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Oxychlorination of Methane in the Presence of Molten Metallic Chlorides

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Catalytic oxychlorination of methane was investigated with the equimolar binary melts of potassium chloride with cupric chloride and ferric chloride in a flow reactor under atmospheric pressure at temperatures of 340 to 410°C. The methane conversion was higher and depended on reaction time considerably with the cupric chloride system, whereas there was little time-dependence with the ferric chloride system. This difference between the above two systems was discussed in view of the reaction mechanism. It was found that, with the cupric chloride system, the selectivity to higher chlorinated products was greater than that obtained in the thermal chlorination and in the chlorination with melts used by previous investigators, and furthermore that the activity decreased drastically at the solidification point.

INTRODUCTION

Molten metallic chlorides have frequently been used as reagents or catalysts of chlorination or oxychlorination of hydrocarbons (*1*), though some of them are corrosive. Chlorination of methane using melts containing copper and potassium chlorides as reagents has been investigated by Gorin *et al.* (*2*) and Kunugi *et al.* (*3*). Many patents have been published on the catalytic oxychlorination of methane by some molten mixtures. However, there are very few reports on the mechanism and kinetics of the reaction catalyzed by molten chlorides. In the present study, therefore, the catalytic activity of binary melts of KCl with $CuCl_2$ and $FeCl_3$ was investigated quantitatively by using a quiescent pool of the melt.

The difference in the activity of the salt between the molten and the solid state was also examined for the $CuCl_2$–KCl salt. This is of interest in connection with the mechanism of catalysis in the solid state. Few reports have so far been published on the change in catalytic activity above and below the melting point of salts. Ruthven and Kenney and Butt and Kenney reported two opposite findings: One is a sharp decrease in the activity for the oxidation of HCl at the solidification point (*4*), and the other is a sudden increase in the activity for the oxidation of naphthalene (*5*).

MATERIALS AND METHODS

A small shallow Pyrex boat, placed horizontally in a tubular reactor, was employed as a pool of the melt with a surface area of 50 cm^2. Little attack on Pyrex by melts was observed under our conditions. The melt was maintained at a constant temperature in a Pyrex-made electric furnace which made it possible to observe directly the surface appearance of the melt. In order to remove the scum on the melt surface, a movable rake-shaped glass rod was used.

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Commercial metallic chlorides were used without further purification. Their purities were 99.5, 99.0, and 99.5% for $CuCl_2$, $FeCl_3$, and KCl, respectively. The melts were prepared by heating equimolar powdery mixtures of KCl with $CuCl_2$ and $FeCl_3$ in an inert atmosphere. The total amounts were 0.64 and 0.50 mol for the cupric and the ferric system, respectively. Care was taken to avoid the contact between the salts and moisture throughout the preparation.

An atmospheric gaseous mixture of CH_4, HCl, O_2, and He (2.0:1.5:1.0:2.0, mole ratio) was passed continuously over the melt. These gases were of commercial grade and methane was 99.5% pure. The flow rate of the mixture was 65 cm^3 (STP)/min. Products were analyzed by gas chromatography, and every isomer of chloromethanes was separated. No burning nor cracking products of methane were detected.

RESULTS AND DISCUSSION

Figure 1 shows methane conversion as a function of reaction time at different temperatures for the cupric chloride system (mp 350°C). It was necessary to make up a fresh melt for each experiment since the change in composition of the melt after the reaction was not negligible. Conversion decreased with time and finally approached zero. As the reaction proceeded, a solid-like film was formed on the melt surface. This deactivation is ascribed to the formation of film in that the activity of the inactive used melt is restored by removing the film from the surface with the rake-shaped glass rod. The activity of the melt renewed by removal of the film was lower than that of the fresh melt. When, therefore, several runs were made repeatedly with the same melt charge, the activity of the melt decreased with an increasing number of runs. The probable cause of this deactivation is the reduction of cupric to cuprous chloride, the existence of which was confirmed by the X-ray diffraction pattern of the solidified used salt. Evidently part of the melt was consumed for chlorinating methane.

