

Kinetics & Mechanism of Oxidation of Primary Alcohols by N-Bromo-3,5-dinitrobenzamide

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The oxidation of nine primary aliphatic alcohols by N-bromo-3,5-dinitrobenzamide (NBDNB) in acid solution results in the formation of corresponding aldehydes. The reaction is first order each in [oxidant] and [alcohol] and is catalysed by hydrogen ions. The observed hydrogen ion dependence of the reaction indicates that both NBDNB and its protonated form are reactive oxidising species. The value of primary kinetic isotope effect (k_H/k_D) in the oxidation of ethanol is 4.20 at 288 K. Addition of the parent amide does not affect the rate. The rates correlate well with Taft's σ^* substituent constants, ρ^* being -2.53 at 2.98 K. The activation parameters of the oxidation have been evaluated. A mechanism involving transfer of a hydride ion to the oxidant in the rate-determining step has been proposed.

We have tried a number of substituted N-halobenzamides as oxidants in the oxidation of organic compounds^{1,2} and found that N-bromo-3,5-dinitrobenzamide (NBDNB) is a very good oxidant, quite stable and easy to prepare. In this paper, we report the kinetics of oxidation of a series of primary alcohols by NBDNB in aqueous acetic acid solution, in the presence of perchloric acid.

Materials and Methods

Alcohols were commercial products and were purified by the usual methods. NBDNB was prepared by the bromination of 3,5-dinitrobenzamide by the reported method³. Perchloric acid was used as a source of hydrogen ions. $[1,1\text{-}^2\text{H}_2]$ Ethanol was prepared by Kaplan's method⁴.

Product analysis

In a typical experiment, a mixture of ethanol (2.3 g, 0.05 mol) and NBDNB (2.2 g, 0.01 mol) was made up to 100 ml in 1:1 (v/v) acetic acid-water, in the presence of 1.0 mol dm^{-3} perchloric acid. The reaction mixture was allowed to stand for nearly 12 hr, treated with an excess (250 ml) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 M HCl and kept in a refrigerator for nearly 10 hr. The precipitated 2,4-dinitrophenylhydrazone (DNP) of acetaldehyde was filtered, dried and recrystallized from ethanol. Its identity as the DNP of acetaldehyde was confirmed by m.p. and mixture melting point determination with an authentic sample, yield 92%; after recrystallization 84%. Similar experiments with other alcohols gave the DNP of the corresponding aldehydes in 81-88% yield after recrystallization. The overall reaction could be expressed by Eq. (1)



Kinetic measurements

The solvent used was always 1:1 (v/v) acetic acid-water. Lower than ambient temperatures were attained with the help of a Haake D-8G refrigerator bath circulator. The other experimental details were similar to those reported earlier¹.

Results

The reaction is first order each in [oxidant] and [alcohol]. The pseudo-first order rate coefficients do not vary with the initial [NBDNB]. The reaction is catalysed by perchloric acid (Table 1).

Table 1—Rate Constants for Oxidation of Ethanol and Propan-1-ol at 288 K

10^3 [NBDNB] (mol dm^{-3})	[Alcohol] (mol dm^{-3})	$[\text{H}^+]$ (mol dm^{-3})	$10^5 k_1$ (s^{-1})	
			EtOH	1-PrOH
1.0	0.10	0.20	36.0	64.1
2.0	0.10	0.20	32.0	63.5
3.5	0.10	0.20	34.5	62.5
5.0	0.10	0.20	33.7	63.5
7.5	0.10	0.20	34.2	63.0
10.0	0.10	0.20	34.8	63.8
5.0	0.05	0.20	17.0	31.7
5.0	0.20	0.20	69.0	128
5.0	0.30	0.20	103	190
5.0	0.10	0.05*	13.5	24.5
5.0	0.10	0.10*	20.5	37.5
5.0	0.10	0.20*	35.0	62.5
5.0	0.10	0.30*	48.0	89.3
5.0	0.10	0.40*	63.0	115
5.0	0.10	0.50*	77.2	142
5.0	0.10	0.60*	91.7	168
5.0	0.10	0.80*	120	220
5.0	0.10	1.00*	147	—

* $I = 1.0 \text{ mol dm}^{-3}$.

