

Generation and reactions of the borate radical – A flash photolysis study

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Abstract. The borate radical is produced by the flash photolysis of an aqueous alkaline solution of NaBO_2 and $\text{K}_2\text{S}_2\text{O}_8$. The absorption spectrum of the transient borate radical shows two maxima. The self decay of this radical is second order. Rate constants for the reactions of this radical with some organic substrates have been determined.

Keywords. Flash photolysis; borate radical; rate constants; organic substrates.

1. Introduction

In recent years there has been great interest in studies relating to the flash photolytic and pulse radiolytic generation of inorganic free radicals and their reactions (Ross and Neta 1979; Morkovnik and Okhlobystein 1979). There has been no report on the radicals arising from the borate ion system. In this study we report results dealing with the transients derived from metaborate ion.

2. Experimental

2.1 Materials

All the reagents used were of analytical grade. In the case of liquid substrates, freshly distilled samples were used for preparing the solutions. In the case of solid substrates, recrystallised samples were used and their purity checked from their melting points. Sodium metaborate tetrahydrate (AR) ($\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$) was recrystallised thrice from distilled water.

2.2 Measurements

Flash photolysis experiments were carried out in a Nortech Flash Photolysis apparatus. The half-width of the flash duration was about 30 μs . The wavelength of the exciting flash source ranges from 215 to 850 nm. The measurements were made

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at $23.0 \pm 1.0^\circ\text{C}$. All solutions were prepared with triply distilled water. The flash experiments were done immediately after making the solutions.

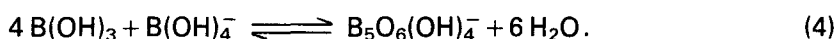
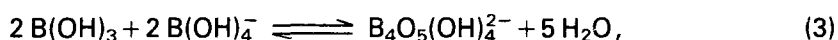
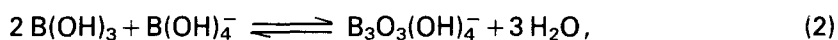
3. Results and discussion

3.1 Spectral and other properties of borate solutions

Aqueous solutions of borate/boric acid display markedly different properties from other inorganic anion systems.

- (i) The solutions exhibit very poor absorption in the UV-visible region and are practically transparent.
- (ii) Borate exists in different forms at various pH and concentration conditions. For example, at concentrations above 0.025 M the solution contains mixtures of polyionic forms (Nies and Campbell 1964; Anderson *et al* 1964). These polymeric forms arise by self reaction accompanied by elimination of water.

Scheme 1 depicts the various processes that can occur in a boric acid/borate solution (Mehri 1963; Salentine 1983).

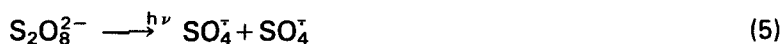


Scheme 1

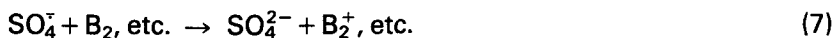
The relative concentrations of the various forms depend upon the pH of the solutions. Polyborate equilibria in water have been studied by IR (Goulden 1959), laser Raman (Maya 1976) and more recently by ^{11}B NMR spectroscopy (Salentine 1983). At pH 11.0 these complexities are absent and only one form, namely B(OH)_4^- is present. Laser Raman spectrum of an aqueous solution of NaBO_2 at pH 11.5 has only one band at 745 cm^{-1} attributable to B(OH)_4^- . This assignment is based on the laser Raman spectral studies on various borate solutions at different pH by Maya (1976). Goulden (1959) has concluded that only B(OH)_4^- is present at pH 11.1. This is based on the observation of the characteristic IR bands at 1160 cm^{-1} and 945 cm^{-1} . Thus at pH 11.0 to 12.0, B(OH)_4^- alone is present, to the exclusion of all other species, while in the pH range 9.0 to 10.5, complex mixtures exist.

3.2 Transients derived from borate solutions

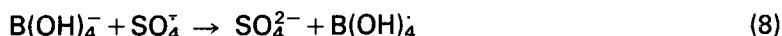
Since borate does not absorb in the UV region, flash photolysis of borate solutions did not yield any transient at any pH. An aqueous solution containing NaBO_2 ($5 \times 10^{-2} \text{ M}$) and $\text{K}_2\text{S}_2\text{O}_8$ ($1 \times 10^{-3} \text{ M}$) was flashed at various pH conditions (NaOH was used to adjust the pH). Scheme 2 depicts the possible reactions.



At pH 9 to 11

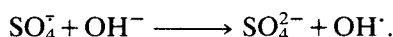


At pH 11 to 12



Scheme 2

There is a possibility that the OH^- competes with the borate ion for the $\text{SO}_4^{\cdot-}$ radical.



