

ASSOCIATION OF ALKYL HALIDES WITH HYDROGEN CHLORIDE AT -78°

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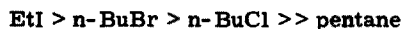
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It was recently reported that 1-chloronorbornene (I) is not hydrochlorinated measurably over an eight-hour interval in CCl_4 at -78° , conditions under which norbornene (II) adds hydrogen chloride quantitatively in two to three minutes (1, 2). This difference in reactivity, at least five orders of magnitude, was attributed to the electron-withdrawing power of the bridgehead chlorine atom (1). This effect is certainly important, but we wish to report evidence suggesting that there exists at -78° an additional mode of deactivation of I by the chlorine atom. When I is injected into the Brown² hydrochlorinator (3) (previously chilled to -78° and flushed with HCl), immediate rapid uptake of over one mole-equivalent of hydrogen chloride takes place. The resulting mixture is stable until warmed to $\sim -50^{\circ}$, when HCl evolution occurs and I is recovered. This behavior is reversible--chilling to -78° results in re-addition of HCl. Evidence that the much-discussed π -complex in hydrohalogenations (4) is not involved here arises from our observation that n-butyl chloride, and in fact a number of alkyl halides of varied structural types readily and reversibly take up HCl at -78° . This behavior has been observed with ethyl iodide, n-butyl bromide, allyl and crotyl bromides and chlorides, and 1-bromo-3-chloropropane (5). We suggest that this phenomenon is due to hitherto unobserved charge-transfer interaction of the n-electrons of the alkyl halides with hydrogen chloride, and possibly also London attractive forces, which are known to be strong between halogens (6). Hildebrand and coworkers have previously accounted for changes in the visible spectrum of iodine dissolved in alkyl halides (as opposed to iodine in saturated hydrocarbons or in the gas phase) in terms of weak solvent-solute charge-transfer interactions (7). To the extent that the halogen in the haloalkenes is associated with hydrogen chloride at -78° , its electronegativity should be increased and the double-bond reactivity decreased.

Further evidence for association between the alkyl halides and hydrogen chloride rests upon relative solubility data. The alkyl halides dissolve 8-12 times as much HCl at -78° as does pentane, despite the fact that the solubility parameter, δ , for alkyl halides as solvents is always greater than for saturated hydrocarbons, such as pentane (7). Since increasing values of δ generally mean decreased solubility if solution occurs without solvent-solute association, we infer again the existence of such association (8). We may also note that the decreasing

order of solvent power toward hydrogen chloride:



is precisely the order of decreasing solvent-solute interaction observed with iodine as acceptor (7).

One consequence of the phenomenon described here should be pointed out. Studies of the hydrochlorination of alkenes have indicated no simple kinetic order (4). If investigations are carried out at low temperatures, the possibility of association of HCl with the reaction products should be recognized; this might alter both the observed stoichiometry and the instantaneous concentration of hydrogen chloride in the organic phase throughout the reaction.

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REFERENCES

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2. H. C. Brown and K.-T. Liu, J. Am. Chem. Soc., 89, 3900 (1967).
3. H. C. Brown and M.-H. Rei, J. Org. Chem., 31, 1090 (1966).
4. P. B. D. de la Mare and R. Bolton, Electrophilic Additions to Unsaturated Systems, Elsevier Publishing Co., New York, N. Y., 1966, Chapter 5.
5. No chemical change takes place under these conditions, eg., n-butyl bromide, allyl bromide, and ethyl iodide are not converted to the corresponding chlorides, the crotyl halides are not isomerized, and treatment of allyl chloride with deuterium chloride results in no incorporation of deuterium.
6. E. L. Eliel, N. C. Allinger, S. J. Angyal, and G. A. Morrison, Conformational Analysis, Interscience Publishers, New York, New York, 1965, p. 16.
7. J. H. Hildebrand and R. L. Scott, Regular Solutions, Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962.
8. Strictly speaking, the solubility parameter correlates the solubility only of non-polar solutes, but its breakdown with polar solutes is principally because of the very possibility of solute-solvent interaction.