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A Study of the Dehydrochlorination of 1,2-Dichloropropane over Silica–Alumina Catalysts

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The conversions of 1,2-dichloropropane (12dcp), 1,3-dichloropropane (13dcp), and allyl chloride (3-chloropropene, 3cp=) over a silica–alumina bed have been investigated. Both 12dcp and 13dcp undergo dehydrochlorination above 500 K, mainly resulting in the two 1-chloropropene (1cp=) geometric isomers, which, above 650 K, further eliminate HCl to give propyne and burn in the presence of oxygen. Small amounts of 3cp= were also observed. 12dcp was found to react more rapidly than 13dcp. The conversion of 3cp= gives essentially CO_x above 700 K and small amounts of benzene in the range 600–700 K. The reaction order is zero. The activation energy for the conversion of 12dcp was found to be 14.4 kcal/mol (60.6 kJ/mol). IR data show that a reversible adsorption step is followed by a nucleophilic substitution by an active surface oxide species, giving rise to an alkoxide species. The slow step is likely the E1 elimination of the alkoxide. The conversion of the primary 3-chloro-1-propyl carbenium ion to a 1-chloro-2-propyl carbenium ion plays a relevant role. The catalyst deactivates progressively at 523 K, its activity being nearly halved after 4 h, but it attains a plateau after 7 h. At higher temperatures, the stable total conversion of 12dcp was obtained after 10 h.

Introduction

The dehydrochlorination of chloroalkanes to give olefins and HCl to be recovered can be performed either thermally or catalytically. The dehydrochlorination of 1,2-dichloroethane to vinyl chloride is performed thermally in cracking furnaces near 800 K and 2–3 MPa with a conversion of 50–60% and recycling of the unreacted dichloroethane.^{1–3} Catalytic processes have also been developed over silicates, metal-promoted aluminas and zeolites,² and polyacrylonitrile-based active carbon fiber catalysts.⁴ In all cases, catalyst deactivation occurs rapidly, and frequent regeneration is needed.

The dehydrochlorination of chlorided linear paraffins to linear olefins in the production of alkylbenzene sulfonate surfactants is performed catalytically in the presence of silica–aluminas or on metal packings of reactor columns acting as catalysts.^{2,3,5,6} In this case, no information is readily available in the open literature concerning catalyst stability.

Recent reports in the open literature describe the dehydrochlorination of different chlorided organics over alumina and silica–alumina,⁷ over transition metal

chlorides,^{8,9} and over silica-supported nickel catalysts in the presence of hydrogen.^{10,11}

The dehydrochlorination reaction can also be proposed as a means of lowering the chlorine content in chlorided organic wastes with recovery of the chlorine as HCl. In our laboratory, the catalytic dehydrochlorination of 2-chloropropane, as a model of a weakly chlorided saturated organic compound, has previously been investigated.¹² Silica–alumina was found to act as an excellent catalyst near 500 K, and some kinetic and mechanistic information was also obtained. In particular, the mechanism proposed consists of a sequence involving a nucleophilic substitution to give a 2-propoxide species followed by an elimination reaction, i.e., it is different from the mechanisms proposed by Noller and Kladnig in their review of elimination reactions.¹³

In the present paper, we report on the dehydrochlorination of 1,2-dichloropropane (12dcp) as an example of a more extensively chlorinated compound. This compound is an excellent solvent for fats, oils, resins, lacquers, asphalt, and bitumen and is used in refineries to adjust the chlorine content of catalysts.² However, because of its harmful health effects, the levels of 12dcp vapors allowed in the workplace are limited by the Occupational Safety and Health Administration to less than 75 ppm for an 8-h workday and to 110 ppm for a 15-min exposure. Some data on the conversions of 1,3-dichloropropane and 3-chloropropene (allyl chloride) are

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also reported. To approach the conditions of processes aimed at the treatment of wastes, the reactions are carried out in the presence of oxygen.

Experimental Section

1,2- and 1,3-Dichloropropane (12dcp and 13dcp, respectively), as well as 1-chloropropane (1cp), 2-chloropropane (2cp), 2-chloropropene (2cp=), and 3-chloropropene (allyl chloride, 3cp=), were from Aldrich. The catalyst was 87% SiO₂–13% Al₂O₃ amorphous silica–alumina from Strem (330 m²/g).

Catalytic tests were carried out at atmospheric pressure in a continuous fixed-bed tubular glass flow reactor (internal diameter 6 mm, length ~2.5 cm). Catalyst (0.1–0.2 g) was loaded into the reactor in the form of fine powder (mesh 60–70) that had been mechanically mixed with 0.4 g quartz powder. The total gas flow was in the range 345–370 mL/min, and the feed composition varied in the ranges 0.1–0.25% 12dcp and 4–5% oxygen, with the balance helium. Most of the experiments were consequently carried out with a contact time of $\tau = 49.75$ ($g_{\text{cat}}/g_{12\text{dcp}}$) min. The reactants and the reaction products were analyzed on-line using a gas chromatograph (HP 5890) equipped with an HP PLOT Q column connected to TCD and FID detectors. A methanizer allowed for the analysis of CO and CO₂. GC-MS analysis of the products was performed using a HP GCD G1800B instrument with an HP-VOC column.

