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KINETICS AND MECHANISM OF Ru(III) CATALYSED OXIDATION OF SOME POLYHYDRIC ALCOHOLS BY N-BROMOSUCCINIMIDE IN ACIDIC MEDIA

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Abstract - Kinetics of oxidation of ethylene glycol, glycerol, erythritol and dulcitol by acidic solution of N-bromosuccinimide (NBS) in presence of ruthenium(III) chloride as a homogeneous catalyst and mercuric acetate as scavenger in the temperature range of 30-50°C have been reported. The reactions follow identical kinetics, being first order in each NBS, substate and Ru(III). Zero effect of $[H^+]$, [mercuric acetate] and ionic strength has been observed. A negative effect of succinimide and acetic acid is observed while $[Cl^-]$ shows the positive effect on reaction velocity. Various activation parameters have been computed. The products of the reaction were identified as the coresponding acids. A suitable mechanism consistent with the experimental results has been proposed.

INTRODUCTION

NBS is a potent oxidant and has been used in the quantitative estimation[1-3] of a large number of organic as well as inorganic compounds. Relatively little work has been done on the oxidation kinetics involving NBS, and the mechanistic interpretations of the results are obscure. Some investigations on oxidation kinetics involving NBS and alcohols,[4] esters,[5] and a few ketones,[6-9] in acidic media have been reported. The mode of NBS oxidation in catalysed reactions is unknown and so far none has attempted to probe the role of ruthenium(III) chloride as catalyst in NBS oxidations. This prompted us to undertake the present investigation which constitutes the studies of kinetics and mechanism of Ru(III) catalysed NBS oxidation of aforesaid polyhydric alcohols in perchloric acid media in presence of mercuric acetate.

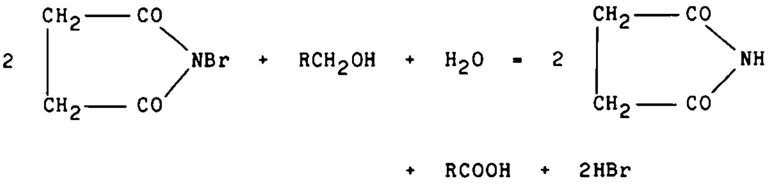
EXPERIMENTAL

An aqueous solution of NBS was prepared afresh each day from a G.R., S. Merck sample of the reagent, and its strength was checked by the iodometric method.[10] Ethylene glycol, glycerol, erythritol and dulcitol of AnalaR grade and E. Merck (Germany) sample of mercuric acetate were used. The solutions of the polyhydric alcohols were prepared by weighing their samples. Ruthenium(III) chloride (Johnson Matthey) solution was prepared by dissolving the sample in hydrochloric acid of known strength. All other reagents, namely perchloric acid, glacial acetic acid and sodium perchlorate, were of AnalaR grade. Triple distilled water was used throughout the investigations. The reaction stills (Jena glass) were blackened from outside.

All the kinetic measurements were carried out at constant temperature (± 0.1°C). The reaction was initiated by rapid addition of NBS to the reaction mixture containing appropriate quantities of alcohol, glacial acetic acid, perchloric acid, ruthenium(III) chloride, mercuric acetate and water and mixing them by vigorous shaking. The progress of the reaction was monitored by estimating the amount of unconsumed NBS at regular time intervals iodometrically.

RESULTS

Stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of NBS over alcohol (in varying ratios) at 50°C for 48 hrs, and estimations of residual NBS in different sets showed that one mole of alcohol consumes two moles of NBS according to the stoichiometric equation (1).



(1)

where R stands for CH_2OH, $CH_2OHCHOH$, $CH_2OH(CHOH)_2$, and $CH_2OH(CHOH)_4$ in ethylene glycol, glycerol, erythritol and dulcitol whose oxidation products, glycollic acid, dl-glyceric acid, erythronic acid and galactonic acid were detected by conventional methods.[11]

