Reports of the Academy of Sciences of the USSR

PHYSICAL CHEMISTRY

1962

SovietRxiv

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Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1962. Volume 147, No. 5

PHYSICAL CHEMISTRY

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FORMATION OF DIARYL NITROXIDE RADICALS IN REACTIONS OF AMINES WITH PEROXIDE RADICALS

(Presented by Academician V. N. Kondrat' ev, July 19, 1962)

Numerous works devoted to the study of the processes of hydrocarbon oxidation in the liquid and solid phases have established that this process is a pronounced radical-chain process (^{1}), in which the growth of kinetic chains occurs through radicals $\dot{R}$ and $RO\dot{O}$, and chain branching occurs through the further transformation of the intermediate hydroperoxide, leading to the formation of active radicals. In close connection with such concepts, it is generally accepted in the literature (^{2,4,5}) that inhibitors (in particular, amines) react with radicals $\dot{R}$ and $RO\dot{O}$, thereby breaking the kinetic chains of oxidation. In some cases inhibitors can interact in a specific manner with hydroperoxides, leading to suppression of chain-branching reactions (^{3}).

Fig. 1. E.p.r. spectra of cumene samples irradiated at −170°: *a* —cumene in the absence of oxygen, *b* —cumene in an oxygen atmosphere, *c* —cumene with an addition of cumene hydroperoxide (∼ 1%).

In our work we made an attempt to investigate the reaction between radicals and molecules of the inhibitor InH under conditions not complicated by other reactions. The method used consisted in irradiating hydrocarbon samples containing the inhibitor with fast electrons of energy about 1.6 MeV. In experiments in which irradiation was carried out at low temperatures, accumulation of considerable concentrations of radicals was observed. Registration of the radicals by the e.p.r. method was performed directly during irradiation (6). Upon warming the samples, a gradual decrease in the intensity of the e.p.r. spectra was observed.

As a model hydrocarbon we used cumene, which readily forms organic glasses upon a sharp lowering of temperature. Among secondary amines, diphenylamine and phenyl-β-naphthylamine were investigated. Upon irradiation of frozen cumene with fast electrons in the absence of oxygen, radicals of the type $\dot{R}$ accumulate; their e.p.r. spectrum is shown in Fig. 1*a*. The spectrum is a triplet with additional structure; it is characteristic of radicals arising under radiation action on aromatic compounds (7) and is a superposition of two spectra, one of which belongs to the radical formed by abstraction of an H atom from the side chain of cumene, and the other as a result of addition of an H atom to the double bond of the benzene ring. In the presence of a large amount of oxygen (in our experiments, 5-10 atm above the cumene sample) such radicals are rapidly converted into $RO\dot{O}$ radicals, whose e.p.r. spectrum is shown in Fig. 1*b*.

It was shown in the work that addition to cumene of 1-3% diphenylamine or phenyl-β-naphthylamine has no substantial effect on the nature of the radicals formed upon irradiation. In this case there occurs only a slight-

a change in the yield of radicals. To detect whether a reaction occurs between the radicals $\dot{R}$ or $\mathrm{ROO^{\cdot}}$ and the amine molecule, we slowly warmed the irradiated samples to temperatures above the melting point. It was established that, in the case of $\dot{R}$ radicals, after passing through the melting point no paramagnetic particles remained in the samples. On the contrary, in the case of $\mathrm{ROO^{\cdot}}$ radicals, as warming proceeded the form of the EPR spectrum of the peroxide radical changed, and after melting a clear regular triplet with a line ratio of $1:1:1$ was recorded, corresponding to the EPR spectrum of the radical $\mathrm{Ar_2\dot{N}O}$ (4,5,8).

Thus, from the results of the work it may be concluded that peroxide radicals vigorously oxidize the secondary amine and that, in this case, processes apparently proceed according to the scheme

$$\mathrm{ROO^{\cdot}} + \mathrm{HNAr_2} \rightarrow \mathrm{ROOH} + \mathrm{\dot{N}Ar_2}, \tag{1}$$

$$\mathrm{ROO^{\cdot}} + \mathrm{\dot{N}Ar_2} \rightarrow \mathrm{\dot{R}O} + \mathrm{O\dot{N}Ar_2}. \tag{2}$$