To analyze HCl and Cl₂, the effluents were contacted with a NaOH–water solution. Chloride and hypochlorite anions were analyzed and quantified by means of ionic chromatography. Actually, hypochlorite anions were never detected. According to this analysis, only HCl is produced and always nearly fulfills the chlorine balance, if organic chlorided compounds analyzed by GC and GC-MS are taken into account. Thus, hereinafter, only conversions and selectivities based on carbon-containing compounds are considered.

The results are presented as conversions (C) and selectivities (S), both calculated on molar bases. The conversions are expressed as

$$(\text{moles of reactant reacted})/(\text{moles of reactant fed}) \%$$

and the selectivities (equivalent to “percentage yields”) are expressed as

$$\frac{(\text{moles of the product obtained})}{(\text{moles of reactant reacted})} \%$$

The experimental error was estimated not to exceed 5%.

Results

1. Thermal and Catalytic Dehydrochlorination and Thermodynamics of the Process. In Figure 1, the conversion of 1,2-dichloropropane (12dcp) in the “empty” reactor (actually the reactor filled with quartz powder only) is shown. The conversion begins to be significant above 700 K. In addition to carbon oxides and HCl, five organic products are observed among the products. At higher temperatures, propyne (P) is observed and identified by mass spectrometry. It is, however, a largely minor product. The main products are all characterized by retention times of ~8 min. We preliminarily called them 7-9, 8-1, 8-2, and 8-3, in order of increasing retention times. They were all identified by mass spectrometry as chloropropene, but the indi-

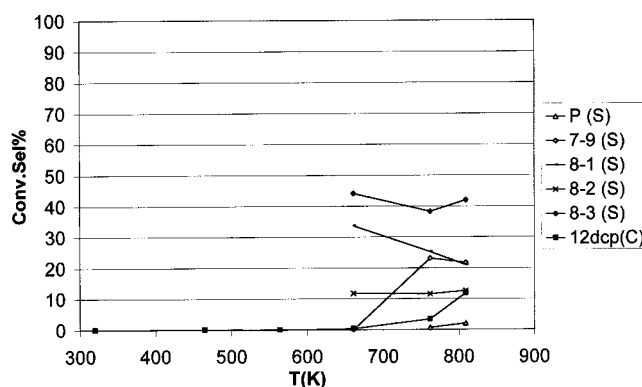


Figure 1. Conversion of 1,2-dichloropropane (C) and organic product selectivities (S) in empty reactor ($p_{12\text{dcp}} = 0.001$ atm and oxygen excess, 350 mL/min total flow rate). 7-9 identified as 2-chloropropene, 8-1 and 8-3 as the two geometric isomers of 1-chloropropene, and 8-2 as 3-chloropropene.

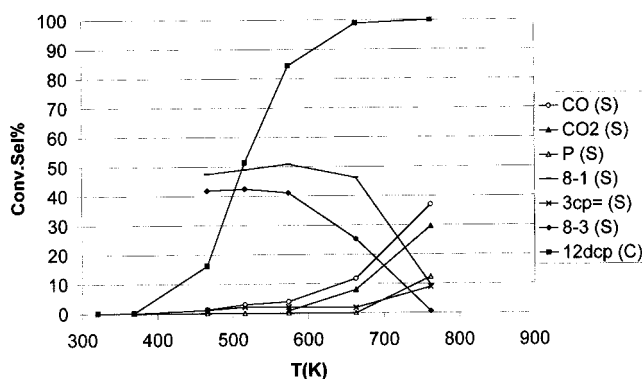


Figure 2. Conversion of 1,2-dichloropropane (C) and product selectivities (S) over silica–alumina catalyst ($p_{12\text{dcp}} = 0.001$ atm and oxygen excess, 350 mL/min total flow rate). 8-1 and 8-3 identified as the two geometric isomers of 1-chloropropene.

vidual isomers could not be specified. A gaschromatographic analysis based on the retention time supports the identification of compounds 7-9 as 2-chloropropene (2cp=) and 8-2 as 3-chloropropene (allyl chloride, 3cp=). These two compounds are available as commercial products. The other two compounds (8-1 and 8-3) should consequently be identified as the two geometric isomers of 1-chloropropene [(*E*)-1-chloropropene and (*Z*)-1-chloropropene]. However, we could not discriminate between them. We can remark that they are more abundant than 3cp= in the empty reactor. The data we obtained are consistent with those reported by McBee et al.,¹⁴ although those researchers found only traces of the 2cp= isomer.

The conversion of 12dcp over a silica–alumina bed is reported in Figure 2. The analyses for each temperature were performed after 90 min on stream, where the product selectivities appeared to be nearly constant with time (see below). Conversion is significant already near 400 K, becoming nearly total at 700 K. The largely predominant products in the range 400–600 K are the two 1-chloropropene isomers 8-1 (particularly more abundant at the higher temperatures in this range) and 8-3, both of which decrease strongly at the highest temperatures (i.e., above 600 K). The allyl chloride (3cp=) is observed in small amounts below 600 K. Above 600 K, the selectivities to 8-1 and 8-3 drops to 0, whereas increasing amounts of 3cp= are produced, together with CO_x and propyne. The total absence of 2-chloropropene among the products substantially agrees with the results previously reported by Mochida et al.⁷

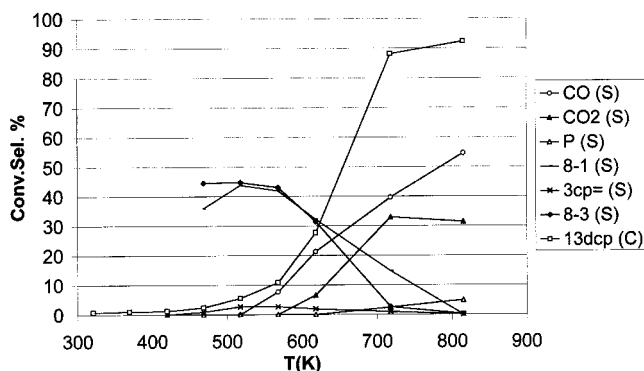


Figure 3. Conversion of 1,3-dichloropropane (C) and product selectivities (S) over silica-alumina catalyst ($p_{13dcp} = 0.001$ atm and oxygen excess, 350 mL/min total flow rate). 8-1 and 8-3 identified as the two geometric isomers of 1-chloropropene.

