KINETICS OF OXIDATION OF CUPROUS CHLORIDE
IN MELTS WITH A MIXTURE OF OXYGEN AND HYDROGEN CHLORIDE

J.Sláma and P.Pacák

Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, Prague 6

Recently an increasing attention has been paid to the catalytic effect of molten salts on reactions in the gaseous phase. This interest was stimulated by the possibility of studying the mechanism of catalysis in the mentioned systems and, on the other hand, by the development of the chemistry of molten salts. One of the problems investigated is the catalytic oxidation of hydrogen chloride by oxygen. Gorin and coworkers[1] and recently also Ruthven and Kenney[2] devoted their work to the study of partial reactions involved in this process. Most of the studies were concerned with the kinetics of oxygen absorption in the molten system cuprous chloride—potassium chloride[1-3]. This absorption is supposed to be the rate determining step of the catalytic process. Oxidation of cuprous chloride with a mixture of oxygen and hydrogen chloride has not yet been studied. Theoretically, the kinetics of this reaction could be calculated on the basis of experimental data, obtained in studying the kinetics of oxygen absorption in the melts of cuprous chloride and potassium chloride, since the reaction of hydrogen chloride with absorbed oxygen is a very fast one[2,3]. On the other hand, it cannot be *a priori* excluded that the kinetics of oxygen absorption is affected by the presence of hydrogen chloride and thus that the reaction mechanism is more complicated. For this reason the present work was performed with the aim to elucidate this problem in more detail.

EXPERIMENTAL

Apparatus

The reactor proper was a glass vessel of the form of a large test-tube (40 mm diameter and 250 mm height). The inlet of gas into the melt was placed 5—10 mm above the bottom of the test-tube. The reaction vessel was thermostated in a stirred bath of molten alkali nitrates. Bath temperature was measured by a calibrated mercury thermometer and was kept constant within ±1°C by means of a compensation thermoregulator. Gases from steel flasks were dried with concentrated sulphuric acid and their flow-rate was measured by a capillary flow-meter. Total flow-rate was 200 ml/min throughout.

Chemicals Used and Analytical Methods

Most of the chemicals used were of the "chemically pure" grade, since it was ascertained that the purity grade of the reaction agents has no effect on the kinetics of the reaction. Cuprous chloride was purified from the always present cupric chloride by washing with dilute hydrochloric acid. For checking experiments cuprous chloride of high purity was used, supplied by the Research Institute of Monocrystals, Turnov. Dried components were weighed and after mixing they were melted in the reaction vessel in nitrogen atmosphere. After stabilization of temperature the experiment was started by feeding the oxygen–hydrogen chloride mixture into the melt. Samples of the melt were taken by means of a glass pipette in suitable time intervals. After cooling and

weighing they were dissolved in water. Copper content was determined chelatometrically and the content of bivalent copper by means of iodometric analysis in an inert atmosphere. The content of chlorine in the gaseous phase was determined, after absorption in potassium iodide solution, by titration of the evolved iodine with thiosulphate.

RESULTS AND DISCUSSION

Oxidation of cuprous chloride with a mixture of oxygen and hydrogen chloride proceeds according to overall stoichiometric equation

$$4\,HCl \;+\; O_2 \;+\; 4\,CuCl \;\;\rightleftarrows\;\; 2\,H_2O \;+\; 4\,CuCl_2 \,. \tag{A}$$
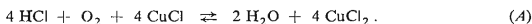
The equilibrium of this reaction is very distinctly shifted towards the formation of products. The steady state is maintained by the effect of thermal dissociation of cupric chloride to cuprous chloride and chlorine, as expressed by the equation
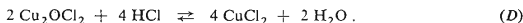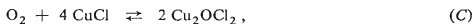
$$2\,CuCl_2 \;\;\rightleftarrows\;\; 2\,CuCl \;+\; Cl_2 \,. \tag{B}$$

Since reactions (A) and (B) proceed simultaneously, the concentration of cuprous chloride in the melt reaches a maximum at a given temperature and oxygen pressure.

