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# THE UNCATALYZED GAS PHASE HYDROCHLORINATION OF ALKENES II. ALLENE

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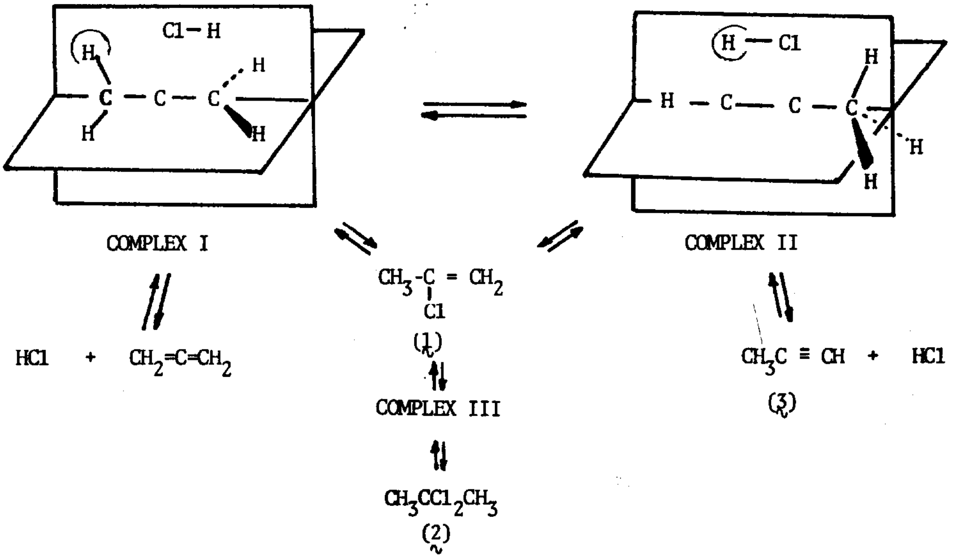
The gas phase reaction between allene and hydrogen chloride at pressures of one to ten atmospheres at 25±2°C and 100±2°C has been monitored in sealed glass and quartz vessels by proton magnetic resonance spectroscopy. The reaction is very slow. The products formed are 2-chloropropene (1), 2,2-dichloropropane (2) and methyl acetylene (3); exactly those expected for a vinyl cation intermediate. The data, TABLE, permits the following conclusions: (a) despite the fact that "free" or solvated ions are not involved, the product composition (Expts.1-6) reflects some charge separation in the direction anticipated if a vinyl cation were present, i.e., no 1-chloro-2-propene nor products which might arise from it are found. This is in concert with previous experimental data obtained in solution[1,2] as well as calculations on the stability of the ions expected[3]; (b) the initial rapidly and reversibly formed gas phase complex (or complexes) between allene and HCl[4] can yield either 1 or 3. Our incomplete data[5] yields a second order rate constant (at both 25°and 100°C) for the disappearance of allene of 5.6±1 X $10^{-3}$ $1.\text{mole}^{-1}\text{day}^{-1}$; (c) the lack of temperature dependence (Expts.1 and 3) illustrates that the activation energy for the conversion of the initial complex of allene with HCl to product is equal to or less than $|\Delta H|$ for the formation of the complex.[6] Also, the gas phase complex between HCl and 1 is formed reversibly and the rate of conversion of 1 to 2 at 25±2°is 4.8±3 X $10^{-1}$ $1.\text{mole}^{-1}\text{day}^{-1}$ (Expt. 7)[7]; (d) a three fold increase in the surface area (Expt. 5) or a change in the nature of the surface[8] (Expt. 4) does not cause, within experimental error, a change in the overall rate of allene disappearance to form products - implying that a surface reaction is not involved; (e) the slow reaction we observe (allene is disappearing to form products at the rate of 3±1 % per month) in the absence of catalysts[2,9] to give the same products normally obtained in solution leads us to believe that the electrophilic addition process in solution may not, in fact, involve exclusively the species as usually written.

The SCHEME illustrates the reactions which are occurring. We write the complex initially formed between HCl and allene (COMPLEX I) which leads to **3** and may or may not lead to **1** as a highly ordered species. Intramolecular rearrangement of COMPLEX I[10]leads to COMPLEX II which can then dissociate to **3** or eventually lead to **1**.[11] We note that the rate of formation of **1** from allene and from **3** (Expt. 6) is, within experimental error, identical and that therefore, the rate determining step for both processes may be the same.