Thomas (5), who investigated the accumulation of $\mathrm{(C_6H_5)_2\dot{N}O}$ radicals during the catalytic oxidation of certain hydrocarbons, came to an analogous conclusion. It should be noted that irradiation of the system cumene $+\mathrm{O_2}$ + $\mathrm{Ar_2NH}$ at temperatures above the melting point does not lead to the formation of $\mathrm{Ar_2\dot{N}O}$. The fact we observed, that stable radicals are not formed when $\dot{R}$ radicals interact with an $\mathrm{Ar_2NH}$ molecule, apparently indicates that the radicals $\mathrm{Ar_2\dot{N}}$

formed in the primary act prove to be active radicals that rapidly recombine with $\dot{R}$ radicals to form stable products

$$\mathrm{Ar_2\dot{N}} + \dot{R} \rightarrow \mathrm{Ar_2NR}. \tag{3}$$

Further, we showed that $\dot{R}$ or $\mathrm{ROO^{\cdot}}$ radicals, when continuously generated, are capable of interacting with $\mathrm{Ar_2\dot{N}O}$ radicals. We synthesized $\mathrm{(C_6H_5)_2\dot{N}O}$ radicals, prepared their solution in cumene, and irradiated it with electrons at room temperature in the absence of air and in an atmosphere of oxygen. In both cases, intense destruction of the $\mathrm{(C_6H_5)_2\dot{N}O}$ radicals was observed. We suppose that in this case the following processes occur:

$$\dot{R} + \mathrm{O\dot{N}(C_6H_5)_2} \rightarrow \mathrm{RON(C_6H_5)_2}, \tag{4}$$

$$\mathrm{ROO^{\cdot}} + \mathrm{O\dot{N}(C_6H_5)_2} \rightarrow \mathrm{RON(C_6H_5)_2} + \mathrm{O_2}. \tag{5}$$

On irradiating cumene containing cumene hydroperoxide, at low temperatures we observed a complex spectrum (Fig. 1*b*), which is a superposition of the spectra of several radicals. Upon warming, this spectrum was transformed and acquired the form shown in Fig. 1*b*, completely coinciding with the form of the EPR spectrum of peroxide radicals. A detailed investigation of this phenomenon led us to the conclusion that, in the radiolysis of cumene hydroperoxide, along with other radicals, radicals of the $\mathrm{ROO^{\cdot}}$ type are also formed. It turned out that irradiation of cumene containing an admixture of hydroperoxide gives a considerably higher radiation yield of radicals in comparison with the cumene + oxygen system.

We investigated the interaction of such radicals with secondary amines by irradiating samples of cumene + cumene hydroperoxide + amine at different concentrations of the last two components.

In this case, too, the formation of diarylnitroxide radicals is observed. Apparently, as in the preceding case, reactions proceeded

(1) and (2). Along with this, upon irradiation of solutions of the amine in cumene containing hydroperoxide, evidently another process of formation of $\mathrm{Ar_2\dot{N}O}$ radicals also takes place. This follows from the aftereffect observed by us, which consists in the following. If cumene containing cumene hydroperoxide and amine is irradiated at temperatures above 0°C, then a noticeable increase in the concentration of $\mathrm{Ar_2\dot{N}O}$ radicals is observed immediately. Further irradiation leads to a decrease in their concentration (apparently, through reactions (4) and (5)) to a certain limit, depending on the intensity of the electron flux. It is noteworthy that after irradiation an increase in the concentration of $\mathrm{Ar_2\dot{N}O}$ radicals is observed for a long time. Repeated irradiation leads to a sharp decrease in the concentration of the radicals. The picture observed in this case is shown in Fig. 2.

Fig. 2

Figure 2: Fig. 2

Fig. 2. Change in the concentration of $Ar_2\dot{N}O$ radicals during irradiation (I), after irradiation (II), and upon repeated irradiation (III) of a solution of cumene hydroperoxide (20%) and diphenylamine (1.7%) in cumene at 40°. Dose rate $\sim 1.5 \cdot 10^4$ rad/sec.

