SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Chloride Ion Oxidation in Molten Alkaline-Earth Metal, Magnesium, and Zinc Chlorides

Yu. S. Chekryshkin, A. N. Chudinov, A. A. Fedorov, and T. A. Rozdyalovskaya

Institute of Technical Chemistry, Ural Branch, Russian Academy of Sciences, ul. Akademika Koroleva 1, Perm, 614000 Russia Received July 26, 2011

Abstract—The interaction of molten alkaline-earth metal, magnesium, and zinc chlorides with oxygen has been investigated. The products of these reactions are molecular chlorine and the respective metal oxides. The reactivity of the chlorides increases linearly with an increasing polarizing power of the cation or with an increasing effective polarizing power of the mixture of cations. The magnesium oxide and magnesium oxide—zinc oxide powders resulting from the oxidation of the respective chlorides have been analyzed.

DOI: 10.1134/S0036023612110058

The interaction of metal chlorides with oxygen is of interest to those who are engaged in the synthesis of vanadates [1-3] and salt lubricants for hot rolling of tubes [4], in the synthesis of metal oxide fine powders or single-crystal films [5-7], in chlorine-containing waste treatment yielding chlorine [8, 9], and in the design of stable catalytic systems for oxidation of halogenated hydrocarbons [10-13]. Production of some metal oxides and oxychlorides, including their recovery from spent nuclear fuel, also includes the oxidation of chlorinated metal-containing mixtures, yielding molecular chlorine [14–17].

There have been studies of the catalytic effect of transition metal oxides on chloride ion oxidation in molten sodium, calcium, zinc, and barium chlorides [5, 11, 12, 18]. This effect is due to the polarizing action (ionic moment) of the oxide's cation, $ze/r_{M^{Z^+}}$, where z is the charge of the metal ion, $e = 4.803 \times 10^{-10}$ esu is the unit charge, and $r_{M^{2+}}$ is the radius of the cation. It was demonstrated that the chlorine formation rate increases with an increasing polarizing power (PP) of the cation. No chloride ion oxidation is observed as oxygen or air is bubbled through molten sodium chloride. The same process conducted in the presence of a variable-valence metal oxide vields chlorine, whose amount is a linear function of the PP of the oxide's cation. The catalytic activity of transition metal oxides decreases in the following order: $CrO_3 > V_2O_5 > MoO_3 >$ $Sb_2O_5 > CuO > Co_3O_4$. This order coincides with the decreasing order of cation PPs [18].

Here, we report the oxidation of the chloride ion in molten strontium and magnesium chlorides and in mixtures of $MgCl_2$ with sodium and zinc chlorides by gas-phase oxygen. We will consider the regularities of the oxidation of Group II metal chlorides. We have determined the particle size and phase composition of the resulting magnesium oxide and MgO–ZnO powders.

EXPERIMENTAL

The chloride ion was oxidized by bubbling air or oxygen (5 L/h) through the chloride melt at the preset temperature. The experimental procedure and apparatus were the same as in our earlier study [11]. For isolation of the resulting oxides, the melt was cooled to room temperature and the cake was dissolved in distilled water and was washed clean of the unreacted chlorides. The residual Cl⁻ concentration in the wash water was determined by capillary electrophoresis on an Agilent G1600 AX system using a proprietary buffer solution (pH 7.7) at a temperature of 20°C and an applied voltage of 30 kV. The constants characterizing the chlorides were taken from a handbook [19].

The particle size of the synthesized magnesium oxide and MgO + ZnO mixture was determined with an Olympus BX51 light microscope. The composition of the reaction products was determined by X-ray diffraction on a Shimadzu XRD 7000 diffractometer (Cu K_{α} radiation, $\lambda = 0.15406$ nm, tube current of 30 mA). The crystallite size of the resulting oxide powders was derived from X-ray diffraction data using the Selya-kov–Scherrer formula [20]:

$$D = K\lambda/\beta\cos\theta_{HKL},$$

where K = 0.94 for X-ray diffraction and β is peak broadening (rad).

