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Abstract

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Certain Features of the Kinetics of the Addition of Hydrogen Iodide to Unsaturated Compounds

We have established that iodine accelerates the addition of HJ to cyclohexene and to allyl chloride, if the reaction is carried out in a benzene solution. Measurements showed that the rate of both reactions is expressed by the equation

$$-\frac{d[\mathrm{HJ}]}{dt} = k_3 M[\mathrm{HJ}][\mathrm{J}_2],$$

where M is the concentration of the unsaturated compound.

The rate of the reaction of HJ with cyclohexene does not depend on temperature, at least in the interval from 4 to 30°. This is revealed in Fig. 1, where data from several kinetic experiments at different temperatures are plotted. It can be seen that, within the limits of experimental error in the measurement of the HJ titer in the mixture, all temperatures correspond to one and the same curve, for which k_3 is equal to 6.7 $\mathrm{l}^2 \cdot \mathrm{mol}^{-2} \cdot \mathrm{sec}^{-1}$. Thus, the temperature coefficient of the rate of the reaction between cyclohexene and HJ in benzene solution is equal to zero. The total activation energy is also equal to zero; and the pre-exponential factor $\alpha = k_3 = 6.7$—a very rare case for reactions in solutions.

If the reaction of cyclohexene with HJ is carried out in glacial acetic acid, then iodine ceases to act as a catalyst and, on the contrary, retards the reaction if it is taken in a concentration comparable with the concentration of HJ. The temperature coefficient of the rate assumes a normal value, equal to ~ 2.4 per 10° (Fig. 2). The rate of the reaction of HJ with cyclohexene in acetic acid is expressed by the equation

$$-\frac{d[\mathrm{HJ}]}{dt} = k_3' M[\mathrm{HJ}]^2,$$

where $k_3' = 0.096$ at 20° and 0.23 at 30° (in the same units), $E = 14.7$ kcal. Additions of LiJ appreciably accelerate the reaction; apparently, LiJ replaces the HJ molecule in the transition complex of the addition reaction.

HJ in benzene and in the presence of iodine adds to allyl chloride much more slowly than to cyclohexene: $k_3 = 0.0088\ \mathrm{l}^2 \cdot \mathrm{mol}^{-2} \cdot \mathrm{sec}^{-1}$. In acetic acid, addition

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

does not take place at all. The rate of addition of HJ to allyl chloride in benzene solution increases by a factor of 2.2 in the interval 12–30°.

1,2-Dimethylcyclohexene-1 reacts with HJ so rapidly that it is impossible to obtain exact values of the rate constants even at a temperature of about 0°. However, the catalytic action of iodine leaves no doubt.

From the data presented it follows that the kinetics of the addition of HJ in these three reactions is determined by the action of an electrophilic agent. Indeed, groups with an electron-donor effect (CH_3) accelerate, while those with an electron-acceptor effect (CH_2Cl) retard the addition reaction. However, we observe an acceleration of the reaction on going from cyclohexene to the dimethyl ester of acetylenedicarboxylic acid—a compound more inclined toward reactions with nucleophilic than with electrophilic reagents.

In the absence of iodine, the addition of HJ to acetylenedicarboxylic ester in benzene obeys a second-order equation:

$$-\frac{d[\mathrm{HJ}]}{dt} = k_2 M[\mathrm{HJ}].$$

The constant of this equation does not depend on temperature in the interval from 3 to 30°. This is evident from Fig. 3, where the same curve 1 represents the values of measurements made at 3, 13, and 30°; k_2 for this reaction is equal to $0.24\ \mathrm{l} \cdot \mathrm{mol}^{-1} \cdot \mathrm{sec}^{-1}$. Iodine retards the reaction of addition of HJ to acetylenedicarboxylic ester, as is shown by curve 2 in Fig. 3, corresponding to experiments with iodine added up to 0.0058 mole/l.

