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The Role of Ionic Point Defects in the Catalytic Activity of Ionic Crystals

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Theoretical considerations suggest that the rate of dehydrohalogenation of alkyl halides on the surface of a metal halide may be enhanced by the presence of ionic point defects such as ad-cations, ad-anions, cation vacancies, and anion vacancies whose concentrations may be increased by appropriate dopes. In accord with these considerations, the rate of the reaction $(CH_3)_3CCl = (CH_3)_2C{:}CH_2 + HCl$ at 100°C on solid AgCl as a catalyst has been found to increase by 1.5 orders of magnitude upon doping AgCl with $CdCl_2$.

The effect of electrons and electron holes on the catalytic activity of metals and semiconductors has been investigated by various authors (*1*). In addition, one may anticipate specific effects of atomic or ionic point defects which have not been investigated so far. In the interior of a binary ionic crystal, e.g., NaCl or AgCl, one has four different kinds of ionic point defects, i.e., interstitial cations and anions and moreover cation and anion vacancies (*2*). At the surface, one has cations and anions on top of the outermost complete lattice plane (denoted as ad-ions) as analogous to interstitial cations and anions in the bulk crystal. Moreover, one has cation and anion vacancies in the outermost lattice plane. Each of these four surface point defects may be expected to make a significant contribution to the catalytic activity of an ionic crystal. Consider, e.g., the decomposition of an ethyl halide

$$CH_3{\cdot}CH_2X = CH_2{:}CH_2 + HX \qquad (1)$$

Fig. 1a shows the mechanism which one may expect at the plane surface of a metal halide crystal with formation of adsorbed H and X atoms followed by desorption of HCl. In the presence of one of the aforementioned point defects the break-away of H and X may be facilitated by virtue of the mechanisms shown schematically in Fig. 1b to 1e.

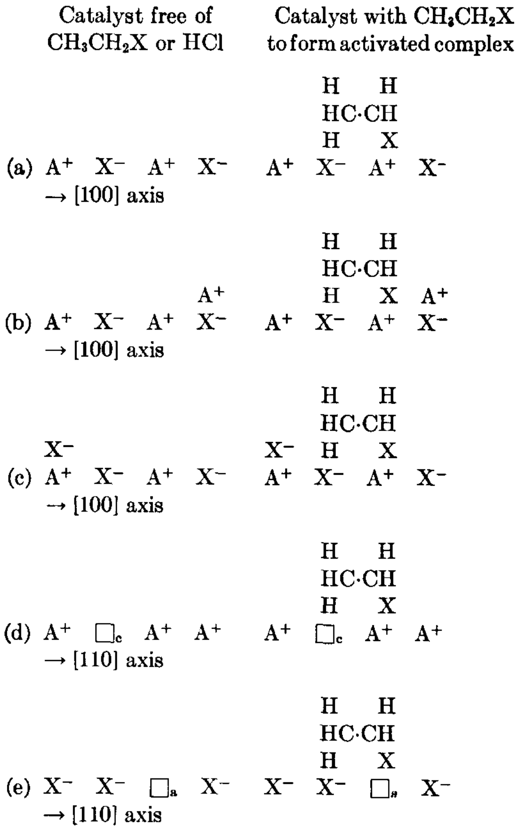

FIG. 1. Mechanisms for the reaction $CH_3{\cdot}CH_2X = CH_2{:}CH_2 + HX$ on the (001) surface of a metal halide A^+X^- with rock salt structure for (a) plane surface, (b) surface with ad-cation, (c) surface with ad-anion, (d) surface with cation vacancy $\square_c$, (e) surface with anion vacancy $\square_a$.

According to Fig. 1b, a hydrogen atom and a halogen atom of the organic compound become attached to an anion in the outermost lattice plane and an ad-cation, respectively, corresponding to the adsorption of H and X on the catalyst. After desorption of HX, the initial state of the surface is restored and the catalytic reaction may go on. As an alternative, a hydrogen atom and a halogen atom of the organic compound may become attached to an ad-anion and a cation in the outermost lattice plane as is shown in Fig. 1c.

If there are cation vacancies, a hydrogen atom of the organic compound may move into a cation vacancy in the outermost lattice plane and simultaneously the halogen of the organic compound may become transferred to a site on top of the outermost lattice plane next to a cation see (Fig. 1d). By virtue of surface diffusion, H and X may come together, may combine and may leave the surface as HX, whereupon the original state of the catalyst is restored.