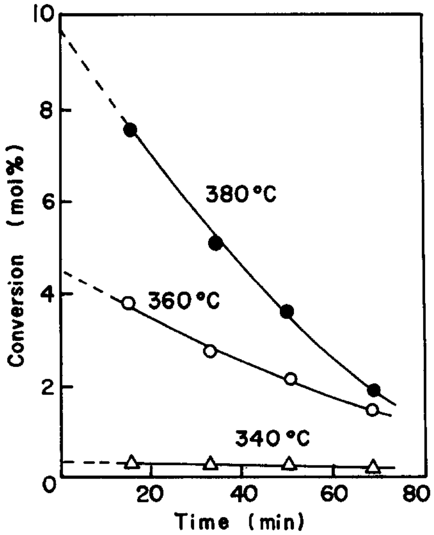

FIG. 1. Methane conversion as a function of reaction time at different temperatures for a $CuCl_2$–KCl melt.

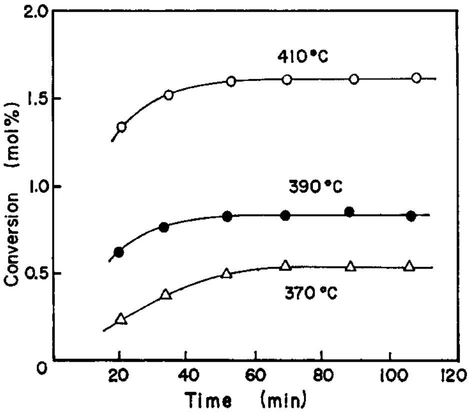

FIG. 2. Methane conversion as a function of reaction time at different temperatures for a $FeCl_3$–KCl melt.

For the ferric chloride system (mp 240°C), as shown in Fig. 2, the dependence of methane conversion on time contrasts with that for the cupric system. The conversion increased to be steady with time. No formation of film was observed and the activity of the melt was unchanged before and after the disturbance of the surface with the rake-shaped rod. Furthermore, when several runs were made using one melt charge, the deactivation of the catalyst did not occur.

These results suggest that the rate-determining step differs between the cupric and the ferric systems, which will be discussed below. The following mechanism is most commonly proposed for the oxychlorination of hydrocarbons on a solid cupric chloride catalyst (*6*). The first step is the chlorination of hydrocarbons either with chlorine liberated by the decomposition of $CuCl_2$ into CuCl or with $CuCl_2$ itself; the second is the oxidation of CuCl with O_2 to form copper oxychloride or cupric oxide; and the third is the regeneration of $CuCl_2$ by the reaction of HCl with the above oxides.

When free chlorine is the chlorinating agent, the product distribution will be similar to that in the thermal chlorination. This case is the oxychlorination of methane on a supported cupric chloride catalyst reported by Meissner and Thode (*7*). The product distribution for the cupric system in this work, however, differed from that in the thermal chlorination (*8–11*), as shown in Fig. 3. This result suggests that the direct reaction between methane and the species containing cupric chloride (*12–15*) at the melt surface is predominant. The chlorine pressure over this melt is estimated to be considerably lower than that over the solid cupric chloride in the work of Meissner and Thode (*7*), for the cupric chloride in the melt forms the complex compound with KCl (*12–15*), and furthermore the reaction temperature is somewhat low. Thus, the melt reacts directly with methane without being decomposed. For the ferric chloride system, there appears to be no reason to suppose that the mechanism is other than the above one.

It is further shown in Fig. 3 that a higher selectivity to polychloromethanes is obtained in this oxychlorination than in any other chlorination given in the figure. Although the cause is not evident, the adsorption mechanism of the reactant at the melt surface may possibly be related to the selectivity.