The OH^{\cdot} radical can subsequently react with the borate ion. The rate constant for the formation of OH^{\cdot} radical is reported to be $4.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (Roebke *et al* 1969). The rate constant for the reaction of $\text{SO}_4^{\cdot-}$ with borate ion is determined to be $5.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at pH 11.5. Further, a large concentration of borate ion ($[\text{NaBO}_2] = 5 \times 10^{-2} \text{ M}$) has been used in the experiments. So it is expected that the predominant reaction is between the borate ion and the $\text{SO}_4^{\cdot-}$ radical. Further, independent experiments suggest that the OH^{\cdot} radical is not responsible for the formation of the borate radical. H_2O_2 on flash photolysis yields OH^{\cdot} radicals (Behar *et al* 1970). When a mixture of borate and H_2O_2 is flashed no borate radicals could be detected. The absence of borate radicals suggests that the borate radical is not formed through the intermediacy of the OH^{\cdot} radical. B_1 , B_2 , etc. are the various borate species present. Table 1 gives the absorption maxima due to various transients observed for solutions at different pH.

Table 1. Absorptions of transients observed in the flash photolysis of $5 \times 10^{-2} \text{ M NaBO}_2$ and $1 \times 10^{-3} \text{ M K}_2\text{S}_2\text{O}_8$ at different pH levels.

pH	λ_{max} (nm)	Ratio of optical densities at various times (ms) after flash	
		$\text{OD}_{650}/\text{OD}_{590}$	$\text{OD}_{420}/\text{OD}_{590}$
10.5	420,590,650	1.20(0.6)	0.96(0.6)
		1.19(0.8)	0.97(0.8)
		1.20(1.0)	0.97(1.0)
10.75	420,590,650	1.11(0.6)	0.98(0.6)
		1.12(0.8)	0.98(0.8)
		1.10(1.0)	0.97(1.0)
11.0	590,650	1.14(0.6)	
		1.13(0.8)	
		1.14(1.0)	
11.5	590,650	1.10(0.6)	
		1.11(0.8)	
		1.10(1.0)	

It is seen from the data in table 1 that below pH 11.0 three absorption maxima (420, 590 and 650 nm) were observed though the ratio of the optical densities were the same. At pH 11.0 to 12.0 only two absorption maxima (590 and 650 nm) were observed. Further the optical density at these wavelengths were a maximum at pH 11.5. As pointed out earlier (Maya 1976) the species present at this pH is $B(OH)_4^-$ and therefore the transient formed must be $B(OH)_4$. So most of the studies were confined to this pH. The absorption spectrum of the transient borate radical at pH 11.5 is shown in figure 1. The flash photolysis without $NaBO_2$ yields the SO_4^- radical absorbing at $\lambda_{max} = 455$ nm (Hayon and McGarvey 1967). This characteristic SO_4^- radical absorption is not observed when $NaBO_2$ was also present in the solution. $B(OH)_4^-$ is a strong base and hence loss of H from $B(OH)_4^-$ via H abstraction by SO_4^- radical is precluded. The more probable reaction that can be visualised between SO_4^- radical and $B(OH)_4^-$ is electron transfer from $B(OH)_4^-$ to SO_4^- [(8) in scheme 2].

The molar extinction coefficient of the borate radical was estimated according to the procedure of Dogliotti and Hayon (1967) using the equation

$$\epsilon_T/\epsilon_R = \frac{OD_T}{OD_R}, \quad (9)$$

where ϵ_T is the value of the transient $B(OH)_4$ and ϵ_R that of SO_4^- . OD_T is the maximum OD of the borate radical in the presence of the sulphate radical and OD_R is the maximum OD of SO_4^- in the absence of borate ($\epsilon_{SO_4^-} = 1100 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{max} = 455$ nm) (Hayon and McGarvey 1967).

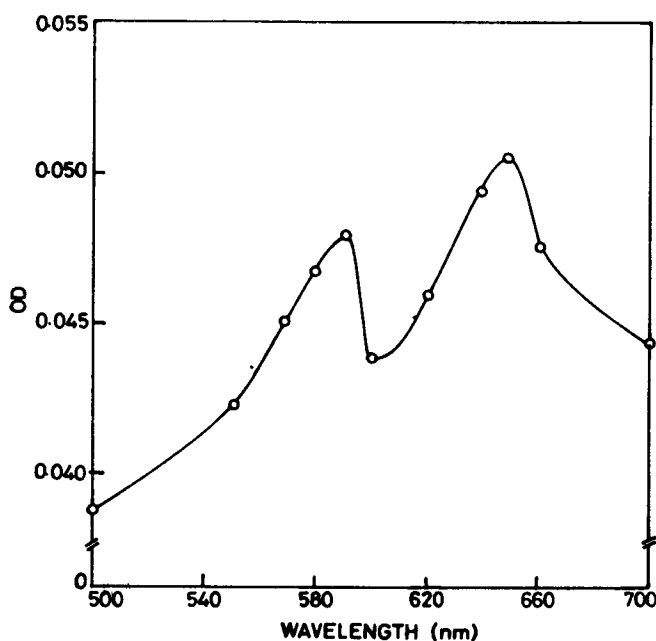
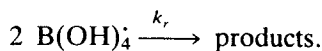