Analysis of experimental data revealed that the kinetic course of the studied reaction can formally be expressed in terms of the following kinetic equation

$$dn_{CuCl_2}/n_t\,dt = kP_{O_2} - k'(N_{CuCl_2}/N_{CuCl})^2 \,, \tag{J}$$

where n_t denotes total number of moles nf the melt, N concentration in mole fractions and P and t stand for pressure and time, respectively. This result is rather unexpected, since the oxidation rate of cuprous chloride was independent of its concentration in the melt which corresponds to a zero-th order reaction with respect to cuprous chloride. Further kinetic course of the reaction is complicated by the influence of simultaneous reaction (B) and therefore the kinetics of direct and reverse reactions will be discussed separately.

Ruthven and Kenney[2] assume, similarly to Fontana and Gorin[1], the absorption rate of oxygen in the melts of cuprous chloride to be the rate determining step of the studied reaction. However, when studying the kinetics of oxygen absorption, Ruthven and Kenney found[2] that the absorption rate of oxygen in melts is directly proportional to the square of cuprous chloride concentration. This obvious disproportion indicates that the mechanism of cuprous chloride oxidation by a mixture of oxygen and hydrogen chloride is more complex and cannot therefore be interpreted in terms of simple schemes (C) and (D)

$$O_2 \;+\; 4\,CuCl \;\;\rightleftarrows\;\; 2\,Cu_2OCl_2 \,, \tag{C}$$

$$2\,Cu_2OCl_2 \;+\; 4\,HCl \;\;\rightleftarrows\;\; 4\,CuCl_2 \;+\; 2\,H_2O \,. \tag{D}$$

For this reason we tried to find the most probable reaction mechanism which would comply with all experimental data. The following mechanism resulted as the single consistent solution:

Oxygen reacts directly with the melt surface, the formed oxichloride being transformed in a fast reaction with hydrogen chloride into cupric chloride. This causes a concentration gradient at the contact surface, *i.e.* concentration of cupric chloride in the surface layer is greater than that in the bulk of the melt. The formed chlorine is not in equilibrium with the composition of the bulk of the melt and in contact with the regenerated surface it is quickly absorbed under the for-

mation of cupric chloride in the surface film. As the result of these reactions the surface film of the melt has a roughly constant composition as far as cuprous and cupric chlorides are concerned and consequently also the absorption rate of oxygen is constant. From this it follows that also the oxidation rate of cuprous chloride with oxygen–hydrogen chloride mixture is independent of the composition of the bulk of the melt and the reaction is apparently of zero-th order with respect to cuprous chloride concentration in the melt. With increasing concentration of cupric chloride in the bulk of the melt the effect of the simultaneously proceeding thermal decomposition of cupric chloride becomes more and more manifest the rate of which is proportional to the ratio of concentration squares of cupric and cuprous chlorides in the melt. In the steady state the partial pressure of chlorine in the vapour phase is in equilibrium with the concentration of cupric chloride both in the surface and in the bulk of the melt.

Some premises of this mechanism may be discussed in more detail. On the basis of their kinetic study of oxygen absorption in melts containing cuprous chloride, Ruthven and Kenney[2] concluded that the assumption of a direct reaction of oxygen with the melt is very probable. Contrary to aqueous solutions, the solubility of gas in melt is very low and thus the reaction of dissolved oxygen with cuprous chloride cannot contribute substantially to the elucidation of this problem. Fast reaction of the formed oxichloride with hydrogen was not only assumed[1,2], but it also has been demonstrated in our experiments. The ability of even thinnest films of copper chlorides to catalyze the oxidation of hydrogen chloride by oxygen has been ascertained in our paper[4]. Also the high rate of reaction of cuprous chloride with gaseous chlorine in melts has been verified in our experiments and besides it also follows from the high rate with which the equilibrium is reached.

