Hot Hydrogen Atom Displacement Reaction at Ethylenic C–H Bonds[1]

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Received November 21, 1960

Reaction of hot hydrogen atoms to replace hydrogen atoms in cis and trans dichloroethylenes proceeds with 70% retention of the original configuration. This indicates the existence at sp² C–H bonds, of a fast single-step displacement mechanism, not involving a common intermediate, and similar to that previously found in saturated systems. The isomerization that does occur can result from rotation about the double bond of product molecules excited in the primary displacement. A hot hydrogen double bond addition mechanism may also yield isomerized dichloroethylenes.

The reaction of hot or high kinetic energy hydrogen atoms to replace other hydrogen atoms has been shown to occur with high efficiency in a wide variety of organic compounds.[3-5] There is considerable evidence showing that when this process occurs at a saturated carbon atom it is a fast single-step displacement that involves no metastable intermediate complex.[5,6] The reaction is apparently initiated by attack at a large angle, near normal, to the C–H bond axis[6] and involves essentially complete retention of configuration.[7] The intent of the present study is to clarify the mechanism of hot hydrogen replacement at ethylenic C–H bonds. The system cis and trans dichloroethylene was chosen since it makes it possible to determine the change of configuration upon reaction without chemical degradation.

Experimental

Recoil tritium from the nuclear reaction He³(n,p)H³ was used as the source of the hot hydrogen. The techniques used to carry out the reaction and to analyze the products have been described previously.[8] In separate but similar experiments the hot tritium was generated by neutron bombardment of 1 cm. Hg pressure of He³ mixed with about one atmosphere of cis and trans dichloroethylene, respectively. Analysis was by gas chromatography using flow counters to detect the tritiated products.[9]

Previous work has shown that not all of the tritium reacts while it is hot. Those atoms reaching thermal energies may be expected to undergo an addition reaction to form a radical. This then decomposes by breaking the relatively weak C–Cl bond yielding tritiated vinyl chloride.

$$CHCl{=}CHCl + T \longrightarrow CHTClCHCl\cdot \qquad (1)$$

$$CHTClCHCl\cdot \longrightarrow CHT{=}CHCl + Cl\cdot \qquad (2)$$
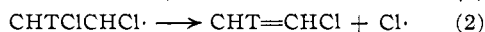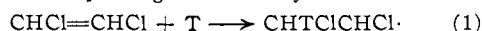
Experiments also were carried out in the presence of an added 1 cm. O₂. Oxygen acts as a radical scavenger and reacts with hydrogen atoms which may reach thermal energies and with any other radicals having a lifetime in excess of 10⁻⁷ seconds. As expected the scavenged runs give a lower relative yield of tritiated vinyl chloride showing that this product originates partially from the reaction of thermal tritium atoms.

Results and Discussion

The results as given in the Table show several notable features. The high vinyl chloride finds no parallel in corresponding saturated systems, such as ethyl chloride, in which direct displacement of a Cl atom to form ethane has only a low prob-

ability.[10] Most of the vinyl chloride therefore probably results, not from one-step Cl atom displacement, but rather from an addition to the double bond similar to that of thermal hydrogen (see reactions (1) and (2) above). Hot addition, followed by de-excitation through breaking the weakest bond, has been observed previously in the reaction of recoil tritium with alkenes.[11] The high yield of acetylene may result from dehydrochlorination of excited vinyl chloride; or from displacement of an HCl molecule by the recoil tritium, followed by Cl elimination from the resulting HClC=CT.

Because of the competing processes involving the C–Cl and double bonds, yields of simple hydrogen abstraction and displacement reactions of the recoil tritium are fairly minor. Nevertheless, for the present inquiry the relatively small yields of the tritiated dichloroethylenes formed by hydrogen atom replacement are most directly relevant. These show a 70% retention of configuration with respect to the original cis or trans molecules. This result demonstrates the existence of a direct displacement mechanism, without formation of a common intermediate, in the reaction of hot hydrogen with ethylenic C–H bonds. The process thus corresponds to the displacement mechanism which has been established for saturated systems.[6]

In contrast to saturated systems,[7] however, there is a 30% loss of configuration. Because of the presence of the double bond this is not surprising and is readily accounted for within the framework of the existing hot hydrogen displacement (A) and addition (B) mechanisms:

(A) The hydrogen displacement mechanism can leave the product with sufficient excitation energy for it to react further. Thus hydrogen displacement in carboxylic acids apparently can cause decarboxylation.[12] With cyclopropane isomerization to propylene, which has an activation energy of 3 ev.,[13] appears to follow at least 15% of the primary displacement events.[14] Rotation about an ethylenic double bond has an activation energy of only about 2 ev.[15] It must be expected therefore that displacement of hydrogen at an ethylenic carbon may frequently result in a product sufficiently