Curves 3, 4, and 5 in Fig. 3 show that the reaction of addition of HJ

Fig. 1. Cyclohexene and HJ in benzene.
$[C_6H_{10}]_0 = 0.13\ M;\ a—4°,\ b—14°,\ c—30°$

Fig. 2. Cyclohexene and HJ in glacial acetic acid.
$[C_6H_{10}]_0 = 0.05\ M;\ a—20°,\ [J_2] = 0.052\ M;\ b—20°,\ [J_2] = 0.0009\ M;\ c—30°,\ [J_2] = 0.0008\ M$

to acetylenedicarboxylic ester is retarded on going from a benzene solution to a solution in petroleum ether and is accelerated on going to more protophilic solvents—mixtures of benzene with dioxane or with acetic acid.

Apparently, HJ acts in the first stage of this reaction not as an electrophilic but as a nucleophilic agent (1). On going from cyclohexene to acetylenedicarboxylic ester, therefore, not only the rate constant changes, but also the mechanism of addition of HJ.

The very small temperature coefficient of the rate of addition of HJ to cyclohexene and to acetylenedicarboxylic ester in benzene solution is apparently explained by the intermediate formation of an active complex, the concentration of which decreases with increasing temperature, thereby compensating for the thermal acceleration of the reaction. Of the various complexes possible in our systems, the π-complex $\mathrm{C_6H_6 \cdots HJ}$ is most probable in this role. If the energy of its formation (ΔH) is close in magnitude to the energy (E_a) of its conversion into the critical complex, then the observed activation energy $E = \Delta H - E_a$ will be close to zero.

This applies to the addition of HJ to cyclohexene and to acetylenedicarboxylic ester. In allyl chloride the energy of formation of the transition complex so greatly exceeds the free energy of formation of the complex $\mathrm{C_6H_6 \cdots HJ}$ that the temperature coefficient of the reaction rate differs little from the normal one.

The catalytic action of iodine in the reactions of HJ with cyclohexene and with allyl chloride is connected, as we believe, with its electrophilic properties.

The reaction probably proceeds through a trimolecular transition complex of the composition

$$\text{(cyclic transition complex with } C{=}C,\ J,\ J,\ H\text{)}$$

in the formation of which the complex $C_6H_6 \cdots HJ$ plays the role of a nucleophilic agent. With elimination of HJ, 1,2-diiodocyclohexane is formed, which is immediately reduced to the monoiodo derivative. The stage of reduction of the diiodide proceeds so rapidly that it does not limit the overall reaction rate and is not reflected in the kinetic equation.

Fig. 3. Dimethyl acetylenedicarboxylate ester and HJ, $[C_6H_6O_4]_0 = 0.02\,M$; 1 —in benzene, $[J_2] = 0.0001\,M$ (a–3°, b–13°, v–30°); 2—in benzene, $[J_2] = 0.0058$, 13°; 3—in petroleum ether, 14°; 4—in a mixture $C_6H_6 + CH_3CO_2H$ $(1:1)$, 14°; 5—in a mixture C_6H_6+ dioxane $(1:1)$, 13°.

Thus, we assume the formation of 1,2-diiodocyclohexane as an intermediate stage in the hydroiodination of cyclohexene and allyl chloride. To confirm this hypothesis it would be necessary to know the rate of formation of the diiodide and the rate of its reduction. It turns out, however, that in the absence of HJ iodine adds to cyclohexene slowly, while in the presence of hydrogen iodide the iodine-addition reaction cannot be observed, because instead of iodine, HJ adds. If the solution contains an iodine adduct to cyclohexene, then after addition of HJ it very rapidly liberates iodine. However, the rate of formation of diiodocyclohexane in the presence of HJ remains unknown, and therefore it is not possible to give exhaustive proof of our assumption.

Experimental Data

Cyclohexene, obtained from cyclohexanol, had b.p. 82°. 1,2-Dimethylcyclohexene-1 was prepared from 1,2-dimethylcyclohexanol-1 by distillation with iodine (^{2}); b.p. 135–136°. Dimethyl acetylenedicarboxylate ester was obtained as in previous work (^{3}). Allyl chloride (from allyl alcohol and HCl) boiled at 44–45°. The solvents were carefully dried and distilled. Gaseous HJ was purified from iodine with a solution of CaJ_2, from water with phosphorus anhydride, and from PH_4J by cooling to $-25°$.

