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Abstract

Full Text

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Stereochemistry and Mechanism of the Addition of Hydrogen Bromide to Dimethyl Acetylenedicarboxylate in Organic Acids

(Presented by Academician B. A. Kazanskii, November 20, 1959)

As was shown earlier[1], hydrogen bromide adds to acetylenedicarboxylic ester in glacial acetic acid at 20°, with the formation of approximately equal amounts of bromofumaric and bromomaleic esters. The reaction rate is described by a third-order equation:

$$v = k_3[\mathrm{A}][\mathrm{HBr}]^2. \tag{1}$$

Similar experiments were carried out in propionic acid, in an equimolar mixture of monochloro- and trichloroacetic acids, and also in glacial acetic acid at various temperatures. Equation (1) proved to be valid for all the cases studied. The rate constants of the reaction k_3 ($\mathrm{l}^2 \cdot \mathrm{mol}^{-2} \cdot \mathrm{min}^{-1}$) are presented in Table 1.

Table 1

t-ra, °C	Propionic acid	Acetic acid	Equimolar mixture of monochloro- and trichloroacetic acids	t-ra, °C	Propionic acid	Acetic acid	Equimolar mixture of monochloro- and trichloroacetic acids
0	0.265	–	–	30	8.0	5.5	–
10	–	0.74	–	45	–	–	54.5
20	1.4	1.4	–	60	37.5	36.0	–
25	–	–	34.2	80	–	167	–

The stereochemical course of the reaction depends on the solvent and the temperature of the experiment. The yield of the cis product is shown in Fig. 1. The greatest yield of the cis adduct is observed in a mixture of monochloro- and trichloroacetic acids; acetic acid occupies an intermediate position, and the smallest yield of bromomaleic ester is obtained in propionic acid. Temperature has a substantial influence only in certain intervals, in which the yield of the cis adduct increases as the temperature is lowered (the first case). Outside this

Figure 1. Yield of cis-product as percent of the sum of stereoisomers. 1 —$C_2H_5CO_2H$; 2 —CH_3CO_2H; 3 —CCl_3CO_2H + CH_2ClCO_2H

Figure 1: Figure 1. Yield of cis-product as percent of the sum of stereoisomers. 1 —$C_2H_5CO_2H$; 2 —CH_3CO_2H; 3 —CCl_3CO_2H + CH_2ClCO_2H

interval, at a higher temperature, the stereochemical course of the reaction is practically independent of it (the second case). In propionic acid, within the range 0—60°, the second case occurs; in acetic acid, both cases occur: one in the range 10—40°, and the other 40—80°; in the mixture of monochloro- and trichloroacetic acids, only the first case occurs at 25—40°.

Table 2

Solvent	Temperature interval, °C	E, kcal/mol (cis-)	E, kcal/mol (trans-)
$C_2H_5CO_2H$	0—60	15.6	13.6
CH_3CO_2H	10—20	6.4	17.4
Same	20—40	10.6	17.1
Same	40—80	19.0	17.1
CCl_3CO_2H + CH_2ClCO_2H	25—45	0.3	20.8

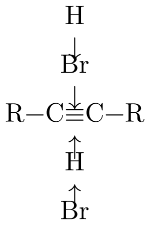
Since the overall third order of the reaction is retained for all temperatures and solvents, equation (1) is also valid for each of the reaction pathways separately. Therefore the quantity k_3 is the sum of the rate constants of the cis- and trans-addition reactions, and the values of the individual constants can be determined from the ratio of the yields of each stereoisomer. Having obtained in this way the rate constants of each process, we calculated their activation energies E, which are presented in Table 2.

It turned out that for trans-addition the activation energies remain constant over the entire range of temperatures studied; for cis-addition, on the contrary, either higher or very low energies are observed.

From the data presented it follows that trans-addition in all cases proceeds by the same mechanism. For cis-addition there are two mechanisms: one of them requires a large activation energy—2 kcal higher than for trans-addition—and therefore manifests itself at a higher temperature; the other mechanism, on the contrary, requires very little activation energy for its occurrence and therefore predominates at low temperatures.

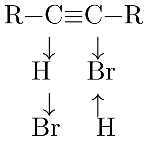
Fig. 1. Yield of cis-product as percent of the sum of stereoisomers. 1 —$C_2H_5CO_2H$; 2 —CH_3CO_2H; 3 —CCl_3CO_2H + CH_2ClCO_2H

We assume that the reactions of trans-addition and cis-addition with high activation energy take place through open trimolecular complexes:



$$\begin{array}{c} \mathrm{H} \\ \downarrow \\ \mathrm{Br} \\ \downarrow \\ \mathrm{R{-}C{\equiv}C{-}R} \\ \uparrow \\ \mathrm{H} \\ \uparrow \\ \mathrm{Br} \end{array}$$

trans

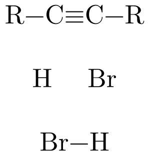


$$\begin{array}{ccc} \mathrm{R{-}C} & \equiv & \mathrm{C{-}R} \\ \downarrow & & \downarrow \\ \mathrm{H} & & \mathrm{Br} \\ \downarrow & & \uparrow \\ \mathrm{Br} & & \mathrm{H} \end{array}$$

cis

Naturally, the course of the reaction through a cis-complex of this type requires a greater activation energy because of steric hindrance in the approach of both hydrogen bromide molecules from one side of the linear molecule.

