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The Metal Bromate Decomposition Reaction in Fused Alkali Nitrates¹

BY FREDERICK R. DUKE AND WALTER W. LAWRENCE

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The decomposition reaction: $6M^{++} + 12BrO_3^- \rightarrow 6Br_2 + 15O_2 + 6MO$ where M^{++} is cobalt, copper, nickel or zinc ion proceeds at a measurable rate in fused KNO_3 - $NaNO_3$ or $LiNO_3$ - KNO_3 - $NaNO_3$ eutectics in the range 170 to 290°. A kinetic study of the reaction demonstrates that the mechanism consists of two steps: the fast equilibrium $M^{++} + BrO_3^- \rightleftharpoons MBrO_3^+$ followed by the slow step $MBrO_3^+ \rightarrow$ decomposition products. The presence of the equilibrium is demonstrated by an experimental technique which leads to separation of the rate and equilibrium constants. Activation energies are also determined and relative reactivities of the four metal ions evaluated. The reactivities of various metal ions toward the reaction are interpreted on the basis of the following factors: (1) ability of the metal ion to complex with bromate in the fused nitrate solvent, (2) a favorable thermodynamic energy relationship between metal ion and its oxide and (3) the ability of the metal bromate complex to reach a favorable electronic configuration for decomposition to occur.

Dilute solutions of alkali bromates in fused alkali nitrate solvents will decompose above 300° but are quite stable at lower temperatures. If a heavy metal ion such as zinc(II) is added the decomposition to bromine and oxygen is catalyzed. Various metal ions effect different rates of reaction. The mechanism may be studied by kinetic observation and the relative reactivities of several metal ions may be evaluated.

Experimental

Materials and Apparatus.—ACS reagent grade chemicals were used. All of the rate determinations were carried out in test-tube-shaped Pyrex reaction vessels immersed in a constant temperature bath consisting of a fused mixture of alkali nitrates. The temperature was maintained to within $\pm 1^\circ$ with a chromel-alumel indicating thermocouple controlling a Brown Potentiometer Pyrometer.

The reaction vessel used for most experiments was made from 31 mm. i.d. Pyrex tubing. A 40/50 standard taper glass joint at the top was used to give easy access to the solution and was fitted with a gas inlet tube which reached to within one-half inch of the bottom of the reaction vessel and an outlet tube extending from the cap. This arrangement allowed one to agitate the solution and to sweep gaseous products out and into absorbing solutions with an inert gas.

The sweep gas was first dried in a tower containing anhydrous $Mg(ClO_4)_2$ and metered through an orifice meter. A mercury manometer was used to observe back-pressure on the system.

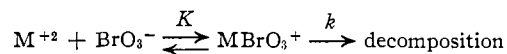
Procedure.—A solution of sodium bromate in the fused eutectic was added to a heavy metal nitrate solution in the same solvent. The solutions were maintained at the bath

temperature. The rate of reaction was studied by collecting evolved bromine in water containing sulfite and titrating with standard silver nitrate. The concentration of the heavy metal ion in the fused solution was determined by dissolving a sample in water and then titrating with standard EDTA, using naphthyl azoxine indicator.² In all cases concentrations are expressed in molality units.

When determining the stoichiometry of the reaction, a special flask was constructed so the system could be evacuated before mixing the thermostated reactant solutions. Product gases were collected in this way without sweeping with an inert gas and the relative amount of bromine and oxygen produced in the reaction was determined by an Orsat-type analysis.

Results and Discussions

Separate solutions of the metal nitrates and sodium bromate in the fused alkali nitrate eutectics were found to be stable below 300° but, when mixed, reaction occurred giving the metal oxide and bromine as products: $6M^{++} + 12BrO_3^- \rightarrow 6Br_2 + 15O_2 + 6MO$. By keeping one of the reactants in much higher concentration than the other, it was found that the reaction was first order both in divalent metal ion and bromate, each at low concentration. The experimental data did not fit a second order mechanism but suggested a fast prior equilibrium followed by rate controlling decomposition



(1) Contribution No. 844. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) J. S. Fritz, W. J. Lane and A. S. Bystrhoff, *Anal. Chem.*, **29**, 821 (1957).

