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The Gas Phase Addition of Hydrogen Chloride to Propylene¹

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Abstract: The neat gas phase addition of hydrogen chloride to propylene in mixtures containing up to 25 atm of hydrogen chloride and 5 atm of propylene has been examined at temperatures between 19 and 70°C. The reaction, in which the only detectable product is 2-chloropropane, was continuously monitored by gas phase proton magnetic resonance (¹H NMR) in glass-, quartz-, and Teflon-lined NMR tubes. Trace quantities of polar molecules (e.g., water and nitrogen oxides) appear to serve as homogeneous catalysts. Removal of the catalysts by repetitive vacuum distillation of both reagents permitted observation of the surface catalyzed process. Both homogeneous catalyzed and surface catalyzed processes are best fit by kinetic expressions first order in propylene and third order in hydrogen chloride, and the rates of both are attended by an inverse temperature dependence. A reaction scheme is proposed that includes a six-center intermediate.

The addition of hydrogen halides to olefins has been explored extensively and has played a fundamental role in the microscopic models used to explain chemical reactivity of organic molecules. For the generalized addition of hydrogen halide to olefin, three distinct pathways, not all of which are available to all alkenes and all hydrogen halides, are recognized. The first, ionic (Markovnikov) addition, takes place in polar solvents, presumably through protonation to yield a carbonium (carbenium) ion, which then goes on to product.² The second, free radical (anti-Markovnikov) addition, extensively studied by Kharasch and coworkers,³ and useful for only hydrogen bromide,⁴ occurs in both the gas phase and in solution. The third is the direct bimolecular addition which occurs in the gas phase and has been examined in detail by Benson and coworkers for the case of hydrogen iodide.⁵ The latter is an example of the microscopic reverse of the thermal elimination of hydrogen halide from alkyl halides. Many such elimination studies have been undertaken.⁶

No gas phase reactions of hydrogen chloride with olefins have been reported. Maass and Sivertz⁷ mixed hydrogen chloride and propylene at 1 atm total pressure and, after 400 days, they could observe no reaction. Kistiakowsky and Stauffer⁸ measured the rate of elimination of hydrogen chloride from *tert*-butyl chloride and the equilibrium constant attending that elimination and suggested that the bimolecular addition of hydrogen chloride to alkenes has too high an activation energy to be observed at room tempera-

ture in any reasonable time. At sufficiently high temperatures for a reasonable addition rate, the equilibrium strongly favors elimination. Using the data from Benson's report,⁵ which includes the Kistiakowsky and Stauffer⁸ data, the time for 1% reaction of hydrogen chloride and propylene *via* the direct bimolecular addition at 20° and 1 atm each is 2.8×10^{11} days!

Maass and Sivertz⁷ did observe a reaction between hydrogen chloride and propylene in the neat liquid phase, giving 2-chloropropane and a "chlorohexane" in a 2:1 ratio. In this reaction, it appeared that a high order in hydrogen chloride was necessary to account for the rapid reaction and the authors suggested that the reaction was "hydrogen chloride catalyzed". The rate was orders of magnitude faster than extrapolation from the gas phase results would give and thus it was suggested⁸ that a different mechanism obtained in the liquid phase and that it might well occur through an HCl-alkene complex. Maass and Wright⁹ interpreted melting point data of hydrogen chloride-alkene mixtures in terms of such complexes.

Mayo and Katz,¹⁰ some years later, also obtained 2-chloropropane and the "chlorohexane" from the reaction of hydrogen chloride with propylene in heptane solution. Their results, while incomplete, suggested that the reaction was first order in propylene and roughly third order in hydrogen chloride. They also found evidence for complexes between hydrogen chloride and alkene.

Finally, recent observations by King, Dixon, and Hersch-



Figure 1. Teflon lined NMR tube with Teflon valve. The lining extends above the "O" ring seal but not into the side arm.

bach¹¹ that six-center gas phase reactions involving halogens can have very low activation energies provide a plausible pathway for such addition processes.

