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The Catalytic Dehydrohalogenation of Alkyl Halides by Fused Zinc Chloride and Other Molten Chlorides

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The thermal and catalyzed eliminations of hydrogen chloride from ethyl, isopropyl, and *n*-propyl chloride have been studied in a stirred flow reactor at atmospheric pressure. The catalysts employed were molten zinc chloride alone, and binary mixtures containing zinc chloride and other metallic chlorides. Both the thermal and catalyzed reactions follow first-order kinetics between 260 and 500°C. It is suggested that the catalyzed reaction occurs largely on the surface of the molten salt and that the active catalytic species is molecular zinc chloride.

INTRODUCTION

The chemistry of molten salts is attracting increased attention, and particular interest is being shown in their use as reaction media (*1*). The kinetics of a number of homogeneous reactions have been described (*2*), but little work has been reported on their behavior as catalysts for reactions between gaseous reactants. We have recently discussed the kinetics of the oxidation of hydrogen chloride (*3*) and sulphur dioxide (*4*) using molten chlorides and pyrosulphates, respectively, and here describe a related investigation of the elimination of hydrogen chloride from ethyl chloride, *n*-propyl chloride, and isopropyl chloride, catalyzed by molten zinc chloride and a number of binary chloride melts containing zinc chloride. The reaction may be written:

$$\mathrm{RCl} \rightarrow \mathrm{RCH{=}CH_2} + \mathrm{HCl}.$$

This reaction was selected after a number of organic reactions had been examined for their suitability for a kinetic study. These included the dehydration of ethanol, the isomerization of *n*-pentane, and isopentane, and the dehydrogenation of isopentane to the olefin. Several molten chlorides were studied, either pure or in binary and tertiary mixtures, over a range of temperatures, but all of these systems were rejected because the molten salts were either catalytically inactive, or were found, after a short reaction time, to be excessively contaminated with organic decomposition products; in some cases the melt sublimed. The hydrogen chloride elimination reaction took place at an experimentally convenient rate between 280 and 380°C, and although a small amount of decomposition was observed in some experiments, the rate data were reproducible, provided that the melt was stirred. Apart from their intrinsic interest, the catalytic properties of molten salts raise a number of questions about the nature of catalytic behavior, in particular whether the reaction takes place on the melt surface or in the bulk of the melt.

EXPERIMENTAL

The apparatus shown in Fig. 1 was used for all experiments and consisted of a stirred tank reactor operated at constant pressure under steady-state conditions. A crystallizing dish was filled with the molten salt catalyst and fitted with a stirrer and two thermocouples as shown.

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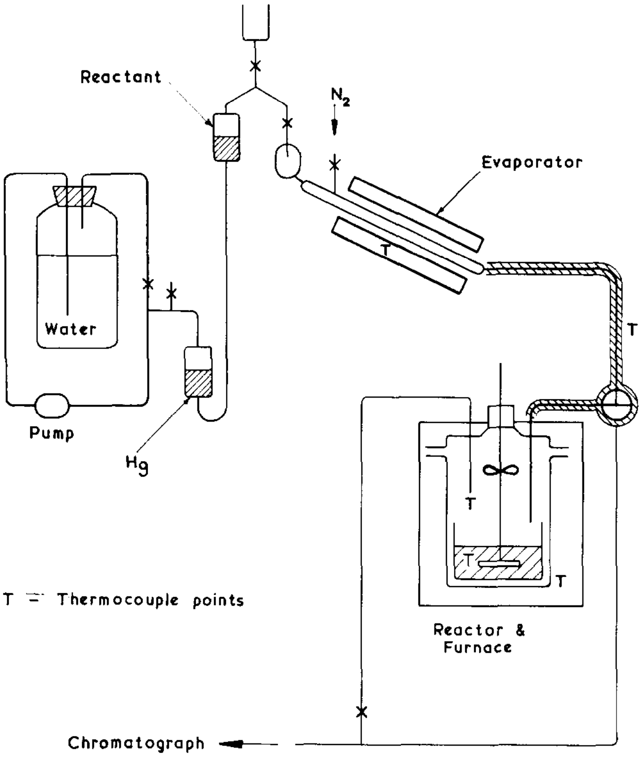

FIG. 1. Diagram of apparatus.

