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ON MACROSCOPIC STAGES IN THE INITIATED REACTION OF BROMINATION OF PHENETOLE BY N,N-DIBROMO-5,5′-DIMETHYLHYDANTOIN IN DICHLOROETHANE

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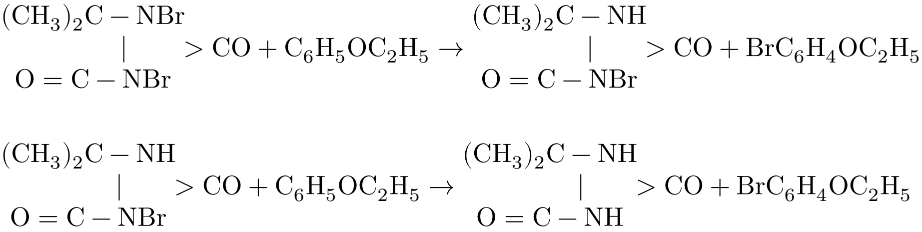
N. M. Emanuel' (1) drew attention to the widespread occurrence, in chain reactions, of phenomena of macroscopic staging. A real chain process, especially in complex chemical systems, is not a simple realization of one and the same sequence of elementary stages from the beginning of the reaction until complete consumption of the substance, but rather a complex reaction with distinct changes in its regime in the course of the reaction. Such a change in the regimes of a chain reaction was noted in its most demonstrative form in oxidation reactions. However, we have succeeded in showing the existence of a macroscopic stage also in such a chain reaction as the bromination of phenetole, initiated by diazoaminobenzene (DAAB), where N,N-dibromo-5,5′-dimethylhydantoin (DBDMH) was used as the brominating agent.

In previous works (2,3) we showed that the process of chlorination of phenetole in the presence of DAAB develops by a chain mechanism with participation of free radicals; moreover, only one chlorine atom participates in the chlorination reaction, apparently forming monochloramine-N-chlorobenzenesulfonamide. The clear difference in the character of the chlorination process of phenetole, which we observed from the consumption of N,N-dichlorobenzenesulfonamide and N-chlorobenzenesulfonamide, was explained by us from the point of view of their chlorinating activity. When N,N-dibromo-5,5′-dimethylhydantoin was used for this reaction instead of N,N-dichlorobenzenesulfonamide, it turned out that, despite the insignificant difference in the activity of the bromine atoms located in position 1 and position 3, in this case also there is a clear manifestation of the character of the consumption of one and the other bromine atoms. Figure 1 presents the kinetic curve for consumption of the halogenating agent in the DAAB-initiated reaction of bromination of phenetole by N,N-dibromo-5,5′-dimethylhydantoin according to the scheme:

Fig. 1. Bromination of phenetole by DBDMH and BDMH in dichloroethane.

Figure 1: Fig. 1. Bromination of phenetole by DBDMH and BDMH in dichloroethane.



$$\begin{array}{l}(CH_3)_2C-NBr\\ \qquad\qquad |\\ O=C-NBr\end{array} > CO + C_6H_5OC_2H_5 \rightarrow \begin{array}{l}(CH_3)_2C-NH\\ \qquad\qquad |\\ O=C-NBr\end{array} > CO + BrC_6H_4OC_2H_5$$

$$\begin{array}{l}(CH_3)_2C-NH\\ \qquad\qquad |\\ O=C-NBr\end{array} > CO + C_6H_5OC_2H_5 \rightarrow \begin{array}{l}(CH_3)_2C-NH\\ \qquad\qquad |\\ O=C-NH\end{array} > CO + BrC_6H_4OC_2H_5$$

As can be seen, the kinetic curve for consumption of the halogenating agent represents a clearly expressed two-stage process. The initially relatively rapid stage of bromination of phenetole, after consumption of one bromine atom, is replaced by a slower stage of the reaction, corresponding to the monobromoamine —N-bromo-5,5′-dimethylhydantoin (BDMH)—formed in the course of bromination.

The formation of monobromoamine (BDMH) and the nature of its brominating action with respect to phenetole were demonstrated by us in separate kinetic experiments with a deliberately known preparation of BDMH, obtained by direct bromination of dimethylhydantoin under the conditions described in the literature (4).

Kinetic experiments with BDMH were carried out under the same conditions as for DBDMH, and differed in that a doubled amount of BDMH was introduced as the halogenating agent, exactly corresponding in bromine content to the experiments with DBDMH.