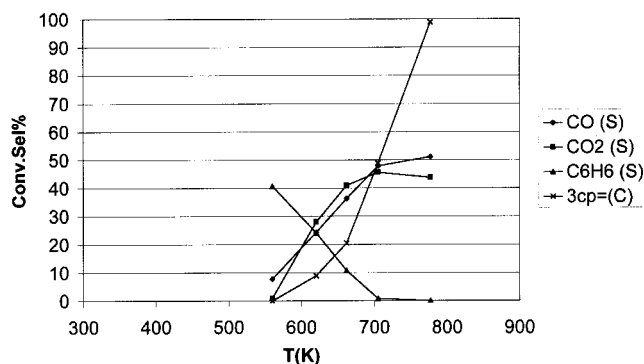


Figure 4. Conversion of 3-chloropropene (C) and product selectivities (S) over silica-alumina catalyst ($p_{3cp=} = 0.001$ atm and oxygen excess, at 350 mL/min total flow rate).

for silica-alumina at 573 K in the presence of hydrogen. However, those authors found a different product distribution, in which (*Z*)-1-chloropropene was most abundant (50% selectivity) and allyl chloride was also produced in substantial amounts (39% selectivity), along with minor amounts of (*E*)-1-chloropropene.

We also investigated the conversion of the 1,3-dichloropropane (13dcp) isomer under the same conditions (Figure 3). The conversion of 13dcp is definitely shifted to higher temperatures with respect to that of 12dcp, but the observed products are the same and have a quite similar selectivity pattern at the same temperature. In particular, also in this case, no products with the retention time characteristic of 2-chloropropene can be observed. Such a finding is, in this case, expected, because the reactant has no chlorine atoms in the 2 position. It also further supports the previous identification of the 8-1, 8-2, and 8-3 products as the three chloropropene isomers other than 2-chloropropene.

In Figure 4, the results of the experiment on the conversion of 3-chloropropene (allyl chloride) over the silica-alumina bed are reported. No isomerization to the other chloropropene isomers was found to occur. Also, no evidence was found for propyne formation. Allyl chloride appears to be very refractory to conversion and gives rise to benzene starting from 600 K and to CO_x as the only detectable products above 700 K.

To obtain more information on the catalytic effect of silica-alumina, we performed thermodynamic equilibrium calculations. We used the experimental data reported by Reid et al.¹⁵ for 12dcp, 3cp=, propyne, allene, and HCl and the method of Yoneda, as reported by Reid et al.,¹⁵ for calculating the values of the

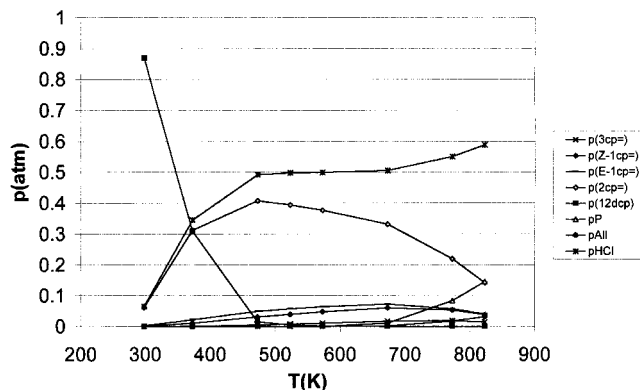


Figure 5. Theoretical reactants and products partial pressure (atm) under equilibrium conditions and at increasing temperatures. Total pressure = 1 atm.

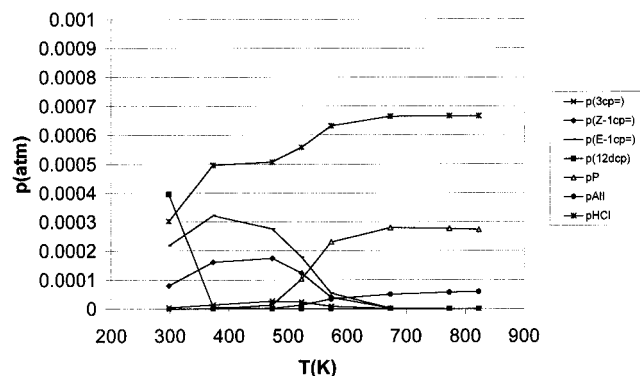


Figure 6. Theoretical reactants and products partial pressure (atm) under equilibrium conditions and at increasing temperatures. Total pressure = 0.001 atm.

thermodynamic variables for the other compounds. According to these data, 2-chloropropene is the most stable among the chloropropene isomers (Figure 5), while allyl chloride is the least stable. The geometric 1-chloropropene isomers have similar intermediate stabilities, with the *E* isomer expected to be slightly more stable than the *Z* isomer.