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Starting material	Trans	Trans + O_2	Cis	Cis + O_2
Products				
Hydrogen	10.0	10.0	10.0	10.0
Ethylene	0.8	0.5	1.2	..
Acetylene	21.7	16.7	22.6	22.6
Methyl chloride	3.6	3.0	3.4	3.5
Vinyl chloride	77	51	72	52
Trans-Dichloroethylene	2.7	2.8	1.8	1.5
Cis-Dichloroethylene	1.3	1.4	3.9	3.1

excited to undergo *cis-trans* isomerization by internal rotation.

(B) Independent evidence also exists for a hot hydrogen addition reaction[11] similar to that for thermal atoms (see reaction 1). However, even for the hot system the resulting radical has been shown to have a strong preference to decompose by rupture of the weakest bond,[11] in this case to form vinyl chloride (see reaction 2). Nevertheless if de-excitation by C–H bond rupture occurs in only a few per cent. of the events, the addition mechanism could contribute significantly to the observed yield of the isomerized dichloroethylene.

Regardless of the relative importance of the isomerization mechanisms (A) and (B), the results demonstrate the existence of a fast hydrogen displacement reaction of hot hydrogen atoms with sp^2 C–H bonds. As with saturated systems this process probably proceeds by attack normal to the bond axis leading to a product of unchanged configuration. The "Impact Model" as the detailed mechanism of the fast displacement reaction is discussed in the two preceding papers.[6,7]

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Studies of "Cage" Reactions

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The recombination of methyl radicals was investigated in the liquid and in the gaseous phases. The same temperature and the same proportion of ingredients were maintained in the respective experiments carried out in both phases. The occurrence of "cage" processes in solution was shown unequivocally. Two methods for methyl radicals generation were utilized in these studies, namely, thermal decomposition of acetyl peroxide and photolysis of azomethane. It was shown that "cage" recombination of acetate radicals leads to formation of methyl acetate since this product was not formed in the gaseous decomposition. By using the O^{18}-labeled peroxide it was demonstrated that the recombination of acetate radicals to the peroxide was not observed under our experimental conditions. From analysis of the results it was possible to estimate the unimolecular rate constant of acetate radical decarboxylation to be 10^9–10^{10} sec.$^{-1}$. It follows therefore that acetate radicals may participate in reactions taking place in the "cage," but the probability of their existence outside the "cage" is negligible. The "cage" recombination of methyl radicals, produced by the photolysis of azomethane, was investigated as a function of temperature and the wave length of actinic light. The close initial location of methyl radicals formed in this process increases greatly the probability of their recombination. Finally, the "cage" recombination of trifluoro-methyl radicals and the "cage" recombination and "cage" disproportionation of ethyl radicals is discussed. The results seem to indicate that the recombination of trifluoro-methyl radicals may require about 1.5 kcal./mole of activation energy. The large increase in the probability of recombination (or disproportionation) of ethyl radicals seems to be due to the larger size of the particle which decreases the probability of escape from the "cage" by decreasing the rate of diffusion.

The concept of "cage" reaction was introduced by Franck and Rabinowitch[1] to account for a peculiar situation created in solution when two radicals or free atoms are formed simultaneously in the same location. Due to the slowness of diffusion processes in liquids, the original partners remain together for about 10^{-10} sec., and this increases greatly the probability of their mutual interaction. This interaction is referred to by Franck and Rabinowitch as a "cage" reaction.

A more sophisticated treatment of "cage" processes is due to Noyes[2] who considered the problem of reunion of two particles starting their random walk through a liquid from adjacent locations and irreversibly reacting whenever they meet. This treatment led him to two concepts: (1) the probability of the initial "cage" reaction arising from an interaction of the original partners at the onset of their "walk," and (2) the probability of their reunion after being separated through diffusion.

Two types of events result from a "cage" reaction. Either the original partners recombine and regenerate the parent molecule, or they produce some new species. The first event contributes in a negative way to the outcome of a reaction. Its occurrence manifests itself only indirectly by slowing down the investigated decomposition process. This may be demonstrated by comparing the rates of a dissociation, proceeding under otherwise identical conditions, in the gas phase and in solution. If the reaction in solution is slower than its corresponding gaseous reaction, one might assume that the reduction in rate is caused by a "cage" process. Such phenomena are studied most conveniently in photo-dissociations where the occurrence of a "cage" reaction manifests itself by a decrease in quantum yield. Indeed, in the extreme case of reactions proceeding in rigid media at very low temperatures, "cage" processes may completely

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