for which the rate expression is

$$\text{rate} = \frac{kK[M^{+2}][\text{BrO}_3^-]}{(1 + K[M^{+2}])} \quad (1)$$

$$= k'[\text{BrO}_3^-]$$

if the metal ion concentration is kept much higher than the bromate concentration; under these conditions, the bracketed terms are total concentrations. This expression was tested by determining a series of k' values at various metal ion concentrations. These could then be used to test the rate expression, since a plot of $1/k'$ vs. $1/[M^{+2}]$ should lead to a straight line from which the equilibrium and rate constants might be evaluated

$$\frac{1}{k'} = \frac{1}{kK[M^{+2}]} + \frac{1}{k} \quad (2)$$

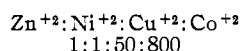
Note that the intercept on the $1/[M^{+2}]$ axis is $-K$. It was found that reaction rates could best be followed in the range 230–290° for zinc(II) and nickel(II) while those for copper(II) and cobalt(II) were best studied in the range 170–210° because of their higher reactivities. When the data are plotted according to eq. 2, reasonably straight lines are obtained from which the slopes and, in most cases, the intercepts can be evaluated. These lead to the rate and equilibrium constants listed in Table I.

TABLE I
RATE AND EQUILIBRIUM CONSTANTS EVALUATED FROM STUDY OF M^{+2} -BROMATE REACTION

Ion	Temp., °C.	k , min. ⁻¹	K , mole ⁻¹
Zn ⁺²	250	0.46 ± 0.15	1.3 ± 0.5
	230	.025 ± .01	12 ± 4
Ni ⁺²	250	.46 ^a	1.3 ^a
	230	.025 ^a	12 ^a
Cu ⁺²	210	.33 ± 0.07	3 ± 1.5
	190	.022 ± .01	9.3 ± 3
Co ⁺²	180	.15 ± .04	45 ± 9

^a Constants estimated from similarity with Zn⁺² data.

Experiments were performed at various temperatures and Arrhenius plots made to determine activation energies. E^* values of about 42 kcal./mole were obtained for all four systems. Also from this plot relative reactivities were evaluated.



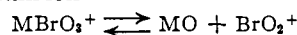
Other metal ions such as Pb(II), Cd(II), Hg(II), Si(II), Y(III), La(III) and some other rare earths were tested and found to be inactive toward decomposition of bromate in this system in the temperature range studied. It is postulated that these ions might be too strongly solvated by nitrate for the bromate complex to be formed.

Two correlations can be made for the experimental results in so far as the reactivities of the metal ions are concerned, both of which involve the basic premise that the ion must be capable of forming a reactive complex with bromate. It will be observed that the reactivity parallels the expected paramagnetic character of the metal ion with the possible exception of nickel. The fused nitrate solutions of nickel nitrate were always brown in color until cooled when they turned green. Also the Ni⁺⁺ solution in fused lithium perchlorate, which is assumed less complexing than nitrate, was bright

green. Color, of course, is not necessarily indicative of magnetic character but in this case is suggestive. This hypothesis that divalent nickel might be diamagnetic in fused nitrate solvents is not substantiated by Gruen,³ who reports the spectrum is much the same as observed in water. Nevertheless, an attempt to study the magnetic character of the hot solution seemed to indicate a possible diamagnetic character. There was no provision for keeping the sample hot in the magnetic field; it was also difficult to keep ferromagnetic nickel oxide out of the solution.

Magnetic catalysis of this sort has been shown by other investigators. In one case Calvin^{4,5} has shown paramagnetic character to be involved in a photosensitive reaction. In another case Gelles, *et al.*,^{6–11} have shown a paramagnetic catalysis in the thermal decarboxylation of some organic acids. It is possible that some favorable electronic configuration for the metal bromate complex is more readily reached when a heavy metal nucleus is present and, in particular, when there are unpaired electrons available to cause a perturbation.