In addition, phenetole in an amount of 0.04 mole was introduced into the experiment in two portions—the second portion of phenetole, in an amount of 0.02 mole, was added after the consumption of one bromine atom.

Fig. 1. Bromination of phenetole by DBDMH and BDMH in dichloroethane.
a—phenetole 0.04 mole, DBDMH 0.02 mole, DAAB 0.0003 mole, hydroquinone 0.0004 mole;
b—phenetole 0.04 mole, BDMH 0.04 mole, DAAB 0.0003 mole, hydroquinone 0.0004 mole.

Under the conditions of these kinetic experiments it was possible to reproduce completely the state of the reaction mixture with respect to its composition, as in the experiments with DBDMH. As in the latter, so also in the experiments with BDMH, by the time of reaction of the second bromine atom the reaction mixture contained: the substance being halogenated—phenetole, the bromination product—bromophenetole, the halogenating agent—BDMH, an inducer, and an antioxidant. The results of the indicated kinetic experiments are presented in Fig. 1 (the kinetic curve is denoted by open circles). It is not difficult to see that it coincides completely with the kinetic curve corresponding to the monobromoamine formed in the experiments with DBDMH.

Thus, the brominating action of DBDMH in its reaction with phenetole manifests itself in two clearly expressed macrostages. The BDMH formed in the course of the bromination reaction enters into reaction with phenetole only after the nearly complete consumption of the first bromine atom of DBDMH. The consumption of both the first and the second bromine atoms of DBDMH is described by the monomolecular law

$$(\Delta X)_\infty - \Delta X = (\Delta X)_\infty \cdot e^{-kt},$$

where ΔX is the amount of halogenating agent consumed by time t, and ΔX_∞ is the same by the end of the reaction for each bromine atom. The difference $(\Delta X)_\infty - \Delta X$ denotes the available amount of halogenating agent at each moment of time.

The semilogarithmic anamorphosis of the kinetic curve of DBDMH and BDMH is a straight line. The rate constants of the reactions calculated from it are $6 \cdot 10^{-2}$ min^{-1} and $1.6 \cdot 10^{-2}$ min^{-1}, respectively.

This phenomenon can be explained on the basis of the following assumptions. Evidently, DBDMH and BDMH decompose in the course of the reaction under the influence of the inductor according to the scheme:

$$\mathrm{DBDMH} \rightleftarrows \mathrm{Br}^{\cdot} + \mathrm{BDMH}^{\cdot}$$
$$\mathrm{BDMH} \rightleftarrows \mathrm{Br}^{\cdot} + \mathrm{DMH}^{\cdot}$$

$$k_1 = \frac{\mathrm{Br}^{\cdot} \cdot \mathrm{BDMH}^{\cdot}}{\mathrm{DBDMH}} > k_2 = \frac{\mathrm{Br}^{\cdot} \cdot \mathrm{DMH}^{\cdot}}{\mathrm{BDMH}}.$$

Let us assume that $k_1 \gg k_2$. Then the concentration of the bromine atom will depend on the concentration of DBDMH, and the dissociation of BDMH will be suppressed. It follows from this that the dissociation of BDMH into an atomic bromine and a radical will be minimal as long as DBDMH is present in the solution in an amount sufficient to make the concentration of DMH$^{\cdot}$ so low that this radical will not participate in the development of the bromination chain reaction. This assumption is confirmed by experiments with the addition of DMH$^{\cdot}$ to the reaction mixture. In the case of the bromination reaction of DBDMH, the addition of DMH inhibits the rate of the bromination reaction, which is probably explained by the fact that DMH reacts with DBDMH to form BDMH. After DBDMH has been consumed, the influence of DMH disappears and DMH, as the experiments showed, has no effect on the course of the bromination reaction of BDMH.

In view of the fact that, under the experimental conditions, the inductor and the antioxidant are brominated by DBDMH, phenetole was introduced after their exhaustive halogenation and after determination of the zero point of the brominating agent.

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REFERENCES CITED

1. N. M. Emanuel, *Problems of Chemical Kinetics, Catalysis, and Reactivity*, Publishing House of the Academy of Sciences of the USSR, 1955, p. 117.
2. K. A. Kornev, DAN, **100**, 1091 (1955).
3. K. A. Kornev, DAN, **105**, 720 (1955).
4. Orfeo O. Orazi, J. Meseri, cited in *Chem. Abstr.* **44**, 1950, p. 4423.

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