130.4 (CH), 124.8 (CH), 82.1 (CH), 70.9 (CH_2), 68.4 (CH_2), 65.9 (C), 47.0 (CH), 45.8 (C), 43.2 (CH), 41.2 (CH), 39.3 (CH), 36.5 (CH), 34.6 (CH_2), 34.4 (CH_2), 28.0 (CH_2), 25.1 (CH_3), 21.3 (CH_3), 21.1 (CH_3), 20.9 (CH_3), 15.3 (CH_3), 13.1 (CH_3).

Diol 4, 5(*R*),16-Dihydroxyspata-13,17-diene. The diol 4 was isolated as an oil as 8.8% and 7.7% from *S. schmittii* and *S. howleii*, respectively. Diol 4 from the former source showed $[\alpha]_D$ +8.2° (*c* 1.05, $CHCl_3$), while 4 from the latter showed $[\alpha]_D$ + 7.3° (*c* 3.9, $CHCl_3$). The diol as isolated from *Steochospermum marginatum* showed $[\alpha]_D$ +6.3 (*c* 1.91, $CHCl_3$). The spectral features of the diols from *Spatoglossum* were superimposable with an authentic sample from *S. marginatum*.[21]

Triacetate Derivative 13 of Tetraol 5, 18-Hydroxy-5(*R*),15,19-triacetoxyspata-13,16(*E*)-diene. The triacetate derivative, 13 of the tetraol 5 was isolated as 1.0% of the *S. howleii* extract. Compound 13 showed $[\alpha]_D$ −51.2° (*c* 1.16, $CHCl_3$) in close comparison to the synthetic triacetate produced from the tetraol as isolated from *Stoechospermum marginatum*, $[\alpha]_D$ −36° (*c* 1.32, $CHCl_3$).[21] The spectral features of 13 were identical with those of the authentic derivative reported earlier.[21]

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Registry No. 1, 76520-52-0; 2, 86887-32-3; 3, 86887-34-5; 4, 77136-83-5; 5, 77136-60-8; 6, 77136-71-1; 7, 86887-30-1; 8, 77136-72-2; 9, 86887-31-2; 10, 86887-33-4; 11, 77136-70-0; 12, 86900-72-3.

Kinetics and Mechanism of the Oxidation of Alcohols by *N*-Bromoacetamide in Alkaline Solution

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The kinetics of the oxidation of seven secondary alcohols by *N*-bromoacetamide has been studied in alkaline solution. The main product of the oxidation is the corresponding ketone. The reaction is first order with respect to the oxidant and alcohol. The oxidation of benzhydrol-α-*d* indicates the absence of a primary kinetic isotope effect. The rate decreases with the increase in the concentration of hydroxide ion. Addition of acetamide decreases the reaction rate. The rates were determined at four different temperatures, and the activation parameters were evaluated. The activation enthalpies and entropies of the oxidation of the seven alcohols are linearly related. Hypobromite ion has been postulated as the reactive oxidizing species. A mechanism involving rate-determining nucleophilic attack of hypobromite ion on the alcohol molecule has been proposed.

Although many reports about the mechanism of the oxidations by *N*-halo amides like *N*-bromosuccinimide[1] and *N*-bromoacetamide[2] (NBA) in acid solution are available, there seems to be no report about the mechanism in alkaline solution. It is known, however, that the mechanisms of several redox reactions change with the changes in the reaction conditions, e.g., reactions of chloramine-T[3] and permanganate ion.[4] We now report the kinetics of the oxidation of several secondary alcohols by NBA in aqueous alkaline solution and discuss the mechanistic conclusions. For the purpose of comparison, the oxidation of some of the alcohols by hypobromite ion was also studied.

