I. M. BARKALOV, Corresponding Member of the Academy of Sciences of the USSR V. I. GOLDANSKII,

GO MIN' -GAO

1963

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

I. M. BARKALOV, Corresponding Member of the Academy of Sciences of the USSR V. I. GOLDANSKII,
GO MIN' -GAO

KINETICS OF THE DECOMPOSITION OF BENZOYL PEROXIDE IN ACETYLENIC HYDROCARBONS

The polymerization of acetylenic hydrocarbons has a number of specific features ([1–5]) that distinguish this process from the well-studied vinyl polymerization. These differences are connected primarily with the fact that, in the course of polymerization, macromolecules with a system of conjugated bonds are formed. The polymerization of acetylenic hydrocarbons—for example, phenylacetylene (PA)—can be induced both by radiation ([1–3]) and thermally ([4]), as well as with the aid of traditional radical initiators: benzoyl peroxide (BP) ([5]) and azobisisobutyronitrile.

As was established in ([5]), during the polymerization of PA under the action of BP an anomalously rapid decomposition of the peroxide is observed, and the rate of decomposition of BP in PA is proportional to the first power of the concentration of both BP and PA. The activation energy of BP decomposition ($E = 21$ kcal/mol) in this case coincides with the activation energy of PA polymerization, but differs from the activation energy of the ordinary monomolecular decomposition of BP ([6]). It was also established that, during the decomposition of BP in PA, benzoic acid is formed, and the rate of its formation coincides with the rate of disappearance of BP. To describe all these facts, in work ([5]) we proposed a scheme for the decomposition of BP in PA based on the assumption of a direct bimolecular interaction of the molecules of these substances. Subsequently we obtained a number of new data, presented in this article; in particular, the kinetics of BP decomposition in PA, deuterated PA (DPA), and methylphenylacetylene (MPA) were compared, and the inhibition of BP decomposition and PA polymerization by additions of benzoquinone (BQ) was also investigated. The totality of all the results makes it possible to establish the presence of a chain decomposition of BP in PA, a possible mechanism of which is considered below.

Experimental procedure. A series of ampoules was filled with a solution of a definite concentration of BP in the monomer. The ampoules were freed from the air dissolved in them (to a pressure of $< 10^{-3}$ mm Hg), sealed, and kept in a thermostat for the time interval required for the experiment. The ampoules

Fig. 1 and Fig. 2 graphs

Figure 1: Fig. 1 and Fig. 2 graphs

were then opened, the polymer yield was determined gravimetrically, and the concentration of unreacted peroxide was determined iodometrically. The yield of benzoic acid was determined by titration. DPA was obtained by decomposition of Na-phenylacetylene with heavy water. The concentration of the completely deuterated product was 98%. MPA was prepared according to the procedure described in ([7]). The BQ used in some experiments as inhibitor was subjected to threefold recrystallization from a benzene solution.

Experimental results and discussion. The kinetic curves for the BP-initiated polymerization reaction of PA and DPA are shown in Fig. 1. The presence of a limiting polymer yield (the same for PA and DPA) is explained by the consumption of all the BP and corresponds to the polymerization of approximately 6.8 PA (or DPA) molecules per one BP molecule. As follows from Fig. 1, the transition from PA to DPA lowers the initial rate of polymerization by approximately a factor of one and a half; in the case of MPA, however, polymerization was not observed at all under the given experimental conditions. In Fig. 2 are presented,

kinetic curves for the decomposition of BP in different media. The rate of BP decomposition in PA is 6.8 times lower than the rate of consumption of the monomer, which is in good agreement with the above-mentioned value of the limiting yield of the polymerization reaction. In MPA the rate of BP decomposition proves to be much lower than in PA (the decomposition is slowed by approximately a factor of 25), and is practically equal to the rate of monomolecular decomposition in CCl_4. These results undoubtedly indicate the important role of the mobile hydrogen $C_6H_5C \equiv CH$ in the PA molecule in the kinetics both of BP decomposition and of BP-initiated polymerization of PA and other similar hydrocarbons. The interrelation of the rate

