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G. N. KOVALEV, G. RAABE, R. M. NALBANDYAN, V. S. GURMAN

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Abstract

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G. N. KOVALEV, G. RAABE, R. M. NALBANDYAN, V. S. GURMAN and G. B. SERGEEV

RAPID PHOTOCHEMICAL HYDROBROMINATION OF ETHYLENE AND PROPYLENE AT LOW TEMPERATURES

(Presented by Academician N. N. Semenov, August 1, 1961)

In 1959 it was shown that chlorine rapidly adds at low temperatures to a series of olefins, giving only addition products ([1]). The reactions of bromination and hydrohalogenation of olefins proceed analogously ([2]).

Along with the study of such reactions, which probably proceed by an ionic mechanism or through molecular complexes, investigation of the possibility of radical and chain reactions initiated by radiation at low temperatures is also of considerable interest.

In the present work the photochemical hydrobromination of ethylene and propylene at low temperatures was studied. The experiments were carried out in a vacuum apparatus of the usual type, in a quartz reaction vessel of cylindrical shape with a base diameter of 2 cm and a height of 5 cm. Mercury quartz lamps PRK-2 and PRK-7 served as the source of ultraviolet illumination. Hydrogen bromide in an amount of 10^{-3}–10^{-4} mole was mixed in the gas phase with an equal amount of olefin. The mixture, gradually condensed onto the bottom of the reaction vessel cooled with liquid nitrogen, was illuminated for a specified time and then thawed.* The extent of reaction was usually monitored from the change in pressure, since by means of gas chromatography it was found that the principal product of the hydrobromination reaction of ethylene is ethyl bromide. In the addition products of hydrogen bromide to propylene only normal propyl bromide was detected.

Figure 1 gives curves of the dependence of the extent of reaction on the illumination time for the reactions of hydrogen bromide with ethylene and propylene. From this figure it is seen that in two hours of illumination more than 80% conversion takes place. It is interesting to note that, for the hydrobromination of ethylene, the yield increases with an increase in the number of thawings at the same illumination times.

Illumination of a layer of hydrogen bromide at −196° and subsequent freezing

onto it of a layer of ethylene, or of a mixture of hydrogen bromide with ethylene, led to the reaction forming ethyl bromide. For a given illumination time, the extent of this reaction did not depend on when the ethylene or the reaction mixture was frozen on. A layer of bromine illuminated at liquid-nitrogen temperature also initiated the hydrobromination reaction of the olefin. Illumination of the olefin and subsequent freezing-on of hydrogen bromide did not lead to reaction. Thus, the experiments described above show that the low-temperature hydrobromination reaction of olefins is initiated by bromine atoms.

The high degree of conversion and the formation of the normal addition product in the hydrobromination reaction of propylene made it possible to suppose that the photochemical hydrobromination of olefins proceeds by a chain mechanism. Using ferrioxalate dosimetry ([3,4]), we

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* It had previously been shown that there is no reaction of hydrogen bromide with ethylene and propylene in the gas phase, or upon repeated freezing and thawing of the mixtures without illumination by ultraviolet light.

the quantum yield was determined in the hydro-bromination reaction of olefins at low temperatures.

Accurate determination of the quantum yield at low temperatures in the systems studied is difficult, since the mixture is opaque and the associated light scattering is hard to take into account. In the measurements, only the number of quanta incident on such a quantity of mixture as practically did not transmit light was estimated. The lower limit of the quantum yield of the hydrobromination reaction of ethylene and propylene obtained in this way proved to be 150. It is interesting to note that, with the aid of gas chromatography, in the interaction of hydrogen bromide with ethylene, dibromoethane was also found among the reaction products in addition to ethyl bromide. The ratio of C_2H_5Br to $C_2H_4Br_2$ was equal

[Figure 1 and Figure 2 diagrams visible on page]