Experimental Section

Materials. All alcohols were commercial products (Fluka). They were dried over anhydrous magnesium sulfate and then fractionally distilled. Benzhydrol-α-*d*[5] and NBA[6] were prepared by reported methods. The isotopic purity of benzhydrol-α-*d* as ascertained by its NMR spectra was 94 ± 4%. While the effect of varying the concentration of sodium hydroxide on the reaction rate was studied, the ionic strength was kept constant at 0.20 M by using sodium perchlorate. Hypobromous acid was freshly prepared by the action of bromine on yellow mercuric oxide.[7] It was then neturalized by sodium hydroxide.

Product Analysis. In a typical experiment propan-2-ol (6.00 g, 0.1 mol), NBA (2.79 g, 0.02 mol), and sodium hydroxide (0.40 g, 0.01 mol) were made up to 100 mL in water. The mixture was kept for ca. 20 h in the dark to ensure completion of the reaction. It was then treated overnight with an excess (200 mL) of a saturated solution of 2,4-dinitrophenylhydrazine in 3 M HCl. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol, and weighed again. The product was identical (melting point and mixture melting point) with an authentic sample of the DNP of acetone. The yields of DNP before and after recrystallization were 4.0 (84%) and 3.5

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g (74%), respectively. Similar experiments with other alcohols yielded the DNP of the corresponding ketones in 70–80% yields after recrystallization.

Stoichiometry. Propan-2-ol (0.60 g, 0.01 mol), NBA (6.95 g, 0.05 mol), and sodium hydroxide (2.0 g, 0.05 mol) were made up to 100 mL in water. When the reaction was complete, the residual NBA was determined iodometrically. Several determinations with various alcohols indicated a 1:1 stoichiometry.

Kinetic Measurements. The reactions were carried out under pseudo-first-order conditions by keeping an excess (×15 or greater) of the alcohol over NBA. All reactions were carried out in blackened flasks to avoid any photochemical reactions and were followed iodometrically for over 70% of the reaction. Rate constants were computed from the linear ($r > 0.98$) plots of log [oxidant] against time. Duplicate kinetic runs showed that the rates were reproducible to within ±3%. The rates of oxidation by sodium hypobromite were also determined iodometrically.

Results

The oxidation of alcohols by NBA in alkaline solution results in the formation of the corresponding ketones. Analysis of products and determination of stoichiometry indicate the overall reaction of eq 1.

$$R_2CHOH + MeCONHBr + OH^- \rightarrow R_2CO + MeCONH_2 + Br^- + H_2O \quad (1)$$

Rate Laws. The rate laws and other experimental data were obtained for all the alcohols investigated. As the results are similar, only those of propan-2-ol are reproduced.

The reaction is found to be first order with respect to the oxidant. Further, the first-order rate coefficient did not vary with the initial concentration of NBA (Table I). The order with respect to the alcohol is also one (Table II). Under the conditions of constant ionic strength the rate decreases with the increase in the concentration of hydroxide ion (Table III).

The oxidation of benzhydrol-α-d indicated the absence of a primary kinetic isotope effect (Table IV).

Addition of acetamide reduces the rate of oxidation of ethanol (Table V).

The oxidation of seven secondary alcohols were studied at different temperatures, and the activation parameters were evaluated (Table VI). The average errors in the values of ΔH^*, ΔS^* and ΔF^* (at 298 K) are ±2 kJ mol^{-1}, ±5 J mol^{-1} K^{-1}, and ±3 kJ mol^{-1}, respectively.

Oxidation by Sodium Hypobromite. The kinetics of the oxidation of propan-2-ol, butan-2-ol, pentan-2-ol, pentan-3-ol, and benzhydrol by hypobromite ion were studied. The reactions are first order with respect to the oxidant and the substrate. The rate decreases with an increase in the concentration of alkali (Table VII). The rates were determined at different temperatures, and the activation parameters were calculated (Table VIII).

Discussion

The activation enthalpies and entropies of the oxidation of the seven alcohols are linearly related ($r = 0.9995$). The correlation was tested and found to be genuine by applying Exner's criterion.[8] The isokinetic temperature computed from this plot is 392 K. Current views do not attach much physical significance to isokinetic temperature.[9] The linear correlation, however, implies that all the alcohols are oxidized by the same mechanism, and the changes in the rate are governed by changes in both enthalpy and entropy of activation.