In Figure 5, the theoretical equilibrium partial pressures of 12dcp, the four chloropropene isomers, HCl, propyne (P), and allene (All) are reported as expected for 1 atm total pressure. The conversion of 12dcp is expected to be nonnegligible already at room temperature and should be more than 90% above 473 K. The predominant product expected up to about 700 K is 2-chloropropene, with minor amounts of the 1-chloropropene isomers and even less allyl chloride. Above 673 K, the dehydrochlorination of the chloropropenes becomes possible, with the formation of propyne and, much less, of allene.

If 2-chloropropene (which we do not detect among the products under catalytic conditions) is not considered, and if the equilibrium is calculated at a total pressure of 0.001 atm (1.013×10^2 Pa), i.e., nearly at our working pressure (neglecting the partial pressure of the inert He), the data show that the conversion of 12dcp is possible and can be as large as 60% at room temperature and above 99% at 373 K. The thermodynamic equilibrium concentrations calculated are shown in Figure 6. The "thermodynamic" selectivity to (*E*)-1-chloropropene is near 65%, whereas that to the *Z* geometric isomer is near 32%, but the difference tends to decrease as the temperature increases. The selectivity to allyl chloride tends to grow with temperature but remains less than

Table 1. Effect of Contact Time on the Conversion of 12dcp and Selectivities to Products at 515 K

contact time (min)	conversion 12dcp (%)	selectivity to 8-1 product (%)	selectivity to 3cp= (%)	selectivity to 8-3 product (%)	selectivity to CO (%)
49.75	51.4	51.9	2.3	44.9	0
74.63	53.0	50.9	1.7	46.2	0
99.5	60.1	46.2	1.5	44.0	3.2

10% in the range 373–473 K. Above this temperature, the further dehydrochlorination of the chloropropenes starts to be thermodynamically possible, so that propyne is expected to be the most abundant product at 573 K, with allene being an additional byproduct. According to the method of Yoneda,¹⁵ 13dcp is expected to be slightly less stable than 12dcp [$\Delta G_f^\circ(298\text{ K}) = -70.7\text{ J/mol}$ for 12dcp, $\Delta G_f^\circ(298\text{ K}) = -64.0\text{ J/mol}$ for 13dcp], so that its thermodynamic conversion is expected to shift slightly toward lower temperature but without changing the product pattern.

These data indicate the following: (i) The conversion of 12dcp (and 13dcp) in the range 400–700 K is kinetically limited and is due to the catalytic activity of silica–alumina. (ii) The formation of the most stable chloropropene isomer, 2-chloropropene, is hindered by kinetics over silica–alumina catalysts. On the other hand, also for the thermal reaction, 2cp= is not the predominant product, even though it is the most stable. This means that its production is kinetically limited also in the gas phase in our temperature range. (iii) The relative amounts of the two 1-chloropropene isomers and of allyl chloride produced by dehydrochlorination are roughly similar to those expected on the basis of thermodynamics at low temperature, but they strongly deviate from prediction at higher temperature. On the other hand, we do not detect any formation of 1-chloropropenes from allyl chloride. This makes it likely that their relative amounts are actually governed by the kinetics of their formation. Thus, silica–alumina, which is well-known to act as a double-bond isomerization catalyst for olefins such as butenes in this temperature range,¹⁶ does not catalyze this reaction for chloropropenes. (iv) the further dehydrochlorination of chloropropenes to propyne is also kinetically limited in the temperature range 473–773 K over silica–alumina beds, as well as in the empty reactor.

2. Kinetic Evaluations. The conversion data at low conversion as a function of the reaction temperature, with the assumption of a differential reactor, allowed us to estimate the apparent activation energy. The values measured from the Arrhenius plots are 23.7 kcal/mol (99.1 kJ/mol) for the thermal reaction in the empty reactor and 14.4 kcal/mol (60.6 kJ/mol) for the reaction over the silica–alumina catalyst bed. This confirms that our data are actually obtained in kinetic regimes where diffusion has a small effect, if any. However, we remark that the value for the catalyzed reaction is at the lower limit of the range determined for the dehydrochlorination of 2-chloropropane over the same catalyst,¹² measured previously to be 14–27 kcal/mol.

We also performed experiments with the same flow and feed conditions but with increasing catalyst amounts, and thus with increasing contact times up to 99.5 min (Table 1). The conversion increases with increasing catalyst amount but not in a proportional way, except perhaps when conversion is very low. This means that the kinetic regime is not purely chemical, as diffusion

Table 2. Effect of 12dcp Partial Pressure on the Conversion of 12dcp at 466 K and 515 K and Selectivities to Organic Products

partial pressure of 12dcp in the feed	conversion of 12dcp at 466 K (%)	selectivity to 8-1 product at 466 K (%)	selectivity to 3cp= at 466 K (%)	selectivity to 8-3 product at 466 K (%)
0.0012	16.1	51.6	1.2	46.3
0.0018	12.8	44.5	1.1	45.4
0.0024	13.9	45.1	1	46.6

partial pressure of 12dcp in the feed	conversion of 12dcp at 515 K (%)	selectivity to 8-1 product at 515 K (%)	selectivity to 3cp= at 515 K (%)	selectivity to 8-3 product at 515 K (%)
0.0012	51.4	51.9	2.3	44.9
0.0018	37.6	44.6	1.2	47.4
0.0024	41.9	44.5	1.1	50.6