An analogous mechanism may take place when anion vacancies are present to which an X atom from an organic compound is transferred while an H atom goes to a site on top of the outermost lattice plane next to a cation (see Fig. 1e).

In each case it may be expected that the energy of the system with H or X attached to one of the various defects is lower than in the case of attachment of H and X to an anion and a cation in the outermost lattice plane according to Fig. 1a. Accordingly, one may except that the activation energy required for the transfer of H and X from $CH_3 \cdot CH_2X$ to a surface involving point defects is lower than the activation energy for transfer to a lattice plane without defects. Thus the rate of the catalytic decomposition may be increased by the aforementioned point defects if the lowering of the activation energy is sufficiently large in order to overcompensate the lower frequency factor for a mechanism involving point defects.

To test this working hypothesis it is necessary to change the concentrations of the point defects in a definite manner. This may be accomplished by doping the base crystal with the help of additions of other ionic compounds involving a greater or smaller cation-to-anion ratio as the base crystal (*3*). For instance, upon doping AgCl with Ag_2S, i.e., providing an excess of cations, one may expect an increase in the concentrations of ad-cations and anion vacancies. Conversely, upon doping AgCl with $CdCl_2$, i.e., providing an excess of anions, one may expect an increase in the concentrations of ad-anions and cation vacancies.

In the case of KCl as the base crystal, the addition of dopes yields cation or anion vacancies in the bulk crystal rather than interstitial ions because of the high repulsion energy to be overcome in the case of the formation of interstitial ions (*2*). This energy term, however, is lacking in the energy balance for the formation of ad-ions. Consequently, formation of ad-ions may be favored in comparison to the formation of vacancies in the outermost lattice plane even in systems where doping produces vacancies rather than interstitials in the bulk crystal.

In addition, the foreign cations or anions of the dopes may exhibit specific effects which have not been considered above.

In order to test the occurrence of an increase of the catalytic activity of an ionic crystal by doping, the decomposition of tertiary butyl chloride,

$$(CH_3)_3CCl = (CH_3)_2C{:}CH_2 + HCl \qquad (2)$$

has been investigated on AgCl doped with $CdCl_2$ and on $PbCl_2$ doped with KCl and $LaCl_3$. Tertiary butyl chloride rather than ethyl chloride was chosen because decomposition of butyl chloride takes place with a convenient rate at lower temperatures and thus the occurrence of side reactions possibly resulting in a poisoning of the catalyst is less likely to occur.

EXPERIMENTAL

Tertiary butyl chloride was obtained from the firm Schuchardt G.m.b.H. und Co., München, Germany. Gas chromatographic analysis and freezing point determinations showed that the mole fraction of impurities was less than 0.003. No further purification seemed necessary.

To prepare AgCl doped with $CdCl_2$ as a catalyst, a melt of weighed amounts of AgCl and $CdCl_2$ was passed through a vertical capillary. The outcoming droplets solidified in air while falling downward over a distance of about 150 cm. Pellets of nearly spherical shape with diameters ranging between 0.25 and 0.50 mm were selected with the help of sieves and annealed in a gentle stream of purified HCl + Cl_2 at 250°C in order to remove traces of metallic silver and silver oxide. Subsequently the catalyst was handled in the dark.

To prepare $PbCl_2$ doped with KCl or $LaCl_3$, a melt of weighed amounts of $PbCl_2$ and the dope prepared under purified HCl was quenched. The solidified material was crushed and pellets of irregular shape with diameters ranging from 0.16 to 0.20 mm were sorted out with the help of sieves.

The kinetics of the homogenous reaction (2) has been investigated, by measuring the rate of the pressure increase in a closed vessel, by Brearley, Kistiakowsky, and Stauffer (*4*), and by Barton and Onyon (*5*). The same method was adopted for measurements of the catalyzed reaction. To avoid errors resulting from sorption of tertiary butyl chloride in the grease of stopcocks and ground joints, a setup with mercury valves, after Stock as described by Lux (*6*), shown in Fig. 2 was used. The volume of the reaction vessel 3 was about 55 cm^3, whereas the volume of the capillary tubing between vessel 6 and manometer 7 was about 3 cm^3, i.e., much smaller than the volume of vessel 3. Thus, for an approximation, the amount of gas outside vessel 3 which does not undergo decomposition can be neglected.