The retarding effect of added acetamide suggests that the preequilibrium step involves a process in which acetamide is one of the products (eq 2). If this equilibrium

$$MeCONHBr + H_2O \rightleftarrows MeCONH_2 + HOBr \quad (2)$$

is involved in the oxidation process, then the rate should be an increase function of acetamide concentration. The rate constants presented in Table V gave a linear plot ($r = 0.9968$) against [acetamide]. Even at the lowest concentration of alkali used, hypobromous acid will exist exclusively as hypobromite ion.

Another possible reaction, disproportionation of NBA to N,N-dibromoacetamide, can be ruled out in view of the strict first-order dependence of the reaction rate on NBA. Thus the most likely oxidizing species is hypobromite ion.

The postulation of hypobromite ion as the reactive species is supported by the results of the oxidation of some of the alcohols by sodium hypobromite.

The effect of [OH$^-$] on the rate of oxidation of propan-2-ol by hypobromite ion is parallel to that observed in the oxidation by NBA.

Similarly the rates of oxidation and the activation parameters in both the cases are of the same order. Moreover, an isokinetic relationship exists between log [rate] of the oxidations of the alcohols by NBA and hypobromite

Table I. Oxidant Dependence of the Rate of Oxidation of Propan-2-ol by N-Bromoacetamide[a]

10^3[NBA], M	2.0	5.0	7.5	10.0	12.5
$10^6 k_1$, s^{-1}	1.25	1.27	1.20	1.30	1.27

[a] [PrOH] = 1.0 M; [OH$^-$] = 0.10 M; temperature 298 K.

Table II. Dependence of the Reaction Rate on the Concentration of Alcohol[a]

[PrOH], M	0.5	1.0	1.5	2.0	3.0	5.0
$10^7 k_1$, s^{-1}	6.50	12.7	19.0	25.2	38.3	65.0

[a] [NBA] = 0.005 M; [OH$^-$] = 0.10 M; temperature 298 K.

Table III. Dependence of the Reaction Rate on the Concentration of Hydroxide Ion[a]

[OH$^-$], M	0.02	0.04	0.08	0.10	0.14	0.20
$10^6 k_1$, s^{-1}	5.47	4.00	2.66	2.23	1.59	1.30

[a] [NBA] = 0.005 M; [PrOH] = 2.0 M; I = 0.20 M; temperature 298 K.

Table IV. Kinetic Isotope Effect in Oxidation of Benzhydrol by N-Bromoacetamide[a]

[benzhydrol], M	type	$10^5 k_1$, s^{-1}
0.10	α-^{1}H	2.95
0.15	α-^{1}H	4.50
0.20	α-^{1}H	5.80
0.05	α-^{2}H	1.50
0.10	α-^{2}H	2.97
0.20	α-^{2}H	5.73

[a] $10^5 k_H = 2.95 \pm 0.05$ M^{-1} s^{-1}; $10^5 k_D = 2.95 \pm 0.07$ M^{-1} s^{-1}; $k_H/k_D = 1.00$; [NBA] 0.002 M; [OH$^-$] = 0.10 M; temperature 298 K.

Table V. Effect of Acetamide on the Rate of Oxidation of Propan-2-ol by N-Bromoacetamide[a]

10^3[acetamide], M	0.0	2.0	4.0	6.0	8.0	10.0
$10^6 k_1$, s^{-1}	3.83	3.40	3.17	2.90	2.61	2.51