The oxides were also examined under a Hitachi-3400 electron microscope with an energy-dispersive X-ray (EDX) spectroscopy attachment. The composition of the MgO–ZnO powder was determined using a Flyuorat 2M instrument, and its specific surface area was measured using an ASAP 2020 analyzer.

Cation	$r_{M^{2+}}, nm$	$ze/r_{M^{2+}}$, esu cm ⁻¹	<i>T</i> , °C	n_{Cl_2} , mol	τ, min
Ba ²⁺ [5]	0.138	0.070	960	0.00008	420
Sr ²⁺	0.12	0.080	890	0.00075	300
$Ca^{2+}[5]$	0.104	0.092	890	0.01284*	300
Zn^{2+} [5]	0.083	0.116	890	0.04050*	300
Mg^{2+}	0.074	0.130	730	0.05949	270
Mg ²⁺ -Na ⁺ (eutectic, 1:1.28 mol/mol)	—	0.085	600	0.00135	300
Mg ²⁺ -Na ⁺ (eutectic, 1:1.28 mol/mol)	—	0.085	750	0.00703	300
$Mg^{2+}-Zn^{2+}$ (1 : 1 mol/mol)	—	0.123	600	0.00292	300

Table 1. Amount of chlorine released by MCl_2 melts and the ionic radii and polarizing powers of the cations

* Calculated from E_a data for reactions occurring under kinetic control.

RESULTS AND DISCUSSION

It was established that the chlorine and metal oxide yields depend on the reaction temperature and on the conditions under which the oxidizer gas is introduced into the melt and are determined by the oxygen partial pressure in the gas phase [5]. The chlorine and oxide formation rate under the given experimental conditions obeys a zeroth-order rate equation. Note that variation of the mass of metal chloride in the reactor (20-50 g) exerts no effect on the chlorine formation rate, because the molten chloride is in stoichiometric excess over the oxygen fed into the reactor.

Investigation of chloride anion oxidation in molten Group II metal chlorides demonstrated that the chlorine formation rate depends on the PP of the chloride's cation. Table 1 lists the conditions and outcomes of Cl⁻ oxidation in the molten metal chlorides and the ionic radii and PP values of the cations.

In the case of a mixed chloride melt, the effective PP value of the cations was calculated as follows:

$$(ze/r)_{\rm eff} = \sum_{i=1}^n N_i ze/r_{\rm M^{2+}},$$

where $ze/r_{M^{2+}}$ is the PP of the cation of a chloride and N_i is the mole fraction of this cation in the mixture containing *n* chlorides. For example, the effective PP of the cations of an equimolar mixture of magnesium and zinc chlorides is $0.5 \times 0.130 + 0.5 \times 1.116 = 0.123$. A similar method for calculating the effective cationic radius for a mixture of alkali metal chlorides was described by Smirnov [21].

Because of the relatively low boiling point of zinc chloride (732°C), the amount of chlorine that could result from its oxidation at 890°C was derived from the temperature dependence of the Cl⁻ oxidation rate constant. The same calculation was carried out for calcium chloride. Figure 1 plots the amount of chlorine evolved as a function of the cation PP for alkaline-earth metal, magnesium, and zinc chlorides. This plot fits the equation $n_{Cl_2} = 1.0380x - 0.0784$ with a corre-

lation factor of 0.9841, indicating that the amount of chlorine evolved by the chloride is proportional to the PP of its cation.

While the *ze* value for the Group II metal cations is the same, the chlorine yield depends on the inverse ionic radius of the cation. The ionization potential of isoelectronic atoms and cations (*I*) is related to their ionic radius by the formula $\sqrt{I} = a/r - b$ [22]. For the Group IIA cations, the ionization potential depends on the inverse radius as $\sqrt{I_{II}} = 0.1056/r + 2.4438$ with a correlation factor of 0.9994.

