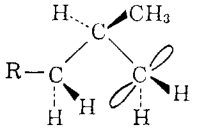
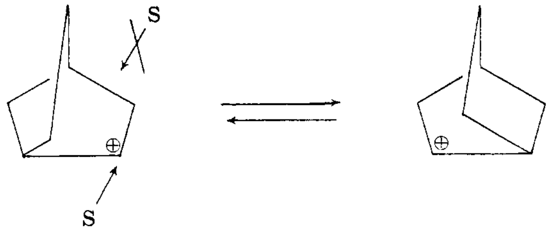
The 1,3-interactions are best rationalized as intramolecular hydride transfers made probable by the favorable geometry of the extended chain (minimum non-bonding repulsions) in acyclic paraffinic systems.



The lifetimes of alkyl carbonium ions under the alkaline conditions of deoxideation (15–50% aqueous KOH solution) must be limited by the rates of diffusion of R^+ and OH^-, since it is reasonable to expect this bimolecular reaction to occur at each collision. Thus a lifetime of $<10^{-9}$ second is indicated for R^+. It is significant that within this time interval 1,2-rearrangements, 1,3-hydride shifts and cyclopropane formations have been observed, emphasizing the high mobility of atoms in alkyl carbonium ion systems.

The conclusions that unimolecular rearrangements are occurring with frequencies in excess of solvent and ion-pair relaxations has bearing on a current controversy relative to the postulate of non-classical carbonium ions. Critics of the non-classical concept have suggested that control of stereochemistry can be explained by rapid interconversion of isomeric classical carbonium ions, as illustrated for norbornyl cation. The suggestion is validated by analogy since this interconversion can be faster than reaction with the solvent, so that *endo* attack is precluded, leading to *exo* products exclusively. Control of stereochemistry is a valid argument in favor of a non-classical structure *only* in those cases where it can be demonstrated that equilibration between classical ions is slower than conversions to products.



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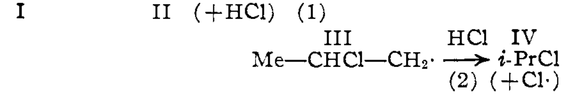
FREE RADICAL ADDITIONS OF HYDROGEN CHLORIDE TO ALKENES

Sir:

It has long been known that the addition of hydrogen bromide to a 1-alkene may be directed to give 95% or more of either primary or secondary bromide.[1] The high yields of either product demonstrate kinetic control of both products since longer or more strenuous treatment of either bromide with a catalyst for either type of addition leads to the same equilibrium mixture of bromides.[2] Reports of primary chlorides from free radical additions of hydrogen chloride to 1-alkenes are relatively rare. This situation has been ascribed[3] to the difficulty in reaction of an alkyl radical, particularly an allyl radical, with hydrogen chloride in the necessary chain. Recent papers from Madison[4] and Moscow[5] throw new light on this explanation and warrant reconsideration of some previous data.

Benson and Willard[4] found that liquid *n*-propyl chloride is isomerized to isopropyl chloride by gamma radiation, that the reaction is catalyzed by hydrogen chloride and retarded by propylene, that hydrogen in the hydrogen chloride exchanges but chlorine does not, and that *G*-values as high as 150 can be obtained for formation of isopropyl chloride. This work establishes the rearrangement mechanism



$$\underset{\text{I}}{n\text{-PrCl}} \xrightarrow{\text{Cl}\cdot} \text{Me—}\dot{\text{C}}\text{H—CH}_2\text{Cl} \longrightarrow \quad \text{II} \ (+\text{HCl}) \quad (1)$$

$$\overset{\text{III}}{\text{Me—CHCl—CH}_2\cdot} \xrightarrow[\text{(2)}]{\text{HCl}} \overset{\text{IV}}{i\text{-PrCl}} \ (+\text{Cl}\cdot)$$

This reaction must be reversible, and the equilibrium mixture, which is high in isopropyl chloride,[6] would undergo extensive exchange with hydrogen chloride in the presence of radicals without change in proportions of chlorides if side reactions did not interfere. The equilibrium between I and IV does not tell us about the relative concentrations of II and III nor about their relative rates of reaction with hydrogen chloride. However, the rearrangement of the bromine analog of III, Me-CHBr-$CH_2\cdot$, to the analog of II in the chlorination of isopropyl bromide[7] suggests that II is more stable than III.

