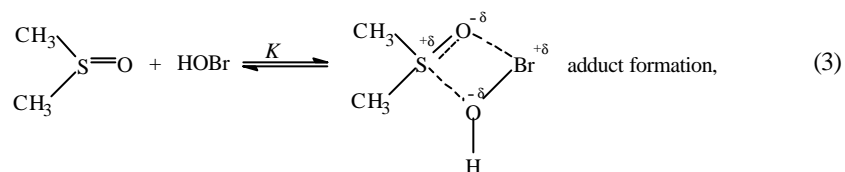
of NaBrO_3 and NaHSO_3 were allowed to react together for two hours to generate HOBr completely first (step 1), and then kinetic run started with substrate DMSO . The course of the reaction was followed by estimating the unreacted HOBr iodometrically at regular intervals of time. The reaction product was identified as dimethyl sulphone. To see the effect of dissolved oxygen on the rates, nitrogen gas was bubbled through the reaction mixture to expel dissolved oxygen and the reaction studied. It was found that there was no effect of oxygen on the rate. The stoichiometry was determined to be 1:1 ($\text{DMSO}:\text{HOBr}$) in accordance with (2) below



3. Results and discussions

Under the conditions $[\text{DMSO}] \gg [\text{HOBr}]$, the plots of $\log[\text{HOBr}]$ versus time are linear indicating first-order dependence on $[\text{HOBr}]$. From the slopes of such plots, the pseudo-first order rate constants (k_{obs}) have been evaluated at different initial $[\text{DMSO}]$. The order in $[\text{DMSO}]$ is fractional when $[\text{DMSO}]$ is between 0.01 and 0.5 mol dm^{-3} . A fractional order in $[\text{DMSO}]$ points to the formation of an intermediate adduct between DMSO and HOBr (step 3). This fact is further supported by the linearity of $1/k_{\text{obs}}$ versus $1/[\text{DMSO}]$ plot with finite intercepts. This adduct decomposes in a rate-determining step to yield the product DMSO_2 .

In this study HOBr has been well established to be the only effective oxidizing species⁸⁻¹⁰. This is further supported by the fact that HOBr in aqueous solution is a weak acid ($K_a = 2 \times 10^{-9}$ at 25°C)^{10a}. Water is relatively a much weaker acid than HOBr (self ionization constant of water = 1×10^{-14} at 25°C)^{10b}. Hence protonation of HOBr (i.e. formation of H_2OBr^+) is ruled out. The rates remain unaffected by added Na_2SO_4 salt indicating that reaction may involve two dipoles, i.e. DMSO and HOBr . Based on the product analysis, experimental observations, stoichiometry and foregoing discussions, the mechanism shown in scheme 1 is proposed for the oxidation of DMSO by sodium bromate-sodium bisulphite reagent in neutral medium at $[\text{DMSO}] > 0.01 \text{ mol dm}^{-3}$ and $< 0.5 \text{ mol dm}^{-3}$.



Scheme 1.

Scheme 1 leads to the rate law,

$$\text{rate} = \frac{kK[\text{DMSO}][\text{HOBr}]}{1 + K[\text{DMSO}]}, \quad (5)$$

or

$$\frac{-2 \cdot 303d \log[\text{HOBr}]}{dt} = k_{\text{obs}} = \frac{kK[\text{DMSO}]}{1 + K[\text{DMSO}]}, \quad (6)$$

where k_{obs} is the observed pseudo-first order rate constant, k the first order rate constant for the decomposition of the adduct, and K the formation constant of the adduct.

Table 1. Order in [DMSO] in DMSO-HOBr reaction.

[NaBrO₃] = 1.00 × 10⁻³ mol dm⁻³; [NaHSO₃] = 2.00 × 10⁻³ mol dm⁻³; [DMSO] = 0.03-0.5 mol dm⁻³; temp. = 313 K

[DMSO] (mol dm ⁻³)	$k_{\text{obs}} \times 10^2 \text{ min}^{-1}$	2 + log[DMSO]	2 + log k_{obs}	1/[DMSO]	1/ k_{obs}
0.030	1.23	0.477	0.090	33.3	66.8
0.050	1.50	0.700	0.176	20.0	62.0
0.080	1.69	0.903	0.228	12.5	57.9
0.100	1.84	1.00	0.265	10.0	49.0
0.200	2.23	1.30	0.348	5.00	43.0
0.300	2.53	1.48	0.403	3.33	41.1
0.400	2.76	1.60	0.441	2.50	39.5
0.500	3.00	1.70	0.477	2.00	37.5

Table 2. Effect of [DMSO] on k_{obs} in DMSO-HOBr reaction when [DMSO] > 0.5 mol dm⁻³.