The effect of changes in surface area could be studied quantitatively by using dishes of different diameter; changes in catalyst composition can be detected by direct weighing and analysis. In the majority of runs, molten salt at a depth of 1.5 cm was placed in a crystallizing dish of 6.5 cm in diameter. This gives a surface area of 33.2 cm^2. For the experiments with isopropyl chloride (bp 36.5°C) and *n*-propyl chloride (bp 46.4°C), a micropump was used to feed the reactants. Water was pumped into a vessel containing mercury which displaced the organic reactant through a capillary nozzle. The reactant flowed into the evaporator, along with a nitrogen stream. The evaporator was a glass tube packed with small glass spheres kept at 200°C. The feed rate of reactant was controlled by changing the stroke of the micropump, and this, together with variations in the nitrogen flow rate, allowed a wide range of reactant concentrations to be obtained. In the experiments with ethyl chloride (bp 13°C), the chloride was contained in a thick-walled glass vessel immersed in water at 30°C in a constant temperature bath. This served as an evaporator and the vapor was mixed with nitrogen, its flow rate being controlled with needle valves and measured with a rotameter. All the reactants were B.D.H. laboratory reagents. Gas chromatography was used to analyze the streams entering and leaving the reactor. Several types of analytical columns were examined, and squalane, absorbed on firebrick and operated at 60°C, using hydrogen as a carrier gas, gave a column which would separate nitrogen, unreacted alkyl halide, and olefin. The hydrogen chloride was removed by bubbling the product gases through a solution of sodium hydroxide. Nitrogen here played a dual role, both as a diluent and as an internal standard, since the chromatograph was calibrated beforehand by making up a set of nitrogen–olefin mixtures. Therefore, by assuming that the total amount of nitrogen remains constant, the amount of olefin produced, and hence the degree of conversion, can be calculated from the nitrogen and olefin peaks.

The kinetic analysis of the experiments assumes that the mixing in the reactor is perfect, and it is necessary to test this assumption. This was done by measuring the distribution of residence times arising from a step change of an inert gas entering the reactor in the absence of reaction. A stream of hydrogen passing through the reactor was rapidly changed to one of nitrogen, and the concentration of nitrogen in the exit stream was monitored with the chromatograph.

Let

$$F = \frac{\text{concentration of exit nitrogen}}{\text{final nitrogen concentration}}$$

and

$$t = \frac{\text{time after switch to nitrogen}}{\text{mean residence time}},$$

then for a perfectly mixed vessel,

$$\log_e (1 - F) = -t.$$

Straight line plots of $-\log(1 - F)$ against t were obtained as required by the theory, passing through $(1 - F) = 0.368$ at $t = 1$ for stirrer speeds of 100, 200, and 300 rpm and gas flow rates of up to 400 ml/min. Even at a stirring rate of 50 rpm, the departure from perfect mixing was only just detectable. The design of the reactor was such that the gas phase and the molten catalyst layer were stirred simultaneously, and the most commonly employed stirring speed was 200–250 rpm, since above 300 rpm the surface of the melt became distorted, leading to an uncertain increase in the gas–liquid interfacial area.

The experimental conditions employed in the study of the catalyzed elimination of hydrogen chloride from isopropyl chloride are shown in Table 1.

TABLE 1

Reaction pressure	778–790 mmHg
Reaction temperature	263–386°C
Inlet gas composition N_2	0.67–0.85 mole fraction
Isopropyl chloride	0.15–0.33 mole fraction
Gas flow rate	80–420 cm^3/min
Stirring speed	200–250 rpm

Noncatalyzed thermal elimination reactions were also examined in the same reactor but without any molten salt present. The range of variables lay within those given in Table 1, apart from temperatures for which much higher values (400–500°C) were necessary in order to observe appreciable conversions. The analytical technique was unchanged. Both the thermal and the catalyzed reactions were found to give only the olefin and hydrogen chloride as products.

RESULTS AND DISCUSSION

The elimination reaction at constant pressure is associated with a volume change, since each molecule of reactant produces two molecules of gaseous product. The inlet and outlet concentrations, C_0 and C_1 respectively, are related to the reactor volume, V, and velocity constant k by the familiar steady-state equation for a well-mixed reactor (*14*). It has been shown that this reactor is "perfectly mixed," and so the concentration at all points in the reactor is the same as the exit concentration, C_1. Hence, assuming that the rate depends only on the concentration of the reactant, and the order of the reaction is 'n', we may write:

$$kV(C_1)^n = U_0C_0 - U_1C_1,$$

where U_0 and U_1 are the inlet and outlet volume flow rates. Thus,

$$\log kV + n \log C_1 = \log (U_0C_0 - U_1C_1),$$

and a straight line plot of log $(U_0C_0 - U_1C_1)$ against log C_1 should be obtained. For a first-order reaction, the line should have unit slope, and such first-order kinetics were observed in both the catalyzed and thermal reactions for conversions up to 60%. Typical plots are shown in Fig. 2 for the elimination of hydrogen chloride from isopropyl chloride over molten zinc chloride. The velocity constants over a range of temperatures between 263 and 386°C are plotted as log