Cis-addition with low activation energy apparently proceeds through a complex of cyclic structure:



$$\begin{array}{c} \mathrm{R{-}C{\equiv}C{-}R} \\ \mathrm{H} \quad \mathrm{Br} \\ \mathrm{Br{-}H} \end{array}$$

Indeed, as shown by the calculations of Ya. K. Syrkin [2], the occurrence of the process through a six-membered transition complex is always associated with a decrease in activation energy in comparison with a complex of any other type.

Apparently, the resultant activation energy of the process (proceeding in two stages [1]) is determined by the energy of proton detachment in the final stage. The proton acceptor may be the solvent, and naturally, the more basic it is, the smaller the activation energy will be, owing to the gain in the energy of proton addition, for example, to the carbonyl of the solvent. Therefore the activation energy of processes proceeding through open complexes decreases in the series: mixture of monochloro- and trichloroacetic acids, acetic acid, propionic acid. In the cyclic complex, proton detachment occurs through formation of a new undissociated molecule of hydrogen bromide, which, of course, is associated with an additional gain in energy.

The difference in the basicity of the solvents with respect to hydrogen bromide also explains the different reaction rates in them: the less strongly hydrogen bromide is bound to the solvent, the faster the reaction proceeds.

Experimental Part

Dimethyl acetylenedicarboxylate, synthesized according to the procedure of (^{3}), was purified by vacuum distillation. Hydrogen bromide was obtained by the action of bromine on naphthalene and, after purification, was condensed on cooling in a mixture of solid carbon dioxide and acetone. By slow evaporation, the hydrogen bromide was distilled into the solvent placed in a special apparatus. After saturation, the solution was forced into preweighed ampoules, which were immediately sealed. For kinetic experiments, thin-walled ampoules of about 5 ml volume were prepared; for preparative work, ampoules of up to 100 ml were used. The concentration of hydrogen bromide for each series was determined by analysis of the solution in several small ampoules from the series.

The kinetic experiments were carried out in an apparatus made entirely of glass (^{4}). Into it were placed a solution of the acetylenedicarboxylate ester and a small ampoule containing a weighed portion of the hydrogen bromide solution. After both solutions had been brought in the thermostat to the experimental temperature, the ampoule was crushed and the reaction components were mixed instantaneously. The course of the reaction was followed from the decrease in the titer of hydrogen bromide in samples. Samples of definite volume were poured into water, which stopped the reaction, and then titrated by the Volhard method. The errors in the determination, including sampling, did not exceed 0.5%.

The data for the addition of hydrogen bromide in a mixture of monochloroacetic and trichloroacetic acids may serve as an example of the typical course of the reaction (the initial concentrations of HBr and A are identical).

Experiment 1; 25°	Experiment 1; 25°	Experiment 1; 25°	Experiment 2; 45°	Experiment 2; 45°	Experiment 2; 45°
Time, min.	HBr	k_3	Time, min.	HBr	k_3
0	0.0435	–	0	0.0350	–
10	0.0290	33.0	10	0.0230	53.9
20	0.0230	34.0	20	0.0183	55.0
30	0.0193	35.9	30	0.0160	53.5
40	0.0175	34.2	40	0.0140	53.8

Preparative experiments were carried out under the same conditions as the kinetic experiments. Solutions brought to the specified temperature were mixed and kept until completion of the reaction. The mixture was poured onto ice, and the reaction products were extracted with ether. After removal of the solvent, the residue was subjected to fractional distillation under vacuum in an apparatus equipped with a column ensuring complete separation of the unreacted acetylenedicarboxylate ester and isolation of a pure fraction of the mixture of bromofumaric and bromomaleic esters. Quantitative determination of their mixture was carried out from the refractive indices (n_D^{25} 1.4935 for the trans adduct and 1.4861 for the cis adduct) and was checked by freezing out the bromofumaric ester from the mixture. We estimate the accuracy of an individual determination as 4% for each component.

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References Cited

[1] I. V. Smirnov-Zamkov, E. A. Shilov, DAN, **67**, 671 (1949).
[2] Ya. K. Syrkin. Izv. AN SSSR, OKhN, 1959, No. 2, 238.
[3] *Syntheses of Organic Preparations*, Collection 2, IL, 1949, p. 21.
[4] I. V. Smirnov-Zamkov, G. A. Piskovitina, Ukr. khim. zhurn., **23**, 208 (1957).

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

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