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REACTIONS OF FREE RADICALS IN SOLUTIONS. THERMAL DECOMPOSITION OF TRIAZENES IN VARIOUS MEDIA

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Recently, much attention has been devoted to the study of the kinetics of decomposition of various compounds that serve as sources of free radicals. This applies especially to organic peroxides and hydroperoxides (1-4). As was shown by Kh. S. Bagdasar' yan and R. I. Milyutinskaya (5), and also by other authors (1, 2), benzoyl peroxide at comparatively high concentrations decomposes by a chain mechanism.

In the present work the kinetics of decomposition of a series of triazenes in various systems was studied. The rate of decomposition was determined from the rate of gas evolution during the reaction.

Table 1

Rate constants of the decomposition reaction
$K_1 \cdot 10^{-4}$ sec^{-1} of ethyldiphenyltriazene in various media at 100°

Solvent	Concentration (C), mol. %	Concentration (C), mol. %	Concentration (C), mol. %	Concentration (C), mol. %
	1.3	4	13	25
Isopropylbenzene	1.2	1.6	2.2	2.7
Styrene	2.4	6.1	–	–

Using ethyldiphenyltriazene (EDT) and propyldiphenyltriazene as examples, it was shown that, with increasing concentration of triazenes in solution, the rate constants of the decomposition reaction increase (Table 1). This fact indicates that, under these conditions, chain decomposition occurs.

Fig. 1. Kinetics of decomposition of propyldiphenyltriazene at 120°: 1–$C = 15$ mol. %, 2–$C = 20$ mol. %.

At concentrations of 15-25 mol. % and a temperature of 120°, when the number of radicals in the system is very large, the chain decomposition of triazenes pro-

Fig. 1. Kinetics of decomposition of propyldiphenyltriazene at 120°: 1–$C = 15$ mol. %, 2–$C = 20$ mol. %.

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ceeds to such an extent that the kinetic curve does not obey the monomolecular law (Fig. 1).

In the decomposition of ethyldiphenyltriazene in styrene, the growth of the rate constant of this reaction with increasing concentration occurs to a much greater extent than in isopropylbenzene, which is connected with a considerable increase in the concentration of free radicals as a result of the development of the chain polymerization process.

Along with the increase in the rate constants of decomposition of triazenes with increasing concentration in solution, a decrease is observed in the yield of RH products formed according to the reaction:

$$\mathrm{R} \cdot + \mathrm{LH} \rightarrow \mathrm{RH} + \mathrm{L}\cdot,$$

where LH is a solvent molecule.

Table 2

Yield of RH products as a function of the initial concentration of triazenes at 120°

Ethylphenyltriazene		
concentration, mole %	1.3	25
yield of RH_1, % of theoretical	37	22

Propylphenyltriazene				
concentration, mole %	1.3	15	20	25
yield of RH_1, % of theoretical	24	22	20	15

It is most probable that this decrease in the yield of products of hydrogen abstraction from the solvent molecule is connected with the development of a chain decomposition process owing to consumption of radicals in reaction with the triazene.

The chain character of the decomposition of triazenes at elevated concentrations is confirmed by the fact that, when sulfur is introduced into the system, the decomposition rate constants decrease (Table 3 and Fig. 2). As established by M. P. Tikhomolova et al. (^{6}), sulfur is a good acceptor of free radicals.

Fig. 2. Kinetics of decomposition of ethylphenyltriazene at 100°: 1 –C = 25 mole % (without S), 2 –C = 25 mole %, 3 –C = 12.5 mole %, 4 –C = 1.3 mole %, 5 –C = 4 mole %

Figure 2: Fig. 2. Kinetics of decomposition of ethylphenyltriazene at 100°: 1 –C = 25 mole % (without S), 2 –C = 25 mole %, 3 –C = 12.5 mole %, 4 –C = 1.3 mole %, 5 –C = 4 mole %

Table 3

Rate constants of the decomposition reaction of ethylphenyltriazene in isopropylbenzene in the presence of sulfur at 100° $\frac{S}{\text{EPT}}$ (wt. %) = 2

Concentration, mole %	1.3	4	13	25
$K \cdot 10^{-4}$ sec^{-1}	1.2	1.2	1.4	1.7

However, sulfur is not able completely to suppress the development of the chain process, which is especially noticeable at higher temperatures. Thus, at 120° and a triazene concentration of 25 mole % in the presence of sulfur, $K_1 = 15 \cdot 10^{-4}$ sec^{-1} (at a concentration of 1.3 mole %, $K_1 = 3.5 \cdot 10^{-4}$ sec^{-1}). Without sulfur under these conditions the decomposition proceeds in 7-10 min almost completely, which excludes the possibility of obtaining accurate kinetic data.