Thus, there is evidence that a fourth pathway for the addition of hydrogen chloride to alkenes might exist. Such a pathway would be expected to have a high order in hydrogen chloride. We report here our observations on the gas phase reaction between hydrogen chloride and propylene, which we undertook in an attempt to elucidate this fourth pathway.

Experimental Section

Rate measurements were carried out by mixing the purified reactants¹² in a nuclear magnetic resonance (NMR) tube as the reaction vessel. Sample pressures ranged from 6 to 30 atm. Reaction times ranged from a few days to several months. Measurements of the reaction extent were made at appropriate time intervals by NMR spectroscopy directly in the reaction vessel.

A. Reactant Purification, Sample Preparation, and Reaction Vessel Treatment. The reactants were purified by trap-to-trap distillation using removable traps on a vacuum system which had never been exposed to mercury vapor. No packed columns or sulfuric acid traps were used so that the entrainment of possible catalytic impurities would be minimized. In all distillations, the initial distillate was pumped away and a residue discarded by removing the trap. The removable traps were cleaned of organic impurities by cycling through an annealing oven at 590°C for several hours. They were then heated under vacuum (10^{-6} Torr) for several hours before use. The propylene was distilled a number of times from a dry ice-acetone bath at -78°C . The hydrogen chloride was distilled from a pentane-liquid nitrogen slush at -135°C , an ethanol-liquid nitrogen slush at -110°C , and a dry ice-acetone bath. After the distillation, the reactant was transferred to a storage bulb with a Teflon valve on the vacuum system that had been previously pumped and heated for several days.

Samples were prepared as follows. A reactant was permitted to leak into the vacuum manifold (having a known volume) from the storage bulb. The reactant pressure was measured using an MKS Baratron capacitance manometer (1000 Torr head). Pressures varied from 5 to 120 Torr. The reactant was then condensed into a permanent trap used only for that reactant, evaporated from a dry ice-acetone bath, and condensed into the reaction vessel. The same procedure was used for the second reactant and the reaction vessel was then sealed and the reactants allowed to evaporate. Most reaction mixtures were maintained at $19 \pm 1^{\circ}\text{C}$. Several runs were made at higher temperatures by keeping the sample in an oven controlled to $\pm 1^{\circ}\text{C}$.

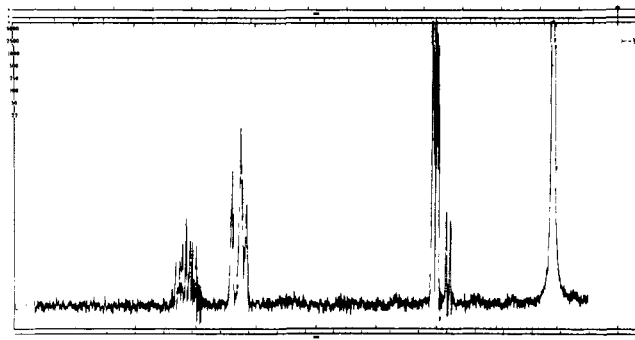


Figure 2. A typical ^1H NMR spectrum obtained on the gas phase reaction mixture of propylene-hydrogen chloride. SW 1000 Hz. The methyl doublet of 2-chloropropane is seen to the right of the large propylene doublet. The reaction, at 22 atm total pressure (5 atm of propylene and 17 atm of HCl), has gone to about 1.4% completion.

The following procedure was used to clean all reaction vessels (except those lined with Teflon). Standard taper joints (10/30) were sealed onto the tubes. The tubes were cleaned with aqua regia (to remove possible metal contaminants) and then rinsed exhaustively with deionized water. Some tubes were subsequently treated with 4 *N* NaOH and rinsed again. The tubes were then placed in an annealing oven at 590°C for several hours to remove possible organic impurities and subsequently stored in a clean, closed vessel until attachment to the vacuum system. Each tube was examined under high magnification to ensure absence of foreign matter prior to attachment to the vacuum system. After attachment, the tubes were evacuated and heated for several hours before filling.