After charging reaction vessel 3 with catalyst and sealing to the manometer at 5, vacuum was applied over the mercury in container 13 in order to lower the Hg column and to connect vessel 4 with the vacuum pump at 8. Then atmospheric pressure was applied over the mercury in container 13 in order to raise the Hg column and to close the valve to the vacuum pump at 8. After the furnace had been heated to 100°C, vessel 4 was evacuated once more for about 5 min and tertiary butyl chloride was admitted by applying vacuum over the mercury in container 14 until a pressure of about 100 mm Hg was reached. Then atmospheric pressure in 14 was applied in order to close valve 10. To

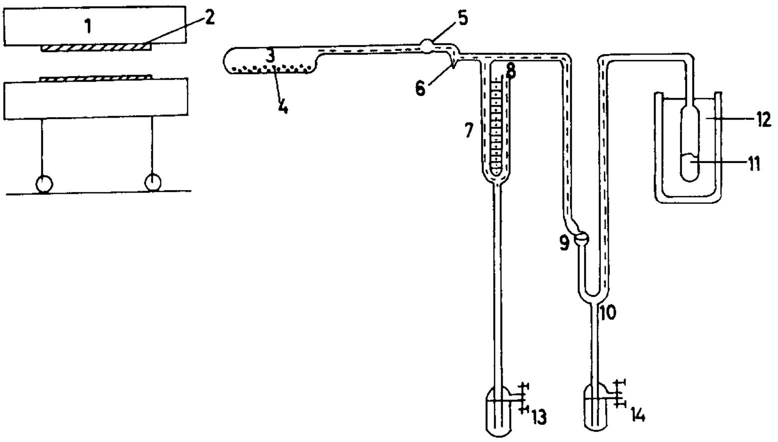

FIG. 2. Apparatus for measuring the decomposition rate of $(CH_3)_3CCl$: 1, movable furnace; 2, Al tube inductor; 3, reaction vessel; 4, catalyst; 5, point at which tube was broken to replace catalyst; 6, small Hg trap; 7, Hg manometer and Hg value between reaction vessel and vacuum pump; 8, connection to HCl absorber and vacuum pump; 9, glass plates serving as obstructions to prevent flow of Hg into reaction vessel; 10, Hg value; 11, tertiary butyl chloride; 12, bath kept at 0°C; 13, 14, Hg containers and stopcocks to vacuum and to atmospheric pressure. Capillary tubing is indicated by broken lines.

follow the reaction, readings at manometer 7 were taken at frequent intervals. Subsequent runs with the same catalyst were made by evacuating the reaction vessel through valve 8, readmitting tertiary butyl chloride, etc.

DISCUSSION

Assuming a first order forward reaction and a second order backward reaction with the rate constants k and k', respectively, one has the rate law

$$-dp_1/dt = kp_1 - k'p_2p_3 = k(p_1 - p_2p_3/K) \tag{3}$$

where p_1, p_2, and p_3 are the partial pressures of tertiary butyl chloride, HCl, and butene, respectively, and K is the equilibrium constant which equals 6.8×10^{-3} atm at 100°C according to Howlett (*7*) corresponding to a decomposition of 21% for an initial pressure $P_0 = 100$ mm Hg. The partial pressures are related to the total pressure P and its initial value P_0 by

$$p_1 = P_0 - (P - P_0), \qquad p_2 = p_3 = P - P_0$$

whereupon Eq. (3) becomes

$$dP/dt = k[(2P_0 - P) - (P - P_0)^2/K] \tag{4}$$

Integration of Eq. (4) yields

$$k = \frac{1}{t}\frac{2}{(1 + 4P_0/K)^{1/2}} \left[\tanh^{-1}\frac{1 + 2(P - P_0)K}{(1 + 4P_0/K)^{1/2}} - \tanh^{-1}\frac{1}{(1 + 4P_0/K)^{1/2}}\right] \tag{5}$$

TABLE 1
DECOMPOSITION OF TERTIARY BUTYL CHLORIDE AT 100°C ON AgCl DOPED WITH CdCl$_2$

Mole % CdCl$_2$ in catalyst	Conductivity $\kappa \times 10^4$ (ohm^{-1} cm^{-1})	Rate constant
0	0.02	5.3×10^{-5}
0.1	0.08	2.0×10^{-4}
0.4	0.24	5.0×10^{-4}
1.5	1.63	1.2×10^{-3}
5	2.88	1.8×10^{-3}