TABLE 1 Effect of Concentrations of Reactants on Reaction Rate

$[Hg(OAc)_2] = 2.00 \times 10^{-3}$ M, pH = 2.58,

$[Ru(III)]$ 0.88×10^{-6} M and $[Cl^-] = 3.60 \times 10^{-3}$ M

$[NBS]10^3$ M	$[Substrate] 10^2$ M	$10^4\ k_1\ sec^{-1}$							
		Ethylene glycol		Glycerol		Erythritol		Dulcitol	
		30°	35°	30°	35°	30°	35°	30°	35°
0.6	1.0	2.60	4.30	3.92	6.07	5.17	7.80	6.78	9.70
0.8	1.0	2.64	4.31	3.68	6.12	5.11	7.72	7.12	9.77
1.0	1.0	2.70	4.40	3.69	6.26	5.16	7.95	6.86	9.90
1.2	1.0	2.62	4.38	4.38	5.95	5.22	7.92	6.93	9.78
1.4	1.0	2.74	4.44	3.80	6.11	5.20	8.20	7.04	9.82
2.0	1.0	2.68	4.36	3.82	6.14	5.16	7.90	7.04	9.76
2.5	1.0	2.74	4.38	3.70	6.20	5.19	7.94	6.88	9.74
1.0	0.5	1.39	2.17	1.98	3.09	2.68	3.91	3.36	4.96
1.0	1.0	2.70	4.38	3.69	6.26	5.17	7.95	6.86	9.90
1.0	1.5	3.67	6.28	5.77	9.16	8.09	11.60	10.19	14.86
1.0	2.0	5.10	8.44	7.61	12.28	10.48	15.84	13.40	19.70
1.0	2.5	6.88	10.10	9.78	15.46	13.04	19.76	16.91	24.72

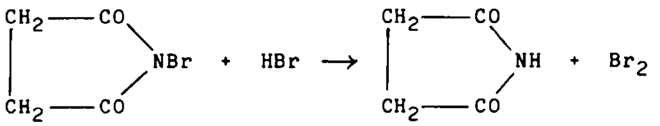
The kinetics of the oxidation of polyhydric alcohols was investigated at several initial concentrations of the reactants (Table 1). First order dependence in NBS was followed at all initial concentrations of NBS.
Pseudo first order constants (k_1) were calculated from the slopes of log-time plots (Fig. 1). Further, a linear increase in the first order rate constants in NBS with an increase in initial concentrations of polyhydric alcohols was

observed. The order in substrates was computed from the slopes of log k_1 vs log [substrate] plots (Fig. 2) and was found to be 0.96 for ethylene glycol and glycerol and 0.95 for erythritol and dulcitol. This established that reactions follow first order kinetics with respect to all polyhydric alcohols. The rate of the reaction was found to be highly influenced by [Ru(III)]. It was observed that with increasing [Ru(III)] the first order rate constants in NBS increased linearly (Table 2 and Fig. 3) and k_1/[Ru(III)] had a fairly constant value, which proves first order dependence on [Ru(III)]. The results of Table 2 also reveal that on increasing pH of the reaction mixtures the first order rate constants in NBS remain unchanged, indicating thereby zero effect of hydrogen ion concentration. Insignificant effect of addition of mercuric acetate and sodium perchlorate (ionic strength variation) was observed.

Successive addition of acetic acid decreased the first order rate constants in NBS, indicating an anion-dipole interaction in the rate-determining step. The first order rate constant in NBS decreased on addition of succinimide while it increased on increasing chloride ion concentration (Table 3). The values of activation parameters were computed from the study of rate measurements at 30°, 35°, 40°, 45° and 50°C and are reported in Table 4.

DISCUSSION

The results of the oxidation of ethylene glycol, glycerol, erythritol and dulcitol, recorded here, have revealed that the reactions have identical kinetics and thus appear to have common mechanism. Insignificant effect of mercuric acetate on reaction rate rules out its involvement in NBS oxidation and acts only as a scavenger[12,13] for any Br^- formed in the reaction. It suppresses completely the oxidation by Br_2, which would have been formed by the interaction of HBr and NBS as follows:



(2)

Mercuric acetate thus ensures the oxidation purely through NBS.

Positive effect of chloride ions on reaction rate suggests that equilibrium (3) is favoured to right side[14] in acidic ruthenium(III) chloride solution.

$$Cl^- + [RuCl_5.H_2O]^{2-} \rightleftharpoons [RuCl_6]^{3-} + H_2O \qquad (3)$$

It may, therefore, be assumed that $[RuCl_6]^{3-}$ is the active species of ruthenium(III) chloride.

NBS is known to exist in acidic media in the following equilibria:

$$>NBr + H^+ \rightleftharpoons >\overset{+}{N}HBr \qquad (4)$$

$$>NBr + H^+ \rightleftharpoons >NH + Br^+ \qquad (5)$$

Thus NBS itself or protonated NBS, i.e. $\overset{+}{N}BSH$ or Br^+ may be the possible oxidising species in acidic media.

