

On the Dehydrochlorination of *tert*-Butyl Chloride on Pure and Doped Silver Chloride

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The catalytic properties of both pure and doped silver chloride in the dark and under illumination were studied by the decomposition of *tert*-butyl chloride between 100° and 150°C. It was found that the freshly rechlorinated silver chloride surface caused a large rate of decomposition. This catalytic activity, however, is diminished by the irreversible surface reaction of chemisorbed chlorine species reacting with silver ions with the generation of silver ion vacancies. A doping with cadmium chloride had no effect on the catalytic properties of silver chloride. However, silver chloride doped with cuprous chloride produced a catalyst which without any chlorine treatment shows a promising catalytic activity for a considerable length of time.

INTRODUCTION

Stimulated by the paper of Schwab and Noller (1) on dehydrochlorination of ethyl chloride on various metal chlorides and the investigation of the decomposition of *tert*-butyl chloride on silver chloride surfaces by Simkovich and Wagner (2), we tried to demonstrate that also in the case of a typical ionic crystal such as, for instance, silver chloride, the decisive step during catalysis is caused by an electronic reaction. Following this concept, it was obvious that under illumination the silver chloride surface should show an additional effect on the rate of decomposition because of the generation of electron-hole pairs which produce a latent image well known in photography.

It is understood that the latent image is composed by a statistically distributed large number of small areas where silver ions in interstitial positions have trapped electrons. This assumption is good enough to lead to the belief that every single spot of the latent image can act as an active center, according to Taylor, where an electron exchange reaction will preferentially take place. Therefore, the light should have a significant influence on the rate of decomposition. As shown in this work, indeed, the light in-

creases the rate of decomposition of *tert*-butyl chloride. In order to get more information on the role of electrons in heterogeneous catalysis, we doped silver chloride with cuprous chloride in the absence of oxygen or air and employed this catalyst for the dehydrochlorination of *tert*-butyl chloride.

EXPERIMENTAL

Chemicals used. Commercial grade silver chloride was used for all the measurements. The powder was passed through the sieve and small grains, approximately 1 mm diameter, were selected for the experiment. The gas chromatographic analysis on *tert*-butyl chloride gave less than 0.5% impurities and thus no further purification seemed necessary.

Deposition of silver on glass. The silver plates were prepared in a standard Edwards vacuum bell jar, at pressure of 10^{-5} to 5×10^{-5} torr. Spectrographically pure silver in the form of wire 0.5 mm in diameter was evaporated from a tantalum boat. A thick deposit of about 10 μ was made on a glass plate measuring 5×3 cm and 2 mm thick. Furthermore, silver foils 99.99% silver and $5 \times 3 \times 0.02$ cm were also employed.

Chlorination of silver plates and foil.

A silver plate so prepared or a silver foil was then chlorinated at 400°C by the thermal decomposition of gold chloride. The chlorine thus liberated, $2\text{AuCl}_3 = 2\text{Au} + 3\text{Cl}_2$, was carried to the silver surface by an inert gas passing through a drying agent such as calcium chloride. The time required for chlorination at 400°C and at standard pressure is about 8 min (3)

Preparation of gold chloride. Extremely pure chlorine in small quantity can be obtained by the thermal decomposition of gold chloride at 255–260°C (4). Hence gold chloride was prepared by the action of technical grade chlorine on fine gold powder at about 240°C. The yield of gold chloride is very poor, about 100–200 mg hr⁻¹. Approximately 10 mm long needlelike crystals were obtained.

Doping of silver chloride. Silver chloride was doped with cadmium chloride by melting known quantities of the two components in a Pyrex glass tube. Then the sample was crushed and small particles were selected for the experiment. The catalyst prior to use was annealed in a gentle stream of purified HCl + Cl₂ at 350°C. Failing to obtain satisfactory results, a doped sample was then prepared according to the method of Simkovich and Wagner (2). The process can briefly be described as follows: A melt of weighed amounts of silver chloride and cadmium chloride was passed through a vertical capillary. The outcoming

droplets solidified in air while falling downward over a height of 150 cm.

To prepare the silver chloride doped with cuprous chloride by a simple method of melting the two components in a glass tube was not possible as it resulted in the oxidation of cuprous into cupric oxide, giving a black precipitate. Weighed amounts of both components were heated to 150°C in vacuum for several hours to remove the moisture. Subsequently the mixture was allowed to melt in a pure and dry nitrogen atmosphere and the molten sample allowed to drop in the outer tube also filled with nitrogen. The solidified material was then crushed and small particles of irregular shapes were used as the catalyst. Finally it was annealed in a stream of nitrogen for about 3 hr at 250°C before being evacuated and used for experiments at 100°C.