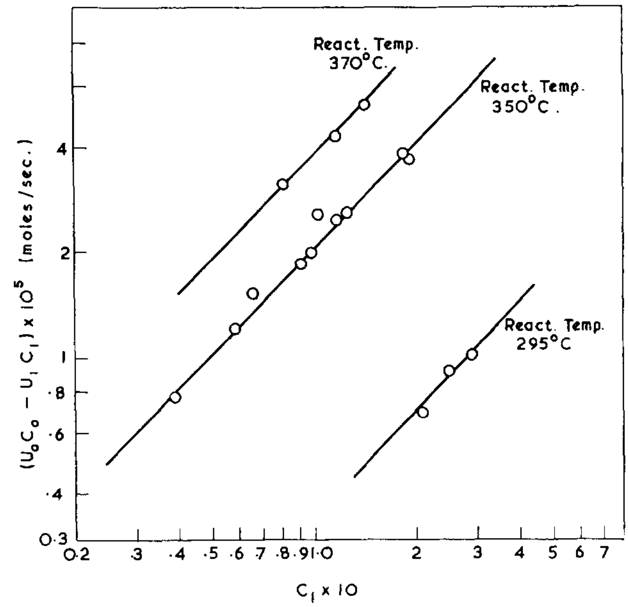

FIG. 2. Rate of hydrogen chloride elimination as function of isopropyl chloride concentration (in atm) over molten zinc chloride. Inlet concentrations and flow rates were varied over the ranges shown in Table 1.

k against $1/T$ in Fig. 3. These give a satisfactory straight line from which the activation energy of 25.8 kcal/mole is obtained. Similar experiments were performed on the decomposition of ethyl chloride and *n*-propyl chloride over molten zinc chloride, and also when no catalyst was present.

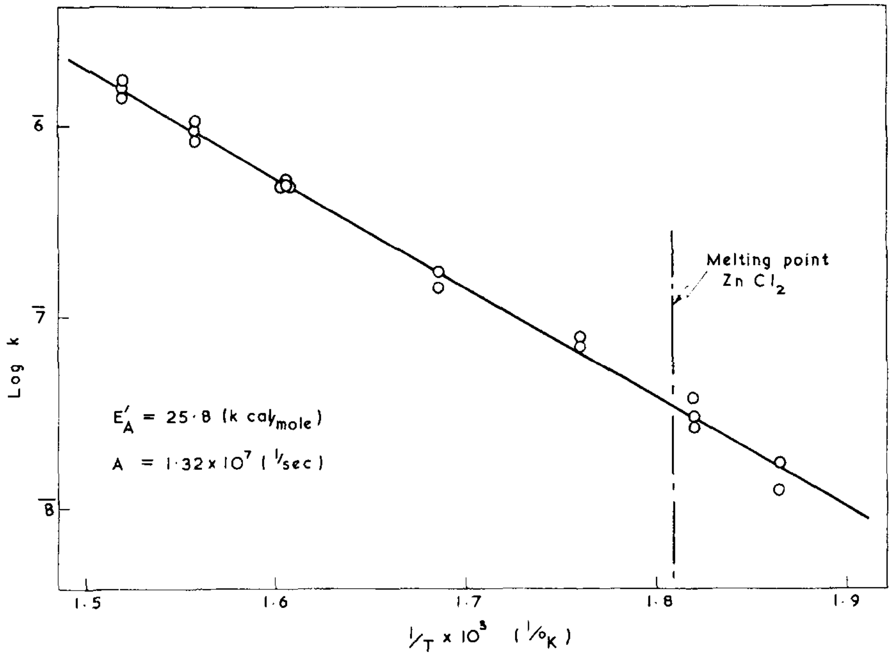

FIG. 3. Arrhenius plot of first-order rate constant for hydrogen chloride elimination from isopropyl chloride over molten zinc chloride.

The purpose of studying the thermal reaction was to verify that the reaction with zinc chloride present was in fact a catalytic one, and further to obtain some indication of the accuracy of the derived velocity constants. The results of the thermal and catalytic reactions are given in Table 2, and since the velocity constants for the thermal decomposition compare favorably with those of other investigations (*11–13*), the value for the catalytic constants would appear to be satisfactory.

