G. N. Kovalev, G. B. Sergeev

1965

SovietRxiv

Abstract

Full Text

Physical Chemistry

G. N. Kovalev, G. B. Sergeev

FEATURES OF A CHAIN PHOTOCHEMICAL REACTION IN FROZEN MIXTURES OF HYDROGEN BROMIDE WITH ETHYLENE

(Presented by Academician N. N. Semenov on 11 VII 1964)

In frozen mixtures of HBr and C_2H_4, under the action of ultraviolet illumination, the reaction forming C_2H_5Br occurs, with a long chain of hundreds of links (^{1}).

In the present work, the course of the reaction was monitored by the method of differential thermal analysis. Thermographic curves obtained during slow heating of pre-illuminated samples are shown in Fig. 1. At low illumination doses, the form of the thermographic curves does not depend on the time for which the samples are kept at a temperature of −196°. This shows that in the illuminated mixture of HBr and C_2H_4, stabilization of the active reaction centers—apparently bromine atoms or C_2H_4Br radicals—takes place, and the ethylene hydrobromination reaction proceeds below the melting temperature of the mixture (−161°C) in the solid phase. As the illumination dose increases, the reaction attains a higher rate at a lower temperature.

When samples are illuminated in liquid nitrogen with light of sufficiently high intensity, after some time from the beginning of illumination (the induction period τ), the thermocouple records a rapid exothermic process, analogous to curve 3 in Fig. 1. During the induction period, a small, smooth, progressively increasing heating is observed, which after a time τ is replaced by an extremely rapid rise in temperature. From the data of Table 1 it is seen that τ is inversely proportional to I over a wide interval

Table 1

Dependence of the induction period of the reaction τ on the illumination intensity (I) at a temperature of −196°

I/I_0	τ, sec	ΔT, °C	ΔT_m, °C	η, %	D_{expl}
1	4.4	0.9	31	17.1	4.4
0.62	6.5	1.1	30	16.4	4.0
0.51	9.0	1.0	31	16.3	4.6
0.34	11.5	1.0	30	16.0	3.9
0.25	16.3	1.3	31	16.2	4.1

I/I_0	τ, sec	ΔT, °C	ΔT_{m}, °C	η, %	D_{expl}
0.10	45.7	1.1	30	15.2	4.6
0.04	no explosion; the reaction depth and the magnitude of heating during subsequent thawing increase monotonically with the illumination dose.				

Note. ΔT is the magnitude of heating at the end of the induction period; ΔT_{m} is the maximum heating; η is the reaction depth; $D_{\mathrm{expl}} = I\tau$ is the illumination dose leading to explosion.

of intensities, i.e., the rapid reaction develops upon reaching a definite illumination dose ($D_{\mathrm{expl}} \simeq 4.3^*$). This illumination dose corresponds to a constant reaction depth, equal to 16%.

All quantities in Table 1 are averages of several experiments.

At an illumination intensity of $0.04I_0$ or less, the rapid exothermic process at $-196°$ ceases to develop even after illumination with doses tens of times exceeding D_{ign}. The rapid reaction is recorded only upon subsequent heating of the mixture. This fact indicates the influence of the time during which the mixture receives D_{ign}. Indeed, if a mixture of HBr and C_2H_4 at a temperature of $-196°$ is illuminated with light of intensity $I \geq 0.1I_0$ (see Table 1) with interruptions of several minutes, then the rapid reaction does not proceed at $D = D_{\mathrm{ign}}$.

Fig. 1. Thermographic curves of equimolecular mixtures of HBr and C_2H_4. Illumination temperature $-196°$. 1 –illumination dose $D = 0.6$ (in arbitrary

---

* Illumination dose in arbitrary units. The unit is taken to be the illumination received by the sample at the maximum intensity I_0 from a PRK-7 lamp in one second.

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

units), reaction depth 15%; 2 $-D = 0.9$, reaction depth 14%; 3 $-D = 39.5$, reaction depth 37%.

The facts considered above show that the onset of the rapid exothermic process is determined by the slow reaction preceding it.

The occurrence of such a reaction in the absence of illumination is also confirmed by experiments with changing the conditions of heat removal from the system (2). Changing the conditions of heat removal from the reaction vessel cooled in liquid nitrogen, accomplished by pumping out the heat-exchange gas*, led to self-heating of the previously illuminated mixture. In this case, the character of the change in the exothermic processes with illumination dose is analogous to the corresponding processes during thermographic recording in the block (see Fig. 1), with the difference, however, that in the present case the temperature rise occurs only as a result of self-heating of the mixture due to the ongoing reaction.

Fig. 2. Change in reaction depth after illumination with a definite dose as a function of holding time in the dark ($t = -196°$). 1 $-D = 0.7$ sec ($\times I_0$), illumination intensity $\sim 3.6 \cdot 10^{-2} I_0$; 2 $-D = 36.7$ sec ($\times I_0$), $I \sim 8 \cdot 10^{-2} I_0$; 3 $-D = 244$ sec ($\times I_0$), $I \sim 8 \cdot 10^{-2} I_0$.