[a] [NBA] = 0.005 M; [PrOH] = 3.0 M; [OH$^-$] = 0.10 M; temperature 298 K

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Table VI. Temperature Dependence and Activation Parameters for Oxidation of Alcohols by *N*-Bromoacetamide[a]

compd	10^7k_2, M^{-1} s^{-1} 298 K	303 K	308 K	313 K	ΔH^*, kJ mol^{-1}	ΔS^*, J mol^{-1} K^{-1}	ΔF^*, kJ mol^{-1}
propan-2-ol	12.7	24.2	44.2	80.5	92.6	−41.2	105
butan-2-ol	10.3	20.2	37.0	68.1	94.6	−36.0	105
pentan-2-ol	8.8	17.6	29.8	61.0	97.1	−29.2	106
pentan-3-ol	7.0	13.7	28.0	53.1	102	−15.2	107
1-chloropropan-2-ol	650	1200	1710	2350	49.8	−150	94.5
1-methoxypropan-2-ol	1100	1470	1900	2530	40.2	−180	93.8
benzhydrol	295	450	675	1000	60.2	−124	97.1

[a] $[OH^-] = 0.10$ M; $k_2 = k_1/[\text{alcohol}]$.

Table VII. Dependence of the Rate of Oxidation of Propan-2-ol by Hypobromite Ion on Alkali Concentration[a]

$[OH^-]$, M	0.02	0.04	0.08	0.10	0.14	0.20
10^6k_1, s^{-1}	4.00	3.35	2.25	1.90	1.45	1.11

[a] $[OBr^-] = 0.005$ M; [PrOH] = 2.0 M; $I = 0.20$ M; temperature 298 K.

is observed in the oxidation of propan-2-ol by both NBA and hypobromite ion ($r = 0.9955$ and 0.9992, respectively; the concerned data are presented in Table III and VII). The slope and intercept have values of 3.36 and 0.12, respectively, for NBA oxidation while the corresponding values for the oxidation by hypobromite ions are 3.74 and 0.16. The similar behavior observed in the two reactions further confirms that the oxidations by NBA and hypobromite ions follow the same mechanistic pathway. The agreement between derived and observed rate laws supports the proposed mechanism.

Table VIII. Temperature Dependence and Activation Parameters for Oxidation of Alcohols by Hypobromite Ions[a]

compd	10^7k_2, M^{-1} s^{-1} 298 K	303 K	308 K	313 K	ΔH^*, kJ mol^{-1}	ΔS^*, J mol^{-1} K^{-1}	ΔF^*, kJ mol^{-1}
propan-2-ol	16.9	30.5	53.3	93.0	85.2	−64	104
butan-2-ol	13.5	24.3	44.4	76.0	87.2	−59	104
pentan-2-ol	11.3	21.0	38.3	66.2	89.3	−53	105
pentan-3-ol	9.73	18.4	34.0	59.8	91.1	−48	106
benzhydrol	365	590	910	1400	67.5	−98	96.7

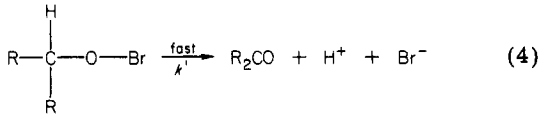
[a] $[OH^-] = 0.10$ M; $k_2 = k_1/[\text{alcohol}]$.

ion ($r = 0.9927$).

The absence of a primary kinetic isotope effect confirms that the C–H bond is not cleaved in the rate-determining step.

The decrease in the rate of oxidation with increasing concentration of hydroxide ion led us to suggest that the rate-determining step is a reversible nucleophilic attack of a hypobromite ion on the alcohol molecule resulting in the formation of a hypobromite ester (eq 3). The hypohalite esters are known to decompose readily[10] to carbonyl products (eq 4).

$$R_2CHOH + OBr^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} R_2CHOBr + OH^- \qquad (3)$$



(4)

A rigorous treatment of the rate equations describing the reaction sequence in eq 3 and 4 is difficult. However, by applying a steady-state approximation for the concentration of hypobromite ester, we can derive the following rate equation (eq 5) for the above mechanism.[11]

$$\text{rate} = \frac{k'k_f[R_2CHOH][OBr^-]}{k' + k_r[OH^-]} \qquad (5)$$

or 1/rate =

$$\frac{1}{k_f[R_2CHOH][OBr^-]} + \frac{k_r[OH^-]}{k'k_f[R_2CHOH][OBr^-]} \qquad (6)$$