The rate of the catalyzed reaction is approximately 100 times as great as the thermal elimination at 300°C per unit volume of gas space, and so the latter may be neglected as a side reaction. At 400°C, however, the catalytic and pure thermal reaction rates are becoming comparable, and the existence of a thermal reaction could lead to an appreciable error in determinations of catalytic velocity constants. At lower temperatures, though, the errors are believed to be of the order of 20–30%. It is sometimes convenient, for the purposes of comparison with the behavior of gas–solid systems, to express the velocity constants in terms of the surface area of the melt surface k', rather than as a homogeneous rate constant k. If the volume of the gas space in the reactor is V, and the melt surface area is S, then $k'S = kV$. The units of k are thus sec^{-1}, and those of k' are cm sec^{-1}, with the multiplying factor V/S for this apparatus being 12.8 cm.

Having established that molten $ZnCl_2$ displayed appreciable activity as a catalyst for hydrogen chloride elimination, the behavior of a number of other metal chlorides was examined. The freezing points of the majority of metal chlorides are unfortunately comparatively high, and hence considerable thermal elimination takes place at temperatures at which the pure chlorides are molten. For this reason, it was preferable to examine the catalytic behavior of a number of binary chloride melts, each of which contained zinc chloride as one component. The metal chlorides used were NaCl, KCl, LiCl, AgCl, $SnCl_2$, CuCl, $FeCl_2$, $CuCl_2$, and $FeCl_3$. All of these compounds gave homogeneous melts over a range of compositions at 350°C, although the decomposition of $FeCl_3$ at this temperature and the sublimation of $SnCl_2$ gave rise to significant errors in the velocity constants obtained with melts containing these compounds. The elimination of hydrogen chloride from isopropyl chloride was examined using the experimental conditions given in Table 1. All the binary melts studied gave a first-order catalyzed reaction, although the velocity constants obtained showed considerable variation, both with the metal chloride and its mole fraction in the binary melts; this can be seen from Fig. 4. The significance of these measurements is discussed below.

The homogeneous gas phase decomposition of alkyl chlorides occurs by a simple unimolecular reaction mechanism (*5*). It is known that solid zinc chloride is a Friedel–Crafts catalyst (*6*), and there is no reason to suppose that the mechanism

TABLE 2

Rate Constants for Alkyl Chloride Elimination Reactions

Reactant	Zinc chloride catalyst $k(\text{sec}^{-1})$	Thermal elimination $k(\text{sec}^{-1})$
isopropyl chloride	$1.32 \times 10^7 \exp - 25.8/RT$	$1.0 \times 10^{13} \exp - 52.5/RT$ $(2.5 \times 10^{13} \exp - 50.5/RT)^{11}$
n-propyl chloride	$2.45 \times 10^7 \exp - 29.7/RT$	$1.62 \times 10^{13} \exp - 57.3/RT$ $(2.8 \times 10^{13} \exp - 55.0/RT)^{12}$
ethyl chloride	$7.59 \times 10^7 \exp - 31.5/RT$	$4.57 \times 10^{13} \exp - 59.2/RT$ $(7.9 \times 10^{13} \exp - 59.0/RT)^{13}$

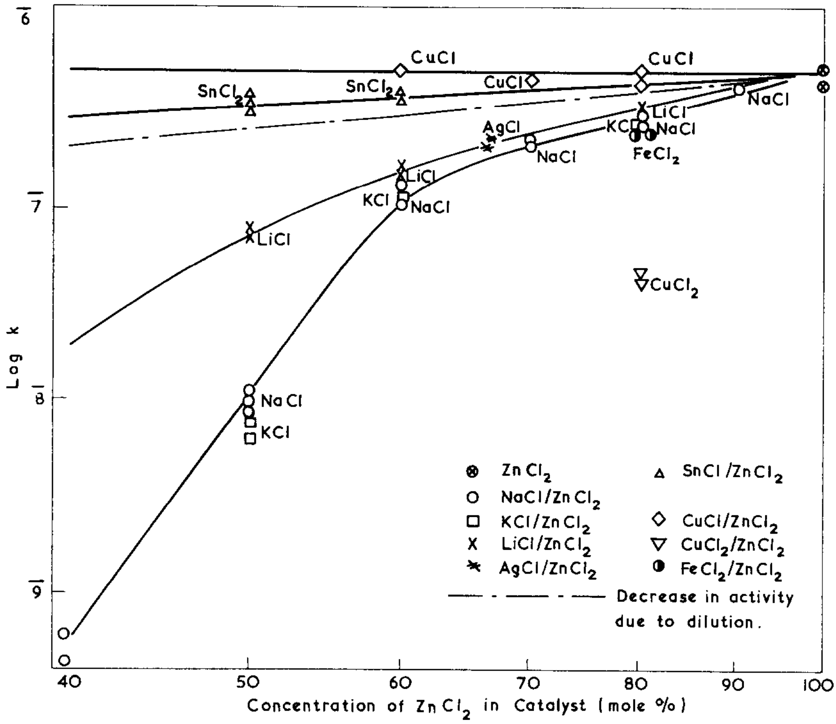

FIG. 4. Variation of first-order elimination rate constants with mole % of zinc chloride in various binary melts at 350°C.