The experimentally determined values of rate constants k are presented in Table I. We tried to compare the effect of partial gas pressures, temperature, concentration of potassium chloride and of rare earths chlorides on the experimentally found values of k with analogous effects on constant k_3, as referred in Ruthven's and Kenney's study of the kinetics of oxygen absorption in melts, containing cuprous chloride[2]. The value of k increases with increasing temperature. This effect is comparable in the case of melts containing 30 mol % KCl, however it does not correspond to the temperature dependence of k_3 at 50 mol % KCl, as Ruthven and Kenney found the activation energy to be practically zero even with melts, containing lanthanum chloride.

TABLE I

Values of Rate Constants (s^{-1} atm^{-1})

P_{O_2} atm	P_{HCl} atm	KCl mol %	NdCl$_3$ mol %	$k \cdot 10^5$		$k' \cdot 10^6$	
				450°C	500°C	450°C	500°C
0·5	0·5	50	0	5	5·9	1	3·1
0·25	0·5	50	0	5	6·1	1	3
0·5	0·25	50	0	4·8	5·8	1·1	3·1
0·5	0·5	45·5	9	12	20	1·7	7
0·5	0·5	40	0	4·4	6·5	5	9·5
0·5	0·5	30	0	4	6	9	19
0·5	0·5	36·4	9	—	20	—	22
0·5	0·5	27·3	9	—	16	—	55

The effect of increasing potassium chloride concentration on the value of k is only poor, whereas in the kinetics of oxygen absorption it is quite distinct, particularly with melts, containing rare earths chlorides. Addition of these chlorides causes a considerable increase in the value of k, however, this effect is much more expressive for k_3. From the above comparison it follows that the kinetics of oxidation of cuprous chloride with oxygen–hydrogen chloride mixture cannot be interpreted merely in terms of oxygen absorption kinetics. The direct proportionality of rate constant to partial pressure of oxygen and its independence of partial pressure of hydrogen chloride is consistent with the dependence of the reaction rate which was found in the study of catalytic effect of melts on the oxidation of hydrogen chloride to chlorine[9] by oxygen. All these findings support our concept of mechanism of cuprous chloride oxidation with a mixture of oxygen and hydrogen chloride in melts.

The equilibrium of reaction (B) in molten mixtures of copper and potassium chlorides was studied by Ruthven and Kenney[5]. In our earlier papers we investigated both the equilibrium and the kinetics of this reaction in the melts of potassium and zinc chlorides[8] and further in an eutectic melt of lithium and potassium chlorides[6,7]. Therefore it is possible to compare the values of rate constants k' as determined in the present paper with other published data. The effect of partial pressures of the gaseous components and that of the melt composition on k' can be seen from Table I. Evidently, composition of the gaseous phase has no effect on k'. With increasing temperature the value of k' increases in all cases. This finding is in accordance with the general course of the dependence of thermal dissociation on temperature. With increasing concentration of potassium chloride the value of k' decreases. Addition of neodymium chloride to the melt causes an increase of k'.

Using thermodynamic data as well as the data of Ruthven and Kenney[5] we can calculate equilibrium constants of reaction (B) or partial pressures of chlorine over melts of corresponding composition. The effect of temperature and potassium chloride concentration on the melt both on equilibrium constant and the rate constant k' can be qualitatively compared. However, Ruthven and Kenney found that addition of lanthanum chloride does not affect the equilibrium constant which is not quite in accordance with our results.