B. Types of Reaction Vessels. The reaction vessels were NMR tubes having a 4 mm inner diameter. Pyrex and quartz tubes were used. Carefully cleaned soft glass capillary tubing was placed in some vessels to increase the surface area. A Teflon lined tube, with a Teflon valve, was obtained from the Wilmad Glass Co, Buena, N.J. The construction of the tube is shown in Figure 1. A standard taper joint was attached to the side arm for introduction of reactants and this was sealed off during a run. A matching glass tube was cemented opposite to the side arm to permit spinning in the probe. The Teflon lined tubes were cleaned with aqua regia, rinsed exhaustively with deionized water, and evacuated with heating at 150°C (10^{-6} Torr) for at least 12 hr prior to use.

C. Analytical Technique. Reaction mixture composition was determined from proton magnetic resonance (^1H NMR) spectra obtained using a Varian XL-100-15 spectrometer in the external lock (water) mode. The spectrometer was tuned internally prior to each run before locking. A typical spectrum is shown in Figure 2. The spectra were integrated 4 to 6 times to determine the product to reactant ratio. It was possible to obtain reproducible measurements when the 2-chloropropane concentration reached 4 mmol l^{-1} . The product could be observed when 0.5 mmol l^{-1} concentrations were reached. These limits were set because a low radiofrequency power was necessary to avoid saturation and because phasing problems arose due to the proximity of the reactant and product methyl peaks.

D. Initial Rate Technique. Because of the high pressures used, the 2-chloropropane condensed after only a few percent reaction. The rates changed after liquid formation so the kinetic run was stopped. A method of initial rates was used to determine the reaction order.

For the reaction



Assuming that the rate can be expressed by an integral order of the reactants, then

$$-da/dt = ka^m b^n \quad (2)$$

where a and b are the concentrations of the corresponding reagents A and B, respectively, and m and n are the exponents of the concentrations. Rearranging and converting the differentials to differences and noting that p (the concentration of product P) = $a_0 - a = -\Delta a$, we have

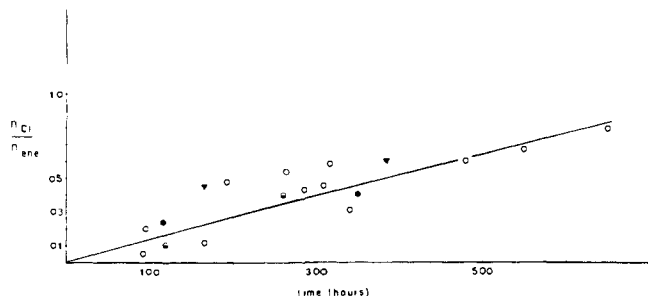


Figure 3. A plot of the ratio 2-chloropropane:propylene vs. time. The initial concentration of hydrogen chloride is held constant at 5 atm. The propylene is varied as follows: ▼, 2.5 atm of propylene, Teflon lined tube; □, 7.5 atm of propylene, Pyrex tube; ○, 5 atm of propylene, Pyrex tube; ●, 5 atm of propylene, Pyrex tube with soft glass capillary tubing added. Surface area increased threefold; ⊙, 5 atm of propylene, quartz tube. (Data for longer times are available for the samples of 2.5 atm of propylene, Teflon lined tube [▼] to confirm the slope of the line drawn but a different scale is needed for representation.)

$$p/a = ka^{m-1}b^n\Delta t \quad (3)$$

Equation 3 will be valid if the reaction only goes to several percent and the initial concentrations of A and B (i.e., a_0 and b_0 , respectively) can be used on the right-hand side of eq 3.

A series of reaction mixtures is prepared holding b_0 constant and varying a_0 . The rate constant is then given by the slope of the line in a plot of p/a vs. Δt . By using this procedure for each reactant, the order of the reaction in both hydrogen chloride and propylene is also obtained.