Finally, in concert with our concept of the high degree of order required for the rearrangement of allene to **3**, the reverse reaction, in which the methyl group is now a "free rotor" shows no sign of occurring even though **3** does lead to **1** and **2**; and recent calculations indicate[2] that as charge develops at the central carbon of allene, the terminal hydrogen moves in the required direction.[12]

SCHEME



TABLE

| Experiment[a] | Initial pressure (atm) |  | Temp (°C) | Time (days)[g] | $\frac{\text{allene}}{\text{allene}_o}$ | $k_2$ ($10^3$) (1.mole$^{-1}$day$^{-1}$) | PRODUCTS[b] |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  | HCl | allene |  |  |  |  | (1) | (2) | (3) |
| 1 | 5.0 | 5.0 | 25 | 119 | 0.90 | 5.3 ± 1 | 34 | 28 | 38 |
| 2 | 2.5 | 2.5 | 25 | 122 | 0.94 | 4.5 ± 1 | 44 | 23 | 33 |
| 3 | 5.0 | 5.0 | 100 | 114 | 0.90 | 4.5 ± 1 | 58 | 4 | 38 |
| 4 | 5.0 | 5.0 | 25 | 95 | 0.89 | 6.8 ± 1 | 37 | 30 | 33 |
| 5 | 5.5 | 5.5 | 25 | 113 | 0.86 | 6.7 ± 1 | 35 | 32 | 33 |
| 6 | 5.0 | c | 25 | 101 | 0.88[d] | 6.7 ± 1 | 57 | 43 | -- |
| 7 | 5.0 | e | 25 | 12 | 0.20[f] | $4.8 \pm 3 \times 10^2$ (h) | -- | 100 | -- |

a. The values presented are for typical runs: Experiments 1,2, and 3 were carried out in glass nmr tubes; Experiment 4 was carried out in a quartz nmr tube; Experiment 5 was in a glass tube to which capillary tubing had been added. The surface area available to the reaction was increased three fold; Experiment 6 used methylacetylene (3) for the substrate; Experiment 7 used 2-chloropropene (1) for the substrate. b. The yields expressed are per cent composition of the total product. The accuracy is ± 10 % of the values given. c. Methyl acetylene, initial pressure = 5.0 atm. d. This ratio is methyl acetylene/methyl acetylene$_o$. e. 2-Chloropropene, initial pressure = 0.61 atm. f. This ratio is 2-chloropropene/2-chloropropene$_o$. g. The reactions were monitored continuously. These times refer specifically to the data in columns 6,8,9, and 10. h. See reference 7.

(1) See, e.g. P. J. Stang, *Progr. Phys. Org. Chem.*, **10**, 205 (1973) and references therein.

(2) See, e.g. K. Greisbaum, *Angew. Chem., Int. Edit.*, **5**, 933 (1966) and references therein.

(3) L. Radom, P. C. Harriharan, J. A. Pople and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 6531 (1973).

(4) Utilizing ethane as external standard, we observe that HCl shifts 8 ± 1 Hz downfield and allene shifts 2 ± 1 Hz upfield, relative to their initial chemical shifts when mixed at partial pressures of 5 atm. each and the spectrum observed at 35° C. Warming the mixture to *ca.* 100° C returns the lines to their original positions.

(5) After the reaction is about 10% complete (TABLE) liquid forms (products) in the tubes and a two phase reaction, with different kinetics, begins. At lower pressures, the reaction time is too long for a feasable study.

(6) Our analysis of the temperature dependence is as follows: $A + B \quad ^{K_1} \quad C \quad ^{k_2} \quad P$. We assume that the rate at which equilibrium is attained is much faster than the rate of product formation, i.e. $dP/dt = k_2C = k_2K_1AB = k_oAB$. Then if $k_2$ follows the Arrhenius rate law, $k_o = k_2K_1 = \{Ae^{\Delta S_1/R}\}e^{-E_A + \Delta H_1)/RT}$ and the overall constant will show no temperature dependence if $E_A + \Delta H_1 \approx 0$.

(7) The large uncertainty here is due to difficulties in purifying 2-chloropropene.

(8) The same reaction has been observed in teflon-lined ir cells but interpretation of the data is more difficult. In the previous paper in this series, we have shown that the reaction of isobutylene with HCl occurs at about the same rate in glass and teflon-lined nmr tubes.

(9) Metal catalysts are usually present, intentionally or otherwise. See, e.g. reference 2. We have found that HCl used without first purging the lines and valves contains traces of catalyst(s) for the reaction with allene. The products obtained are the same but they are formed much (*ca.* $10^3$) more rapidly.

(10) Since we consider some charge separation present, the extent to which this very slow reaction is, or should be, concerted is open to question. See, e.g. N. D. Epiotos, *J. Amer. Chem. Soc.*, **94**, 1924 (1972) and references therein.

(11) Again, using ethane as external standard, we observe that the HCl signal shifts 15 ± 1 Hz.

(12) About 4% of allene should be present at equilibrium. This much allene could have been observed were it present. We did not see it.