Because the amount of chlorine released by the chlorides and the ionization potential of the metals depend on the inverse radius of the metal atom, there is a linear correlation between $n_{\rm Cl_2}$ and $\sqrt{I_{\rm II}}$: $n_{\rm Cl_2} = 0.0892\sqrt{I_{\rm II}} - 0.2906$ (Fig. 2). The correlation factor in this case (0.9630) is smaller than in the $n_{\rm Cl_2}$ - $ze/r_{\rm M^{2+}}$ relationship (Fig. 1). The linearity of the correlation breaks down if the amount of chlorine resulting from zinc chloride oxidation is included in the data array.

Chloride ion oxidation in $MCl_2-V_2O_5$ systems (M = Mg, Ca, Sr, Ba, Zn) was also studied. The process was carried out by passing air at a rate of 5 L/h



Fig. 1. Amount of chlorine released by the chloride melt as a function of the polarizing power of the cation.

RUSSIAN JOURNAL OF INORGANIC CHEMISTRY Vol. 57 No. 11 2012



Fig. 2. Amount of chlorine released by molten MCl_2 (M = Mg, Ca, Sr, Ba) as a function of the M⁺ \rightarrow M²⁺ ionization potential.

over the surface of the reaction mixture at 800° C (730°C for MgCl₂ and 550°C for ZnCl₂). The initial vanadium pentoxide concentration was 10 wt %. For the MCl₂–V₂O₅ (M = Mg, Ca, Sr, Ba) systems, the amount of chlorine released increases with an increasing effective PP of the M²⁺ and V⁵⁺ cations

In order to elucidate the effect of cations having a smaller PP value than the Group II cations, we investigated chloride ion oxidation in molten zinc + sodium, magnesium + sodium, and magnesium + zinc chloride mixtures. It was demonstrated earlier that sodium chloride does not evolve chlorine under the given experimental conditions [11]. The addition of sodium chloride to zinc chloride leads to a decrease in the chlorine yield. This effect is particularly strong at sodium chloride concentrations of 60 mol % and above. A study of NaCl-ZnCl₂ melts varying in composition demonstrated that the Na₂ZnCl₄ complex forms at sodium chloride mole fractions of 0.7 and above. This compound can be resistant to oxygen. At the same time, at zinc chloride concentrations of 40-100 wt %, the chlorine yield depends on the effective PP value of the sum of the mole fractions of sodium and zinc cations (r = 0.9612).

A similar inhibiting effect of the sodium cation is observed in the oxidation of the MgCl₂–NaCl mixture. The dilution of magnesium chloride with sodium chloride causes a marked decrease in the chlorine yield relative to the yield observed for pure MgCl₂.

Table 2. Rate constants of Cl^- oxidation in $MgCl_2$ and eutectic NaCl-MgCl₂ melts

Composition	<i>T</i> , °C	$k_0 \times 10^7$, mol/s
NaCl-MgCl ₂ (eutectic)	600	0.79 ± 0.07
NaCl-MgCl ₂ (eutectic)	700	2.45 ± 0.24
NaCl-MgCl ₂ (eutectic)	750	4.22 ± 0.43
MgCl ₂	750	34.38 ± 4.84

Table 2 lists the rate constants for chloride ion oxidation in the MgCl₂ and NaCl-MgCl₂ melts.

From the temperature dependence of the rate constant of Cl⁻ oxidation in the NaCl-MgCl₂ melt, we determined the apparent activation energy of Cl⁻ oxidation: $E_a = 82$ kJ/mol. The small E_a value for magnesium chloride oxidation is due to the high rate of the reaction, so the reaction is dependent on oxygen diffusion across the gas/molten salt interface. It is due to the oxygen diffusion effect that the activation energy of chloride ion oxidation in molten calcium and zinc chlorides decreases with increasing temperature [5]. Under the assumption that the interfacial oxygen diffusion rate is the same for all of the melts examined, the role of diffusion will be greatest in magnesium chloride oxidation because of the high rate of this reaction.