Results

A. Products. Significantly, within the limits of detection, 2-chloropropane was the only product formed. We acknowledge, however, that in the gas phase spectra, an amount of gas phase "chlorohexane" on the order of several percent of 2-chloropropane might have gone undetected. In several reactions that had gone to completion, i.e., all propylene was consumed, and in which there was a significant quantity of liquid, no product (<0.5%) other than 2-chloropropane could be detected.

The 2-chloropropane invariably condensed at a pressure lower than that of the pure vapor and the condensation pressure decreased as the hydrogen chloride pressure increased. This implies a significant association or a molecular complex formation between the hydrogen chloride and the 2-chloropropane.

B. Rate Measurements. The order determination was carried out for two different sets of conditions. In the first series (series 1), a homogeneous gas phase reaction which was catalyzed by small amounts of impurities was observed, while in the second series (series 2), where the impurities had been removed, a heterogeneous reaction intruded.

Series 1. In this series of reactions, purification of hydrogen chloride was accomplished by a single distillation from pentane-liquid nitrogen slush (-135°C) and subsequent distillation from dry ice-acetone. The results of these experiments are shown in Figures 3 and 4.

In Figure 3, the product to propylene ratio is plotted (ordinate) against time. The large scatter at short times arises from the difficulties in the NMR measurements mentioned earlier (Experimental Section) and the scatter was reduced somewhat as analytical techniques improved. Regardless of the scatter, however, it is clear that a single line best fits the data for the several initial propylene concentrations. Since the slope of the line for each different initial concentration is proportional to the initial concentration to the $m - 1$ power where m is the order of the reaction (Experimental

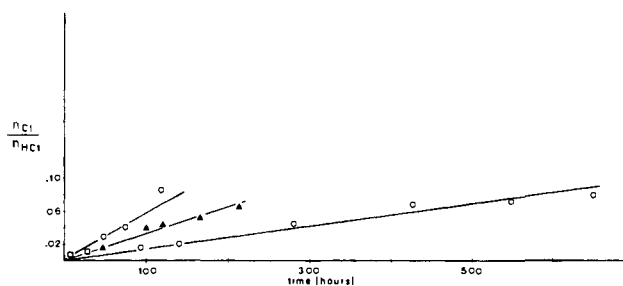


Figure 4. A plot of the ratio 2-chloropropane:hydrogen chloride vs. time. The initial concentration of propylene is held constant at 5 atm. The hydrogen chloride is varied as follows: □, 10 atm of HCl, Pyrex tube; ▲, 7.5 atm of HCl, Pyrex tube; ○, 5.0 atm of HCl, Pyrex tube.

Section) and all slopes are the same, $m - 1 = 0$, and the reaction is first order in propylene.

In Figure 4, the product to hydrogen chloride ratio is plotted (ordinate) against time. Here, each different concentration requires a different straight line. From the slopes of the lines in this family we determine a best fit to be third order (i.e., $m - 1 = 2$) in hydrogen chloride.

Reactions in Pyrex-, quartz-, and Teflon-lined vessels and in Pyrex vessels containing soft glass capillary tubing (*a threefold surface area increase*) show no differences in rate. These results imply that there are *no* surface effects; the reaction is homogeneous. In addition, although the data are not shown for this series, several rate measurements were made at higher temperature. An *inverse* temperature dependence was observed and the rate, at $70 \pm 1^\circ\text{C}$, was roughly one-third that at $19 \pm 1^\circ\text{C}$.

Series 2. For this series, the hydrogen chloride taken from the cylinder was purified by three distillations from pentane-liquid nitrogen slush, three distillations from an ethanol-liquid nitrogen slush, and a single distillation from dry ice-acetone. Cylinder HCl is known to contain nitrogen oxide impurities¹³ that can be removed by this technique. Hydrogen chloride was also synthesized from the reaction of sulfuric acid with sodium chloride and purified as above. The hydrogen chloride from these two different sources gave identical results.

