

## Kinetics and mechanism of the oxidative regeneration of carbonyl compounds from oximes by tetrabutylammonium tribromide

Ashok Kumar, Kirti Choudhary, Pradeep K. Sharma & Kalyan K Banerji\*

Department of Chemistry, J.N.V. University, Jodhpur 342 005, India

Received 3 October 2000; revised 10 November 2000

The oxidative deoxygenation of several aldo- and keto-oximes by tetrabutylammonium tribromide (TBAT) in 1:1 (v/v) acetic acid-water exhibits a first order dependence on each the oxime and TBAT. The oxidation of ketoximes is slower than that of aldoximes. The rates of oxidation of aldoximes correlate well in terms of Pavelich-Taft dual substituent-parameter equation. The low positive value of polar reaction constant indicates a nucleophilic attack by a tribromide ion on the carbonyl carbon. The reaction is subject to steric hindrance by the alkyl groups. A mechanism involving the formation of a cyclic activated complex in the rate-determining step has been proposed.

Regeneration of carbonyl compounds from their derivatives under mild conditions is an important process in synthetic organic chemistry. Several oxidative methods are available for deoxygenation<sup>1</sup>. Tetrabutylammonium tribromide (TBAT) has been reported as a useful reagent for the formation of carbonyl compounds from the corresponding alcohols<sup>2</sup>. There seems to be no report about the kinetics and mechanism of oxidative deoxygenation by a polyhalogen derivative. We report here the kinetics of the oxidative deoxygenation of several aldo- and keto-oximes by TBAT in 1:1 (v/v) acetic acid-water. Mechanistic aspects are discussed.

### Materials and Methods

Oximes were prepared by the reported standard methods and their mps were checked with the literature values. TBAT also was prepared by the reported method<sup>2</sup>. Acetic acid was refluxed with CrO<sub>3</sub> and acetic anhydride for 6 h and then fractionated.

### Product analysis

The oxidation of the oximes results in the regeneration of corresponding carbonyl compounds, as confirmed by TLC (eluent: CCl<sub>4</sub>/Et<sub>2</sub>O). Isolation of the product was attempted in the oxidation of oximes of benzaldehyde and acetophenone. In a typical experiment, the oxime (0.2 mol), KBr (0.2 mol) and TBAT (0.04 mol) were dissolved in 50 ml of 1:1 (v/v) acetic acid-water and allowed to stand for ca. 10 h for the completion of the reaction. Silica gel (5 g) was then added to the reaction mixture and the mixture

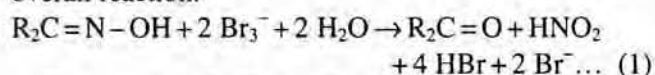
was stirred<sup>3</sup> for 15 min. It was then filtered and the solid residue was washed with the solvent (2 × 15 ml). The solvent was removed on a rotary evaporator and the residue was purified on a silica-gel column (eluent: CCl<sub>4</sub>/Et<sub>2</sub>O). Evaporation of the solvent afforded the pure carbonyl compound. Yields of benzaldehyde and acetophenone were 1.82 g (86%) and 2.02 g (84%) respectively.

### Kinetics measurements

The reactions were studied under pseudo-first order conditions by keeping a large excess (× 10 or greater) of the oxime over TBAT. The solvent was 1:1 (v/v) acetic acid-water, unless mentioned otherwise. Tribromide ion is known to dissociate to a large extent to bromine and bromide ion. The value<sup>4</sup> of the dissociation constant, in 1:1 (v/v) acetic acid-water, is ca. 0.02 mol dm<sup>-3</sup>. To suppress the dissociation, all kinetic runs were carried out in the presence of an excess (0.2 mol dm<sup>-3</sup>) of potassium bromide. The reactions were studied at constant temperature (± 0.1 K). The reactions were followed by monitoring the decrease in [TBAT] at 394 nm spectrophotometrically. The pseudo-first-order rate constant,  $k_{\text{obs}}$ , was evaluated from the linear least squares plots of log [TBAT] versus time. Duplicate kinetic runs showed the rate constants to be reproducible within ± 4%. We have used coefficient of determination ( $R^2$  or  $r^2$ ), standard deviation (sd) and Exner's<sup>5</sup> parameter,  $\psi$ , as the measures of goodness of fit. The second order rate constant,  $k_2$ , was determined from the relation:  $k_2 = k_{\text{obs}} / [\text{oxime}]$ .

## Results

The analysis of products indicated the following overall reaction.



The reaction is first order with respect to TBAT. Individual kinetic runs exhibited first order kinetics. Further, the pseudo-first-order rate constant,  $k_{\text{obs}}$ , does not depend on the initial [TBAT]. The rate of reaction increases linearly with an increase in the concentration of the oxime (Table 1). An addition of tetrabutylammonium bromide (TBABr) had no effect on the rate of the oxidation (Table 1).