Zero effect of ionic strength suggests involvement of at least a neutral molecule in the rate controlling step. Observed positive dielectric effect (retarding effect of acetic acid) shows that the rate determining step must involve an interaction between a neutral molecule and a negatively charged ion. These facts require involvement of either NBS or polyhydric alcohol as neutral molecule in the rate controlling step. Absence of Michaelis-Menten reciprocal relationship[15] (a kinetic proof for the complex formation involving substrate and catalyst), strict first order requirement in polyhydric alcohols, and lack of any spectrophotometric evidence for the complex formation between polyhydric alcohol and Ru(III) species suggest the involvement of alcohol as neutral molecule. This leads to the conclusion that either NBS itself or its protonated form or Br^+ is involved in the complex formation with Ru(III) species. Complexation of Ru(III) species with Br^+ seems to be unreasonable and its direct involvement as such will negate the positive dielectric constant effect. Hence Br^+ as reactive species of NBS is ruled out. Protonated NBS as the reactive species involved in complexation with Ru(III) to give the desired negatively charged species would require first order in H^+ ions and zero effect of succinimide contrary to observed zero effect of H^+ ions and negative effect of succinimide addition. Thus possibility of protonated NBS acting as reactive species is remote. This leaves NBS itself as the only choice to be the reactive species. Formation of complex by NBS with Ru(III) species followed by its interaction with the polyhydric alcohol molecule to form the activated complex seems to be more reasonable, because the complex so formed will exert greater power on account of the involvement of electron pair on nitrogen in coordinate bond formation. Ru(III) in its 8 coordination state gets complexed with NBS and then tries to bring polyhydric alcohol molecule nearer to the reagent, leading to the chemical reaction. During this process, dissociation possibility of Cl^- ion does not exist as equilibrium (3) is towards its association. It is, therefore, concluded that the reaction proceeds with complex formation between Ru(III) species and NBS.

Considering the above statements and kinetic results, the following reaction paths are proposed, where M is succinimide.

$$[RuCl_5.H_2O]^{2-} + Cl^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [RuCl_6]^{3-} + H_2O \qquad (i)$$

$$[RuCl_6]^{3-} + NBS \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A\ (\text{Complex}) \qquad (ii)$$

$$A + RCH_2OH \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} X + M \qquad (iii)$$

$$X \xrightarrow[\text{slow and rate determining}]{k_4} [RuCl_6H]^{4-} + \text{Products} \qquad (iv)$$

$$[RuCl_6H]^{4-} + NBS + H^+ \xrightarrow{k_5} [RuCl_6]^{3-} + HBr + M \qquad (v)$$

Here X stands for the activated complex.

Application of the steady state treatment with the reasonable approximations yields the rate law (6).

$$\frac{d[NBS]}{dt} = \frac{2K_1K_2k_3k_4\ [NBS]\ [RCH_2OH]\ [Ru(III)]_T\ [Cl^-]}{k_{-3}\ [M]\ +\ k_4K_1\ [Cl^-]} \qquad (6)$$

where $K_1 = \frac{k_1}{k_{-1}}$ and $K_2 = \frac{k_2}{k_{-2}}$

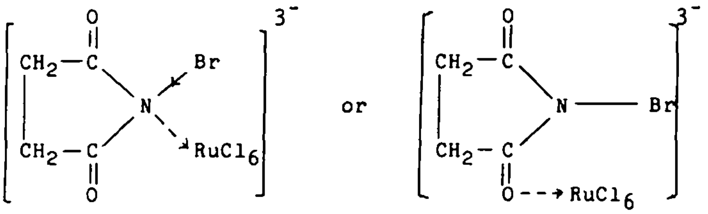
The rate law (6) is in excellent agreement with the experimental results. The equation (6) can be rearranged in the following form:

$$\frac{1}{rate} = 1\ /\ -\frac{d[NBS]}{dt}$$

$$= \frac{[M]}{2K_1K_2K_3k_4\ [NBS]\ [RCH_2OH]\ [Ru(III)]_T\ [Cl^-]} + \frac{1}{2K_2k_3\ [NBS]\ [RCH_2OH]\ [Ru(III)]_T} \qquad (7)$$

where $K_3 = \frac{k_3}{k_{-3}}$

A plot of 1/rate against $1/[Cl^-]$ at constant [NBS], $[RCH_2OH]$ and $[Ru(III)]_T$ should yield a straight line with a positive intercept on 1/rate axis and this was found to be so (Fig. 4). Positive effect of chloride ions on reaction rate is thus proved. This observation favours the equilibrium (3) to the right side and supports the assumption that $[RuCl_6]^{3-}$ is the active species of ruthenium(III) chloride. The structure of the complex (A) formed in step (ii) is not known, but in order to explain its hydride ion abstracting capacity, it may be assigned structures (I) or (II).