It turned out that the increase in the concentration of $Ar_2\dot{N}O$ radicals in the aftereffect proceeds up to a certain limit. The magnitude of this limit increases with the irradiation dose and the temperature at which irradiation was carried out, and depends only weakly on the hydroperoxide concentration. Thus, for example, in pure hydroperoxide and in its 20% solution the observed effects differed by no more than 10%. Analysis of the curve for the accumulation of $Ar_2\dot{N}O$ in the aftereffect shows that the accumulation of radicals obeys the law of first-order reactions. The aftereffect is especially strongly manifested in the case of phenyl-β-naphthylamine. It should be noted that the yield of $Ar_2\dot{N}O$ in the aftereffect period, as measurements show, is approximately a thousand times smaller than the radiation yield of $RO\dot{O}$ radicals in the preceding irradiation period. The kinetic curve (Fig. 2) for the accumulation of $Ar_2\dot{N}O$ radicals during radiolysis of cumene hydroperoxide solutions, passing through a maximum, is unusual for the kinetics of radical accumulation under radiolysis. In most cases, a tendency is observed for the radical concentration to reach saturation.

It turned out that upon irradiation of frozen cumene containing additions of hydroperoxide and diphenylamine, certain specific features appear. We studied the radiation yield of paramagnetic particles at low temperatures in samples of pure cumene and in samples of cumene containing hydroperoxide and diphenylamine. It turned out that additions of hydroperoxide substantially increase the yield of paramagnetic particles, diphenylamine has practically no effect, and introduction of a mixture of peroxide and amine increases the radiation yield of paramagnetic particles especially strongly. The results of these experiments are presented in Fig. 3. In the presence of different additives, the character of the EPR spectrum also changes, which indicates the formation of different kinds of paramagnetic particles. A possible explanation for the increase in the radiation yield of paramagnetic particles (radicals or ion radicals) may be the assumption of the existence of a molecular complex between ROOH and Ar_2NH, where the association of the compounds is due to a hydrogen bond. In the course of radiolysis such complexes may decompose with the formation of paramagnetic particles.

The formation of complexes between peroxide compounds and amines is postulated in a number of works (9, 10).

The available experimental data do not make it possible to explain the char-

Figure 3 graph

Figure 3: Figure 3 graph

acteristic course of the change in concentration with irradiation dose for liquid samples (Fig. 2). One can only assert that there are at least two mechanisms for the formation of these radicals, one of which is associated with reactions (1) and (2), and the other with a bimolecular reaction proceeding through the excited complex $[\mathrm{ROOH}\cdot\mathrm{HNAr_2}]^*$. The recombination processes (4) and (5) undoubtedly play a substantial role. However, they cannot explain the decrease in concentration that is observed after its initial increase (Fig. 2). This decrease is probably associated with the formation of some radiolysis products that slow the processes of radical generation.

Fig. 3. Effect of additions of diphenylamine and cumene hydroperoxide on the radiation yield of paramagnetic particles: *a*—pure cumene, *b*—with addition of diphenylamine (3%), *v*—with addition of cumene hydroperoxide (1%), *g*—with additions of diphenylamine (3%) and cumene hydroperoxide (1%). Temperature −180°.

The cause of the aftereffect is also unclear. However, we think that its most probable explanation is the formation, in the process of radiolysis, of products of incomplete oxidation of $\mathrm{Ar_2\dot{N}H}$ (for example, diarylhydroxylamine), which in the presence of hydroperoxide will be oxidized to $\mathrm{Ar_2\dot{N}O}$. (It is known (8) that $\mathrm{Ar_2NOH}$ compounds are readily oxidized to $\mathrm{Ar_2\dot{N}O}$ by silver oxide.)

Possible processes in this case may be:

upon irradiation

$$\mathrm{RO\dot{O}} + \mathrm{HNAr_2} \to \mathrm{ROOH} + \mathrm{Ar_2\dot{N}}, \qquad \mathrm{ROOH} + \mathrm{Ar_2\dot{N}} \to \mathrm{R\dot{O}} + \mathrm{Ar_2NOH}$$

and after irradiation

$$\mathrm{ROOH} + \mathrm{Ar_2NON} \to \mathrm{R\dot{O}} + \mathrm{H_2O} + \mathrm{Ar_2\dot{N}O}.$$

At high hydroperoxide concentration the formation of $\mathrm{Ar_2\dot{N}O}$ radicals will obey the laws of a first-order reaction.

It follows from the experimental data presented that the presence of peroxide compounds strongly affects the overall pattern of behavior of secondary amines in radical processes. In this case it is necessary to take into account the interaction between amines and peroxide compounds, or the products of their further transformation.

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Received
11 VII 1962

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