Figure 1. Transient absorption spectrum of borate radical produced in the flash photolysis of 50 mM sodium metaborate and 1.0 mM potassium persulphate at pH 11.5. Optical densities (OD) measured 300 μ s after start of flash.

3.3 Reactions of the borate radical

The decay of the borate radical, $B(OH)_4^{\cdot}$, is second order in the absence of any scavenger.



The self decay constant obtained from the slope of the linear plot of $1/OD$ vs. time (see figure 2) according to (10), at both 590 and 650 nm is found to be $(1.0 \pm 0.1) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

$$\frac{1}{(OD)_t} = \frac{kt}{\epsilon l} + \frac{1}{(OD)_0} \quad (10)$$

The self decay constants and the values of the borate radical are reported in table 2.

The correspondence of the values of k at the two wavelengths is in agreement with the conclusion that both the absorptions are due to one and the same species.

In the presence of an organic substrate, the disappearance of the borate radical will be governed by a competition between self decay and its reaction with the organic substrates.

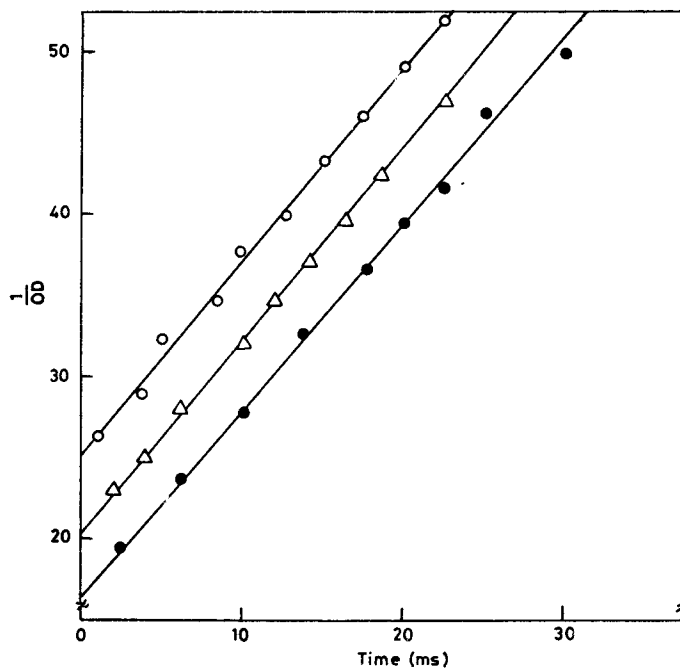
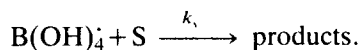


Figure 2. Second order plot for the decay of borate radical at 650 nm produced in flash photolysis of aqueous solution of $1 \times 10^{-3} \text{ M K}_2\text{S}_2\text{O}_8$ and NaBO_2 at pH 11.5: ○— $2.5 \times 10^{-2} \text{ M NaBO}_2$; △— $5.0 \times 10^{-2} \text{ M NaBO}_2$; ●— $1.0 \times 10^{-1} \text{ M NaBO}_2$.

The overall disappearance of the borate radical is given by

$$-\frac{d[\text{B(OH)}_4]}{dt} = k_r[\text{B(OH)}_4]^2 + k_s[\text{B(OH)}_4][\text{S}] \quad (11)$$

With an excess of the substrate the self-decay becomes negligible and a pseudo-first-order reaction with the substrate takes place. The rate equation (11) is then reduced to

$$-\frac{d[\text{B(OH)}_4]}{dt} = k'_s[\text{B(OH)}_4], \quad (12)$$

from which k'_s , the pseudo-first-order rate constant, can be calculated. The second order rate constant, k_s , is given by

$$k_s = \frac{k'_s}{[\text{S}]_0}, \quad (13)$$

Table 2. Decay constants and ϵ values of the borate radical produced by the flash photolysis of 5×10^{-2} M NaBO₂ and 1×10^{-3} M K₂S₂O₈.

pH	λ_{max} (nm)	$k/\epsilon \times 10^{-4}$	ϵ (M ⁻¹ cm ⁻¹)	$k \times 10^{-7}$ (M ⁻¹ s ⁻¹)
11.25	590	1.19	806	0.98
	650	1.18	910	1.01
11.50	590	1.25	806	0.99
	650	1.13	910	1.02
11.75	590	1.27	806	1.02
	650	1.14	910	1.03
12.00	590	1.31	806	1.05
	650	1.12	910	1.01

Table 3. Rate constants for the reactions of B(OH)₄⁻ with various substrates at pH 11.5 (k_s for PO₄³⁻ and CO₃²⁻ given for comparison).

