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Abstract

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ON THE QUESTION OF THE FORMATION OF THE CARBONIUM ION IN ADDITION REACTIONS TO OLEFINS

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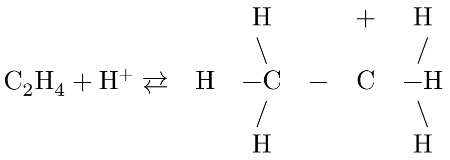
Heterolytic addition reactions at multiple bonds proceed by a stepwise donor-acceptor mechanism (see, for example, (1)). In the first stage, intermediate active compounds are formed, the subsequent reactions of which lead to formation of the product. In particular, in acid-catalyzed processes (hydrohalogenation, hydration, addition of acids) the reaction proceeds through the stage of formation of a protonated form of the olefin. For example:

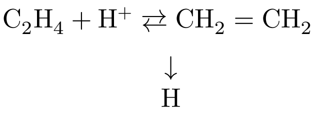
$$C_2H_4 + H^+ \rightleftarrows (C_2H_4 \cdot H)^+ \xrightarrow{HA} C_2H_5A + H^+.$$

The presence of an established acid-base equilibrium in the first stage is demonstrated by the linear dependence of the rate constant on the acidity of the medium (2). As for the nature of the ion formed in the first stage, it is at present the subject of broad discussion. In many works it is assumed that the reaction proceeds through a carbonium ion:



$$C_2H_4 + H^+ \rightleftarrows \begin{array}{ccccc} & H & & + & H \\ & \backslash & & & / \\ H & -C & - & C & -H \\ & / & & & \backslash \\ & H & & & H \end{array} \qquad (1)$$

On the other hand, beginning with Dewar (3), it is often assumed that the ion formed has the structure of a π-complex, in which the π-bond of the olefin does not pass completely into a σ-bond C—H:



$$C_2H_4 + H^+ \rightleftarrows \underset{\underset{H}{\downarrow}}{CH_2} = CH_2 \qquad (2)$$

For an experimental test of one or the other hypothesis, one may use the fact that in the π-complex the newly formed bond with the proton must have a nature different from that of the remaining C—H bonds, i.e., the added H atom must be nonequivalent to the other atoms. In the carbonium ion, the H atoms of the CH_3 group must be equivalent. Therefore, if one takes an acid with labeled hydrogen (for example, D_2SO_4), then in the case of reaction (1) a rapid exchange of the deuterium of sulfuric acid with ethylene should be observed, whereas in the case of reaction (2) there should be no exchange.

The widespread view of the easy exchange of olefins with acids (4, 5) would seem to confirm the carbonium-ion mechanism. However, closer consideration shows that from the exchange data one cannot draw such an unambiguous conclusion. In particular, the exchange of ethylene with deuterosulfuric acid was studied under conditions (10) when the rate of the reaction reverse to the gross reaction (3) was apparently not very small:

$$C_2H_4 + D_2SO_4 \rightleftarrows C_2H_4DOSO_3D. \tag{3}$$

Naturally, in this case exchange should be observed independently of the nature of the intermediate ion, since there can be no doubt that in ethylsulfuric acid the H atoms in the CH_3 group are equivalent.

We studied the absorption of ethylene in D_2SO_4 under conditions of almost complete absence of reverse decomposition of ethylsulfuric acid. For this purpose the reaction was carried out at elevated ethylene pressures (about 4 atm.) at room temperature. A U-shaped glass vessel served as the reaction vessel. Deuterosulfuric acid was placed in one arm, while ethylene was frozen out through a tube connecting the vessel with the vacuum system into the other. After this the connecting tube was sealed off under vacuum, and the ethylene began to be absorbed in sulfuric acid upon mechanical shaking of the vessel. To create the required ethylene pressure, the arm of the vessel containing liquid ethylene was placed in a cooling mixture at a temperature of −75°.

To determine the D composition of the ethylsulfuric acid formed, it was hydrolyzed with water to ethyl alcohol, which, by reaction with HCl in the presence of zinc chloride(6), was converted into ethyl chloride. The ethyl chloride thus obtained was analyzed on an MS-1A mass spectrometer(7).

To determine the isotopic composition of the acidic hydrogen, the acid, after dilution with a definite amount of water, was converted by reaction with CH_3MgJ into methane, which was analyzed on the mass spectrometer for CH_3D content(9).

Table 1 gives the distribution of line intensities in the calibration spectrum of ordinary ethyl chloride and in the mass spectra of the analyzed reaction products. The intensity values are given as percentages relative to the intensity adopted in the given mass spectrum as the standard.

Table 1

Mass spectrum of ethyl chloride
(electron energy 85 eV, temperature in the ionization chamber ~200°C)

m/e	C_2H_5Cl	Ethyl chloride from reaction products
69	–	–
68	–	6.3
67	2.3	100
66	100	30.8
65	13	348
64	342	36
63	21	–

The compositions of the products formed, calculated from the data of Table 1, are given in Table 2. In the calculation it was assumed that, to a first approximation, the probabilities of cleavage of each H atom and D atom during dissociative ionization in the mass spectrometer are equal.