A slight change in the conditions of heat removal in samples preliminarily illuminated with doses $D > D_{\text{ign}}$ (for example, $D \simeq 30$) led to a rise in temperature which remained constant for some time and then slowly decreased. The process described, proceeding without the occurrence of a rapid reaction, could be repeated several times, but each time at a higher temperature. These experiments indicate the influence of burn-out at a definite temperature of stabilized active centers in the slow dark reaction. The rate of this reaction under unchanged heat-removal conditions, depending on the previously received dose, was studied from the change in reaction depth with holding time at the temperature of liquid nitrogen. It is seen from Fig. 2 that at an illumination dose $D \simeq 37$, the depth of the dark reaction can reach 11%, whereas at $D \simeq 0.75$ the total depth of the reaction does not change, i.e., as the concentration of stabilized active centers increases, the rate of the dark reaction rises.

* To improve heat exchange between the thermocouple of the sample and the walls of the reaction vessel, hydrogen was admitted in an amount corresponding to 9 mm Hg.

Fig. 3

Figure 3: Fig. 3

Thus, the accumulation of stabilized active centers in frozen mixtures of HBr and C_2H_4 is accompanied by a slow reaction whose rate depends on their concentration and on the temperature. Under certain conditions the reaction rate increases sharply, which leads to the development of a rapid exothermic process. These conditions apparently arise when the rate of heat input from the reaction exceeds the rate of heat removal from the system, i.e., the rapid exothermic process develops by the mechanism of a thermal explosion. In this case, when the heat-removal conditions change, the value of the reaction rate leading to explosion (the critical rate) must change. And indeed, decreasing the heat removal from samples irradiated at -196° led to a shortening of the induction period, all other experimental conditions remaining unchanged.

Fig. 3. Dependence of the reaction depth on the irradiation dose at different temperatures.
1 –temperature -161°, intensity $I \sim 3.6 \cdot 10^{-3} I_0$;
2 –temperature -196°, $I \sim 3.6 \cdot 10^{-2} I_0$

In experiments at a temperature of -196°, the conditions of heat removal from the samples and the pre-explosion heating were identical and, consequently, explosion occurred upon reaching one and the same critical reaction rate. Initiation of explosion by a definite irradiation dose (see Table 1) shows that at short irradiation times the critical reaction rate is determined by the corresponding critical concentration of stabilized active centers. As the heat-removal conditions change, the magnitude of the critical reaction rate changes and, accordingly, so does the irradiation dose leading to explosion.

At low irradiation intensities the critical reaction rate is not reached. This feature of the reaction could be explained by a decrease in the concentration of active centers due to the reaction proceeding. However, the data of Fig. 2 and Table 1 show that burn-out during the time required to obtain D_{expl} is insignificant.

Apparently, the reaction is initiated mainly only by active centers that diffuse relatively easily at the given temperature. As a result, at constant temperature the critical reaction rate can be reached only when a sufficient rate of accumulation of readily diffusing active centers of the reaction is provided. If this condition is not fulfilled, the heat of reaction has time to be removed and the reaction rate does not increase, although the total concentration of stabilized active centers may increase. Accordingly, at a constant initial concentration of stabilized active centers, attainment of the critical reaction rate is possible only at a sufficiently high rate of increase of the sample temperature.

The development of the reaction in the solid phase is apparently also influenced by features of chain termination. It is seen from Fig. 3 that the dependence of the reaction depth on the irradiation dose in the liquid phase (curve 1) and in the solid phase (curve 2) is different. The change in the slope of the initial portions of the curves is probably explained by a decrease in the quantum yield of the active centers of the reaction in the solid phase. The decrease in the reaction depth with irradiation dose

(curve 2), apparently indicates a change in the chain length with increasing concentration of stabilized active centers. Chain termination in the solid phase probably occurs as a result of recombination of active centers that are propagating the chain with stabilized active centers of the reaction.

Thus, it has been shown that the rapid exothermic process in frozen mixtures of HBr and C_2H_4 is a thermal explosion.

However, on the other hand, it may also be regarded as a peculiar chain explosion, in which the increase in the number of stabilized active centers entering into reaction occurs at the expense of the heat of the reaction taking place. A possible reaction mechanism may be represented as follows. Stabilized active centers cannot enter into reaction, and only in rare cases—for example, upon recombination of two active centers near a third—can an individual reaction chain of several hundred links arise. Since the hydrobromination reaction of ethylene is exothermic ($\Delta H = -16$ kcal/mole), the course of such a chain is accompanied by an intense thermal wave. The latter, propagating through the solid mixture and reaching the nearest stabilized active center of the reaction, may make it possible for that center, in turn, to initiate another chain. Such a reaction mechanism was called by N. N. Semenov the development of a direct chain branching by means of elementary thermal waves ([3]). As the irradiation dose increases, the concentration of stabilized active centers increases, and with it the rate of such thermal branchings increases. The influence of heat-removal conditions amounts to the fact that the number of branchings increases especially intensively after the critical reaction rate is exceeded.

The phenomena described in this work are characteristic not only of the hydrobromination reaction of ethylene. Rapid exothermic processes, apparently of the same nature, were recorded by us in ultraviolet-irradiated mixtures of HBr with propylene, 1-octene, cyclohexane, and certain other olefins.

Moscow State University
named after M. V. Lomonosov

Received
10 VII 1964

REFERENCES CITED

[1] G. N. Kovalev, T. Raabe et al., DAN, **142**, 396 (1962). [2] G. N. Kovalev, T. B. Sergeev, Proceedings of the Symposium on Elementary Processes in High-Energy Chemistry, “Nauka,”1964. [3] N. N. Semenov, Report at the VIII Congress on Pure and Applied Chemistry, Montreal, Canada, 1961.