Direct comparison of the constant k' with our earlier papers is impossible owing to different forms of kinetic equations. Therefore we tried to compare partial pressure of chlorine which, under given experimental conditions, was present in the reaction products. The calculation considers equimolar concentrations of cuprous and cupric chlorides in the melt. Then the partial pressure of chlorine at 450°C for melts containing 50 mol % KCl is $2 \cdot 1 \cdot 10^{-3}$ atm and for melts with 30 mol % KCl $1 \cdot 85 \cdot 10^{-2}$ atm. In eutectic melt of lithium and potassium chlorides at 450°C and at 0·1M concentration of cuprous and cupric chloride the calculated value was $3 \cdot 1 \cdot 10^{-4}$ atm (see[7]). From this comparison it is evident that increasing concentration of alkali chlorides in the melt causes a decrease in the partial pressure of chlorine. This conclusion is in agreement with the comparison of the free enthalpy of reaction (B), as performed by Ruthven and Kenney[5]. For melts of zinc chloride with an admixture of 30 mol % of potassium chloride the calculated value of the partial pressure of chlorine at 385°C is $1 \cdot 5 \cdot 10^{-3}$ atm. Taking into account that the reaction is strongly temperature dependent, we can state that the agreement with the corresponding values found at 450°C is very good.

REFERENCES

1. Gorin E., Fontana C. H., Meredith C. S.: Ind. Eng. Chem. *44*, 363 (1952).
2. Ruthven D. M., Kenney C. N.: Chem. Eng. Sci. *22*, 1561 (1967).
3. Ruthven D. M., Kenney C. N.: Chem. Eng. Sci. *23*, 981 (1968).
4. Sláma I., Kodejš Z.: This Journal *34*, 2378 (1969).

5. Ruthven D. M., Kenney C. N.: J. Inorg. Nucl. Chem. *20*, 931 (1968).
6. Sláma I.: This Journal *28*, 518 (1963).
7. Sláma I., Regner A.: This Journal *31*, 915 (1966).
8. Sláma I., Regner A.: This Journal *31*, 970 (1966).
9. Kenney C. N.: *Fourth Intern. Congress on Catalysis, Moscow 1968.* Preprint of paper 86.

Translated by V. Čermáková.

CATALYTIC OXIDATION OF HYDROGEN CHLORIDE
WITH OXYGEN IN MELTS OF COPPER CHLORIDES

I.Sláma and J.Pacák

Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, Prague 6

In our previous paper[1] we studied the kinetics of oxidation of cuprous chloride with a mixture of oxygen and hydrogen chloride in melts. We have ascertained that the oxidation rate of cuprous chloride does not depend on its concentration in the melt. This finding was explained by assuming a reaction of oxygen with hydrogen chloride, taking place at the surface of the melt which causes that the composition of the contact surface layers is different from that of the bulk of the melt. The composition of contact layers changes only unsignificantly and consequently also the rate of reactions which is determined by absorption, is independent of the average concentration of cupric chloride in the melt. Under this assumption the oxidation of hydrogen chloride with oxygen should proceed in the given region at a practically constant rate, too. According to the presumed mechanism of catalytic effects of melts the rate determining step is the absorption of oxygen which is followed by the fast, practically irreversible reaction of the formed oxichloride with hydrogen chloride[2−4]. The formed cupric chloride is in equilibrium with chlorine in the gaseous phase. Since the governing factor in this equilibrium is the concentration of cupric chloride at the interphase boundary, the oxidation rate of hydrogen chloride at the beginning of the reaction should be much greater than would correspond to the average concentration of cupric chloride in the melt. This could serve as a proof of the assumption that the concentration of cupric chloride at the surface of contact layer is greater.

The second aim of the present study was to verify the kinetic equation of catalytic oxidation of hydrogen chloride by oxygen at the surface of molten copper chlorides, as it was derived by Kenney[2]. This equation is based on the assumption that the concentration of chlorine in the gaseous phase, which is a function of hydrogen chloride conversion, *i.e.* of the reaction rate and of the partial pressure of hydrogen chloride, determines unambiguously the ratio of cupric chloride to cuprous chloride in the melt. In this way it also determines the reaction rate, as the absorption rate of oxygen depends on the square of cuprous chloride concentration. Experimental verification of this presumption, however, is not quite convincing, as in the steady state catalysis the ratio of cuprous to cupric chlorides is always greater than unity and changes