It is seen that the only deuterium-containing product present in the mixture in any appreciable amount is monodeuteroethyl chloride. The formation of small amounts of $C_2H_3D_2Cl$ in experiments 1 and 2 is apparently connected with the reversibility of reaction (3). In experiment 3 the isotopic composition is given for the acidic hydrogen of the initial sulfuric acid and of the mixture of sulfuric and ethylsulfuric acids formed. It is seen that the light hydrogen from ethylene does not pass into the acid during the reaction.

Similar results were obtained by us for the case of hydration of isobutylene in 4M and 6M deuterosulfuric acid. The reaction was carried out in a closed–

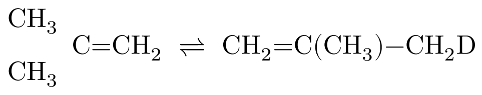
Table 2

No.	Conc. of sulfuric acid, %	$(D_2SO_4)+$ (H_2SO_4) / (C_2H_4) absorbed	D in the initial sulfuric acid, %	D in acidic hydrogen of the formed mixture, %	Isotopic composition of ethyl chloride, %	Isotopic composition of ethyl chloride, %	Isotopic composition of ethyl chloride, %	Isotopic composition of ethyl chloride, %
No.	Conc. of sulfuric acid, %	$(D_2SO_4)+$ (H_2SO_4) / (C_2H_4) absorbed	D in the initial sulfuric acid, %	D in acidic hydrogen of the formed mixture, %	C_2H_5Cl	C_2H_4DCl	$C_2H_3D_2Cl$	Remaining polydeuterides
1	99.9	1.1	100	–	9.3	89	2.4	0.5
2	99.9	2	100	–	5.8	91	3.6	0.1
3	94.5	3.4	74	77	40	59	0.07	0.01
4	99.7	4.7	26	–	86	14	0.2	0.01

sealed ampoule at room temperature. After the hydrogen sulfate had been washed off with light water, the trimethylcarbinol obtained was analyzed directly on a mass spectrometer. The deuteriosulfuric acid was analyzed for deuterium content before and after the reaction. It turned out that in this case as well the reaction proceeds without significant exchange between the sulfuric acid and the olefin, and the reaction product is almost exclusively monodeutero alcohol.

From these results it follows unambiguously that, in the reactions of addition of sulfuric acid to ethylene and of addition of water to isobutylene, there is no stage of reversible formation of a carbonium ion (reaction (1)). Apparently, the hypothesis of a π-complex thus finds experimental confirmation.

It is interesting to note that from the absence of exchange it follows that in these reactions there is absent not only reversible isomerization of the π-complex into a carbonium ion, but also isomerization of the π-complex into an isomeric π-complex.



$$(CH_3)_2C{=}CH_2 \rightleftharpoons CH_2{=}C(CH_3){-}CH_2D \qquad (4)$$

Meanwhile, at first glance it seems that this reaction should proceed readily, since it is associated with neither energetic nor steric difficulties (especially for isobutylene, where the added proton should be shifted toward the CH_2 group). We believe that the absence of such isomerization confirms the recently advanced view of I. I. Moiseev and Ya. K. Syrkin ⁽⁸⁾ of the π-complex as a formation that includes the whole acid molecule and is close in structure to an ion pair. In this case isomerization (4), naturally, should be hindered.

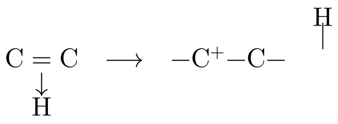
In a recently published work by Taft and Purlee ⁽¹¹⁾ it was also shown that hydration of olefins in dilute acids proceeds without exchange of the hydrogen of water and of the olefin. The authors established the absence of exchange by using heavy water for the hydration and analyzing the olefin that had failed to react. A necessary condition for the conclusion that exchange is absent is, in this case, proof that equilibrium has been established between the gas-phase and dissolved olefin. Apparently, this condition is indeed fulfilled. Together with the data obtained in the present work, these results indicate that over a wide range of acid concentrations there is no stage of reversible formation of a carbonium ion.

From the data on the addition of sulfuric acid to ethylene, the isotope effect of this reaction can be determined. From experiment 4 (Table 2) (carried out with a large excess of acid) it follows that

$$\frac{k_H}{k_D} = \frac{[C_2H_5Cl]}{[C_2H_4DCl]} \cdot \frac{[D^+]}{[H^+]} \sim 2.2.$$

The ratio k_H/k_D for hydration in dilute acids ⁽¹¹⁾ is close to unity*.

We believe that the small isotope effects in addition reactions to olefins indicate that the rate-limiting step of the reaction is scarcely or there may be irreversible isomerization of the π-complex into a carbonium ion



$$\underset{\overset{\downarrow}{H}}{C = C} \longrightarrow -C^{+}-\overset{\overset{H}{|}}{C}-$$

(as is assumed in the works of Taft and of some other authors), since such a process, apparently, should proceed with the maximum isotope effect. An exact

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* The values of isotope effects obtained by Taft, in particular the inverse isotope effect ($k_H/k_D < 1$) for one case, unambiguously indicate the presence of reversible protonation of the olefin in the first stage of the reaction. It follows from this that the proposal of Syrkin and Moiseev ⁽⁸⁾ concerning a six-membered transition complex, even if correct, in any case cannot be put forward in place of an intermediate protonated ion.

interpretation of the isotope effect is difficult, however, because of the multistage character of the reaction.

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Note: Figure translations are in progress. See original paper for figures.