We investigated the interaction of the magnesium chloride-zinc chloride mixture (1:1 mol/mol) with oxygen at 600°C. Below this temperature, the system is solid; above 600°C, there is marked reactant carryover from the reaction zone. The chlorine formation rate constant for the MgCl₂–ZnCl₂ mixture is $1.71 \times$ 10^{-7} mol s⁻¹. For zinc chloride, the rate constant under the same conditions is 1.70×10^{-7} mol s⁻¹. In the resulting powder, the magnesium oxide : zinc oxide ratio is 4.65 and the cation ratio is 9.42 (Flyuorat 2M). This cation ratio is close to the ratio of the Cl⁻ oxidation rate constant for molten MgCl₂ ($32.87 \times 10^{-7} \text{ s}^{-1}$) to the same rate constant for molten $ZnCl_2$ (3.33 × 10^{-7} s⁻¹), which is 9.86. This finding is evidence that, in the oxidation of the chloride mixtures, the observed Cl⁻ oxidation rate constants are equal to the oxidation rate constants of the individual chlorides and the decreases in the chlorine yield is due to the decrease in the reactant concentration in the mixture (dilution effect).

It was demonstrated by X-ray diffraction that the resulting oxide mixture contains only magnesium and zinc oxides. However, the magnesium-to-zinc atomic ratio determined by EDX spectroscopy indicates the presence of hydroxides in the sample.

For determining the particle size of magnesium oxide and MgO-ZnO powders, the powders were dispersed in ethyl acetate and were examined by light microscopy. Most of the MgO particles were in the 2– 5 μ m range; most of the particles of the MgO–ZnO mixture, in the 1-2 µm range. Both samples contained <1- and >5 μ m particles. This wide range of particle sizes is explained by the long duration of the process and by the comparatively high solubility of the metal oxides in the molten chlorides. As a consequence, the particles grew larger via recrystallization. The mean crystallite size determined using the Selvakov-Scherrer formula [20] was 62 nm for magnesium oxide (both pure and mixed with ZnO) and 58 nm for zinc oxide. The specific surface area of the MgO-ZnO powder, determined by the BET method, was 20.26 m² g⁻¹, the pore volume of the mixture was $0.14 \text{ cm}^3 \text{ g}^{-1}$, and the The ionic structure of the metal chlorides and the dependence of their oxidizability on the PP of the cation suggest that the reaction takes place via an ionic mechanism. Coming into contact with a molten metal chloride, dioxygen dissolves in it by occupying "defects" of the ionic stricture of the melt. This gives rise to the following chemical reaction [21]:

$$O_{2(g)} + 4Cl^{-} \rightarrow 2O^{2-} + 2Cl_{2(g)}$$
.

Oxygen in the melts can exist as O_2^- and O_2^{2-} species [24, 25]. It was demonstrated that the dissolution of oxygen in chloride melts brings about three parallel reactions and, under equilibrium conditions, the dominant oxygen compounds are superoxides and the minor ones are peroxides [26, 27].

Thus, the study of chloride ion oxidation in molten Group II metal chlorides demonstrated that the chlorine yield in the MCl_2-O_2 system is linearly correlated with the PP of the cation and with the square root of its ionization potential. The observed dependence of chloride oxidation on the PP of the cation can be used in kinetic studies and thermodynamic analysis, as well as in the estimation of the reactivity of chlorides and oxides in their chlorination. The mural effect of cations should be taken into account in the oxidation of metal chloride mixtures for obtaining metals and their oxides.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (project 10-03-00187a) and by the Presidium of the Russian Academy of sciences (program no. 18: "Synthesis and Isolation of Nanosized Powders of Metal Oxides in Chloride Melts").

REFERENCES

- M. Trypuc', K. Białowicz, and K. Mazurek, Ind. Eng. Chem. Res. 40 (3), 731 (2001).
- M. Trypuc', Z. Torski, and U. Kiełkowska, Ind. Eng. Chem. Res. 40 (4), 1022 (2001).
- M. Trypuc, K. Białowicz, and K. Mazurek, Chem. Eng. Sci. 59 (6), 1241 (2004).