Apparatus. Since the reaction is characterized by a volume increase according to the overall reaction $(\text{CH}_3)_3\text{CCl} \rightleftharpoons (\text{CH}_3)_2\text{C}:\text{CH}_2 + \text{HCl}$ we employed a static system to investigate the rate of decomposition (5, 6). The setup of the apparatus is represented in Fig. 1. The reservoir of *tert*-butyl chloride is directly connected by means of a greaseless stopcock (G. Springham & Co. Ltd; Harlow New Town, Essex, England) with the reaction vessel. The outlet tube from the reaction chamber is connected to the quartz spiral manometer (Bodenstein Manometer). Subsequently this is joined to

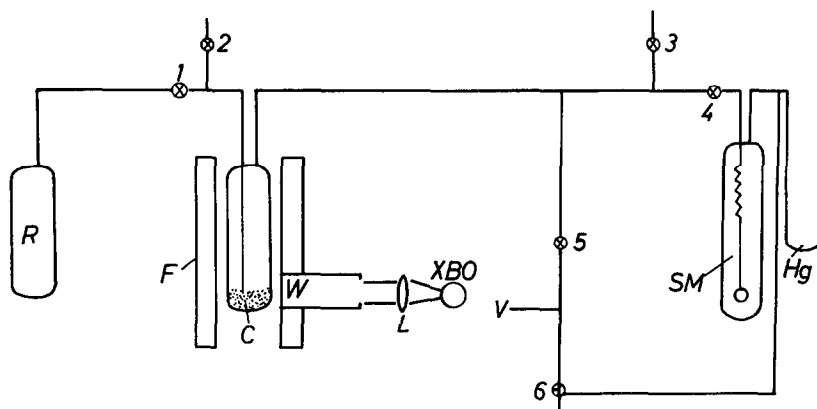
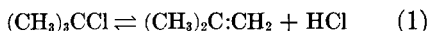


FIG. 1. Static apparatus for the decomposition measurements of *tert*-butyl chloride: R, reservoir for *tert*-butyl chloride; F, furnace; C, catalyst; W, window; L, lens; XBO, XBO high-pressure lamp; SM, quartz-spiral manometer; 1, 2, 3, 4, and 5 are greaseless stopcocks; 6, a two-way stopcock.

the mercury manometer and then finally to the vacuum system, as shown in the Fig. 1. The reaction vessel was heated externally by a furnace. A small window, 7×4 cm, was cut in the furnace to illuminate the catalyst surface. In order to prevent any condensation in the other part of the system it was heated by a laboratory heating tape. The *tert*-butyl chloride reservoir was placed in the thermostat to obtain various partial pressures.

After the apparatus, was evacuated *tert*-butyl chloride vapor was admitted by opening valve number 1. The initial pressure P_0 was recorded and subsequent readings resulting from the increase in pressure were read at intervals of a few minutes for about 30 min. Once this was done the whole apparatus was flushed with pure and dry nitrogen via valves 2 and 3 before once again being evacuated.

Calculation. The reaction occurring on the surface of the catalyst may be written as follows:



If the initial pressure is P_0 and the final pressure P_f and assuming these to be perfect gases, then according to eq. (1) we have, for the degree of dissociation

$$\alpha = (P_f - P_0)/P_0 \quad (2)$$

Also for an initial pressure of P_0 the equilibrium constant K_p was evaluated by the following equation:

$$K_p = \alpha^2 P_0 / (1 - \alpha) \quad (3)$$

According to Simkovich and Wagner (2) we have a rate law,

$$\begin{aligned} -dp_1/dt &= kp_1 - k'p_2p_3 \\ &= k(p_1 - p_2p_3/K_p) \end{aligned} \quad (4)$$

where p_1 , p_2 , and p_3 are the partial pressures of *tert*-butyl chloride, isobutene, and hydrogen chloride, respectively; k and k' are the rate constants for the forward and the backward reaction; and K_p is the equilibrium constant. Equation (4) on integration becomes

$$k = \frac{1}{t} \frac{2}{(1 + 4P_0/K_p)^{1/2}}$$

$$\times \left[\tanh^{-1} \frac{1 + 2(P_f - P_0)/K_p}{(1 + 4P_0/K_p)^{1/2}} - \tanh^{-1} \frac{1}{(1 + 4P_0/K_p)^{1/2}} \right]. \quad (5)$$