From this, it may be seen that the inverse of the rate of reaction will vary linearly with $[OH^-]$. Such a linearity

The rate-determining bimolecular nucleophilic substitution is also supported by the effect of structure on the reactivity of the alcohols. As in other bimolecular nucleophilic substituions, branching at the α- or β-carbon decreases the rate of reaction,[12] and the introduction of electron-withdrawing groups like chlorine and methoxy increases the rate sharply.[13] The structure–reactivity relationship obtained here is opposite that observed in the oxidation of alcohols by NBA in acid solution.[2] In that case introduction of electron-withdrawing groups decreased the reaction rate while alkyl-substituted alcohols reacted faster than methanol.[2]

The negative entropy of activation also supports the above mechanism. When two reacting molecules combine to form a single activated complex, the restrictions on their motion obviously increase,[14] for they can no longer move independently. This results in a large negative entropy of activation.

An alternate route for the formation of hypobromite ester, involving an attack of the alkoxide ion on hypobromous acid (eq 7) can be ruled out on two grounds.

$$R_2CHO^- + HOBr \rightleftharpoons R_2CHOBr + OH^- \qquad (7)$$

First, the formation of an alkoxide ion is catalyzed by alkali, and the inverse dependence on $[OH^-]$ observed here is not compatible with reaction 8. Second, hypobromous acid will not exist free in an alkaline solution.

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$$R_2CHOH + OH^- \rightleftarrows R_2CHO^- + H_2O \quad (8)$$

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Registry No. Propan-2-ol, 67-63-0; butan-2-ol, 78-92-2; pentan-2-ol, 6032-29-7; pentan-3-ol, 584-02-1; 1-chloropropan-2-ol, 127-00-4; 1-methoxypropan-2-ol, 107-98-2; benzhydrol, 91-01-0; *N*-bromoacetamide, 79-15-2; sodium hypobromite, 13824-96-9.

Notes

A Facile Intramolecular Tertiary Amine Displacement Reaction

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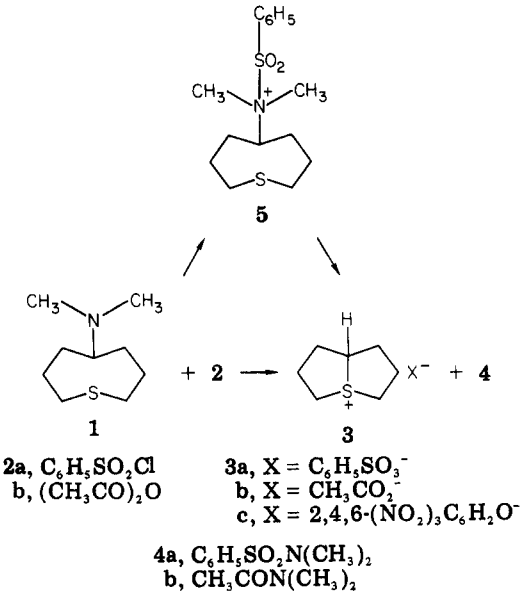
Facile carbon–nitrogen bond-cleavage reactions of tertiary amines are rare. Common exceptions are the reaction between a tertiary amine and cyanogen bromide (the Von Braun reaction)[1] and the nitrous acid dealkylation reaction.[2] When the leaving group is either benzylic or an otherwise stabilized carbocation, the C–N bond can be cleaved by acetic anhydride after lengthy refluxing.[3,4]

Tertiary amines are normally stable when treated with benzenesulfonyl chloride under the conditions of the Hinsberg test[5] although some C–N bond cleavage can occur.[6] We have seen no examples of an intramolecular displacement reaction that causes C–N bond cleavage in amines in contrast to those causing C–O bond cleavage in alcohols.