A (Complex)

I II

The lone-pair of electrons on the nitrogen atom of NBS can coordinate with Ru(III) of $(RuCl_6)^{3-}$ to form a n-π complex (Structure I). Alternatively, the n-electrons of one of the carbonyl groups form a coordinate bond with Ru(III), giving rise to a n-π complex (Structure II). In either case, the N atom will become electron deficient, which will make the electron-pair of N-Br bond shift towards N, making Br slightly positive. Consequently, the electrophilic character and, hence, the hydride ion abstracting capacity of NBS is enhanced considerably after complexation leading to its interaction with polyhydric alcohol. The hydride ion transfer theory is also supported by Littler,[16] Lee,[17] Jones *et al*[18] and Freeman *et al*.[19] It is not possible to establish the existence of Structure (I) or (II) with the present data.

In the light of the above discussion, the sequence of the reaction may, therefore, be pictured as given in the Scheme.

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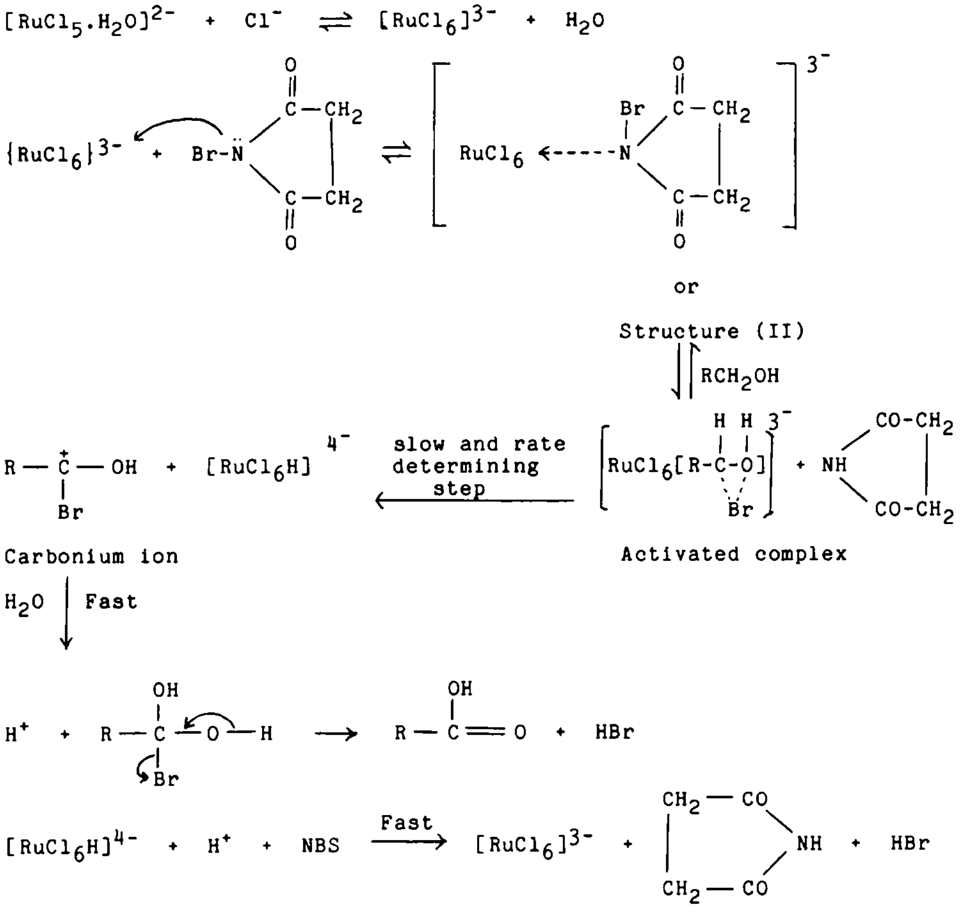

