PHOTOCHEMICAL HYDROBROMINATION REACTION IN GLASSY AND CRYSTALLINE MIXTURES OF ALLYL CHLORIDE AND HYDROGEN BROMIDE

PHYSICAL CHEMISTRY

1965

SovietRxiv

Abstract

Full Text

UDC 54.161.6+541.117+541.12.012.2

PHYSICAL CHEMISTRY

G. N. KOVALEV, M. N. MASTEROVA, G. B. SERGEEV

PHOTOCHEMICAL HYDROBROMINATION REACTION IN GLASSY AND CRYSTALLINE MIXTURES OF ALLYL CHLORIDE AND HYDROGEN BROMIDE

(Presented by Academician N. N. Semenov, April 13, 1965)

Upon rapid cooling to 77° K, allyl chloride and its liquid mixtures with hydrogen bromide form transparent glasses. Thawing such glasses, previously irradiated at 77° with UV light from a PRK-7 mercury-quartz lamp, leads to a hydrobromination reaction occurring in the solid phase below the melting temperature of the mixture C_3H_5Cl–HBr. Gas-chromatographic analysis established that the principal reaction product is 1-chloro-3-bromopropane. The addition of hydrogen bromide against Markovnikov' s rule indicates a free-radical mechanism of the reaction. Comparison of the depth of reaction with the number of light quanta incident on the sample shows that low-temperature hydrobromination of allyl chloride proceeds by a chain mechanism.

The changes occurring during the thawing of mixtures of allyl chloride and hydrogen bromide were monitored by differential thermal analysis (DTA). Details of the method are described in works ([1], [2]). By the DTA method (Fig. 1, 1 and 2) and by visual observations it was shown that allyl chloride frozen in the glassy state crystallizes at 110° K. It is interesting to note that the crystallization temperatures of glassy mixtures of C_3H_5Cl and HBr of different compositions differ little from 110° K. When glassy samples previously irradiated at 77° K are heated, a new exothermic process appears on the thermograms (Fig. 1, 3 and 4) at a temperature of about 88° K.

The data of Table 1 and Fig. 2 show that the intensity of the exothermic peak at 88° K and the depth of reaction after thawing increase with irradiation time, which indicates a connection between this process and the hydrobromination reaction of allyl chloride.

From the data presented in Table 1 it is evident that the temperature at which the exothermic addition reaction begins is practically independent of the irradiation time. This fact is the most interesting feature of the chain reaction of

photochemical hydrobromination in glassy mixtures of allyl chloride and hydrogen bromide.

This feature is not connected with prior occurrence of the addition reaction at 77° K, since during irradiation no heat evolution associated with the reaction could be detected, and keeping the irradiated samples in the dark at 77° K did not lead to noticeable changes in the character of the thermographic curves. It must also be noted that the temperature at which the hydrobromination reaction begins depends only weakly (85-95° K) on the composition within the range HBr/C_3H_5Cl (in moles) = 0.5-12.0.

In our opinion, the remarkable fact that the temperature at which the reaction begins is independent of the duration of prior irradiation, and its weak dependence on the composition of the mixture, can be explained if it is assumed that at 85-88° K there is a low-temperature boundary of the softening interval of the glass composed of allyl chloride and hydrogen bromide. Then initiat-

tion of the reaction by active centers stabilized at 77° K can be associated with a sharp change in a number of properties of the system (heat capacity, viscosity, thermal and electrical conductivity, specific volume, dielectric constant, etc.), which, as is known (3-5), occurs in the softening interval. In the present case, apparently, the principal role is played by the decrease in the viscosity of the system, leading to an increase in the mobility of the reacting particles.

A qualitative indication that

Fig. 1

Fig. 2

Fig. 1. Change in the temperature difference between the sample and the block, ΔT (deg.), with increasing temperature T (°K) in allyl chloride and its mixtures with hydrogen bromide (calculated from experimental d.t.a. curves). 1 —glassy sample of C_3H_5Cl ($3 \cdot 10^{-3}$ mole), obtained by rapid freezing; 2 — the same sample, but crystalline; 3 —glassy sample of an equimolar mixture ($3.8 \cdot 10^{-3}$ mole) of HBr and C_3H_5Cl, irradiated with ultraviolet light at 77° K for 5 sec. The reaction depth after thawing of the mixture is 7%; 4 —a sample analogous to the preceding one. Irradiation time 180 sec. Reaction depth 41%. Rate of heating of the block in the temperature interval 77-110° K —3.7°/min, in the temperature interval 150-170° K —2.2°/min.