In series 2, rate measurements in different types of vessels gave different results, just the opposite of series 1. The rate is fastest in Teflon (about the same as it was in series 1), probably because of impurities in the Teflon surface introduced during polymerization or coating. An increase in the surface area causes an increase in rate. Relative to Pyrex, the rate in quartz is slower by a factor of about 10.

The graphical data representation for this series is given in Figures 5 and 6. The overall rate is observed to be eight times slower than it was in series 1. The reaction is still first order in propylene (Figure 5) using a series of samples that vary the initial propylene pressure by a factor of 10.

One of the most significant results is that the *order* in hydrogen chloride in series 2 is about the same as it was in series 1. The slopes of the lines in Figure 6 do, in fact, suggest an order somewhat greater than three for hydrogen chloride, but there is some variation for the order determined between different pairs of initial hydrogen chloride pressures. When compared to the lowest initial pressure, the highest pressure results give a significantly higher order than the others. **But**, the hydrogen chloride-propylene-2-chloropropane mixtures exhibit extreme nonideal behavior at the higher pressures used. Indeed, as mentioned earlier, the 2-chloropropane product condensed at significantly lower vapor pressures than the equilibrium vapor pressure and this deviation increased sharply with increasing hydro-

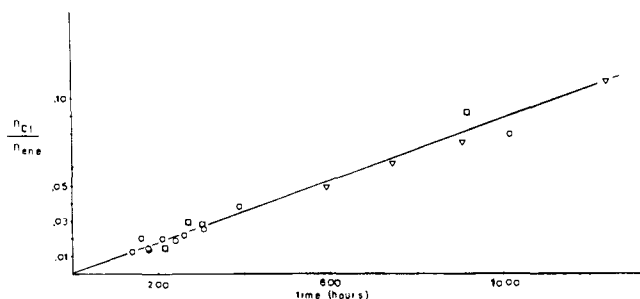


Figure 5. A plot of the ratio 2-chloropropane:propylene vs. time. The initial concentration of hydrogen chloride is held constant at 17 atm. The propylene is varied as follows: \circ , 10 atm of propylene, Pyrex tube; \square , 5 atm of propylene, Pyrex tube; ∇ , 1 atm of propylene, Pyrex tube.

gen chloride pressure. It has been suggested¹⁴ that an aerosol mechanism may be important at this high hydrogen chloride pressure. If then, we exclude the measurements at the higher pressures from consideration while computing the order of the reaction, the best estimate from the other pressures is about 3.3, i.e., the order in hydrogen chloride is somewhat higher than three. Inclusion of the high pressure data gives an estimated order of 3.5 and suggests an increase in the order with increasing pressure. Our present interpretation is that the reaction is third order; the observation of a slightly higher order arises then from the extreme nonideal gas behavior. The observed rate constant in Pyrex is $k_0 = 3.2 \times 10^{-4} \text{ l.}^3 \text{ mol}^{-3} \text{ hr}^{-1}$ at $19 \pm 1^\circ\text{C}$.

The inverse temperature effect is observed and is similar to that observed in series 1. Figure 7 presents data for rates at several different temperatures. The measurements at higher temperatures were carried out for several different pressures and the measurement at $27 \pm 1^\circ\text{C}$ has a somewhat larger uncertainty than the others.

Discussion

As we have pointed out earlier, based upon an assumption that the reaction between hydrogen chloride and propylene was the microscopic reverse of the elimination of hydrogen chloride from 2-chloropropane, at initial pressures of 1 atm in each reactant, a 1% reaction should occur in 2.8×10^{11} days.

Using the rate constant from Pyrex (series 2) and eq 3, the time for 1% reaction at 1 atm in each reactant is 2.2×10^4 days, giving an increase in rate of 10^7 over the bimolecular mechanism. Even in quartz, where the rate is about ten times slower than in Pyrex, there is still a rate enhancement of 10^6 over that expected for the bimolecular reaction. In addition, assuming that Maass and Sivertz⁷ could have seen (manometrically) 0.2% reaction, we calculate, using the rate constant observed in Pyrex NMR tubes, that it would have taken them about 2×10^4 days!