[NaBrO₃] = 1.00 × 10⁻³ mol dm⁻³; [NaHSO₃] = 2.00 × 10⁻³ mol dm⁻³; temp. = 313 K

[DMSO] (mol dm ⁻³)	0.60	0.70	0.80	0.90	1.00
$k_{\text{obs}} \times 10^2$	3.07	3.15	3.11	3.19	3.07

Table 3. Effect of [DMSO] on k_{obs} in DMSO-HOBr reaction when [DMSO] < 0.01 mol dm⁻³.

[NaBrO₃] = 1.00 × 10⁻³ mol dm⁻³; [NaHSO₃] = 2.00 × 10⁻³ mol dm⁻³; temp. = 313 K

[DMSO] (mol dm ⁻³)	$k_{\text{obs}} \times 10^3 \text{ (min}^{-1}\text{)}$	3 + log[DMSO]	3 + log k_{obs}
0.007	8.55	0.845	0.936
0.008	9.54	0.903	0.982
0.009	10.9	0.954	1.00
0.010	11.8	1.00	1.07

Table 4. Thermodynamic and activation parameters in HOBr–DMSO reaction under different conditions of the reactivity of DMSO. Units of ΔH^\ddagger and ΔH are kJ mol^{-1} and of ΔS^\ddagger and ΔS are $\text{J K}^{-1} \text{mol}^{-1}$

Temp.	When order in [DMSO] is one				When order in [DMSO] is fractional				When order in [DMSO] is zero			
	$k'' \times 10^2$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	ΔH^\ddagger	ΔS^\ddagger	K ($\text{dm}^3 \text{mol}^{-1}$)	ΔH	ΔS	$k \times 10^4$ (s^{-1})	ΔH^\ddagger	ΔS^\ddagger	$k \times 10^4$ (s^{-1})	ΔH^\ddagger	ΔS^\ddagger
308	1.80			18.4			4.08			4.48		
313	2.04	17.2	-225	23.8	50.0	-60.0	4.70	15.6	-261	5.12	15.8	-260
318	2.27			36.0			5.17			5.63		
323	2.59			46.0			5.70			6.27		

Equation (5) accounts for the first-order dependence of rate on [HOBr] and fractional order dependence on [DMSO].

Taking the reciprocal of (6) at constant [DMSO],

$$\frac{1}{k_{\text{obs}}} = \frac{1}{kK[\text{DMSO}]} + \frac{1}{k}. \quad (7)$$

A plot of $1/k_{\text{obs}}$ versus $1/[\text{DMSO}]$ is linear, the slope of which is equal to $1/kK$ and the intercept equal to $1/k$. The ratio of intercept to slope gives the value of K and the reciprocal of intercept gives the value of k .

At $[\text{DMSO}] > 0.5 \text{ mol dm}^{-3}$ a zero order dependence in [DMSO] is observed, which may be explained as follows: When $[\text{DMSO}] \gg [\text{HOBr}]$, $[1 + K[\text{DMSO}]] \approx K[\text{DMSO}]$. Hence (5) can be rewritten as

$$\text{rate} = k[\text{HOBr}], \quad (8)$$

which explains the zero-order dependence on [DMSO]. At $[\text{DMSO}] < 0.01 \text{ mol dm}^{-3}$, a first-order dependence on [DMSO] is observed. When $1 + K[\text{DMSO}] \approx 1$, (5) reduces to,

$$\text{rate} = k''[\text{DMSO}][\text{HOBr}], \quad (9)$$

where $k'' = kK$, the second-order rate coefficient. All the results are tabulated in tables 1-3.

4. Effect of temperature

The reaction rates of oxidation of DMSO increase with increase in temperature and the values of K and k also increase with temperature. Thermodynamic parameters for the adduct formation (step 3) and the activation parameters for the decomposition of the adduct (step 4) were evaluated from Eyring plots, when order in [DMSO] is fractional. Also the activation parameters were determined for the other two conditions, i.e. when order in [DMSO] is zero and one and are tabulated in table 4. The negative ΔS^\ddagger for all the three conditions is due to the strong solvation of HBr. The negative ΔS when order in [DMSO] is fractional is due to the formation of an ionic 4-membered cyclic transition state, which may be solvated to a greater extent.

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