Fig. 1. Dependence of the percentage of polymerization on time at 70° for: 1 —phenylacetylene; 2 —deuterated phenylacetylene; 3 —phenylacetylene with added benzoquinone (0.044 mol/l)

Fig. 2. Kinetics of BP decomposition at 70° in different media: 1 —PA; 2 —PA + 0.044 mol/l quinone; 3 —MPA; 4 —CCl_4

of BP decomposition and polymerization of acetylenic hydrocarbons under the conditions of our experiments, as well as the chain character of both of these processes, is also demonstrated by the sharp decrease in their rate under the action of a typical radical inhibitor—benzoquinone (BQ). As is seen from Fig. 1, addition of 0.044 mol/l BQ decreased the rate of PA polymerization by more than 15 times. At the same time the initial rate of BP decomposition also decreased sharply (Fig. 2), whereas the ratio of the rates of polymerization and BP decomposition changed only slightly (decreased by 30%).

Obviously, in contrast to the picture of BP decomposition in vinyl monomers, the process of BP decomposition in acetylenic hydrocarbons proves to be closely connected with the polymerization of the latter. To describe all the experimental results presented above, as well as the previously noted characteristic features of polymerization of acetylenic hydrocarbons [1–3], one may propose a scheme in which the radical formed at some stage of growth of the polymer chain, already being inactive toward polymerization (as we had already assumed earlier [1]), nevertheless causes continuation of the BP decomposition chain by entering with the BP molecule into a bimolecular reaction. Leaving aside here the questions of the action of the inhibitor BQ, we present the reaction scheme in the following form:

$$\text{П} \rightarrow 2\dot{\text{B}} \tag{0}$$

$$\dot{\text{B}} + M \rightarrow \text{BK} + \dot{\text{R}} \tag{1}$$

$$\dot{\text{B}} \rightarrow \text{termination} \tag{2}$$

$$\dot{\text{R}} + M \rightarrow \dot{\text{R}} \tag{3}$$

$$\dot{\text{R}} + M \rightarrow \dot{\text{A}} \tag{4}$$

$$\dot{\text{R}} \rightarrow \dot{\text{A}} \tag{5}$$

$$\dot{\text{A}} + \text{П} \rightarrow \dot{\text{B}} + \text{polymer} \tag{6}$$

where $\text{B}^{\cdot}$ is a benzoyl radical; BK is benzoic acid; $\text{R}^{\cdot}$ is the radical $\text{C}_6\text{H}_5{-}\text{C}{\equiv}\text{C}{-}$, as well as a growing polymer radical; $\text{A}^{\cdot}$ is an inactive polymer radical incapable of further addition of monomer but ensuring chain decomposition of PB. Reaction (1) is abstraction of a labile acetylenic hydrogen with formation of BK. This reaction is somewhat retarded in DFA and is practically absent in MFA. The termination reaction (2) may be interpreted as decomposition of the benzoyl radical

$$\text{C}_6\text{H}_5\text{COO}^{\cdot} \rightarrow \text{C}_6\text{H}_5^{\cdot} + \text{CO}_2$$

with subsequent formation of an inactive radical of the type

$$\text{C}_6\text{H}_5{-}\text{CH}{=}\text{C}^{\cdot}{-}\text{C}_6\text{H}_5.$$

The possible causes of the decay of the activity of the polymer radical as it becomes longer, represented in our scheme by the transformation of R· into A·, are due to the specific properties of polymers with conjugated double bonds ([8]) and have already been discussed in the literature (see, for example, ([1])). Such decay of activity may, in principle, also occur upon interaction of a growing polymer radical with a monomer molecule (reaction 4), and by monomolecular rearrangement of the radical (reaction 5). The observed reaction orders both for the decomposition of PB and for the polymerization of FA when initiated by PB correspond to predominance of decay of radical activity by reaction (4) at not too low monomer concentrations. Therefore, in what follows in this article we exclude reaction (5) from consideration. As a result we arrive at the following expressions for the rates of polymerization of FA (W_{polym}), decomposition of PB (W_{PB}), and formation of benzoic acid (W_{BK}):