- 4. V. P. Kochergin, M. K. Korshunova, M. S. Ulanova, and Z. A. Shevrina, Zh. Neorg. Khim. 14, 521 (1969).
- Yu. S. Chekryshkin, A. N. Chudinov, T. A. Rozdyalovskaya, and A. A. Fedorov, Russ. J. Appl. Chem. 83 (8), 1461 (2010).
- K. Kopalko, M. Godlewski, J. Z. Domagala, et al., Chem. Mater. 16 (8), 1447 (2004).
- V. N. Gaprindashvili, L. V. Bagaturiya, Ts. G. Sulakadze, and L. A. Tskalobadze, Izv. Akad. Nauk Gruzii, Ser. Khim., Nos. 3–4, 332 (2004).
- 8. US Patent No. 6994636.
- K. Takefumi, S. Toshimitsu, I. Kazunori, et al., Ind. Eng. Chem. Res. 42 (24), 6040 (2003).
- 10. Yu. S. Chekryshkin, T. A. Rozdyalovskaya, Z. R. Ismagilov, et al., Eurasian Chem. Technol. J. **5** (2), 137 (2003).
- 11. T.A. Rozdyalovskaya, Yu. S. Chekryshkin, V. N. Nekrasov, et al., Rasplavy, No. 4, 75 (2004).
- 12. A. N. Chudinov, T. A. Rozdyalovskaya, Zh. A. Vnutskikh, et al., Khim. Tekhnol., No. 11, 524 (2007).
- 13. H. C. Yang, Y. J. Cho, H. C. Eun, and E. H. Kim, Chem. Eng. Sci. 62 (18–20), 5137 (2007).
- 14. R. I. Kraidenko, Khim. Tekhnol., No. 1, 8 (2011).
- H. C. Eun, H. C. Yang, Y. Z. Cho, et al., J. Hazard. Mater. 160 (2–3), 634 (2008).
- N. Fu, I. Iwasaki, T. Tamagawa, and M. Kobayashi, Chin. J. Process Eng. 9 (6), 1080 (2009).
- D. M. Smith, M. P. Neu, E. Garcia, and V. R. Dole, J. Alloys Compd. **319** (1–2), 258 (2001).
- T. A. Rozdyalovskaya, Yu. S. Chekryshkin, A. N. Chudinov, and A. A. Fedorov, Russ. J. Appl. Chem. 82 (9), 1510 (2009).
- 19. Properties of Inorganic Compounds: A Handbook, Ed. by A. I. Efimova (Khimiya, Leningrad, 1983) [in Russian].
- N. A. Shabanova, V. V. Popov, and P. D. Sarkisov, *Nano-disperse Oxide Chemistry and Technology* (Akademkniga, Moscow, 2007) [in Russian].
- 21. M.V. Smirnov, *Electrode Potentials in Molten Chlorides* (Nauka, Moscow, 1973) [in Russian].
- L. T. Bugaenko, S. M. Ryabykh, and A. L. Bugaenko, Vestn. Mosk. Univ., Ser. 2: Khim. 49 (6), 363 (2008).
- 23. S. J. Shaw and G. S. Perry, Thermochim. Acta **157** (2), 329 (1990).
- 24. M. L. Deanhardt and V. H. Starn, J. Electrochem. Soc. **127** (12), 2600 (1980).
- F. L. Whitting, G. Mamantov, and I. P. Young, J. Inorg. Nucl. Chem. 34 (8), 2475 (1972).
- 26. M. V. Smirnov and O. Yu. Tkacheva, Rasplavy, No. 3, 57 (1991).
- 27. M. V. Smirnov and O. Yu. Tkacheva, Rasplavy, No. 3, 66 (1991).

RUSSIAN JOURNAL OF INORGANIC CHEMISTRY Vol. 57 No. 11 2012