Another possible correlation of metal ion reactivity can be seen. The metal ion–bromate complex could be in equilibrium with the metal oxide and bromonium ion



The bromonium ion decomposition then could be responsible for the final products. In the case of the existence of this equilibrium, the rate should be dependent on the free energy change upon going from the metallic ion in solution to the precipitated metallic oxide. (Note that MBrO_3^- is in equilibrium with M^{++} .) No data on the free energy of metal ions in fused nitrates were available; aqueous solution data were therefore used, assuming identical free energy changes for all ions upon changing solvent. Table II contains a listing of such data, showing that indeed Zn⁺⁺ and Ni⁺⁺ should have about the same reactivities and Cu⁺⁺ and Co⁺⁺ greater activities. (Co_3O_4 was the oxide found as product and is therefore the one listed in Table II.)

TABLE II
THERMODYNAMIC FREE ENERGY DATA FOR AQUEOUS METAL IONS AND THEIR SOLID OXIDES^{12,13}

Element	$M^{++}(\text{aq.})$, kcal.	F° MO, kcal.(s)	(MO– M^{++}), kcal.
Zn	–35.18	–76.050	–40.86
Ni	–11.1	–51.7	–40.60
Cu	15.53	–30.4	–45.9
Co	–12.3	–59.8 ^a	–47.5
Cd	–18.58	–53.79	–35.21
Pb	–5.81	–45.05	–39.24
Hg	39.38	–13.99	–53.37

^a Value for Co_3O_4 per cobalt.

- (3) (a) D. M. Gruen, *J. Inorg. and Nuclear Chem.*, **4**, 74 (1957).
- (b) D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, **63**, 393 (1959).
- (4) M. Calvin and G. D. Dorough, *J. Am. Chem. Soc.*, **70**, 699 (1948).
- (5) M. Calvin, *ibid.*, **71**, 4024 (1949).
- (6) K. Pitzer and E. Gelles, *ibid.*, **75**, 5132 (1953).
- (7) E. Gelles and K. Pitzer, *ibid.*, **77**, 1974 (1955).
- (8) E. Gelles and R. I. Reed, *Nature*, **176**, 1262 (1955).
- (9) E. Gelles and R. I. Reed, *ibid.*, **176**, 925 (1955).
- (10) E. Gelles and J. J. Clayton, *Trans. Faraday Soc.*, **52**, 353 (1956).
- (11) E. Gelles and G. H. Nancollas, *ibid.*, **52**, 680 (1956).

Two difficulties with this point of view are: (1) Many of the metal ions having the proper free energy relationship are not catalysts; and (2) BrO_2^+ might well be expected to provide some NO_2^+ by reaction with the nitrate ion of the solvent

(12) F. T. Wall, "Chemical Thermodynamics," W. H. Freeman and Company, San Francisco, Calif., 1958, pp. 402-414.

(13) W. M. Latimer and J. H. Hildebrand, "Reference Book of Inorganic Chemistry," The Macmillan Company, New York, N. Y., 1955, pp. 537-540.

in which case NO_2 ought to be a reaction product,^{14,15} which was found not to be the case. Thus, unless ions such as Pb^{++} and Hg^{++} do not associate with bromate for some reason and unless BrO_2^+ is a very much weaker acid than NO_2^+ , this latter correlation is coincidental.

(14) F. R. Duke and M. L. Iverson, *J. Am. Chem. Soc.*, **80**, 5061 (1958).

(15) F. R. Duke and S. Yamamoto, *ibid.*, **81**, 6378 (1959).

[CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

Reactions in Fused Salts. The Metal-Bromide-Bromate Reaction¹

BY FREDERICK R. DUKE AND WALTER W. LAWRENCE

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The reaction $3\text{Zn}^{+2} + 5\text{Br}^- + \text{BrO}_3^- \rightarrow 3\text{ZnO} + 3\text{Br}_2$ proceeds at a measurable rate in alkali nitrate eutectic solutions at 250°. A kinetic study of the reaction indicates that the mechanism involves two general steps: equilibria of the type $\text{Zn}^{+2} + n\text{Br}^- + m\text{BrO}_3^- \rightleftharpoons \text{ZnBr}_n(\text{BrO}_3)_m^{-(n+m-2)}$ followed by slow steps of the type $\text{ZnBr}_n(\text{BrO}_3)_m^{-(n+m-2)} \rightarrow$ decomposition products. The bromide further complicates the reaction by forming zinc bromide complexes which are inert toward the reaction. Formation constants for these complexes were evaluated from the kinetic data.