SCHEME

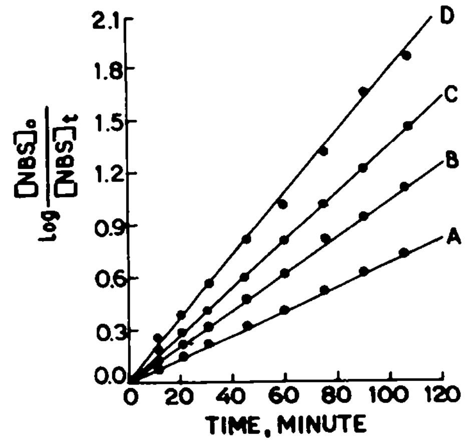

FIGURE 1 First order rate plots at 30°C
[NBS] = 1.20 x 10^{-3} M, [Ru(III)] = 0.88 x 10^{-6} M,
[Cl^-] = 3.60 x 10^{-3} M, [$Hg(OAc)_2$] = 2.00 x 10^{-3} M
[Substrate] = 1.00 x 10^{-2} M in A (Ethylene glycol), B (Glycerol), C (Erythritol) and D (Dulcitol)

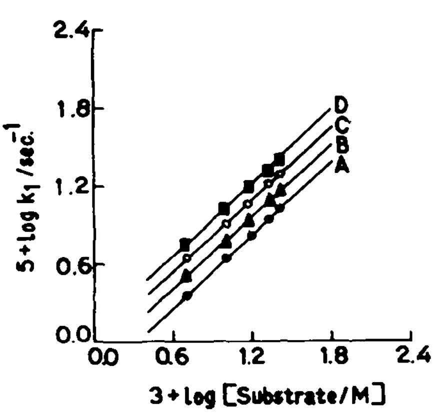

FIGURE 2 Plot of log k_1 vs log [substrate] at 35°C. $[NBS] = 1.00 \times 10^{-3}$ M, pH = 2.58, $[Ru(III)] = 0.88 \times 10^{-6}$ M, $[Cl^-] = 3.60 \times 10^{-3}$ M, and $[Hg(OAc)_2] = 2.00 \times 10^{-3}$ M, A (Ethylene glycol), B (Glycerol), C (Erythritol), D (Dulcitol).

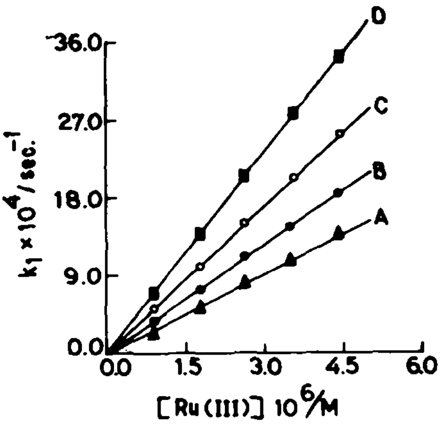

FIGURE 3 Plot of k_1 vs [Ru(III)] at 30°C. Conditions as in Table 2, A (Ethylene glycol), B (Glycerol), C (Erythritol), D (Dulcitol).

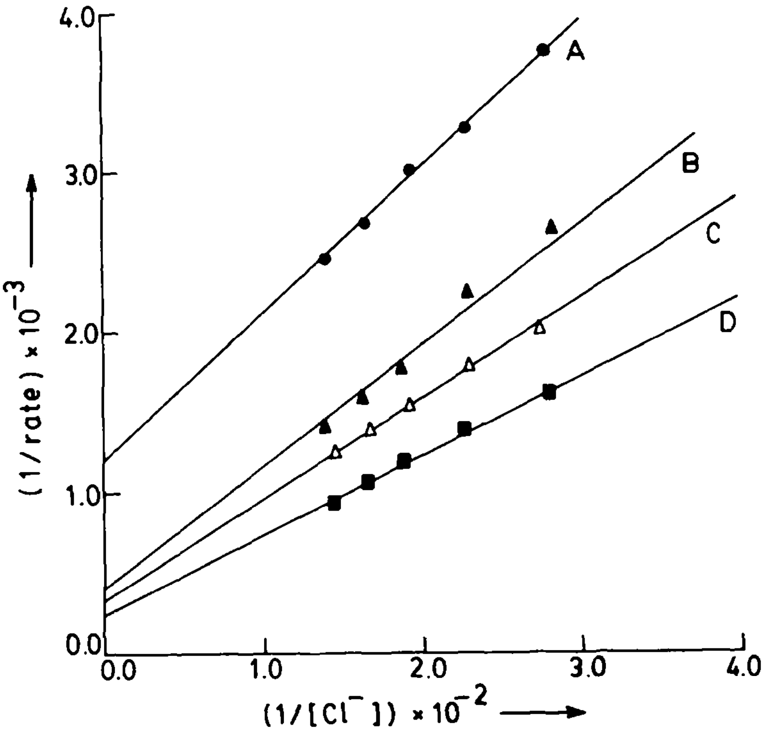

FIGURE 4 Plot of 1/rate vs $1/[Cl^-]$ at 30°C. Conditions as in Table 3, A (Ethylene glycol), B (Glycerol), C (Erythritol), D (Dulcitol).

