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THE UNCATALYZED GAS PHASE HYDROCHLORINATION OF ALKENES I. PROPENE AND ISOBUTYLENE

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In 1925 it was reported that after 400 days at one atmosphere total pressure, no gas phase reaction between propene and hydrogen chloride could be detected.[1]

Twelve years later, after a thorough study of the high temperature decomposition of t-butyl chloride to isobutylene and hydrogen chloride, the propene-hydrogen chloride result was justified on the basis of the activation energy which would be required if the pathway for addition of hydrogen chloride was the reverse of the decomposition reaction.[2]

Between that time and this, many decomposition reactions have been studied.[3] A few gas phase addition reactions with hydrogen iodide, using conditions where both the forward and back reactions could be observed, have been carried out.[4] However, the uncatalyzed gas phase reaction between hydrogen chloride and alkenes at room temperature has been left aside.

We report here our initial results with two alkenes, propene and isobutylene, in their reaction with hydrogen chloride in the gas phase. The reactions, in glass and quartz nmr tubes at moderate pressures (between one and ten atmospheres) and in teflon lined glass tubes (1 atmosphere) are continuously monitored by gas-phase proton magnetic resonance spectroscopy.[5]

In the absence of metal catalysts[6] at room temperature, in the gas phase, propene reacts with hydrogen chloride to yield only 2-chloropropane. Our incomplete kinetic data indicates the reaction is first order in each component until, at the higher pressures, the product begins to liquefy and two phases are present (at which time the kinetic expression becomes more complex). The reaction proceeds at a convenient rate at roon temperature ($t_{1/2}$ = 4 days at ten atmospheres, $k_{25^o\ C} = 4.2 \pm 1 \times 10^{-6}$ l. $mole^{-1}$ $sec.^{-1}$). A three fold increase in the surface area (added capillary tubing) has, within experimental error, no apparent effect on the rate. An increase in the temperature (100 ± 2° C) retards the reaction. We attribute this to reversible complex formation between propene and hydrogen chloride.[7]

In the case of isobutylene, where the same inverse temperature dependence is observed,[7] the second order reaction with hydrogen chloride to yield only t-butyl chloride is much faster ($t_{1/2}$ = 200 minutes at one atmosphere, $k_{25^o\ C} = 3.3 \pm 1 \times 10^{-3}$ l. $mole^{-1}$ $sec.^{-1}$). This reaction has been carried out in sealed glass and teflon-lined[8] glass nmr tubes both by freezing the two components before sealing the tube and by permitting them to diffuse together. In the first case (sealed tubes - gasses frozen), if the isobuytlene and hydrogen chloride are co-frozen (in contrast to freezing the hydrogen chloride at the bottom and the isobutylene at the top of the nmr tube) a very rapid reaction, in which as much as 50% of the product has formed in less than five minutes occurs. Even when frozen in different parts of the tube, some initial surge is present. We attribute the initial surge to reaction of a solid phase alkene-hydrogen chloride complex before evaporation can occur. In the second case, where the gasses diffuse together and the tube is closed with a stopcock, no rapid initial surge is observed.

When the reaction between isobutylene and hydrogen chloride is carried out by the diffusion method in teflon-lined glass tubes, the rate appears slower by a factor of about 2 although in all glass systems, increasing the surface area three-fold by the addition of capillary tubing has no apparent effect on the rate. The retardation, where a teflon-liner is present, may be attributed to catalytic sites on the glass no longer being available (in which case the experiments where additional glass is present cannot be interpreted) or to adsorption of hydrogen chloride by the teflon.[9] Regardless, however, even under these circumstances, the reaction is ca. 10^9 faster than is predicted by consideration of the equilibrium established at high temperature.[11]

We conclude, therefore, that there is a low energy pathway for the gas phase reaction of alkenes with hydrogen chloride, not available at the higher temperatures, where the complexes formed here are unstable. This pathway, which is not the reverse of the decomposition pathway, does not involve "free" or strongly solvated ions but nevertheless, some charge separation must be present since no 1-chloropropane was obtained from propene and no 1-chloro-2-methylpropane from isobutylene.

More complete kinetic data on these and other systems where teflon-coated (rather than lined) tubes have been used will be the subject of our full report.

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References

(1) O. Maas and C. Sivertz, *J. Amer. Chem. Soc.*, **47**, 2883 (1925).

(2) G. B. Kistiakowsky and C. H. Stauffer, *ibid*, **59**, 165 (1937).

(3) See, e.g. A. Maccoll in "The Chemistry of Alkenes", S. Patai, ed., Interscience, New York, N. Y. (1964).

(4) See, e.g., (a) S. W. Benson and A. N. Bose, *J. Chem. Phys.*, **39**, 3463 (1963); (b) D. H. R. Barton and P. F. Onyan, *Trans. Faraday Soc.*, **45**, 725 (1949).

(5) Proton magnetic resonance spectra were obtained on a Varian XL-100-15 spectrometer. Glass, quartz and teflon lined tubes were cleaned thoroughly before use and the glass and quartz tubes heated in an annealing oven to remove trace organic impurities. All tubes were nominally 5 mm o.d. The external lock (H_2O) was utilized throughout.

(6) As pointed out in the accompanying paper, metal catalysis is a major problem here. We have found that traces of metals from valves and lines must be removed by purging and several low temperature bulb-to-bulb distillations of hydrogen chloride are desirable. In general, the same products are formed in the presence of catalysts but they are formed much more rapidly.

(7) This observation, which is discussed more fully in the accompanying paper for the case of allene (where more data is available) appears to be confirmed by the rapid

initial reaction, before evaporation can occur, between isobutylene and hydrogen chloride when they are co-frozen (*vide infra*).

(8) The teflon liner was made by machining a 6 mm o.d. (3 mm i.d.) teflon tube to the required i.d. of the 5 mm tube. The top of the liner was flanged to permit the teflon valve, attached to the top of the tube, to seat directly into the liner. The teflon liner was cleaned with xylene, trichloroethane (to remove traces of machining lubricant), aqua regia and distilled water. After drying overnight in a vacuum oven, the entire assembly was heated, under high vacuum, for 12 hours before filling with gaseous hydrogen chloride and isobutylene.

(9) It has been pointed out[10] that the fabrication of teflon tubing (from which the insert was made) is through the use of a scintering process which leaves micro voids in the teflon. We are currently attempting to circumvent this problem by fabricating teflon coated tubes.

(10) D. F. Schriver, "The Manipulation of Air-sensitive Compounds", McGraw-Hill, Inc., New York, N. Y. (1969) p.239.

(11) From table V of reference 4(a), rate and equilibrium data for the system *t*-butyl chloride - isobutylene - HCl at equilibrium between $200 > T < 300^{\circ}C$ can be obtained. The preexponential factor log A (l. mole^{-1} sec.$^{-1}$) = 6.1 and the energy of activation E_a = 25.4 kcal mole^{-1} lead to a $k_{25^{\circ} C} = 4.2 \times 10^{-13}$ l. mole^{-1} sec.$^{-1}$.