Fig. 2. Kinetics of decomposition of ethylphenyltriazene at 100°: 1 –C = 25 mole % (without S), 2 –C = 25 mole %, 3 –C = 12.5 mole %, 4 –C = 1.3 mole %, 5 –C = 4 mole %.

In the case of isopropylphenyltriazene, the presence of sulfur causes an unexpected effect—a strong acceleration of the decomposition process. The kinetic curve, calculated according to the monomolecular law, has a break at the point corresponding to 70% decomposition. Below this point $K_1 = 20.8 \cdot 10^{-4}$ sec^{-1}, above it $K_1 = 10 \cdot 10^{-4}$ sec^{-1}. In the absence of sulfur, $K_1 = 9.0 \cdot 10^{-4}$ sec^{-1}. The acceleration of decomposition in the presence of sulfur in this case is possibly explained by the fact that the sulfide radicals formed prove sufficiently active for the development of chain decomposition of the triazene. As Kooyman showed (^{7}), RS • radicals, where R is an alkyl substituent of iso-structure ($(CH_3)_2CH$, $(CH_3)_2C$), have greater activity in the hydrogen-abstraction reaction than those in which R has a normal structure.

As is known, recently, for trapping free radicals and preventing the chain decomposition of various compounds, in particular peroxides and azo compounds, α,α-diphenyl-β-picrylhydrazyl has been used. In the case of triazenes this method proved inapplicable, since α,α-diphenyl-β-picrylhydrazyl greatly accelerates their decomposition.

Fig. 3. Dependence of the rate constant of the decomposition reaction of triazenes on temperature: 1 —methyl-, 2 —ethyl-, 3 —benzyl-, 4 —hexylphenyltriazenes

Figure 3: Fig. 3. Dependence of the rate constant of the decomposition reaction of triazenes on temperature: 1 —methyl-, 2 —ethyl-, 3 —benzyl-, 4 —hexylphenyltriazenes

From the data given in Tables 2 and 3 it follows that at a concentration of 1.3 mol % chain decomposition is practically absent. The kinetic data obtained at this concentration were used to determine the activation energy of the decomposition reaction of methyl-, ethyl-, benzyl-, and hexylphenyltriazenes. For methyl- and ethylphenyltriazenes the measurements were duplicated in the presence of sulfur. In these two cases the rate constants of decomposition at various temperatures are the same as without sulfur. The values of the rate constants and activation energies are given in Table 4 and in Fig. 3.

Fig. 3. Dependence of the rate constant of the triazene decomposition reaction on temperature: 1 —methyl-, 2 —ethyl-, 3 —benzyl-, 4 —hexylphenyltriazenes

Table 4

Rate constants and activation energy of the thermal decomposition reaction of triazenes*

Triazene	E, kcal/mol	$K_1 \cdot 10^{-4}$, sec.$^{-1}$, temperature, °C: 100	$K_1 \cdot 10^{-4}$, sec.$^{-1}$, temperature, °C: 110	$K_1 \cdot 10^{-4}$, sec.$^{-1}$, temperature, °C: 120	$K_1 \cdot 10^{-4}$, sec.$^{-1}$, temperature, °C: 130
Methylphenyltriazene	31 ± 2	–	2.4	6.6	18.8
Ethylphenyltriazene	29 ± 2	1.2	3.1	8.5	–
Benzylphenyltriazene	28 ± 2	1.5	4.1	10.5	–
Hexylphenyltriazene	31 ± 2	1.6	4.9	13.8	–

* Data published earlier proved to be erroneous (8), since the starting substances were not sufficiently pure.

Experimental Part

All triazenes were synthesized by the action of magnesium bromo derivatives on phenyl azide (9, 10). The decomposition of the triazenes was carried out in an atmosphere of nitrogen in accordance with the procedure described earlier (11).

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