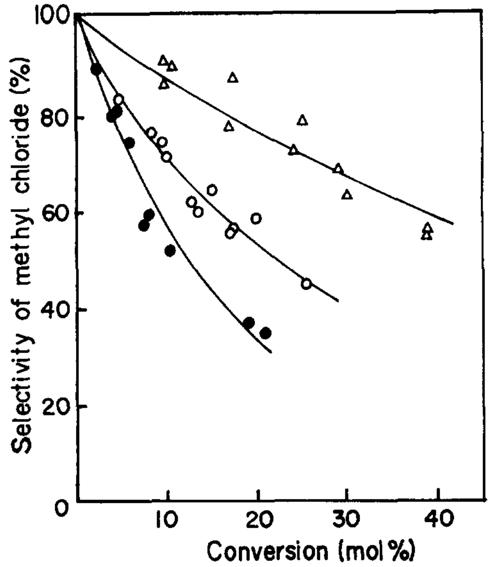

FIG. 3. Comparison of the selectivities to methyl chloride obtained by previous investigators. (△) Thermal chlorination, (○) chlorination using melts as reagents, (●) this work.

The lower valent chlorides, formed probably by the direct reaction between methane and the melts, are expected to be regenerated to the original chlorides via the second and third steps of the commonly proposed mechanism. For the cupric system, however, the regeneration of the original chloride was not easy because of slow reaction of surface oxides with HCl. Therefore, the methane conversion decreased with time (Fig. 1), and the lower valent chloride such as K_2CuCl_3 was detected by X-ray diffraction of the used salt. The apparent activation energy, obtained from the variation of the initial rate with temperature (Fig. 4), was 41 kcal/mol (1 kcal/mol = 4148 J/mol). This value is somewhat high, compared to an activation energy of 28 kcal/mol for the oxidation of HCl over molten salt catalyst (*4*). This may be ascribed to the difference in catalyst composition and reaction temperature between the two.

While, with the ferric system, the regeneration of the original chloride was easy,

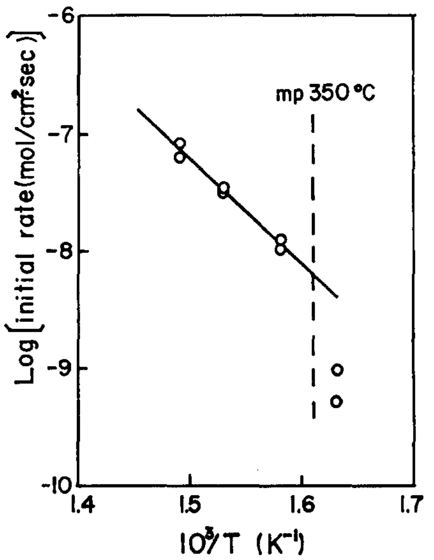

FIG. 4. Arrhenius plots for a $CuCl_2$–KCl salt.

resulting in no formation of surface oxides and no change in activity of the melt with an increasing number of runs, the reaction of CH_4 with the melt was slow in the absence of HCl and O_2. Thus, the reaction is probably the rate determining step for the ferric system.

Noteworthy is a drastic change in the activity at the melting point of the $CuCl_2$–KCl salt, as shown in Fig. 4. The initial rate in the molten state is remarkably faster than that in the solid state. As mentioned above, Ruthven and Kenney (*4*) reported that the rate for the oxidation of HCl decreases markedly below the melting point of the salt containing copper, potassium, and lanthanum chlorides, and they stated that this decrease certainly arises from the freezing out of $LaCl_3$ as a promotor. In our salt, however, such a compound was absent, and thus other speculations should be made about the change in the activity in this work. It may arise from the difference in the rate of mass transfer between the molten and the solid state. As the active species at the surface was consumed for the reaction with methane, it would be supplied extremely faster to the surface from the bulk of the melt than from the bulk of the solid. Consequently, the rate increased drastically above the melting point of the $CuCl_2$–KCl salt.

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