The application of formula (5) to evaluate the rate constant k becomes critical near the equilibrium value of the final pressure P_f because a small experimental error in the measurement of P_f can lead to a value of the argument in Eq. (5) greater than unity and thus making \tanh^{-1} meaningless. Therefore, for the determination of the rate constant k it is advisable to use the value of P_f close to the initial pressure P_0 , i.e., a value of P_f that belongs to a short reaction time t . In this case the equation can considerably be simplified by employing the first term of Taylor's series

$$\tanh^{-1}x = x + x^3/3 + x^5/5 + \dots \quad (6)$$

This gives

$$k = \frac{4}{(K_p + 4P_0)} \frac{P_{t_1} - P_0}{t_1} \quad (7)$$

where P_{t_1} is the change in pressure after a time interval t_1 . If the change in pressure ($P_{t_1} - P_0$) is smaller or equal to 4.2 torr at $P_0 = 100$ torr or 5.7 torr at $P_0 = 150$ torr then the error introduced by using Eq. (7) is less than 3%. Hence in this work the rate constant k has been estimated by Eq. (7). Also, in most of the runs in Tables 1, 2, and 3 an average value of the rate constant k at different intervals of time has been tabulated.

EXPERIMENTAL RESULTS

Chlorinated Silver Plates and Foils as Catalyst

Experiments were carried out on chlorinated silver plate at 100°C and poor or no catalytic activity was observed. Therefore, the experiments were performed on chlorinated silver foils measuring $5 \times 3 \times 0.02$ cm at 150°C. The results are recorded in Table 1 and plots of change of pressure ($P_f - P_0$) against time t are represented in Fig. 2. After the first run in Fig. 2 the silver chloride foil was reactivated at 400°C for a period of 30 min and approximately at atmospheric

TABLE 1
DECOMPOSITION OF *tert*-BUTYL CHLORIDE ON CHLORINATED SILVER FOIL AT 150°C

No. of runs	Pressure (torr)			<i>tert</i> -Butyl chloride decomposed, α (%)	Equilibrium constant K_p (atm)	Rate constant k (sec ⁻¹)
	Initial P_0	Final P_t	Change $P_t - P_0$			
1	85	94	9	10.5	1.4×10^{-3}	7.2×10^{-5}
2 ^a	84	108	24	28.6	12.6×10^{-3}	4.8×10^{-4}
3 (light)	91.5	97	5.5	6.0	4.6×10^{-4}	6.5×10^{-5}
4 ^b	87.5	112.5	25	28.5	12.6×10^{-3}	5.1×10^{-4}
5	85	95	10	11.8	1.8×10^{-3}	8.8×10^{-5}

^a First rechlorination.

^b Second rechlorination.

pressure of chlorine. Run 4 confirms the reproducibility of Run 2. Without rechlorination of silver chloride surface (see Runs 3 and 5) the catalytic activity is strongly decreased. Under these conditions even illumination cannot increase the rate of decomposition (Run 3).

In order to study the effect of illumination on the catalytic activity of silver chloride surface, five consecutive runs were performed

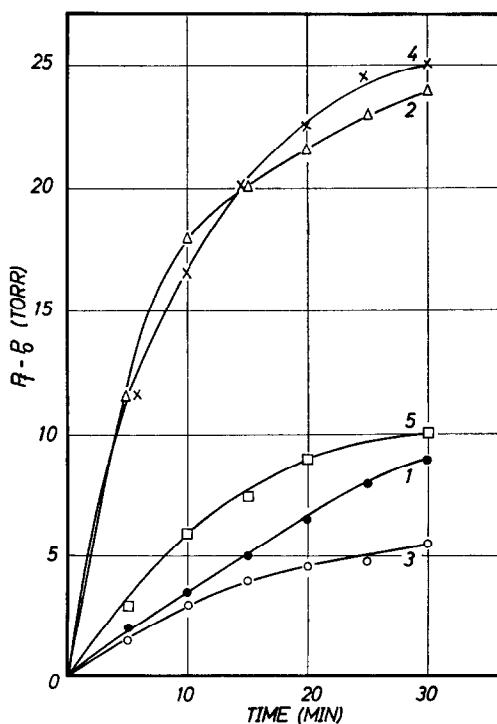


FIG. 2. Rate of decomposition of *tert*-butyl chloride on silver chloride foils at 150°C; 1-5 are the run numbers (for further details see Table 1).

