OXIDATION OF BROMIDE IONS WITH CHLORINE IN MOLTEN ZINC CHLORIDE–POTASSIUM CHLORIDE MIXTURE

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In our earlier work we investigated equilibrium and kinetics of the reaction of chlorine with bromide ions in molten eutectic mixture of lithium and potassium chlorides[1,2]. The analytically determined ratio of bromine to chlorine in the gaseous phase was found to be directly proportional to the ratio of concentrations of bromides to chlorides in the melt. This finding was explained by assuming simultaneously proceeding equilibrium reactions that must be taken into account in the presence of bromine monochloride in the gaseous phase. Reaction rate of the oxidation of bromide ions with chlorine was directly proportional to the partial pressure of chlorine; however, the reaction order with respect to bromide ions concentration varied from zero to unity in dependence on the concentration of bromide. This phenomenon was interpreted in terms of the simultaneous course of equilibrium reactions.

Oxidation–reduction reactions of gaseous halogen with halides in melts are of great interest, as they represent the simplest kind of reactions in which only anion participates in the reactions in ionic liquids. Equilibrium constant of these reactions is a measure of the relative thermodynamic stability of halide ions. From both theoretical and practical point of view it is important in which way this stability can be influenced by changing the cation in the melt. Since this question is of fundamental importance not only for the investigation of the structure of molten salts, but also for the interpretation of reactions in molten salts, we have dealt this problem in more detail. The first subject of our studies was the mixture of zinc and potassium chlorides that had proved to be a suitable reaction medium in our previous studies[3,4].

EXPERIMENTAL

Apparatus

The reaction vessel was formed by a large test tube of 40 mm diameter and 250 mm height, made of boro silicate glass. The melt of the mixture of zinc and potassium chlorides with a given amount of bromides was bubbled through by a stream of chlorine–nitrogen or bromine–nitrogen mixture. The gaseous reaction products were analysed as to the content of chlorine and bromine. The agreement of the analysis of products in the reaction of chlorine or bromine with the melt containing the same amount of bromides indicated that the equilibrium was attained, at a given flow rate of the gases. The reaction vessel was thermostated on a stirred bath of alkali nitrates the temperature of which was maintained constant with an accuracy of ± 1°C.

Chemicals and Analytical Methods

All chemicals used were of reagent grade purity. The mixtures of zinc chloride with potassium chloride or bromide were obtained by weighing the previously dried substances in a appropriate ratio. The basic chloride melt contained 30 mol% potassium chloride (m.p. 268°C). The amount of bromide added was chosen so as to make the content of potassium salts in the resulting melt 30 mol%. Chloride melt was purified, after melting, by long-term bubbling of hydrogen chloride

and chlorine. The flow-rate of chlorine and nitrogen was controlled by a liquid manostat and measured by means of a capillary flow meter. Bromine in the gaseous phase was obtained by leading nitrogen through liquid bromine at a chosen temperature. Reaction gases were absorbed in sulphite solution and the content of bromine or chlorine was determined by argentometric titration with potentiometric indication.

RESULTS AND DISCUSSION

In the reaction of chlorine with bromide the following simultaneous chemical equilibria take place

$$Cl_2 + 2\,Br^- = 2\,Cl^- + Br_2\,, \qquad (A)$$

$$Cl_2 + Br_2 = 2\,BrCl\,, \qquad (B)$$

$$Cl_2 + Br^- = Cl^- + BrCl\,, \qquad (C)$$

$$BrCl + Br^- = Cl^- + Br_2\,. \qquad (D)$$

Equilibrium constants are defined by the relations

$$K_A = (N^2_{Cl^-}/N^2_{Br^-})\,(P_{Br_2}/P_{Cl_2})\,, \qquad (1)$$

$$K_B = P^2_{BrCl}/P_{Br_2}\,.\,P_{Cl_2}\,, \qquad (2)$$

$$K_C = (N_{Cl^-}/N_{Br^-})\,(P_{BrCl}/P_{Cl_2})\,, \qquad (3)$$

$$K_D = (N_{Cl^-}/N_{Br^-})\,(P_{Br_2}/P_{BrCl})\,, \qquad (4)$$

where N are mole fractions and P partial pressures of the respective reacting species.