Solutions of HJ in organic liquids were used in kinetic experiments protected from light in an atmosphere of carbon dioxide, to prevent oxidation by air, which occurs especially readily in solutions in acetic acid.

The kinetic experiments were carried out in special vessels connected with a dosing pipette (^{4}). To determine hydrogen iodide, 1-ml samples were mixed in a separatory funnel with several milliliters of CCl_4 and shaken with water. HJ was determined in the aqueous layer by titration according to Folgard. Iodine in the CCl_4 layer was titrated with thiosulfate.

In each individual experiment the values of the constants, within the limits of experimental error, were constant. As an example, the data of two experiments are given. Concentrations are given in moles per liter; the concentrations of HJ were taken from the curves.

Cyclohexene and HJ in benzene
$[C_6H_{10}]_0 = 0.123,\ [J_2] = 0.00515\ M,\ 17°$

t, min	$[HJ]$	k_2, $\mathrm{l \cdot mol^{-1} \cdot sec^{-1}}$
0	0,097	–
5	0,042	0,0314
7	0,032	0,0301
10	0,0245	0,0297
15	0,016	0,0301
20	0,011	0,0313
25	0,008	0,031
		0,0307

Acetylenedicarboxylic acid diethyl ester and HJ in benzene
$[C_6H_6O_4]_0 = 0.0316\ M,\ 13°$

t, min	$[HJ]$	k_2, $\mathrm{l \cdot mol^{-1} \cdot sec^{-1}}$
0	0,0300	–
5	0,0144	0,111
10	0,0092	0,113
15	0,0086	0,115

t, min	$[HJ]$	k_2, l • mol^{-1} • sec^{-1}
20	0,0059	0,113
		0,113

$$k_3 = \frac{k_2}{[J_2]} = 6.0 \text{ l}^2 \cdot \text{mol}^{-2} \cdot \text{sec}^{-1}$$

Some of the mean values of the constants k_2 and k_3 are given in summary Tables 1 and 2. It should be noted that the discrepancies between the values of the constants

Table 1

Cyclohexene and HJ in benzene

T, $^\circ C$	$[HJ]_0$	$[C_6H_{10}]_0$	$[J_2]$	$k_2 \cdot 10^4$, l • mol^{-1} • sec^{-1}	$k_3 = \frac{k_2}{[J_2]}$, l^2 • mol^{-2} • sec^{-1}
30	0,120	0,380	0,0004	24,6	
30	0,120	0,649	0,0004	23,6	
17	0,097	0,123	0,0014	89	6,3
17	0,097	0,123	0,00255	158	6,2
17	0,097	0,123	0,00515	307	6,0
4,4,30	0,096	0,131	0,0026	185	6,7
14	0,091	0,131	0,0025	170	6,8
4,30	0,094	0,131	0,00105	50	5,0
					6,2

Table 2

Allyl chloride and HJ in benzene

T, $^\circ C$	$[HJ]_0$	$[C_3H_5Cl]_0$	$[J_2]$	$k_2 \cdot 10^4$, l • mol^{-1} • sec^{-1}	$k_3 \cdot 10^3$, l^2 • mol^{-2} • sec^{-1}
30	0,102	0,408	0,012	0,93	7,9
30	0,098	0,408	0,024	2,03	8,5
30	0,105	0,408	0,049	4,0	8,2
30	0,118	0,408	0,125	11,7	9,4
30	0,17	0,408	0,025	2,26	9,0
30	0,098	0,408	0,049	4,37	8,9
30	0,10	0,10	0,058	6,1	9,9

T, $^\circ C$	$[HJ]_0$	$[C_3H_5Cl]_0$	$[J_2]$	$k_2 \cdot 10^4$, l · mol^{-1} · sec^{-1}	$k_3 \cdot 10^3$, l^2 · mol^{-2} · sec^{-1}
					8,8
12	0,10	0,10	0,078	2,4	3,0

from different experiments are rather considerable, which is explained by the inaccuracy of the analytical determinations of elementary iodine in the samples.

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