An increase in the amount of acetic acid, in the solvent mixture of acetic acid and water, increases the rate slightly. For example, under the conditions [TBAT] = 0.001 mol dm<sup>-3</sup>, [acetaldoxime] = 0.5 mol dm<sup>-3</sup>, [Br<sup>-</sup>] = 0.20 mol dm<sup>-3</sup>, Temperature = 298 K,  $10^4 k_{\text{obs}}$  increased from 26.7 to 54.5 s<sup>-1</sup> when % HOAc (v/v)

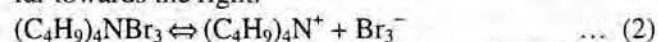
was increased from 30 to 80.

The rate constants were determined at different temperatures and the activation parameters were calculated (Table 2).

## Discussion

An isokinetic plot between enthalpies and entropies of activation of the oxidation of the eleven oximes is not linear ( $r^2=0.8206$ ,  $sd=3.7$  and  $\psi=0.32$ ). However, an Exner's plot<sup>6</sup> between  $\log k_2$  at 288 K and at 318 K is linear ( $r^2=0.9799$ ,  $\psi=0.11$ , slope =  $0.870 \pm 0.025$ ). The value of the isokinetic temperature is  $788 \pm 52$  K. A linear isokinetic relationship is a necessary condition for the validity of linear free energy relationships. It also implies that all reactions so correlated follow a similar mechanism<sup>6</sup>.

We have carried out some conductivity measurements to determine the nature of TBAT in aqueous acetic acid solution. It was observed that acetic acid has very low conductivity. Addition of TBAT increases the conductivity of acetic acid. The conductivity of TBAT was measured in solvents containing different proportions of acetic acid (100 - 30%) and water also. It was found that the conductivity increased sharply as the water content was initially increased but reached a limiting value in about 60% acetic acid-water mixture. Therefore, TBAT can be considered as an ionic compound, which exists under the present reaction conditions as tetrabutylammonium and tribromide ions [Eq. (2)]. That added tetrabutylammonium ion does not have any effect also indicates that the equilibrium (2) lies far towards the right.



Tribromide ion is known to dissociate to bromine and bromide ion and the value of the dissociation

Table 1—Rate constants for the oxidation of acetaldoxime by TBAT at 298 K

$10^3$ [TBAT] (mol dm <sup>-3</sup> )	[oxime] (mol dm <sup>-3</sup> )	$10^4 k_{\text{obs}}$ (s <sup>-1</sup> )
1.0	0.1	7.12
1.0	0.2	14.3
1.0	0.3	21.4
1.0	0.5	35.7
1.0	0.8	57.4
1.0	1.0	71.4
1.0	1.5	110
0.5	0.8	56.8
2.0	0.8	57.2
3.0	0.8	56.3
4.0	0.8	58.1
5.0	0.8	57.0
1.0	1.0	71.4*

\*Contained 0.01 mol dm<sup>-3</sup> TBABr

Table 2—Rate constants and activation parameters of the oxidation of oximes (R<sup>1</sup> R<sup>2</sup> C=N-OH) by TBAT

Substituent	$10^4 k_2$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )				$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	$\Delta S^\ddagger$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G^\ddagger$ (kJ mol <sup>-1</sup> )	
	288	298	308	318 K				
H	H	1250	1590	2140	3130	20.7 ± 1.1	-199 ± 5	77.5 ± 1.2
H	Me	40.3	71.4	127	225	41.1 ± 0.6	-148 ± 2	85.2 ± 0.5
H	Et	29.0	52.2	96.8	182	44.1 ± 1.0	-141 ± 3	86.0 ± 0.8
H	Pr	17.2	30.5	59.1	105	43.8 ± 0.9	-146 ± 3	87.3 ± 0.7
H	Pr <sup>1</sup>	9.97	20.9	40.1	81.6	50.4 ± 0.7	-128 ± 2	88.3 ± 0.6
H	ClCH <sub>2</sub>	136	206	330	460	28.2 ± 0.6	-183 ± 2	82.6 ± 0.5
H	Ph	233	372	506	937	33.5 ± 1.1	-160 ± 3	81.0 ± 0.9
Me	Me	10.1	16.3	27.8	45.0	36.3 ± 1.5	-176 ± 3	88.7 ± 2.0
Me	Et	8.32	13.3	22.0	37.0	36.2 ± 1.0	-178 ± 3	89.2 ± 0.8
Et	Et	5.32	9.17	15.8	26.2	38.7 ± 0.8	-173 ± 3	90.2 ± 0.6
Me	Ph	3.75	6.89	12.7	22.4	43.7 ± 0.6	-159 ± 1	90.8 ± 0.5

Table 3—Reaction constants for the oxidative deoxygenation of aliphatic aldoximes by TBAT<sup>a</sup>

Temp./K	$\rho^*$	$\delta$	$R^2$	sd	$\psi$
288	$0.72 \pm 0.03$	$0.91 \pm 0.03$	0.9988	0.03	0.03
298	$0.64 \pm 0.01$	$0.84 \pm 0.01$	0.9998	0.01	0.01
308	$0.54 \pm 0.02$	$0.78 \pm 0.01$	0.9995	0.02	0.02
318	$0.47 \pm 0.01$	$0.74 \pm 0.01$	0.9999	0.01	0.01

<sup>a</sup>No. of compounds = 6

constant has been reported<sup>4</sup>. However, in the presence of the large excess of bromide ion, the reaction will be suppressed. Thus in the present reaction the reactive oxidising species is the tribromide ion.