The oxidation of [1,1-²H₂]ethanol shows a substantial kinetic isotope effect. The value of k_H/k_D is 4.20 at 288 K. This is in contrast to the absence of kinetic isotope effect in the oxidation of ethanol by N-bromoacetamide¹.

The reaction has also been studied in acetic acid-water mixtures of different compositions. The rate increases with an increase in the proportion of acetic acid in the solvent system. In acetic acid-water mixtures containing 30, 40, 50, 60 and 70% acetic acid (v/v), the rate constants ($10^5 k_1$) are: 7.02, 10.1, 17.0, 27.5 and 42.3 s⁻¹ respectively at [NBDNB]=0.005 mol dm⁻³, [EtOH]=0.05 mol dm⁻³, [H⁺]=0.20 mol dm⁻³ and temp. = 288 K. The addition of reaction product 3,5-dinitrobenzamide does not affect the rate. In the presence of 3,5-dinitrobenzamide at the concentration of 0.0, 2.0, 4.0, 8.0, 10.0 and 12.5 × 10⁻³ mol dm⁻³, the rate constants ($10^5 k_1$) are: 33.7, 34.0, 33.2, 33.5, 33.9 and 34.5 s⁻¹ respectively at [NBDNB]=0.002 mol dm⁻³, [EtOH]=0.10 mol dm⁻³, [H⁺]=0.20 mol dm⁻³ and temp. = 288 K.

The rates of the oxidation of the primary alcohols were determined at different temperatures between 288 K and 318 K and the activation parameters were evaluated (Table 2). The error limits in the values of ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger (at 298 K) are ± 3 kJ mol⁻¹, ± 5 J mol⁻¹ K⁻¹ and ± 4 kJ mol⁻¹, respectively.

Discussion

The activation enthalpies and entropies of oxidation of nine alcohols are linearly related ($r=0.9974$; $\beta=544$ K). The correlation was tested and found genuine by applying Exner's criterion⁵. The linear correlation is a necessary condition for the validity of linear free energy relationships. It also implies that all the alcohols are oxidised by the same mechanism⁶.

Since the parent amide does not affect the rate, the possibility of hydrolysis and/or disproportionation of

NBDNB to yield the oxidising species is ruled out. This also precludes the formation of a hypobromite ester in a pre-equilibrium step. This is in sharp contrast to the retarding effect of the parent amide observed in the oxidations by N-bromoacetamide¹ and N-bromosuccinimide⁷. Thus the most probable oxidising species is NBDNB itself.

A plot of observed rate against [H⁺] is linear with a non-zero intercept, indicating that the pre-equilibrium between the protonated and unprotonated forms of the oxidant is rapid, the protonation constant is small and both the forms are reactive⁸. It is, therefore, suggested that NBDNB is protonated to give a stronger electrophile and oxidant (Eq. 2) and both ArCONHBr + H₃O⁺ \rightleftharpoons (ArCONH₂Br)⁺ + H₂O... (2) ArCONHBr and (ArCONH₂Br)⁺ are the reactive oxidising species. The above situation leads to the experimental rate law (3)

$$k_1 = k_2 + k_3 [H^+] \quad \dots (3)$$

The values of k_2 and k_3 , in the oxidation of ethanol were, 6.47×10^{-5} s⁻¹ and 1.41×10^{-3} dm³ mol⁻¹ s⁻¹ respectively at [EtOH]=0.10 mol dm⁻³, [NBDNB]=0.005 mol dm⁻³, $I=1.0$ mol dm⁻³ and temp. = 288 K. The specific rate constant, k , of the catalysed reaction was obtained from the relation $k = k_3 / [\text{alcohol}]$. The specific rate constant (k) was calculated at different temperatures and the activation parameters were evaluated.

