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).

Reactions in Fused Salts. The Metal–Bromide–Bromate Reaction[1]

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The reaction $3Zn^{+2} + 5Br^- + BrO_3^- \rightarrow 3ZnO + 3Br_2$ 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 $Zn^{+2} + nBr^- + mBrO_3^- \rightleftarrows ZnBr_n(BrO_3)_m^{-(n + m - 2)}$ followed by slow steps of the type $ZnBr_n(BrO_3)_m^{-(n + m - 2)} \rightarrow$ 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. Sigalla[2] 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 ± 1° 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 $Mg(ClO_4)_2$ and metered through an orifice meter. A

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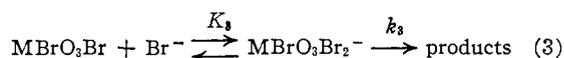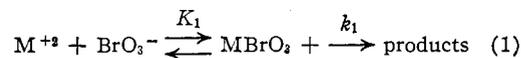
(3) J. O. Edwards, Chem. Revs., 50, 455 (1952).

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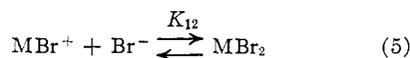
After the M^{+2}–bromate reaction had been studied and the rate expression tested, it was thought that a similar mechanism might be involved for the case when bromide is added but with metal bromide complexes forming which were inactive toward reaction and metal bromate–bromide complexes forming which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

$$M^{+2} + BrO_3^- \underset{\xleftarrow{}}{\overset{K_1}{\rightleftharpoons}} MBrO_3 + \xrightarrow{k_1} \text{products} \quad (1)$$

$$MBrO_3^+ + Br^- \underset{\xleftarrow{}}{\overset{K_2}{\rightleftharpoons}} MBrO_3Br \xrightarrow{k_2} \text{products} \quad (2)$$

$$MBrO_3Br + Br^- \underset{\xleftarrow{}}{\overset{K_3}{\rightleftharpoons}} MBrO_3Br_2^- \xrightarrow{k_3} \text{products} \quad (3)$$

$$M^{+2} + Br^- \underset{\xleftarrow{}}{\overset{K_{01}}{\rightleftharpoons}} MBr^+ \quad (4)$$

$$MBr^+ + Br^- \underset{K_{23}}{\overset{K_{12}}{\rightleftharpoons}} MBr_2 \quad (5)$$

$$MBr_2 + Br^- \overset{K_{23}}{\rightleftharpoons} MBr_3^- \quad (6)$$

$$Rate = k_1[MBrO_3^+] + k_2[MBrO_3Br] + k_3[MBrO_3Br_2^-] \quad (7)$$

The total concentration of divalent metal will then be divided among uncomplexed and complexed species. In the previous study of zinc bromate decomposition at 250°, values of $K_1 = 1.3$ mole^{-1} and $k_1 = 0.46$ min.$^{-1}$ were obtained. In the experiments reported in the present article, the bromide concentration was kept high and [Zn^{++}] also high, with bromate concentration lower than either. However, due to the formation of the zinc–bromide complexes, it turned out that the free zinc ion was much lower than the bromate; therefore, the mixed zinc–bromate–bromide complexes were assumed to be insignificant in their contribution to the material balance of the zinc species

$$(Zn^{+2})_T = [Zn^{+2}] + [ZnBr^+] + [ZnBr_2] + [ZnBr_3^-] + [ZnBrO_3^+] \quad (8)$$

Combining eq. 8 with the various equilibrium constant equations and solving for the three Zn species in the rate equation in terms of [Zn^{++}]$_T$, one obtains the rate expression

$$Rate = \frac{[Zn^{++}]_T[BrO_3^-]\{k_1K_1 + k_2K_1K_2[Br^-] + k_3K_1K_2K_3[Br^-]^2\}}{1 + K_1[BrO_3^-] + K_{01}[Br^-] + K_{01}K_{12}[Br^-]^2 + K_{01}K_{12}K_{23}[Br^-]^3} \quad (9)$$