at 150°C at an initial pressure of *tert*-butyl chloride of 87.5 torr. The first run in Fig. 3 with the large rate of decomposition is due to the simultaneous effect of the fresh rechlorination of the catalyst surface and illumination (XBO lamp without filter). The successive runs were carried out after flushing the reaction vessel with pure and dry nitrogen and then evacuating for a period of about 24 hr without any further fresh rechlorination. As can be seen from Fig. 3 and Table 2, the catalytic activity has been decreased from run to run.

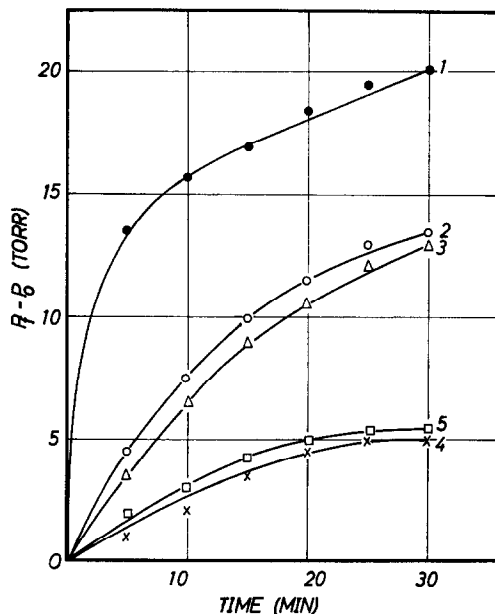


FIG. 3. Rate of decomposition of *tert*-butyl chloride on silver chloride foils at 150°C and under illumination (full light of XBO lamp). Only before the first run was a rechlorination carried out.

TABLE 2
DECOMPOSITION OF *tert*-BUTYL CHLORIDE ON CHLORINATED SILVER FOIL
AT 150°C AND UNDER ILLUMINATION

No. of runs	Pressure (torr)			<i>tert</i> -Butyl chloride decomposed, α (%)	Equilibrium constant K_p (atm)	Rate constant k (sec ⁻¹)
	Initial P_0	Final P_f	Change $P_f - P_0$			
1	87.5	107.5	20	22.8	7.7×10^{-3}	2.2×10^{-3}
2	87.5	101.0	13.5	15.5	3.2×10^{-3}	1.7×10^{-4}
3	87.5	100.5	13.0	14.8	2.9×10^{-3}	1.3×10^{-4}
4	87.5	92.5	5.0	5.7	3.9×10^{-4}	6.5×10^{-5}
5	87.5	93.0	5.5	6.3	4.8×10^{-4}	6.0×10^{-5}

Silver Chloride Grains as Catalyst

After obtaining unsatisfactory results with chlorinated silver foil catalysts, we decided to continue the investigation by employing silver chloride grains. Therefore, similar experiments were made with commercial grade silver chloride powder at 100°C.

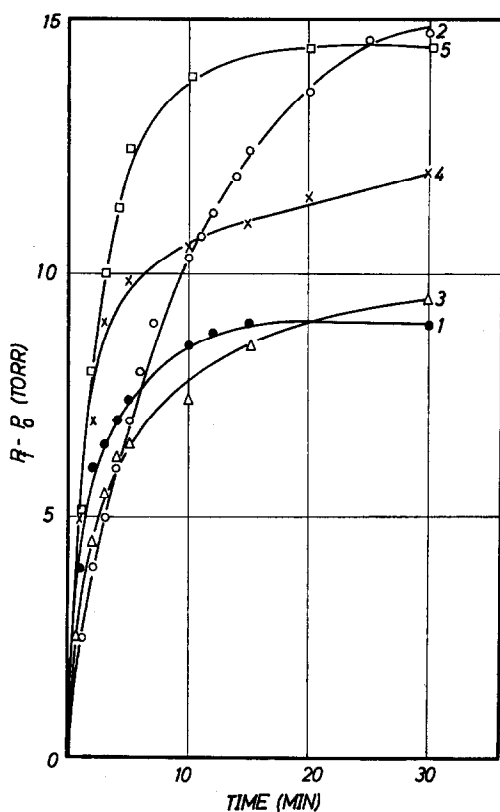


FIG. 4. Rate of decomposition of *tert*-butyl chloride on silver chloride grains at 100°C. Run 1, 99 torr; 2, 99 torr (with light); 3, 96.5 torr; 4, 145 torr; and 5, 161 torr of *tert*-butyl chloride.