over the molten salt is other than an ionic one which may be written as follows:

$$C_3H_7Cl + ZnCl_2 \rightarrow C_3H_7^+ (ZnCl_3)^-,$$
$$C_3H_7^+ \rightarrow C_3H_6 + H^+,$$
$$(ZnCl_3)^- + H^+ \rightarrow HCl + ZnCl_2.$$

The zinc chloride thus acts as an electron acceptor (Lewis acid), with coordination compounds such as $(ZnCl_3)^-$ being formed. It is less clear though whether the catalytic action takes place in the bulk of the melt or if it is confined to the surface, and from the results reported here it is impossible to decide unequivocally between these possibilities. There is evidence that the unstirred catalyst is poisoned by decomposition products, but the fall of activity could arise from either the poisoning of the surface, or the reduced rate of transport into the melt. The fact that the rate of reaction is proportional to the surface area but not to the volume suggests that the reaction takes place on the melt surface or in a surface layer, rather than in the bulk of the melt. A Langmuir type isotherm would give first-order kinetics if the reactant were only weakly adsorbed. However, the strongest evidence in support of a surface mechanism is the relatively smooth change in rate at the melting point of the zinc chloride. A surface process might show this. A mechanism involving diffusion almost certainly would not, since the diffusion coefficients in solids are several orders of magnitude lower than those in liquids, and the transport of the reactants into the melt would be markedly reduced when the melt solidified. The solubility of gaseous reactants in a molten salt can be appreciable, particularly if stable compounds are formed, and this has been confirmed in our work on the oxidation of hydrogen chloride and sulphur dioxide. The solubility of alkyl halides, olefins, and hydrogen chloride in molten zinc chloride on the other hand, although unknown, would be expected to be extremely low ($< 10^{-6}$ mole cm^{-3}). Further, if diffusional restrictions were dominant, the measured activation energy would be one half the true value. This would imply an activation energy of ca. 50 kcal for the catalyzed reaction, which is improbably high.

In the solid state, zinc chloride possesses a double layer network with an octahedral configuration around each zinc atom, and fragments of this molecular structure are retained well above the melting point (*7*). No conclusions can be drawn at present as to whether the monomeric molecular zinc chloride or the polymeric species are particularly active, but in the temperature range examined (260–380°C), the presence of molecular species seems necessary for catalytic activity. Thus it may be supposed that the addition of alkali metal halides to zinc chloride leads to the formation of complex ions such as $ZnCl_3^-$ or $ZnCl_4^{2-}$, which would be unable to participate in the carbonium ion mechanism, thus leading to a fall in activity consistent with that shown in Fig. 4. The inhibition by LiCl is smaller than that of NaCl or KCl, which would be expected, given its lower polarizing strength and smaller propensity to form complexes. This picture is in accord with experimental data from a number of sources. From the study of the Rama spectra of zinc chloride, it has been inferred that the addition of KCl breaks down the network structure of molecular zinc chloride, since the lines associated with $ZnCl_2$ in pure solid or liquid zinc chloride completely disappear when the concentration of KCl rises to 50 mole % (*8*). Bergman (*9*) has reported that the addition of KCl and NaCl produces a sharp decrease in the high viscosity of $ZnCl_2$, presumably through the formation of less polymerized species, and accompanied by the appearance of several distinct compounds of the type $2KCl \cdot ZnCl_2$. In general, it appears that molecular $ZnCl_2$ shows catalytic activity through its properties as an electron acceptor. The addition of other molecular chlorides slightly reduces the activity, whereas highly ionic compounds have a much stronger deactivating effect. The principal exception is cuprous chloride which appears to have an activity comparable with zinc chloride. In general, however, the qualitative behavior of adding other chlorides to the zinc chloride may be estimated from the degree of ionic or covalent character which they display in the solid or fused state. Addition of alkali metal halides leads to a drop in activity to levels comparable with that shown by the solid alkali halides alone (*10*).

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