Nesmeyanov, Freidlina and co-workers[5] have demonstrated rapid rearrangements of radicals like II. Their simplest example is the peroxide-catalyzed addition of hydrogen bromide to 3,3-dichloropropene. Here, the products show that 90% of the $Cl_2CH\text{-}\dot{C}H\text{-}CH_2Br$ reacting rearranged to $\cdot CHCl\text{–}CHCl\text{–}CH_2Br$ before reaction with hydrogen bromide.

The above considerations suggest: (1) In reactions of both II and III which require little activation energy, the products correspond to the more stable radical, II, at least when the halogen is bromine. (2) In reactions of II and III which are

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[1] M. S. Kharasch and F. R. Mayo, *J. Am. Chem. Soc.*, **55**, 2468 (1933); F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 351 (1940).

[2] F. R. Mayo and A. A. Dolnick, *J. Am. Chem. Soc.*, **66**, 985 (1944).

[3] F. R. Mayo, *ibid.*, **76**, 5392 (1954), and references therein.

[4] H. L. Benson, Jr., and J. E. Willard, *ibid.*, **83**, 4672 (1961).

[5] A. N. Nesmeyanov, R. Kh. Friedlina, V. N. Kost and M. Ya. Khorlina, *Tetrahedron*, **16**, 94 (1961).

[6] T. I. Crowell and G. L. Jones, Jr., *J. Am. Chem. Soc.*, **73**, 3506 (1951), report that the equilibrium mixture of propyl chlorides contains less than 0.8% primary chloride. R. H. Wiley, W. Miller, C. H. Jarboe, J. R. Harrell and D. J. Parish, *Radiation Research*, **13**, 479 (1960), were able to isomerize *n*-propyl but not *i*-propyl chloride with γ-rays although hydrogen chloride was split out of both chlorides. On the other hand, the 12% primary chloride found by addition of hydrogen chloride[3] is consistent with the negligible difference in heats of combustion of the two chlorides (0.04 kcal./mole, Beilstein, Vol. I, third supplement, pp. 219, 222) and the 9% primary bromide in the equilibrium mixture of propyl bromides.[2]

[7] P. S. Skell, R. G. Allen and N. D. Gilmour, *J. Am. Chem. Soc.*, **83**, 504 (1961).

relatively difficult, as with hydrogen chloride, then the more stable product, IV, is formed from minor proportions of the less stable[4] but more reactive radical, III. (3) When radicals like II and III contain several halogen atoms,[5] their stabilities and reactivities are altered. (4) Free radical-chain additions of hydrogen chloride to 1-alkenes cannot give high proportions of primary chlorides because of rearrangements such as reaction 1. (5) Reported proportions of primary chlorides in such additions[3] (12% with propylene, 24% with t-butylethylene, 30% with allyl chloride) may be, or approach, equilibrium mixtures of monohalides and the highest proportions of primary halides theoretically attainable by addition of hydrogen chloride. (6) The structure of the allyl chloride-hydrogen chloride telomerization product[3] is now uncertain because of possible rearrangement. (7) In view of chain-branching due to hydrogen shifts in the free radical polymerization of ethylene, the telomerization of ethylene with hydrogen chloride cannot give exclusively primary chloride, although the proportion of this may be higher than in 1:1 addition. (7) Rearrangement of alkyl bromides need not always involve complete elimination and readdition of hydrogen bromide.[2]

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RECEIVED AUGUST 13, 1962

THE STRUCTURE OF WATER AT ROOM TEMPERATURE

Sir:

Many reports on theoretical and experimental studies of the structure of water, although differing in basic conclusions, have made considerable contribution to an understanding of its properties. We present a preliminary report on an X-ray diffraction study undertaken in an attempt to consolidate results and remove conflicts from past studies.