Fig. 1. Dependence of the extent of reaction on the illumination time. **1** — hydrobromination of a mixture of $5 \cdot 10^{-4}$ mole of hydrogen bromide and $5 \cdot 10^{-4}$ mole of ethylene; **2** —hydrobromination of a mixture of $2.5 \cdot 10^{-3}$ mole of hydrogen bromide and $2.5 \cdot 10^{-3}$ mole of propylene (each point on **1** and **2** was obtained by illumination of a freshly prepared mixture)

Fig. 2. Thermographic heating curves. **1** —illuminated mixture of C_2H_4 with HBr; **2** —unilluminated mixture. The plateau at -175° corresponds to melting of the eutectic mixture HBr—C_2H_4; **3** —mixture HBr, C_2H_4, and C_2H_5Br. The ratio of the components corresponds to the composition of a reacted mixture of HBr and C_2H_4

to 500 : 1. From these data the chain length of the reaction of addition of hydrogen bromide to ethylene is equal to 250, if it is assumed that dibromoethane

is formed only upon recombination of the chain-carrying radicals. Apparently, this value is also underestimated. Thus, the totality of the facts described above indicates that low-temperature hydrobromination of olefins proceeds by a chain mechanism with participation of bromine atoms.

To determine the temperature at which the reaction of addition of hydrogen bromide to olefins takes place, a thermographic analysis was carried out. The ethylene–hydrogen bromide system was studied in greatest detail. A copper–constantan thermocouple was placed in the quartz tip of the reaction vessel, 5 mm in diameter. The vessel was filled with a mixture of HBr and C_2H_4, disconnected from the vacuum apparatus, and illuminated in a quartz Dewar at the temperature of liquid nitrogen. Then the reaction vessel was placed in a cryostat and heating curves were recorded. The resulting thermographic curves, recorded under a preselected heating regime, are shown in Fig. 2. From this figure it is seen that the temperature at which the reaction begins is considerably lower than the melting temperature of the unilluminated mixture; i.e., the hydrobromination reaction of ethylene begins and, at least partially, takes place in the solid phase below the melting temperature of the eutectic mixture of hydrogen bromide and ethylene, equal, according to our data and the data of Maass and Wright, to $-175°$ ([5]).

It should be noted that the shape of the thermographic curve of the illuminated mixture (Fig. 2, **1**) indicates that the reaction of low-temperature hydrobromination of ethylene proceeds very rapidly. Preliminary experiments with a differential thermocouple also showed that a rapid exothermic process of explosive type occurs at a temperature of $-196°$. The heating recorded by the differential thermocouple occurs some time after illumination. Thus, the hydrobromination reaction of ethylene be-

begins only upon attainment of a certain concentration of bromine atoms. The heat released in the initial steps, and the favorable energetics of the chain-propagation reactions, promote the further course of the chain reaction in the solid phase. Heating during the reaction reaches the melting temperature of the eutectic mixture (see Fig. 2). As is known^(6-8), in a solid near phase transitions there is considerable mobility of molecules, which in turn may also facilitate the addition reaction of hydrogen bromide to olefins at low temperatures.

The course of the reaction at the temperature of liquid nitrogen apparently explains the absence of electron paramagnetic resonance spectra in mixtures of hydrogen bromide with ethylene (compositions $1:1$, $10:1$, and $1:10$) irradiated for several hours at $-196°$. Photolysis of hydrogen bromide and ethyl bromide under analogous conditions likewise gave no EPR spectra.

The EPR spectrum of the radical C_2H_4Br, recently found^(9) upon radiolysis with γ-rays from Co^{60} of a mixture of hydrogen bromide and ethylene at $-196°$, in our opinion should probably be explained not by the reaction $Br + C_2H_4 \rightarrow C_2H_4Br$, as the authors believe, but by the radiolysis of ethyl

bromide, rapidly formed from HBr and C_2H_4 at the temperature of liquid nitrogen under the action of radiation.

We are currently carrying out experiments for a more detailed study of the phenomena described, and are also investigating the possibility of other chain reactions proceeding at low temperatures.

Moscow State University
named after M. V. Lomonosov

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