As can be observed from Fig. 4, the rate of decomposition is increased by illumination and is independent of the partial pressure of *tert*-butyl chloride. Furthermore, it could be detected that after an initial fast decomposition, the decomposition rate diminishes noticeably and often the reaction comes to a standstill.

Stimulated by the experiments of Simkovich and Wagner (2) with doped silver chloride catalyst, we doped the silver chloride with 4 mole % cadmium chloride and used this for the catalytic study both at 100° and 150°C. In Fig. 5, the experimental

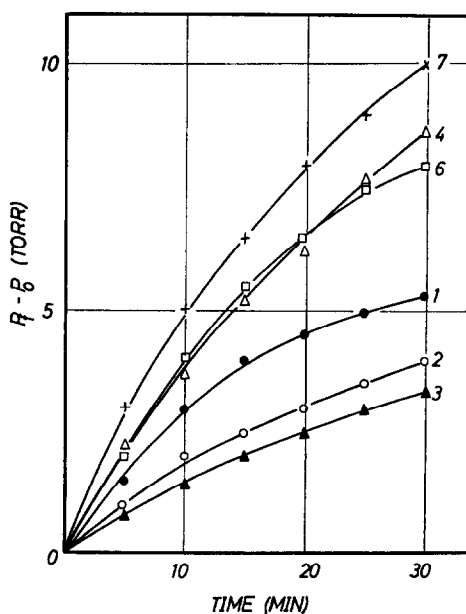


FIG. 5. Rate of decomposition of *tert*-butyl chloride on silver chloride doped with 4 mole % cadmium chloride surface at 100°C (Runs 1, 2, 3) and 150°C (4, 6 with light, 7). Except for run 7 ($P_0 = 128$ torr) all runs were made at $P_0 = 88$ torr.

data are plotted as before. As can be seen from Runs 1, 2, and 3 made at 100°C, a continuous decrease of the catalytic activity was recognized. In spite of rechlorination of the catalyst, the catalytic activity of the doped sample ($\text{AgCl} + \text{CdCl}_2$) showed no effect, unlike the large effect obtained with pure silver chloride after fresh rechlorination. A similar catalytic behavior was observed at 150°C. The illumination of the doped catalyst had no influence on the rate of decomposition.

In contrast to the undoped silver chloride grains (see Fig. 4) here the reaction does not come to a standstill. Even after a period of 30 min the reaction continues. On the basis of the experimental results obtained, no increase in the rate of decomposition could be found on silver chloride catalyst doped with 4 mole % cadmium chloride. A successful activation of the catalytic property of silver chloride was achieved with 1 mole % cuprous chloride. Here for the first time a catalyst was obtained whose catalytic activity continues for a considerable length of time. Some of the typical runs are plotted in Fig. 6. In Table 3 the rate constants under the employed conditions are recorded. The

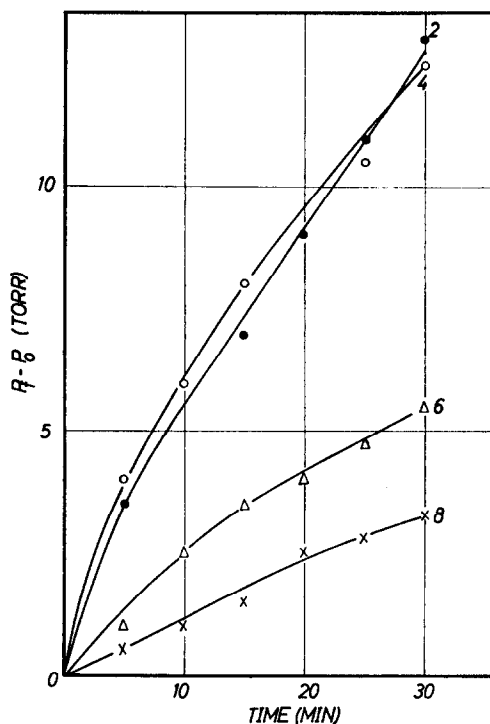


FIG. 6. Rate of decomposition of *tert*-butyl chloride on silver chloride doped with 1 mole % cuprous chloride surface at 100°C. Run 2, 100 torr; 4, 152 torr; 6, 56 torr; and 8, 23 torr of *tert*-butyl chloride.

