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The Effect of γ-Radiation on the Oxidation Reaction of Cetane

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The effect of ionizing radiation on the course of chemical reactions may be of fundamentally different character: on the one hand, it proves possible to induce processes that are practically unattainable by other methods—for example, to obtain phenol from a mixture of benzene and water in the presence of oxygen ([1]); on the other hand, radiation may sharply accelerate a number of slowly proceeding reactions. The latter should be especially pronounced if the reaction proceeds by a chain mechanism. This is supported both by the known facts concerning the photochemical action on chain reactions and by direct experiments on the initiation of polymerization reactions by ionizing radiation ([2]).

In the case where a chain mechanism is not realized, the yield of reaction products is equivalent to the number of initial particles formed by the action of secondary electrons on the molecule. However, to achieve this limiting yield it may prove necessary to resort to the action of catalytic additives that increase the "utilization coefficient" of the initial chemically active particles, as was shown by two of the authors of the present article in the example of the radiolytic oxidation of benzene ([3]). The possibility of radiation initiation of short chains in the oxidation of hydrocarbons was indicated in the works of N. A. Bakh ([4]).

However, especially complex and interesting relationships may arise in the case of reactions with branching or degenerate branching ([5]). Reactions of this type are characteristic, for example, of the practically important case of the oxidation of paraffin hydrocarbons by molecular oxygen.

In the works of V. K. Tsiskovskii ([6]), D. N. Chernyaev ([7]), and especially N. M. Emanuel' ([8]), the role of catalytic additives in the oxidation reactions of these hydrocarbons was elucidated. It is mainly reduced to the fact that the catalyst is the initiator of the reaction—it causes the formation of certain active chemical substances which then conduct the reaction. The catalyst itself may be removed from the reaction mixture at this stage. Radiation may also play the role of such an initiator, as was indicated in many works on chain theory ([5]) and was demonstrated experimentally in the example of the polymerization process ([2]). Recently, N. M. Emanuel' has pointed to the advisability of using

Fig. 1. Schematic of the apparatus

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radiation to initiate the oxidation of high-molecular-weight hydrocarbons.

We carried out experiments on the oxidation of cetane by molecular oxygen under the action of γ-radiation from Co^{60}.

The experiments were carried out using a specially equipped source with an activity of 300 g-equiv ([9]). The design made it possible to remove the source behind shielding and to study the kinetics of accumulation of oxidation products by taking liquid samples both during irradiation and in the post-radiation period.

Figure 1 shows a schematic of the apparatus, the reaction vessel, and its position relative to the radiation source. The temperature in the furnace was maintained —

was kept constant to an accuracy of $±$1° by means of contact galvanometer 3, connected to thermocouple , mounted in the furnace. The temperature of the reaction mixture was determined with the aid of another thermocouple (in finger), the readings of which were recorded by self-recording potentiometer .

In Fig. 2, by way of example, a curve obtained during such recording over the course of one experiment is shown. The arrow indicates the moment at which irradiation was stopped. The small brief drops in temperature on the graph correspond to the moments when samples were taken.

Fig. 1. Schematic of the apparatus: —vessel in which irradiation is carried out, —finger for the thermocouple, —tubes through which oxygen is continuously passed, —apparatus for purifying oxygen, and —traps with liquid air, —furnace for heating the reaction vessel, —galvanometer, —thermocouple, —self-recording potentiometer, —oxygen cylinder

The volume of cetane poured into the apparatus was 100 cm^3. For the experiments a fraction of technical cetane was used, boiling in the range 120-125° at a pressure of 1-2 mm, $n_D^{20} = 1.4374$, $\rho_4^{20} = 0.7783$, iodine number = 0.2. Determination of the dose rate was carried out by the ferrous sulfate method in a calibration experiment, in which, instead of cetane, a solution of Mohr' s salt (10^{-3} n) in 0.8 n H_2SO_4 was placed in the reaction vessel. The yield of this reaction was taken to be 15.6 molecules per 100 eV [(10)]. The average dose rate was 80 r/sec. Analyses were carried out chiefly for the sum of nonvolatile carbon acids, by the method of titration with alkali [(11)]. The experiments were conducted at a temperature of 130° and at atmospheric oxygen pressure. Cetane samples were placed in the preheated reaction vessel, after which oxygen was passed through while irradiation was simultaneously switched on. Samples were taken by forcing several cubic centimeters of the reaction mixture out of

Fig. 2. Temperature stability during the experiment

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Figure 3

Figure 3: Figure 3

the vessel with oxygen for analysis. This procedure made it possible to maintain a stationary regime inside the vessel.