The results obtained in the gas phase differ most significantly from what has been obtained in neat liquid and in heptane solution in that no chlorohexane is observed. If the rate constant we find in Pyrex is used to calculate the rate that might be expected in the pure liquid¹⁵ the reaction we observe is still about 500 times faster than that observed by Maass and Sivertz.⁷ But, this can be adjusted to a factor of about 20 if account is taken of the relatively reduced surface available in the liquid and we believe the factor of 20 could be due to slower diffusion rates in the liquid state. Regardless, the proximity of the extrapolated gas phase rate to the liquid phase rate and the similar high order in hydrogen chloride lead us to conclude that a similar mechanism obtains to produce 2-chloropropane. Accordingly, the "chloro-

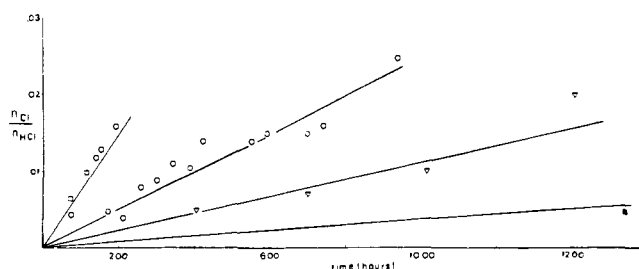


Figure 6. A plot of the ratio 2-chloropropane:hydrogen chloride vs. time. The initial concentration of propylene is held constant at 5 atm. The hydrogen chloride is varied as follows: \square , 25 atm of HCl, Pyrex tube; \circ , 17 atm of HCl, Pyrex tube; ∇ , 12 atm of HCl, Pyrex tube; \triangle , 8 atm of HCl, Pyrex tube. (Data for longer times are available for the samples of 5 atm of propylene and 8 atm of HCl [\blacksquare] to confirm the slope of the line drawn but a different scale is needed for representation.)

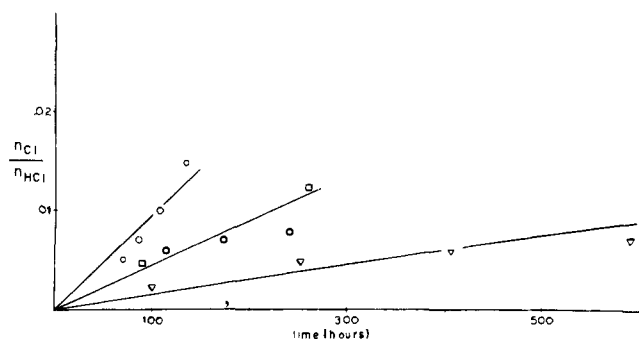
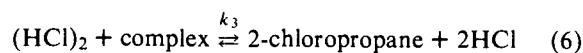
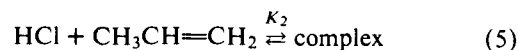
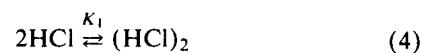


Figure 7. A plot of the ratio 2-chloropropane:hydrogen chloride vs. time. The concentrations of hydrogen chloride (25 atm) and propylene (5 atm) are held constant. The temperature is varied as follows: \circ , $19 \pm 1^\circ\text{C}$; \square , $27 \pm 1^\circ\text{C}$; ∇ , $70 \pm 1^\circ\text{C}$.

hexane" is produced by an additional liquid phase interaction missing under the gas phase conditions.

Thus, in accord with these observations, and the overall order of four for the reaction, we set forth below (eq 4-6) a mechanistic proposal which accounts for the formation of 2-chloropropane. We note that other mechanisms might be written but that the one we suggest is consonant with all observations in solution and in the gas phase.