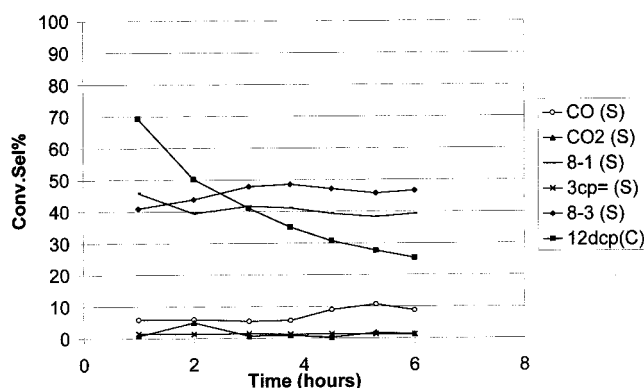


Figure 7. Conversion of 1,2-dichloropropane (C) and product selectivities (S) over silica–alumina catalyst at increasing time-on-stream ($p_{12dcp} = 0.001\text{ atm}$ and oxygen excess, 350 mL/min total flow rate, $T = 518\text{ K}$). 8-1 and 8-3 identified as the two geometric isomers of 1-chloropropene.

limitations have an effect in the relatively high-temperature range.

Measurements performed at the usual contact time (49.75 min) but at different partial pressures of 12dcp (and different amounts of catalysts) show that the conversion at the same temperature is nearly unchanged (Table 2), suggesting that the reaction order with respect to the reactant is nearly zero. This agrees with the zero order found previously for the dehydrochlorination of 2-chloropropane over the same catalyst.¹² Measurements done with the exclusion of oxygen from the feed reveal that it has no significant effect on either the first dehydrochlorination step or the intermediate product selectivities.

3. Catalyst Stability Tests. Two different experiments were performed to study the stability of silica–alumina upon dehydrochlorination of 12dcp. An experiment performed at 518 K (Figure 7) shows that the conversion of 12dcp decreases considerably with increasing time on stream. The conversion after 1 h is 70%, but it is nearly halved after 4 h. However, a plateau is observed above 20% conversion after 7 h. Under these conditions, the selectivities to 8-1 and 8-3 invert after 2 h, but at later times, they stay quite constant.

Another experiment was performed at higher temperatures, i.e., 705 K. Under these conditions, the conversion is 100% and stays complete even after 10 h. However, the product selectivities change significantly

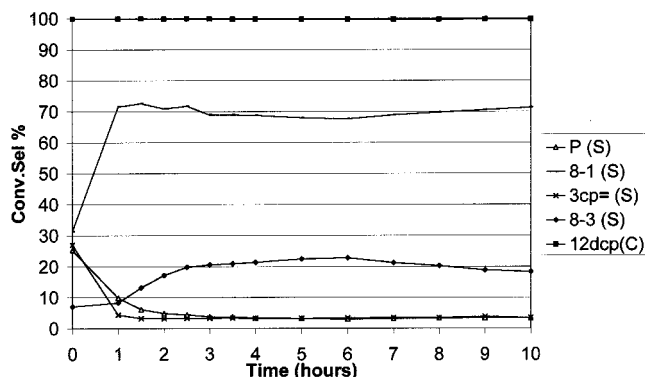


Figure 8. Conversion of 1,2-dichloropropane (C) and product selectivities (S) over silica-alumina catalyst at increasing time-on-stream ($p_{12dcp} = 0.001$ atm and oxygen excess, 350 mL/min total flow rate, $T = 705$ K). 8-1 and 8-3 identified as the two geometric isomers of 1-chloropropene.

in the first period and later stay constant. In particular, the production of CO_x decreases strongly to a stable level on the order of 10% after 2 h. The selectivities to organics are reported in Figure 8. Interestingly, the selectivity to allyl chloride (3cp=), which is 28% at this temperature for short times on stream, falls to less than 5%. Also, the selectivity to propyne decreases strongly. In contrast, the selectivities to the two 1-chloropropenes strongly increase in the first 1–3 h. The 8-1 compound is, however, produced in larger amounts than the 8-3 compound.

4. Infrared Mechanistic Experiments. The dehydrochlorination experiments were also performed in an IR cell as a static reactor with monitoring of both the catalyst surface and the gas phase, as described elsewhere.¹⁷ The IR spectra of the species adsorbed on the silica-alumina catalyst are reported in Figure 9, and the IR spectra of the gaseous species in contact with