TABLE 3
DECOMPOSITION OF *tert*-BUTYL CHLORIDE ON SILVER CHLORIDE DOPED WITH
1 MOLE % CUPROUS CHLORIDE AT 100°C

No. of runs	Pressure (torr)			<i>tert</i> -Butyl chloride decomposed, α (%)	Equilibrium constant K_p (atm)	Rate constant k (sec ⁻¹)
	Initial P_0	Final P_f	Change $P_f - P_0$			
1	107.5	122	14.5	13.4	2.9×10^{-3}	9.3×10^{-5}
2	100.0	113.0	13.0	13.0	2.5×10^{-3}	1.0×10^{-4}
3	100.0	113.5	13.5	13.5	2.7×10^{-3}	1.2×10^{-4}
4	152.0	164.5	12.5	8.2	1.4×10^{-3}	8.8×10^{-5}
5	156.0	168.0	12.0	7.7	1.3×10^{-3}	6.4×10^{-5}
6	56	61.5	5.5	9.8	7.8×10^{-4}	5.9×10^{-5}
7	52	57.0	5.0	9.6	7.0×10^{-4}	7.5×10^{-5}
8	23	26.2	3.2	14.0	6.8×10^{-4}	7.1×10^{-5}
9	26	26.5	3.5	15.0	8.0×10^{-4}	7.1×10^{-5}
10	77	82.7	5.7	7.4	5.9×10^{-4}	6.5×10^{-5}
11	76	81.5	5.5	7.3	5.7×10^{-4}	6.0×10^{-5}
12 (light)	107	114.0	7.0	6.6	6.4×10^{-4}	3.1×10^{-5}
13 ^a	106.5	114.5	8.0	7.5	8.3×10^{-4}	5.8×10^{-5}
14 ^b	102.0	118.5	16.5	16.2	4.1×10^{-3}	1.5×10^{-3}

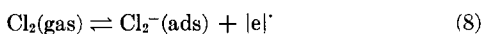
^a Rechlorination at 250°C for 1 hr.

^b Reduction with H_2 at 250°C for 30 min.

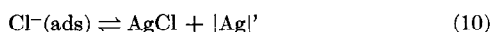
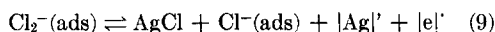
addition of cuprous chloride in silver chloride stabilizes and improves the catalytic properties of the catalyst significantly. Once again it can be seen from the Table 3 that the rate constant is independent of the partial pressures of *tert*-butyl chloride.

DISCUSSION

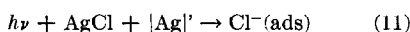
From the experimental results, it can be concluded that the surface of undoped silver chloride becomes highly active catalytically for the decomposition of *tert*-butyl chloride when the surface is pretreated at 400°C with chlorine vapor at atmospheric pressure. Unfortunately the catalytic activity decreases, often to small values, after a period of 30 min. Since the rate of decomposition regains a large effect at the start of the new experiment soon after flushing with pure and dry nitrogen and then evacuating the reaction vessel, we may conclude that by this treatment the undesired surface reaction, (8) to (10), is partly shifted to the left-hand side, thus reproducing the chemisorbed chlorine species which are necessary for the catalysis. A rechlorination of the silver chloride surface causes a combined increase in the concentration of electron holes $|e|'$ and of silver ion vacancies $|Ag|'$ near the surface and also the simultaneous increase in the concentration of chemisorbed chlorine molecules and atoms, as for instance



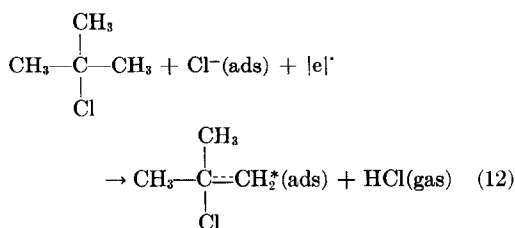
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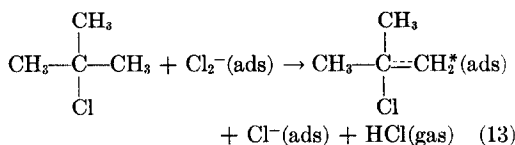
Since immediately after the rechlorination of the silver chloride surface a rather high concentration of $\text{Cl}_2^-(\text{ads})$ and $\text{Cl}^-(\text{ads})$ is available which will slowly be consumed by the reaction steps (9) and (10), the assumption does not seem to be unreasonable that these species can act as "active centers." Further proof for the validity of this concept is the increase of the catalytic activity of the catalyst by illumination. As is known, during illumination chlorine species on the surface are provided, as, for instance.