The log k_1 varies linearly with the inverse of the dielectric constants of the solvent mixtures, with a positive slope, indicating interaction between a positive ion and a dipolar molecule in the rate-determining step⁹.

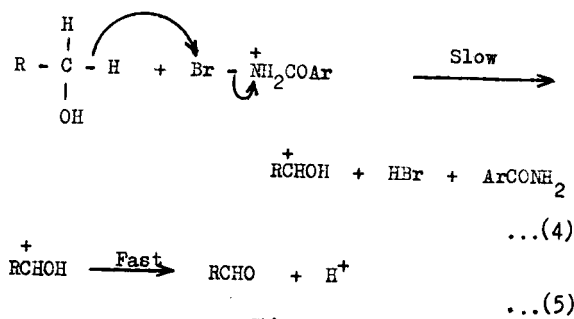
The presence of a substantial primary kinetic isotope effect confirms that the α -C-H bond is cleaved in the rate-determining step. The observed kinetic isotope effect is also rather large for the non-linear transition state implied in the ester mechanism.

The rates of the oxidation of nine primary alcohols correlate very well with Taft's σ^* substituent constants¹⁰ with negative reaction constants. The values of ρ^* at 288, 298, 308 and 318 K are -2.73 (0.9979), -2.53 (0.9993), -2.34 (0.9890) and -2.18 (0.9937) respectively (correlation coefficients are given in parentheses). This indicates that in the transition state of the reaction, the positive charge is highly localised at the carbon atom, to which the substituent R is attached. The carbon atom thus acquires a carbonium ion character. Therefore, a hydride ion transfer from the alcohol to the oxidant is proposed (see Schemes 1 and 2).

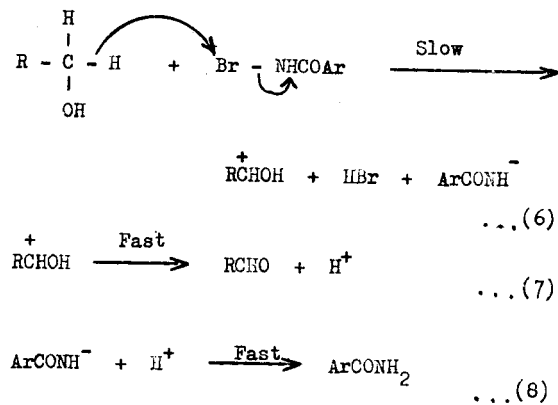
The observed negative entropy of activation also supports the above mechanisms. When two molecules combine to form a single activated complex, the

Table 2—Rate Constants and Activation Parameters for Oxidation of Primary Alcohols (RCH₂OH) by NBDNB

Substituent R	$10^5 k$ (dm ⁶ mol ⁻² s ⁻¹)				ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (J mol ⁻¹ K ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)
	288	298	308	318 K			
H	63.2	180	490	1200	75.0	-48.4	89.4
Me	1400	1350	6900	15000	61.5	-68.6	81.9
Et	2600	5670	12000	23500	56.1	-83.3	80.9
<i>n</i> -Pr	2840	6100	13000	26000	57.0	-79.7	80.7
<i>i</i> -Pr	4470	9600	19500	38000	54.3	-85.0	79.6
<i>n</i> -Bu	3200	6800	14000	27000	54.4	-87.7	80.5
MeCH-							
(OMe)CH ₂	5500	11500	23000	43600	52.5	-89.8	79.3
ClCH ₂	1.90	7.10	24.0	75.7	93.1	-14.5	97.4
MeOCH ₂	54.0	150	420	1030	75.1	-49.5	89.8



Scheme 1



Scheme 2

restrictions on their motion obviously increase, for they can no longer move independently¹¹. This results in a decrease in entropy.

Acknowledgement

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