Substrate	B(OH) ₄ ⁻ k_s (M ⁻¹ s ⁻¹)		PO ₄ ³⁻ k_s (M ⁻¹ s ⁻¹)	CO ₃ ²⁻ k_s (M ⁻¹ s ⁻¹)
	590 nm	650 nm		
Aniline	2.90×10^8	3.30×10^8	7.10×10^{8a}	5.00×10^{8c}
Triethylamine	4.10×10^7	4.18×10^7	7.23×10^{7b}	6.40×10^{6d}
Anthranilic acid	1.01×10^8	1.07×10^8		
Phenoxide	1.45×10^8	1.52×10^8	5.90×10^{8c}	2.20×10^{7c}
Ethanol	5.46×10^6	5.52×10^6	1.90×10^{7c}	1.50×10^{4c}
Isopropanol	4.81×10^6	4.92×10^6	1.80×10^{7c}	3.90×10^{4c}
Benzene	3.13×10^6	3.26×10^6		3.00×10^{3c}
Toluene	2.80×10^6	2.92×10^6		4.30×10^{4c}
Benzoic acid	1.06×10^7	1.13×10^7	$< 10^{7c}$	

^aSubramanian et al 1986; ^bSubramanian et al Unpubl work; ^cElango et al 1984;

^dElango et al 1985; ^eRoss and Neta 1979.

where $[S]_0$ is the initial concentration of the substrate added. The slope of the plot of the pseudo-first-order rate constant vs. [substrate], yields the second-order rate constant.

The reactions of the borate radical with a variety of organic substrates were studied at pH 11.5. The kinetics were followed by monitoring the decay of the borate radical at both the absorption maxima ($\lambda_{\text{max}} = 590, 650 \text{ nm}$). The rate constants observed are reported in table 3. The data are subject to the errors inherent in flash photolysis studies ($\pm 10\%$).

The reactivity of the borate radical with the various organic substrates follows the order: aniline > phenol > anthranilic acid > triethylamine > benzoic acid > ethanol > isopropanol > benzene > toluene.

In general borate radical is less reactive than phosphate radical (Subramanian *et al* 1986; Rose and Neta 1979) and more reactive than carbonate radical (Ross and Neta 1979; Elango *et al* 1984, 1985) towards the various organic substrates.

Further studies on the reactions of the borate radical are in progress.

References

- Anderson J L, Eyring E M and Whittaker M P 1964 *J. Phys. Chem.* **68** 1128
Behar D, Czapski G and Duchovny I 1970 *J. Phys. Chem.* **74** 2206
Degliotti L and Hayon E 1967 *J. Phys. Chem.* **71** 2511
Elango T P, Ramakrishnan V, Vancheesan S and Kuriacose J C 1984 *Proc. Indian Acad. Sci. (Chem. Sci.)* **93** 47
Elango T P, Ramakrishnan V, Vancheesan S and Kuriacose J C 1985 *Tetrahedron* **41** 3837
Elango T P, Ramakrishnan V and Kuriacose J C 1985 *J. Indian Chem. Soc.* **62** 1033
Goulden J D S 1959 *Spectrochim. Acta* **9** 657
Hayon E and McGarvey J J 1967 *J. Phys. Chem.* **71** 1472
Ingri N 1963 *Acta Chim. Scand.* **17** 581
Maya L 1976 *Inorg. Chem.* **15** 2179
Morkovnik A F and Okhlobystein O Yu 1979 *Russ. Chem. Rev. (Engl. Transl.)* **48** 1055
Nies N P and Campbell G W 1964 in *Boron, metallo-boron compounds and boranes* (ed) R M Adams (New York: Interscience) p. 80
Roebke W, Renz M and Henglein A 1969 *Int. J. Radiat. Phys. Chem.* **1** 39
Ross A B and Neta P 1979 *National standard reference data series* (Washington: US Natl. Bur. Stand.) No. 65
Salentine C G 1983 *Inorg. Chem.* **22** 3920
Subramanian P, Ramakrishnan V, Rajaram J and Kuriacose J C 1986 *Proc. Indian Acad. Sci. (Chem. Sci.)* **97** 573