Fig. 2. Dependence of the depth of the hydrobromination reaction in glassy equimolar mixtures of allyl chloride and hydrogen bromide in the reaction vessel for d.t.a. on the time of irradiation with ultraviolet light at 77° K.

softening of the glass of allyl chloride and hydrogen bromide occurs in the temperature interval below 90° K is the fact that cracks form in the glass at 77° K and heal at 90° K. The region of glass softening can also be determined by d.t.a. from the jump in heat capacity. Indeed, in our experiments, on thermograms of allyl chloride (see, for example, Fig. 1, 1) and thermograms of

unirradiated mixtures of C_3H_5Cl and HBr, a weak endothermic process ($\sim 2.5°$) is recorded, beginning at about 87° K. At small doses of preliminary irradiation, this endothermic process precedes the exothermic reaction (Fig. 1, 3).

Thus, the development of the reaction in glassy mixtures is, apparently, determined by the decrease in the viscosity of the mixture. With increasing dose of preliminary irradiation, an appreciable reaction rate is attained at higher values of viscosity, but because of the rapid change in viscosity in the softening interval, the observed shift of the temperature at which the reaction begins is small. The vigorous increase in the reaction rate is mainly associated with the decrease in viscosity as a result of self-heating of the mixture. At the same time, as in the case of low-temperature photochemical hydrobromination of ethylene (1), an important role may be played by the ratio of the rates of heat input from the reaction and heat removal from the sample.

The coincidence of the temperature interval of the second exothermic process on the thermograms of irradiated mixtures with the crystallization temperature interval of nonirradiated mixtures makes it possible to assume that this process is also caused by crystallization of the mixture. From a comparison of the thermograms shown in Fig. 1 and from Table 1, it is seen that in irradiated mixtures the intensity of the crystallization process decreases with increasing irradiation time. DTA of nonirradiated glassy mixtures

Table 1

Effect of irradiation time on the character of thermographic curves of glassy equimolar mixtures of allyl chloride and hydrogen bromide

t	T_1	θ_1	T_2	θ_2	M.p.	θ_3
0	–	–	110	> 12	130	8
1	88	11	110	7,0	128	7,0
5	86,5	25,5	119	3,5	125	4,5
15	88	28,5	112,5	2	126	3
45	85,5	33,5	108	5,5	126	3
80	87,5	36	?	0,2	129	2
120	88	36	115	2	127	2
240	89,5	39	–	–	–	–

Note. t is the time of irradiation of the samples at 77° K, in minutes; T_1, T_2, M.p. (°K) are the temperatures of the hydrobromination reaction, crystallization, and melting of the mixtures, respectively. θ_1, θ_2 are the maximum heat evolutions during the reaction and crystallization, respectively; θ_3 is the magnitude of the melting peak (in degrees).

with 1-chloro-3-bromopropane shows that such a change is apparently associated with the accumulation of the reaction product, which hinders crystallization. At

high concentrations of 1-chloro-3-bromopropane, crystallization of the mixture does not occur.

UV irradiation at 77° K of polycrystalline mixtures of C_3H_5Cl and HBr also leads to a chain reaction, during which significant amounts of 1-chloro-3-bromopropane are formed. At 77° K the reaction does not proceed.

In crystalline mixtures of allyl chloride and HBr, the temperature interval of the reaction observed during thawing depends on the time of preliminary irradiation of the mixture at 77° K. The character of the hydrobromination reaction in crystalline HBr–C_3H_5Cl mixtures is, in its main features, analogous to the reaction in frozen mixtures of ethylene and hydrogen bromide ([1]). With weak initiation in crystalline mixtures of allyl chloride and HBr, the reaction is observed only in the temperature interval 110—130° K, i.e., at the crystallization temperatures of glassy mixtures. With an increase in the irradiation dose, the hydrobromination reaction of allyl chloride in crystalline samples begins below 110° K, but proceeds at significant rates only upon reaching 100—110° K. It is also interesting to note that, by the thermographic method, in crystalline mixtures even after very long irradiation times of the samples at 77° K it was not possible to observe a noticeable hydrobromination reaction below 85° K, i.e., below the temperature at which the reaction begins in the glass.

Moscow State University
named after M. V. Lomonosov

Received
2 IV 1965

CITED LITERATURE

1. G. N. Kovalev, G. B. Sergeev, DAN, **160**, 390 (1965).

2. G. N. Kovalev, G. Raabe, R. M. Nalbandyan, V. S. Gurman, G. B. Sergeev, DAN, **142**, 396 (1962).

3. P. P. Kobeko, *Amorphous Substances*, Publishing House of the Academy of Sciences of the USSR, 1952.

4. G. Tammann, *The Glassy State*, Moscow–Leningrad, 1935.

5. W. Kauzmann, Chem. Rev., **43**, 218 (1948).

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