We could not find any report about the mechanism of the reaction between a C=N bond and a polyhalogen derivative. Olefinic bonds are not usually subject to a nucleophilic attack. However, carbon-nitrogen double bonds, being dipolar in nature, can be easily attacked by a nucleophile. The data in Table 2 show that the rate of oxidation of ketoximes is much less as compared to that of the aldoximes. The reason for the slower reaction of ketoximes must be steric. As the central carbon changes from a trigonal to a tetragonal state, the crowding around it increases. This increase in the steric crowding will be more in the case of ketoximes as compared to that in aldoximes. This observation is supported by the correlation analysis of the reactivity of the aliphatic aldoximes also. The rate of oxidation of the aliphatic aldehydes did not yield significant correlation separately with Taft's  $\sigma^*$  and  $E_s$  values. The rates were, therefore, correlated with Pavelich-Taft's<sup>7</sup> dual substituent-parameter [Eq. (3)].

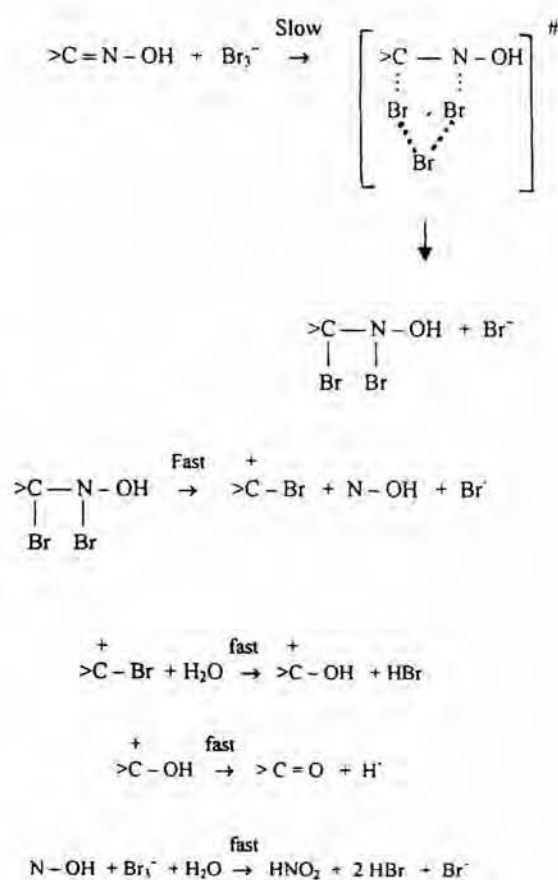
$$\log k_2 = \rho^* \sigma^* + \delta E_s + \log k_0 \quad \dots (3)$$

The rates exhibited excellent correlations in terms of the Pavelich-Taft equation (Table 3); the reaction constants are being positive.

The low positive polar reaction constant points to an almost cyclic transition state in which the formation of the bond between tribromide-bromine and the carbon is somewhat ahead of the formation of N-Br bond. This supports a nucleophilic attack by the tribromide ion on the carbon. The positive steric reaction constant points to a steric hindrance by the substituents. Therefore, the following mechanism (Scheme 1) is proposed for the reaction. The mechanism is supported by the values of activation parameters also. The low values of enthalpy of activation indicate that the bond-cleavage and bond-formation are almost synchronous. The large negative

entropies of activation support the formation of a rigid cyclic activated complex from two acyclic molecules.

The increase in the reaction rate with a decrease in the polarity of the solvent also supports a reaction involving a neutral species and an anion in the rate-determining step. As the oxime and a tribromide ion combine to form the activated complex, the charge density obviously decreases. Therefore, the formation of the activated complex is facilitated by a decrease in the polarity of the medium.



Scheme 1

Hydroxynitrene (N-OH) has been recently reported as a very reactive intermediate<sup>8</sup>.

**Acknowledgement**

Thanks are due to the CSIR, New Delhi, for the financial support.

**References**

- 1 Firouzabadi H & Sadarian A, *Synth Commun*, 13 (1983) 863; Drabowicz J, *Synthesis* (1980) 125; Hopkins P B, Kim S, Yoo S, Nambiar K P & Flack J R, *J Am chem Soc*, 101 (1979) 7131.
- 2 Choudhari M K, Khan A T & Patel B K, *Tetrahedron Lett*, 39 (1998) 8163
- 3 Baltork I M, Sadegi M M, Mahmoodi N & Kharamesh B, *Indian J Chem*, 36B (1997) 438
- 4 Bradfield A E, Jones B & Orton K J P, *J chem Soc*, 1929, 2810.
- 5 Exner O, *Collect Czech Chem Commun*, 31 (1966), 3222.
- 6 Exner O, *Prog phys org Chem*, 10 (1973) 411.
- 7 Pavelich W A & Taft R W, *J Am chem Soc*, 79 (1957) 4935.
- 8 Maier G, Reisenauer H P & Marco M D, *Angew Chem Int Ed*, 38 (1999) 108.