Fig. 2. Temperature stability during the experiment (on the ordinate axis, 1 mm corresponds to 1°C)

In Fig. 3 the kinetic curves are presented for the nonvolatile carbon acids formed during oxidation. The portions of the curves corresponding to

period of irradiation are shown by a dashed line. The vertical lines denote the moment at which irradiation was stopped. Curves 1-5 were obtained in experiments with different irradiation durations (from 0.25 to 3 h). In the experiment corresponding to curve 6, no irradiation was carried out.

Fig. 3. Formation of nonvolatile carboxylic acids as a function of time under the action of different radiation doses (integral dose, r/cm^3): 1–5.76; 2–1.44; 3 –8.64; 4–2.88; 5–7.2; 6–without irradiation.

From the curves presented it is evident that, when radiation acts on the reaction mixture, the rate of the cetane oxidation reaction increases to a considerable extent. However, when the irradiation period exceeds ~30 min, the reaction rate practically ceases to depend on the duration of irradiation. In other words, further increase of the irradiation period does not increase the oxidation rate.

Thus, under the conditions of our experiments, initiation of the cetane oxidation process by radiation is most rationally carried out by irradiating the reaction mixture for ~30 min and then stopping the irradiation. Undoubtedly, there is a close analogy between the phenomenon described and the phenomena occurring in the catalytic oxidation of hydrocarbons, when the catalytic additive can be removed from the reaction mixture some time after the start of the reaction, while the reaction continues to proceed at the same rate.

An explanation of this phenomenon was given by N. M. Emanuel' from the standpoint of the theory of degenerate branching ([8]). Assuming that degenerate branching occurs on the final product, while chain termination follows a linear law, he showed that, beginning from some time t, the action of the catalyst does not cause a further increase in the reaction rate. This time is determined by the relation:

$$t \gg k \ln \left(1 - \frac{\omega_{0k}}{\omega_{0k}}\right),$$

Fig. 4. Formation of peroxide compounds under the action of radiation: 1—irradiation period 3 hr, 2—without irradiation

Figure 4: Fig. 4. Formation of peroxide compounds under the action of radiation: 1—irradiation period 3 hr, 2—without irradiation

where ω_0 is the rate of chain initiation in the absence of the catalyst, ω_{0k} is the rate of chain initiation in the presence of the catalyst, and k is a coefficient that is a combination of the elementary reaction constants.

If such a scheme proves, at least formally, valid for reactions initiated by irradiation, then, since ω_{0k} may be regarded as approximately proportional to the dose rate, the expression for t in this case takes the form:

$$t \gg k \ln \left(1 - \frac{a}{p}\right),$$

where p is the dose rate and a is a quantity constant at constant temperature. It may be assumed, however, that this dependence must have a more complex form, since it is more probable to suppose that chain termination occurs not linearly, but quadratically. In this case, in the expressions describing the macroscopic rate of the reaction, instead of p, as often occurs in photochemical reactions, $\sqrt{p}$ should appear.

Thus, the question of the relationship between t and p is very important from the standpoint of the theory of the process. The practical significance of this question is evident. Therefore further investigations should be directed toward its solution. We shall note only that from the consideration carried out it can already be seen that, with an increase in the dose rate, one should expect not only an increase in the rate of oxidation, but also a decrease in the required irradiation period.

Fig. 4. Formation of peroxide compounds under the action of radiation: **1**—irradiation period 3 hr, **2**—without irradiation.

Along with the determination of nonvolatile acids, in a number of experiments we analyzed the acids volatile at the experimental temperature, frozen out from the stream of oxygen leaving the reactor, and also peroxide compounds according to K. I. Ivanov [12]. It was found that, under the action of irradiation, the rate of formation of these products also increases. The kinetic curves for the formation of peroxides are shown in Fig. 4.

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