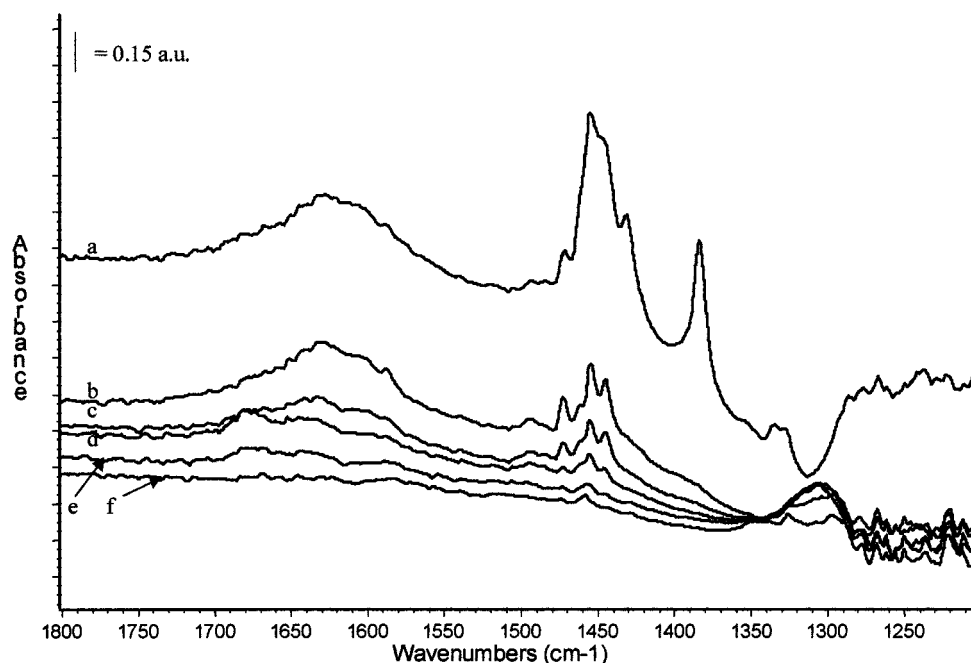


Figure 9. FT-IR spectra of adsorbed species arising from 1,2-dichloropropane adsorption over silica-alumina catalyst (a) in the presence of the gas at room temperature, (b) after outgassing at room temperature, (c) at 373 K, (d) at 423 K, (e) at 523 K, and (f) at 623 K. The activated surface spectrum has been subtracted.

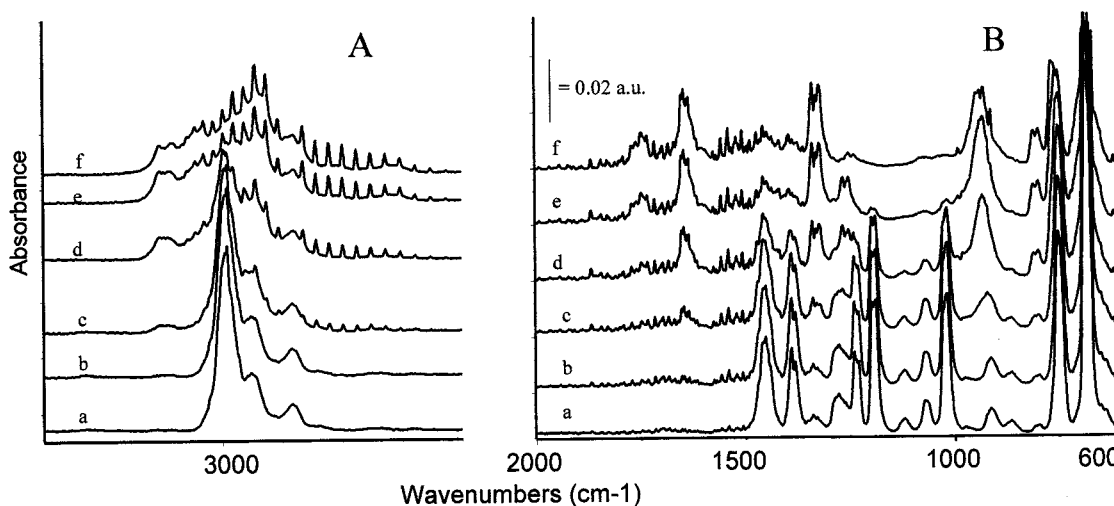


Figure 10. FT-IR spectra of gas-phase species arising from 1,2-dichloropropane conversion over silica-alumina catalyst at (a) 373, (b) 423, (c) 473, (d) 523, (e) 573, and (f) 623 K.

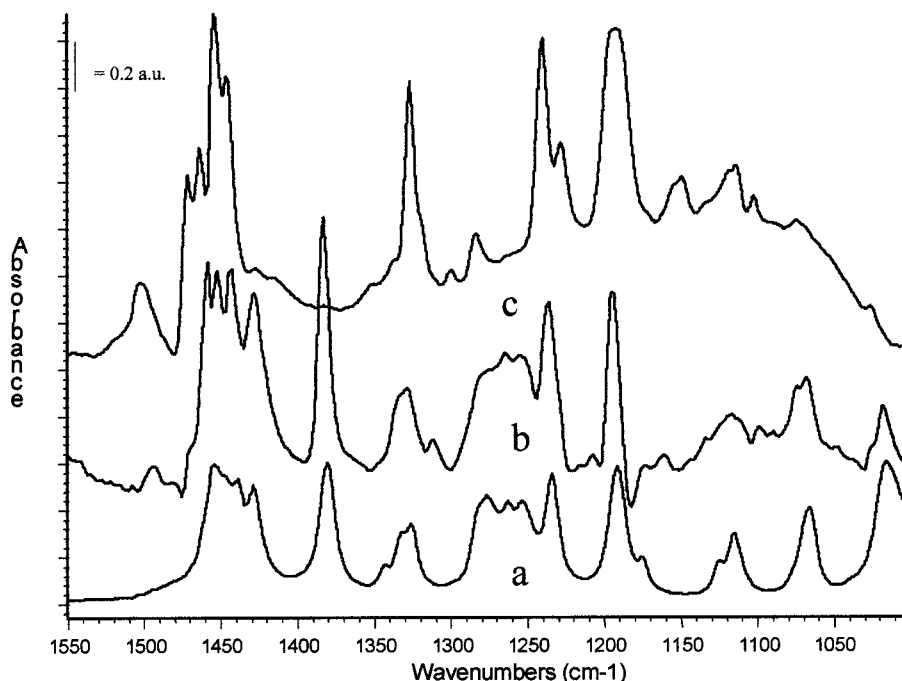


Figure 11. FT-IR spectra of (a) liquid 1,2-dichloropropane and the species arising from adsorption of 1,2-dichloropropane over alumina catalyst (b) in the presence of gas and (c) after outgassing at room temperature.