In these equations, the species labeled "complex" is a 1:1 hydrogen chloride-propylene adduct of undetermined structure; reactions 4 and 5 remain in equilibrium and reaction 6 is the slow step. The overall rate is then given by eq 7,

$$d[\text{RCI}]/dt = k_3 K_1 K_2 [\text{HCl}]^3 [\text{CH}_3\text{CH}=\text{CH}_2] \quad (7)$$

where the product $k_3 K_1 K_2 = k_0$, the observed rate constant determined from the kinetic studies.

In support of the proposed mechanism, we wish to point out: (a) with regard to eq 4, hydrogen chloride dimers have been observed in the gas phase by infrared spectroscopy¹⁶ and we estimate that at 10 atm pressure at 20°C , at least 1% of the dimer is in equilibrium with the monomer; (b) in accord with eq 5 Maass and Wright⁹ measured the melting point curves of numerous hydrogen halide-olefin mixtures at temperatures where no reaction occurred and found that

strong hydrogen halide-olefin complexes were formed. They suggested that a complex between hydrogen chloride and propylene must play a significant role in the reactions of these molecules. We have demonstrated¹⁷ that strong interactions exist in the gas phase since the normal chemical shifts of allene and hydrogen chloride (relative to external ethane) are different when they are mixed; (c) catalysis in the rate-determining step 6 could be effected by homogeneous impurities (water or oxides of nitrogen) and, when these are removed, by the surface.

The inverse temperature dependence is extremely informative as to the suggested mechanism. From eq 7 it can readily be shown that

$$k_0 = Ae^{(\Delta S_4 + \Delta S_5)/R} e^{-(\Delta H_4 + \Delta H_5 + E_a)/RT} \quad (8)$$

The rate will increase as the temperature decreases if $E_a < |\Delta H_4 + \Delta H_5|$. The latter quantities must both be negative.

A value for $\Delta H_4 = -2.5$ kcal/mol has been measured¹⁶ and the studies of Maass⁷ suggest ΔH_5 would have a similar value. This implies that E_a for reaction 6 is quite small, on the order of 1 or 2 kcal/mol. Because the observed kinetic behavior for both homogeneous and heterogeneous reactions is identical in their order in HCl and propylene and because the temperature dependence for both is almost identical, the catalysis must occur in reaction 6, *but it is unlikely to be affecting the activation energy*. Thus, the role of the catalyst is to stabilize the high ordering required in the intermediate *or* to effectively remove the excess energy in the dissociation of the intermediate to products.

Strong support for this involved mechanism is provided by the recent observations of King, Dixon, and Herschbach¹¹ who used molecular beam techniques to show that certain reactions involving halogens proceed through a six-center intermediate with a *near zero activation energy*. Thus, a plausible pathway in the hydrogen chloride-propylene reaction is one in which the alkene, complexed on one face to a single hydrogen chloride, presents the opposite face to the hydrogen chloride dimer for reaction through a six-center intermediate. The initial complex between hydrogen chloride and propylene is thus required to polarize the alkene while the dimer approaches to consummate the reaction.

Although the proposed mechanism must be considered highly tentative at this time, we believe that suitable experiments can be devised for testing it. Such experiments are underway.

Conclusion

The gas phase reaction between hydrogen chloride and

propylene has been examined at various temperatures and pressures. In the presence of homogeneous catalysts, which can be removed by multiple distillation of the reactants, the reaction is ca. 10^8 faster than that predicted by consideration of the unimolecular decomposition of 2-chloropropane and its bimolecular microscopic reverse. When the catalysts are removed, the reaction is still about 10^7 faster than predicted for the bimolecular reaction but the reaction becomes heterogeneous.

Regardless of the nature of the catalyst, the reaction that is observed remains first order in propylene and about third order in hydrogen chloride. These orders, which are about the same as had been observed in heptane solution and in the neat liquids, can be interpreted as a scheme of reactions which include hydrogen chloride dimer and alkene-hydrogen chloride adduct, these being the products of rapid equilibria, and a rate-determining step possessing a six-center reaction intermediate.

Additional work is underway on hydrogen halide reactions with alkenes to attempt to verify our proposed mechanism.

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