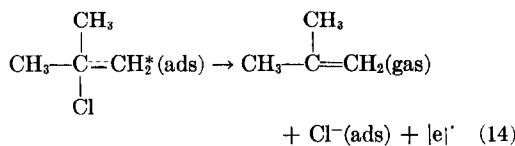
With this matter of fact, we tentatively propose the following reaction mechanism for the decomposition of *tert*-butyl chloride on an undoped silver chloride surface:



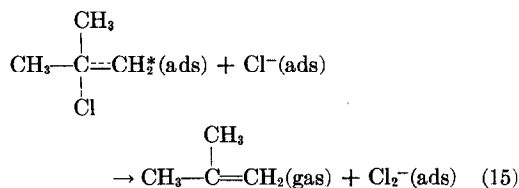
or



The asterisk denotes the activated adsorbed radical. Step (13) is an electrically neutral reaction. After the start of the reaction, (12) and (13), the following steps are possible:



or



This reaction mechanism, however, is based on the existence of $\text{Cl}^-(\text{ads})$ and $\text{Cl}_2^-(\text{ads})$ besides electron holes $|e|'$ on the surface of silver chloride. But during the catalysis these species are consumed, as can be seen by reaction steps (9) and (10). Therefore, the conclusion suggests itself that silver chloride is not a good catalyst for the decomposition of *tert*-butyl chloride because of the small lifetime of the Cl^- and Cl_2^- adsorbed on the surface.

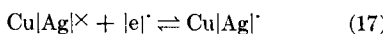
On the basis of this mechanism, it can be expected that a rechlorination of the catalyst surface is effective the very first time but becomes insignificant with subsequent re-

chlorinations. This phenomenon is understood by reaction steps (8) to (10) in which the silver chloride surface becomes saturated with silver ion vacancies and electron holes and thus any further chemisorption of chlorine species is prevented.

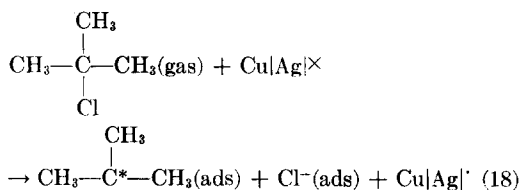
The high catalytic activity of cuprous chloride incorporated in silver chloride, for instance,



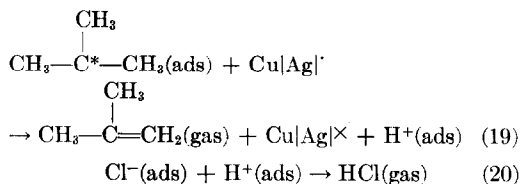
is based on the redox equilibrium



Here Cu|Ag^\times denotes a Cu^+ ion and Cu|Ag^{\cdot} , a Cu^{2+} ion in a Ag^+ lattice site. It can be said that this redox equilibrium seems to be very important for the catalysis. Correspondingly the decomposition begins with the following steps, because in this case no pretreatment with chlorine vapor was carried out:



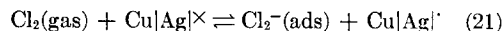
and



In contrast to the first mechanism where the electron holes $|e|$ and adsorbed chlorine species are the catalytically active particles here the incorporation of copper ions in

silver chloride is responsible for the catalytic activity.

In a similar way as described for chemisorption of chlorine in Eq. (8), we can formulate for the chlorination of the silver chloride-cuprous chloride surface,



followed by the reaction mechanism (9) and (10). Contrary to the activation of the pure silver chloride catalyst by rechlorination, the cuprous chloride doped catalyst gave only a poor effect after the same treatment. This reveals that the additional chlorine species at the surface do not act remarkably as "active centers."

This important role of the Cu|Ag^\times species as catalytic centers is confirmed by the reactivation with hydrogen treatment, whereby the equilibrium in Eq. (17) is shifted towards the left-hand side (see Run 14 in Table 3).

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