the catalyst at different temperatures are reported in Figure 10. Figure 10a is the spectrum of gaseous 12dcp. In Figure 11a, the IR spectrum of liquid 12dcp is also reported. It is evident that the spectrum of the weakly adsorbed species of 12dcp on the silica–alumina catalyst (Figure 9a) is very similar to that of the liquid adsorbate (Figure 11a). However, the spectrum of the strongly adsorbed species that resists outgassing (Figure 9b–f) is definitely different and provides evidence of a strong vibrational perturbation. In particular, we note a spectacular decrease in intensity of the band at 1380 cm^{-1} due to the symmetric deformation of the methyl group. On the other hand, all stretching and deformation modes of the C–H groups are shifted and undergo relative intensity modifications; no new bands appear. In any case, we determined that the spectra observed do not correspond to those of adsorbed chloropropenes. The observed spectrum disappears above 523 K. The gas-phase spectra recorded during the same experiment (Figure 10) show that to the spectrum of gaseous 12dcp new bands are progressively added. In particular, at 473 K (Figure 10e), a new rotovibrational band appears near 1640 cm^{-1} (with a shoulder at 1610 cm^{-1}). This band can be assigned to the C=C stretching vibrations of a mixture of chloropropenes. In particular, the $800\text{--}700\text{ cm}^{-1}$ region of the spectrum shows the presence of sharp bands centered at 805 and 755 cm^{-1} assigned to the CCl stretching of the E and Z isomers of 1-chloropropene, respectively.¹⁸ At the same time, we cannot exclude the presence of the allyl chloride species, characterized by a strong band centered around 1250 cm^{-1} ,¹⁹ which is present but very weak at high temperatures (Figure 10f). An analysis of the region $3200\text{--}2800\text{ cm}^{-1}$ also allows us to identify the formation of “internal” olefins such as the two 1-chloropropene isomers (rotovibrational bands in the region $3080\text{--}3020\text{ cm}^{-1}$, asymmetric CH stretchings of H–C=C–H groups). Terminal CH₂ stretching vibrations of allyl chloride should occur in the range $3090\text{--}3010\text{ cm}^{-1}$, thus very close to the corresponding 1-chloropropene IR bands.

At higher temperatures (523 K), a carbonyl compound is also formed (C=O band at 1745 cm^{-1}), likely acrolein, which should be intermediate in the combustion of 12dcp. Additionally, the spectrum of gaseous HCl is also observed starting from 473 K (sharp rotovibrational components in the range $2900\text{--}2700\text{ cm}^{-1}$), showing that, at this temperature, the desorption of HCl is relatively rapid.

The opacity of silica–alumina below 1300 cm^{-1} prevents further information from being obtained from the IR spectra. To overcome this limitation, we also performed experiments on alumina, whose catalytic activity seems to be lower than but similar to that of silica–alumina. Actually, the spectra of the adsorbed species arising from 12dcp on alumina (Figure 11b) are closely similar to those detected on silica–alumina. The possibility of also analyzing, in this case, the region down to 1000 cm^{-1} , allows us to detect the formation of a new band at 1150 cm^{-1} and the important broadening of the band near 1190 cm^{-1} . In this region, bands due to C–C and C–O stretching occur. The formation of new bands here strongly suggests that the hydrolysis of C–Cl bonds has occurred to give rise to C–O– components of alkoxy groups. Previous studies^{12,20} have shown that alkyl chlorides easily undergo nucleophilic substitution over oxide surfaces to give rise to the corresponding alkoxides. In particular, 2-chloropropane was previously found to give rise to 2-propoxides, which are characterized by multiple strong bands in the range $1200\text{--}1100\text{ cm}^{-1}$.¹² Consequently, it seems very likely that such a nucleophilic substitution also occurred from 12dcp in this case.

Discussion

The data reported here show that silica–alumina catalyzes the dehydrochlorination of 12dcp to the two isomers of 1-chloropropene and to 3-chloropropene (allyl chloride) as a minor product. The reaction occurs in the temperature range 400–700 K. The further dehydro-

chlorination of at least some of the three chloropropene isomers to propyne also occurs above 700 K. The data clearly show that both reactions are under kinetic control. A similar product pattern is obtained from conversion of 13dcp, but in this case, the reaction is slower. We previously observed that, under the same conditions, the dehydrochlorination of 2-chloropropane is faster than that of 1-chloropropane.¹² This suggests that reaction could occur through the formation of a carbenium ion according to a heterolytic scission of a C–Cl bond. The faster reaction of 12dcp with respect to 13dcp can be explained on the basis of the location of Cl atoms exclusively in primary positions in the latter case, with the formation of primary carbenium ions. For 12dcp, the rupture of the CCl bond in the secondary position is easier because it allows for the formation of the more stable secondary carbenium ion. This also agrees with the lack of formation of 2-chloropropene not only from 13dcp but also from 12dcp. Thus, the products observed are those in which the Cl atoms are in terminal positions, with Cl in secondary positions not being formed for kinetic reasons.