A quantity that can be determined analytically is the total concentration of bromine or chlorine in the vapour phase, defined by the relations

$$Br_{anal} = (2n_{Br_2} + n_{BrCl})/V\,, \qquad (5)$$

and

$$Cl_{anal} = (2n_{Cl_2} + n_{BrCl})/V\,, \qquad (6)$$

where n denotes the number of mol and V the volume.

The ratio of analytically determinable total concentrations of bromine and chlorine can be expressed as follows

$$\frac{Br_{anal}}{Cl_{anal}} = \frac{2n_{Br_2} + n_{BrCl}}{2n_{Cl_2} + n_{BrCl}} = \frac{2P_{Br_2} + P_{BrCl}}{2P_{Cl_2} + P_{BrCl}}\,. \qquad (7)$$

After rearrangement we obtain the expression

$$\frac{Br_{anal}}{Cl_{anal}} = \frac{2(K_A/K_B)^{1/2}\,(N_{Br^-}/N_{Cl^-}) + 1}{[2N_{Cl^-}/(K_A K_B)^{1/2}\,N_{Br^-}] + 1}\,, \qquad (8)$$

which describes the dependence of the gaseous phase composition on the composition of the melt in terms of measurable quantities. The value of the equilibrium constant K_B is independent of the

TABLE I

Measured Values of Equilibrium Constants

t, °C	K_A	K_C	K_D
300	416 000	1 780	237
325	235 000	1 330	176
350	138 000	1 180	135

kind of system under study and is known from several independent measurements[5,6]. Consequently, analytical data can serve for calculating the values of equilibrium constants K_A, K_C and K_D that are summarized in Table I.

As can be seen from this Table, equilibrium constant K_A decreases with increasing temperature. The change of reaction enthalpy, $\Delta H = 15$ kcal/mol. On extrapolating its value to higher temperatures, we can compare quantitatively the studied system with melts of alkali halides which were studied in preceding papers[1,2]. So, *e.g.*, at 400°C the value of K_A is 68 600 for the molten mixture of potassium and zinc chlorides, whereas in an eutectic melt of lithium and potassium chlorides K_A was found to be 208 200 at 400°C. This means that in alkali halides the value of the equilibrium constant is three times higher than that in the molten zinc and potassium chlorides mixture, the necessary partial pressure of chlorine is three times lower than it is in the melts containing zinc chloride. From this we can conclude that the presence of zinc chloride has a stabilizing effect on bromide ions in the melt or that it decreases the relative reactivity of bromide with respect to chloride.

This phenomenon can be explained by the change of melt structure. Zinc(II) chloride is a distinctly covalent substance, only slightly dissociated to ions. Addition of alkali halogenides to its melt causes the formation of associates of the type $ZnX_n^{(n-2)-}$. The stability of bromide associates in melts is considerably higher than that of chloride associates. This could explain the effect of substituting alkali chlorides by zinc(II) chloride in the melt on the increase of the thermodynamic stability of bromide ions.

Kinetics of the Reaction

Since, according to experimental results the gaseous reaction mixture is under the given conditions in equilibrium with the melt, kinetic equations can be derived using the equilibrium data. If we denote the number of gramions of bromide, reacting with one mol of chlorine in the initial mixture as $2x$ and the number of moles of bromine monochloride in the gaseous phase $2y$, then we can express constants K_A to K_D in terms of x and y (see[2]). Solving any arbitrary two of the four equations obtained, we can calculate the dependence of x on the concentration of bromide in the melt. The true kinetic equation, *i.e.*, the dependence of reaction rate on the concentration of reacting substances, is then obtained in the form

$$r = \frac{2n_0}{W} \frac{2K_A(N^2_{Br^-}/N^2_{Cl^-}) + K_C(N_{Br^-}/N_{Cl^-})}{2K_A(N^2_{Br^-}/N^2_{Cl^-}) + 2K_C(N_{Br^-}/N_{Cl^-}) + 2} \cdot P_{Cl_2}, \tag{9}$$

where n_0 is the total number of moles coming into contact with the melt per one second. From this kinetic equation it is evident that the reaction order with respect to the partial pressure of chlorine

TABLE II

Values of Reaction Rate at 300°, 325° and 350°C
$W = 0{\cdot}0545$ kg.