For these reasons we are reporting the surprisingly exothermic C–N bond cleavage reaction of 5-(dimethylamino)-1-thiacyclooctane (**1**) with benzenesulfonyl chloride under the conditions of the Hinsberg test. A similar reaction occurs with acetic anhydride to give *N,N*-dimethylacetamide and **3b** (NMR experiment).

Treatment of pure **1** with excess benzenesulfonyl chloride (**2a**) produces a vigorous exothermic reaction accompanied by the immediate formation of a solid material. Subsequent separation and identification confirmed the products as 1-thioniabicyclo[3.3.0]octane benzenesulfonate (**3a**) and *N,N*-dimethylbenzenesulfonamide (**4a**) in nearly quantitative yields. The reaction is initiated by a nucleophilic displacement by the amine on the sulfonyl chloride to form the intermediate $C_6H_5SO_2NR_3^+$ salt **5** (Scheme I). Subsequent displacement at C-5 by the transannular thioether leads to formation of **3a** and **4a**. Precedence for such a mechanism was deduced from a similar C–O bond-cleavage reaction of 5-hydroxy-1-thiacyclooctane with phosphoric anhydride[7] to give **3**.

Scheme I



2a, $C_6H_5SO_2Cl$
b, $(CH_3CO)_2O$

3a, X = $C_6H_5SO_3^-$
b, X = $CH_3CO_2^-$
c, X = 2,4,6-$(NO_2)_3C_6H_2O^-$

4a, $C_6H_5SO_2N(CH_3)_2$
b, $CH_3CON(CH_3)_2$

In this C–N cleavage reaction neither a stabilized carbocationic center nor a good leaving group is present so this reaction must proceed via direct displacement of *N,N*-dimethylbenzenesulfonamide by attack of the strongly nucleophilic thioether group on the transannular carbon.

Experimental Section

Reaction of 5-(Dimethylamino)-1-thiacyclooctane with Benzenesulfonyl Chloride. To 0.110 g (0.637 mmol) of **1** was added 0.281 g (1.59 mmol) of **2a**. A rapid exothermic reaction ensued accompanied by the formation of a white solid. Aqueous sodium hydroxide (4 mL of 5% solution) was added and the mixture agitated for 1 h to produce an oily layer. Extraction with ether (5 × 10 mL) provided 0.123 g (0.661 mmol, 104%) of **4a** as white crystals, mp 43.0–45.0 °C (compared with authentic **4a**).

The aqueous layer was saturated with potassium carbonate and extracted with chloroform (5 × 10 mL). Removal of the chloroform produced a pale yellow oil, which crystallized rapidly on cooling to give 0.174 g (0.608 mmol, 95%) of **3a** as an off white, very hygroscopic solid: ^1H NMR ($CDCl_3/Me_4Si$) δ 7.8 (m, 2 H, *o*-H), 7.3 (m, 3 H, *m*- and *p*-H), 4.68 (p, 1 H, CH), 3.60 (t, 4 H, CH_2S), 2.1 (m, 8 H, CH_2); IR (KBr) 3060 (w), 1440 (m), 1230 (s), 1220 (vs), 1202 (vs), 1185 (s), 1125 (s), 1035 (m), 1015 (m), 1000 (m), 760 (m), 730 (s), 695 (m), 615 (s), 656 (m) cm^{-1}. On addition of **3a** in water to a saturated aqueous picric acid solution, yellow needles of **3c** precipitated: mp 256.0–258.0 °C (lit.[8] mp 257–258 °C); ^1H NMR (CD_3COCD_3/Me_4Si) δ 8.58 (s, 2 H, Ar H), 4.90 (p, 1 H, CH), 3.7 (m, 4 H, CH_2S), 2.5 (m, 8 H, CH_2).

Reaction of 1 with 2b. A solution of 3 drops each of **1** and **2b** in 0.5 mL of $CDCl_3$ was monitored by ^1H NMR. After warming

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