A comparison of the data presented here for 12dcp and 13dcp with those reported previously for the two chloropropane isomers 2cp and 1cp also supports the intermediacy of carbenium-ion-like species. In fact, 2cp converts faster by dehydrochlorination than both 1cp and 12dcp. This agrees with the expected destabilizing effect of the chlorine atom, which destabilizes the 1-chloro-2-propyl carbenium ion with respect to the 2-propyl carbenium ion. Thus, the reaction rate is roughly determined by the stability of the corresponding carbenium ion.

The three products first observed upon conversion of 12dcp can all be obtained from the 1-chloro-2-propyl carbenium ion. The predominance of the two geometric isomers of 1-chloropropene indicates that the elimination of the protons at position 1 (at the chloromethyl group Cl–CH₂–) is favored over the elimination at the methyl group. In fact, the experiments on the conversion of allyl chloride show that isomerization at the double bond position does not occur under these conditions.

Starting from 13dcp, the intermediate species is expected to be the unstable primary 3-chloro-1-propyl carbenium ion. Proton elimination from this species is expected to give rise to allyl chloride as the only product. In contrast, also in this case, 1-chloropropenes are the predominant products. This strongly suggests that a fast hydride shift occurs, converting the primary 3-chloro-1-propyl carbenium ion into the 1-chloro-2-propyl carbenium ion before deprotonation to the olefin.

The detection of a different product distribution from 12dcp in the thermal reaction in the empty reactor at 800 K, which also includes the formation of 2-chloropropene, is evidence of a lower “selectivity” of the mechanism involving radicals, which likely occurs in the gas phase.

The IR spectra of the adsorbed species whose evolution gives rise to gaseous chloropropenes suggests that, as previously shown for chloropropanes,¹² alkoxide species can be formed as strongly adsorbed species in a previous fast nucleophilic substitution step. According to the apparent fast adsorption/desorption equilibrium of intact 12dcp, this suggests that the rate-determining step of the overall dehydrochlorination reaction is the further evolution of such alkoxide species. The fast saturation of the sites allowing for the formation of this

intermediate alkoxide also justifies the zero reaction order that we determined experimentally. The activation energy that we found is in a range typical for dehydrochlorination reactions (30.4–91.3 kJ/mol),⁸ as well as for alcohol dehydration reactions, where the elimination from an alkoxide is also likely to be rate-determining.²¹

In our experiments, at higher temperatures, further dehydrochlorination occurs to produce propyne; combustion also occurs to produce CO_x (in the presence of oxygen). However, conversion of allyl chloride does not give rise to significant amounts of organic products. Only CO_x species are observed. This suggests that propyne is produced from 1-chloropropenes. Such a result agrees with expectations. Dehydrochlorination of allyl chloride would give rise to allene, which is even more unstable and is probably immediately burned to CO_x (at 800 K). Interestingly, one of the two 1-chloropropene isomers (which we call 8-3, characterized by longer retention times in the GC column) converts more quickly than the other. According to basic organic chemistry,²² “anti” elimination is expected to be faster than “sin” elimination. This suggests that the 8-3 isomer could be identified as (*Z*)-1-chloropropene, in which H and Cl are in anti positions, whereas isomer 8-1 should be (*E*)-1-chloropropene. Possibly for this reason, the latter compound is the predominant one in the long-term experiments (Figure 8, 10 h at 705 K).

Our catalyst stability experiments show that deactivation occurs despite the presence of oxygen in the reaction mixture. However, deactivation is apparently not total and mainly limits the second dehydrochlorination step and the total oxidation. The catalyst seems to retain high dehydrochlorination activity in an oxidizing atmosphere even after 10 h. It seems likely that the deactivation phenomena can be attributed to coking. Coking of Bronsted acidic catalysts such as silica–alumina is frequently attributed to the oligomerization–cyclization–dehydrogenation of olefins. The apparently limited extent of coking of the catalyst under our conditions can be attributed to the low concentration of the reactants, the presence of oxygen (that could burn carbonaceous materials), and the refractoriness of chloro-olefins to reaction with the Bronsted sites of silica–alumina. In fact, the lack of isomerization at the double bond position activity with respect to chloropropenes (in contrast to what happens with respect to, e.g., butenes) possibly also limits the coking phenomena. This low reactivity with respect to Bronsted sites is likely due to the electron-attracting effect of chlorine on the C=C double bond electrons.

The use of oxygen in our experiments possibly helps in maintaining sufficient cleanliness of the catalyst surface. We did not detect (within the sensitivity of our analytic apparatuses) heavy products either among the gaseous reactor effluents or in the spent catalyst bed.

Conclusions

(i) Silica alumina is an active catalyst in the dehydrochlorination of polychlorinated compounds.

(ii) Dichlorinated compounds are converted to monochlorinated compounds in the 500–700 K range, whereas at higher temperatures, a second dehydrochlorination step takes place. CO_x and HCl are the final products in the presence of oxygen, thus showing the potential of this reaction to destroy polychlorinated compounds with possible recovery of chlorine as HCl.

(iii) A relevant deactivation effect is observed with a progressive reduction of the conversion, especially at lower temperatures. Upon deactivation, the selectivity to monochlorinated compounds grows, whereas the second dehydrochlorination step becomes more suppressed.

(iv) Activity data and IR studies indicate that the reaction mechanism could be an E1 elimination step through alkoxide formation at the surface. Isomerization of the 3-chloromethyl carbenium ion produced from 13dcp to 2-chloromethyl carbenium ion also likely occurs before proton elimination.

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