$n_0 \cdot 10^4$ mol s^{-1}	P_{Cl_2} atm	N_{Br^-}	$r \cdot 10^4$, g-ion kg^{-1} s^{-1} calculated	found
		$t = 300°C$		
0·394	0·131	0·0196	1·72	1·70
0·420	0·186	0·0196	2·61	2·58
0·480	0·288	0·0196	4·58	4·61
0·394	0·131	0·0100	1·59	1·54
0·420	0·186	0·0100	2·40	2·36
0·480	0·288	0·0100	4·22	4·33
0·394	0·131	0·0050	1·39	1·30
0·420	0·186	0·0050	2·10	1·99
0·480	0·288	0·0050	3·69	3·83
0·394	0·131	0·0030	1·21	1·07
0·420	0·186	0·0030	1·83	1·67
0·480	0·288	0·0030	3·21	3·30
0·394	0·131	0·0020	1·05	0·87
0·420	0·186	0·0020	1·59	1·36
0·480	0·288	0·0020	2·79	2·75
		$t = 325°C$		
0·394	0·131	0·0196	1·67	1·68
0·420	0·186	0·0196	2·54	2·57
0·480	0·288	0·0196	4·45	4·54
0·394	0·131	0·0100	1·51	1·52
0·420	0·186	0·0100	2·29	2·30
0·480	0·288	0·0100	4·02	4·17
0·394	0·131	0·0030	1·1	1·10
0·420	0·186	0·0030	1·66	1·76
0·480	0·288	0·0030	2·92	3·18
0·394	0·131	0·0020	0·93	0·92
0·420	0·186	0·0020	1·42	1·44
0·480	0·288	0·0020	2·49	2·79
		$t = 350°C$		
0·394	0·131	0·0196	1·62	1·66
0·420	0·186	0·0196	2·45	2·54
0·480	0·288	0·0196	4·31	4·32
0·603	0·433	0·0196	8·14	7·3
0·394	0·131	0·0100	1·43	1·52

TABLE II

(*Continued*)

$n_0 \cdot 10^4$ mol s^{-1}	P_{Cl_2} atm	N_{Br^-}	$r \cdot 10^4$, g-ion kg^{-1} s^{-1} calculated	found
		$t = 350°C$		
0·420	0·186	0·0100	2·17	2·21
0·480	0·288	0·0100	3·81	3·81
0·603	0·433	0·0100	7·21	6·93
0·394	0·131	0·0050	1·19	1·30
0·420	0·186	0·0050	1·81	1·93
0·480	0·288	0·0050	3·17	3·01
0·603	0·433	0·0050	5·99	5·43
0·394	0·131	0·0030	0·99	1·07
0·420	0·186	0·0030	1·50	1·62
0·480	0·288	0·0030	2·64	2·38
0·603	0·433	0·0030	4·98	4·11
0·394	0·131	0·0020	0·83	0·89
0·420	0·186	0·0020	1·26	1·32

equals unity, however, with respect to bromide concentration in the melt it is not constant, being a function of bromide concentration. Results of kinetic measurements are presented in Table II. Reaction rates, as calculated according to Eq. (*9*), are given in the last but one column of the Table and the experimentally obtained values are in the last column. Good agreement of both these data which lies within the limits of possible experimental error, proves that the reaction rate can be interpreted in terms of a sequence of simultaneously proceeding reactions of chlorine with bromide in the melt according to the above mentioned Scheme.

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