TABLE 2 Effect of [Ru(III)], pH, [Hg(OAc)$_2$] and ionic strength (μ) variation on reaction rate at 30°C. [NBS] = 1.00 x 10^{-3} M, [Substrate] = 1.00 x 10^{2} M, pH = 2.58 (unless otherwise state and [Hg(OAc)$_2$] = 2.00 x 10^{-3} M (unless otherwise mentioned, [Cl$^-$] = 3.60 x 10^{-3} M

[Ru(III)] x 10^6 M	k_1 x 10^4, sec^{-1}			
	Ethylene glycol	Glycerol	Erythritol	Dulcitol
0.88	2.67	3.69	5.16	6.86
1.76	5.52	7.36	10.38	13.88
2.64	8.40	11.33	15.88	20.22
3.52	10.88	14.85	20.81	28.12
4.40	13.66	17.98	25.92	34.70
0.88[a]	2.72	3.76	5.24	6.66
0.88[b]	2.70	3.60	5.00	6.94
0.88[c]	2.68	3.62	5.10	6.76
0.88[d]	2.60	3.70	5.20	6.80
0.88[e]	2.67	3.69	5.16	6.86
0.88[f]	2.64	3.76	5.12	6.60
0.88[g]	2.70	3.70	5.22	6.70
0.88[h]	2.66	3.74	5.18	6.80
0.88[i]	2.64	3.72	5.16	6.78
0.88[j]	2.66	3.72	5.19	6.77
0.88[k]	2.65	3.70	5.16	6.78
0.88[l]	2.67	3.73	5.17	6.76
0.88[m]	2.66	3.74	5.19	6.78

[a] pH = 1.42; [b] pH = 1.86; [c] pH = 2.08; [d] pH = 2.20; [e] pH = 2.78.
[f] [Hg(OAc)$_2$] x 10^3 M = 4.00;
[g] " " 6.00;
[h] " " 8.00.
[i] (μ) 10^2 M = 1.24;
[j] " 1.64;
[k] " 2.00;
[l] " 2.48;
[m] " 3.00.

TABLE 3 Effect of addition of succinimide, acetic acid and chloride ions on reaction rate at 30°C, [NBS] = 1.00 x 10^{-3} M, [Substrate] = 1.00 x 10^{-2} M, [Ru(III)] = 0.88 x 10^{-6} M, pH = 2.58, [Acetic acid] (v/v) = 2% (unless otherwise stated) and [Hg(OAc)$_2$] = 2.00 x 10^{-3} M

[Cl$^-$]$_M$ x 10^3	k_1 x 10^4, sec^{-1}			
	Ethylene glycol	Glycerol	Erythritol	Dulcitol
3.60	2.67	3.69	5.16	6.86
4.40	3.05	4.28	5.66	7.05
5.20	3.28	5.81	6.22	7.98
6.00	3.82	6.61	6.76	9.12
6.80	4.11	7.34	7.55	10.22
3.60[a]	1.96	3.69	3.68	5.04
3.60[b]	1.46	2.63	2.60	3.60
3.60[c]	1.05	1.91	1.85	2.57
3.60[d]	0.72	1.36	1.32	1.84
3.60[e]	2.03	3.05	4.06	5.20
3.60[f]	1.55	2.50	3.32	4.10
3.60[g]	1.28	2.06	2.64	3.28
3.60[h]	1.02	1.62	2.06	2.48

[Acetic acid] (v/v) = 16[a], 30[b], 44[c] and 60%[d];
[Succinimide] x 10^3 M = 0.8[e], 1.0[f], 1.2[g] and 1.4[h]

TABLE 4 Activation parameters for NBS oxidation of polyhydric alcohols

Substrate	ΔE^* (Kcal/mol)	A (1/mol sec)	ΔS^* (e.u.)	ΔH^* (Kcal/mol)	ΔF^* (Kcal/mol)
Ethylene glycol	19.48	4.57×10^{11}	-6.12	17.85	19.76
Glycerol	17.34	1.74×10^{11}	-8.03	17.12	19.62
Erythritol	15.82	1.10×10^{10}	-13.53	15.20	19.43
Dulcitol	14.75	2.29×10^{9}	-16.64	14.13	14.33

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