In this expression, the [Zn^{++}]$_T$ is the total zinc ion concentration in all forms, but the [BrO$_3^-$] and [Br$^-$] are actual concentrations and as the equilibrium constants are evaluated from the data, successive approximations must be made to correct the [Br$^-$] particularly. The data in Table I were programmed for the IBM Magnetic Drum calculator and the equilibrium constants evaluated. The constants, K_2 and K_3 are not separable from the rate constants; K_{01}, K_{12} and K_{13} were found to be 250, 40 and 10 mole^{-1}, respectively. The products of the constants $k_2K_1K_2$ and $k_3K_1K_2K_3$ were, respectively, 1500 min.$^{-1}$ mole^{-2} and 500–1300 min.$^{-1}$ mole^{-3}. The precision is reasonably good for K_{01} but K_{12} and K_{23} are approximate values.

Infrared Spectra of Metal Chelate Compounds. III. Infrared Spectra of Acetylacetonates of Divalent Metals[1]

By Kazuo Nakamoto, Paul J. McCarthy and Arthur E. Martell

The infrared spectra of acetylacetonates of six divalent metals have been measured in the range between 4000 and 400 cm.$^{-1}$. The vibrational frequencies have been calculated for each metal by the perturbation method. The calculated frequencies and assignments were used to (1) elucidate the complex spectra in the 1600 ~ 1400 cm.$^{-1}$ region; (2) correlate the electronic structures of strong and weak chelates with the calculated force constants and (3) show the relationship between the force constant and thermodynamic data based on formation constants from solution equilibria. Also, three chelate compounds of beryllium were studied to locate the characteristic infrared absorption bands of the Be–O bonds.

Introduction

Relationships between infrared spectra and the stability of the metallic complexes have been a subject of considerable interest. For example, Bellamy and Branch[2] have found a linear relation between the carbonyl stretching frequency and the stability constant in a series of metallic salicylaldehydes. They concluded, however, that no such simple relation exists in a series of metallic acetylacetonates. Holtzclaw and Collman[3] and West and Riley,[4] on the other hand, claim that the order of the carbonyl stretching frequency is the same as the stability order of the divalent acetylacetonates if the highest frequency band near 1600 cm.$^{-1}$ is selected as the carbonyl stretching band. Harkins, et al.,[5] have

also found for a series of divalent metal chelates of imidazole derivatives that the order of frequencies of the band near 1250 cm.$^{-1}$ is shifted regularly according to the stability order of Mellor–Maley.[6]

In view of the conflicting nature of previous work, it is of considerable importance to determine whether a relationship between stability and infrared frequency really exists in a series of divalent metal acetylacetonates and, more generally, whether such a simple correlation can be justified on theoretical grounds.

In the previous paper of this series,[7,8] vibrational frequencies and force constants have been calculated for trivalent metal acetylacetonates through the use of perturbation theory. The metal-oxygen force constants thus obtained seem to be more suited to the examination of the relationship between stability and spectra than are the frequencies of the infrared bands, since the latter involve the

(1) This work was supported by the Office of Ordnance Research under contract no. DA-19-020-ORD-5119.

(2) L. J. Bellamy and R. F. Branch, *J. Chem. Soc.*, 4487, 4491 (1954).

(3) H. F. Holtzclaw and J. P. Collman, *J. Am. Chem. Soc.*, **79**, 3318 (1957).

(4) R. West and R. Riley, *J. Nuclear Inorg. Chem.*, **5**, 295 (1958).

(5) T. R. Harkins, J. L. Walter, O. E. Harris and H. Freiser, *J. Am. Chem. Soc.*, **78**, 260 (1956).

(6) D. P. Mellor and L. E. Maley, *Nature*, **159**, 379 (1947); **161**, 436 (1948).

(7) K. Nakamoto and A. E. Martell, *J. Chem. Phys.*, **32**, 588 (1960).

(8) K. Nakamoto, H. J. McCarthy, A. Ruby and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1066 (1961).