Values of k calculated with the help of Eq. (5) were found to be fairly constant for a particular run with fresh catalyst and to increase from 5×10^{-5} sec^{-1} for pure AgCl to 1.8×10^{-3} sec^{-1} for AgCl doped with 5 mole % CdCl$_2$, (see Table 1). Values of k for repeated runs with the same catalyst were somewhat lower than for runs with fresh catalyst. Seemingly, the catalyst was poisoned in the course of time, probably by the product of a side reaction. As a whole, doping AgCl with CdCl$_2$ has a large effect. Since the concentration of cation vacancies is essentially proportional to the electrical conductivity except for pure AgCl, where interstitial Ag$^+$ ions determine the conductivity (*8*), rate constants have been plotted in Fig. 3 versus the conductivity of the samples in purified N$_2$, which was determined at 100°C with the help of a philoscop operated with ac. Figure 3 shows that in essence the rate constant increases linearly with the conductivity, i.e., with the concentration of cation vacancies in the bulk catalyst.

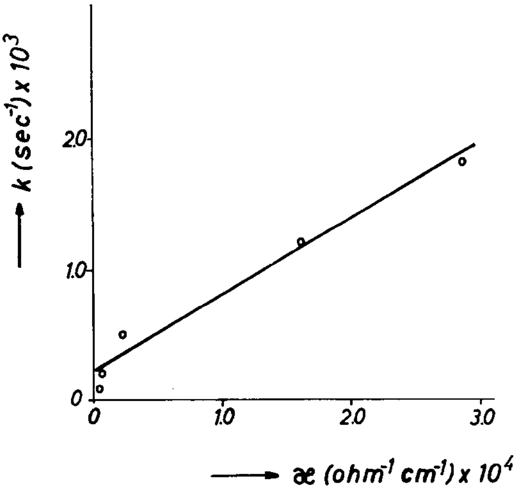

FIG. 3. Rate konstant k for decomposition of tertiary butyl chloride at 100°C on pure AgCl and AgCl doped with 0.1, 0.4, 1.5, and 5 mole % CaCl$_2$ vs. conductivity of catalyst.

This finding, however, does not prove the mechanism shown in Fig. 1d, because both the concentration of ad-anions on AgCl doped with CdCl$_2$ and the concentration of Cd^{2+} ions in the surface are proportional to the concentration of cation vacancies and, therefore, also proportional to the conductivity. Thus, the mechanisms shown in both Fig. 1c and Fig. 1d are equally compatible with the experimental results. Likewise, a mechanism involving transfer of Cl from tertiary butyl chloride to a site next to a Cd^{2+} ion in the outermost lattice plane may account for the results.

In contrast, measurements of the decomposition of tertiary butyl chloride on $PbCl_2$ doped with KCl and with $LaCl_3$ at 100°C did not show a significant change in the rate constant outside the rather large scatter of results, although the conductivities of the doped samples determined in purified N_2 covered a wide range, *viz.*, from 5×10^{-9} to 10^{-4} ohm^{-1} cm^{-1}. Thus point defects due to doping have no spectacular effect on the catalytic activity of $PbCl_2$ as a catalyst for the decomposition of tertiary butyl chloride. The negative result may be due to the fact that at a temperature as low as 100°C, the solubility of the doping agents in $PbCl_2$ is exceeded, as is indicated by irregularities of plots of the logarithm of the conductivity vs. the reciprocal of the absolute temperature. Thus there is a tendency to demixing, especially at the surface where the movement of ions is facilitated by surface diffusion.

Although the prevailing mechanism for the decomposition of tertiary butyl chloride on AgCl doped with $CdCl_2$ cannot be ascertained at present, it is noteworthy that the working hypothesis of specific catalytic contributions due to the presence of point defects such as ad-ions or vacancies has a heuristic value. This hypothesis is to be tested further with the help of other reactions. In particular, it seems worthwhile to investigate whether the rate of the removal of water from organic compounds, e.g., from ethanol,

$$CH_3CH_2OH = CH_2{:}CH_2 + H_2O$$

is increased when the concentration of adions or vacancies is increased by doping an oxide base catalyst.

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