$$W_{\text{polym}} \approx 2k_1/k_2\, k_0\, (2 + k_3/k_4)\, [\text{P}][M] \tag{I}$$

$$W_{\text{PB}} = k_0[\text{P}] + 2k_1' k_0/k_2[\text{P}][M] \tag{II}$$

$$M_{\text{BK}} = 2k_1/k_2\, k_0[\text{P}][M] \tag{III}$$

From these expressions it is evident that the rate of formation of BK is equal to the rate of decomposition of PB to within the small rate of monomolecular decomposition $k_0[\text{P}]$. During decomposition of PB in DFA an isotope effect is manifested in a decrease of the rate constant k_1. In MFA reaction (1) is entirely absent, and therefore neither appreciable polymerization nor chain decomposition of PB is observed. The average degree of polymerization

$$\bar{p} \simeq 2 + k_3/k_4,$$

whence, comparing with the average molecular weight of the polymer, we obtain

$$k_3/k_4 \simeq 5\text{–}6.$$

Owing to the closeness of the activation energies of reactions (3) and (4), the degree of polymerization is practically independent of temperature. Under radiation initiation of FA polymerization, the primary chain-initiation reaction is:

$$M \dashrightarrow R^{\cdot}, \tag{0'}$$

which is followed by reactions (3) and (4), and, in the general case, also by (5) of the scheme presented above. It is easy to verify that in this case also

$$\bar{p} \simeq 2 + k_3/k_4.$$

Thus, the length of the polymer chain depends neither on temperature nor on monomer concentration, nor on the type of initiation, which was also established experimentally. The total activation energy of FA polymerization and PB decomposition is

$$E = E_0 + E_1 - E_2 = 21 \text{ kcal/mol},$$

whereas

$$E_0 = 30 \text{ kcal/mol}.$$

Therefore, within the framework of the proposed scheme, the activation energy of the chain-termination reaction (2) must exceed by approximately 9 kcal/mol the activation energy of reaction (1)—chain propagation by transfer of the labile acetylenic hydrogen.

The inhibiting action of BH is reduced to capture of benzoyl radicals by the inhibitor, which suppresses reactions (1) and (2). The reaction of growing polymer radicals with BH, apparently, does not lead to inhibition, since there is no inhibiting action of BH on the polymerization of FA initiated by radiation and by the action of azobisisobutyronitrile.

Thus, the chain decomposition of PB in acetylenic hydrocarbons is due, on the one hand, to abstraction of the labile acetylenic hydrogen and, on the other, to the specificity of acetylenic polymerization, as a result of which

which form comparatively high concentrations of low-active polymer radicals that do not continue the polymer chain but are capable of decomposing benzoyl peroxide.

Institute of Chemical Physics,
Academy of Sciences of the USSR

Received
15 IV 1963

REFERENCES

[1] I. M. Barkalov, A. A. Berlin et al., *Vysokomolek. soed.*, **2**, 1103 (1960).
[2] I. M. Barkalov, V. I. Goldanskii et al., *Proceedings of the Second All-Union Conference on Radiation Chemistry*, Publishing House of the USSR Academy of Sciences, 1962.
[3] I. M. Barkalov, V. I. Goldanskii et al., *Vysokomolek. soed.*, **5**, No. 3 (1963).
[4] A. A. Berlin, L. A. Blumenfeld et al., *Vysokomolek. soed.*, **1**, 1361 (1959).

[5] I. M. Barkalov, A. A. Berlin et al., *Vysokomolek. soed.*, **5**, No. 3 (1963).
[6] Kh. S. Bagdasar' yan, R. I. Minyushinskaya, *ZhFKh*, **27**, 420 (1953).
[7] J. Campbell, S. O' Connor, *J. Am. Chem. Soc.*, **61**, 2897 (1939).
[8] K. W. Doak, *J. Am. Chem. Soc.*, **72**, 4691 (1950).
[9] A. A. Berlin, *Khim. prom.*, No. 12, 881 (1962); Report at a scientific colloquium under the Scientific Council of the Department of Chemical Sciences of the USSR Academy of Sciences on the problem "Theory of Chemical Structure, Kinetics, and Reactivity," December 26, 1962.

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