Reactions of halate with halide in aqueous solution have been studied by many investigators. Most recently, J. Sigalla² has examined kinetically the reaction of bromate with chloride and bromide and discussed his results in relation to those of other investigators. In all cases a first order dependence on bromate and second order dependence on hydrogen-ion concentrations have been reported. The order in bromide seems to be uncertain with some reports of simple first order dependence and others of two terms, the second containing a second order dependence on bromide concentration. One proposed mechanism involves a fast equilibrium to form a complex (H_2BrO_3^+) followed by rate determining reaction with halide.³ An alternate mechanism involves the formation of BrO_2^+ ion; since the latter is indistinguishable from H_2BrO_3^+ in aqueous solution, it was considered interesting to investigate the reaction in fused alkali nitrate medium, where a possible distinction of an intermediate such as BrO_2^+ might be made.

Experimental

Materials and Apparatus.—ACS reagent grade chemicals were used. All the rate determinations were carried out in erlenmeyer flask-shaped Pyrex reaction vessels immersed in a constant temperature bath consisting of a fused mixture of alkali nitrates. The temperature was maintained to within $\pm 1^\circ$ with a chromel-alumel indicating thermocouple controlling a Wheelco model 404 Capacitral.

The reaction vessel used for the experiments was a 500 ml. erlenmeyer flask with a 40/50 standard taper glass joint at the top to give easy access to the solution. The cap was a separate piece fitted with a gas inlet tube which reached to within one-half inch of the bottom of the reaction vessel and with an outlet tube extending from the cap. This arrangement allowed one to agitate the solution and to sweep gaseous products out and into absorbing solutions with an inert gas.

The sweep gas was first dried in a tower containing anhydrous $\text{Mg}(\text{ClO}_4)_2$ and metered through an orifice meter. A

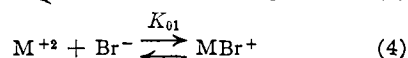
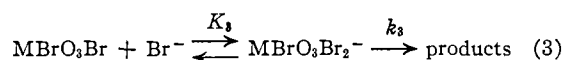
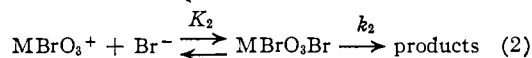
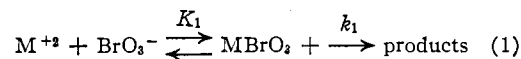
mercury manometer was used to observe back-pressure on the system.

Procedure.—A solution of sodium bromate in fused nitrate eutectic was added to a zinc nitrate and sodium bromide solution in the same solvent. The solutions were maintained at 250° in a constant temperature bath. The rate of reaction was studied by collecting bromine evolved from the reaction in water containing SO_2 and titrating with standard silver nitrate, using eosin indicator. The concentration of bromide in the melt was determined by taking a sample with a hot dropper and dissolving in water. This was also titrated in the same manner. The concentration of the heavy metal ion in the fused solution was determined by dissolving another weighed sample in water and then titrating with standard EDTA, using naphthyl azoxime indicator.

Results and Discussion

By keeping two of the reactant concentrations much higher than the third, in order to keep them essentially invariant during a run, the kinetic order in metal ion and bromate were found to be each first order. Since high concentrations of metal ion and bromate were not stable together,³ the order in bromide was not obtained at low bromide concentrations. Furthermore, the effect of bromide on the rate of the M^{+2} -bromate decomposition reaction was not a simple function of the bromide concentration.

After the M^{+2} -bromate reaction had been studied and the rate expression tested, it was thought that a similar mechanism might be involved for the case when bromide is added but with metal bromide complexes forming which were inactive toward reaction and metal bromate-bromide complexes forming which were more reactive than the simple metal bromate complexes



(1) Contribution No. 845. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) J. Sigalla, *J. chim. phys.*, **55**, 758 (1958).

(3) J. O. Edwards, *Chem. Revs.*, **50**, 455 (1952).