The X-ray diffractometer used has been described briefly in previous publications.[1] MoKα radiation was monochromatized after scattering from the free surface of the sample. As the diffraction pattern showed interference throughout the observable range of the instrument (to $s_{\max} = (4\pi/\lambda) \sin \theta_{\max} = 16$, θ being half the scattering angle), the data are appreciably more extensive than the earlier ones.[2-11]

The radial distribution curve (Fig. 1) shows a well-resolved peak at 2.9 Å., followed by a minimum at 3.4 Å. and a broad region of scattering density rising to a barely resolved maximum at 4.9 Å. Thus, the nearest neighbors of a water molecule occur at an average distance about 5.5% greater than in ice, and others occur in considerable numbers in the intermediate region between the first and second neighbor distances of ice (2.75 and 4.50 Å., respectively). A distinct maximum at r = 1.1 Å. is attributed to the closest O–H distance in H_2O. Any suitable model must clearly provide such a radial distribution while conforming to the proper density.

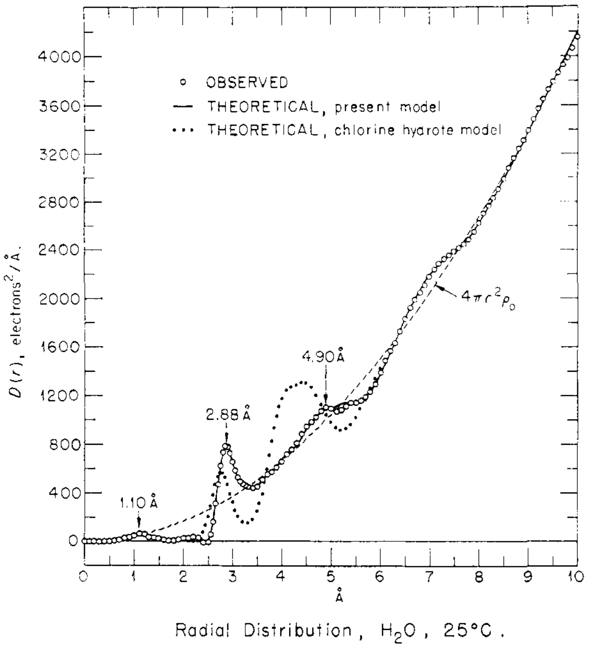

Figure 1.

We have constructed a model, based on the normal ice structure as a point of departure, which fulfills both of these requirements; it proved capable of refinement by a least-squares procedure to give a remarkably close fit to the observed diffraction pattern.

The model consists of an ice-like framework in which each oxygen atom is tetrahedrally surrounded by other oxygen atoms, forming layers of puckered six-membered rings. Two adjacent layers, related by mirror symmetry, form polyhedral cavities with 12 vertices, point symmetry $\bar{6}m2$. The model is accommodated to the required density and distance spectrum by permitting some of the cavities to be occupied by "interstitial" water molecules and by permitting expansion of the framework from that occurring in ice. For simplicity, the model retains the hexagonal symmetry of the ice-like framework and restricts the position of the "interstitial" molecule to the triad axis; however, anisotropic expansion of the framework is permitted.

The initial agreement being promising, the model was subjected to systematic refinement by iterative non-linear least squares, in which the reduced intensity function was fitted to values derived from the measurements. The observational equations contained terms for all discrete distances in the model less than 10 Å. and a term for the scattering from a continuous medium beyond this distance. The usual "temperature factor"

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(1) H. A. Levy, P. A. Agron, M. A. Bredig and M. D. Danford, *Ann. New York Acad. Sci.*, **79**, 762 (1960).

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