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Abstract

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THE INITIATING ACTION OF RADON RADIATION IN THE PROCESS OF OXIDATION OF ISODECANE (2,7-DIMETHYLOCTANE)

(Presented by Academician V. N. Kondrat' ev, December 28, 1957)

The proposal to use the radiation of radioactive inert gases to initiate chain reactions was put forward by one of us as a logical consequence of the principle of gas initiation by chemically active gases (^1) and of the effect of the stimulating action of penetrating radiation (^2).

At present, in the arsenal of the experimental chemist, in addition to radioactive emanations—radon, thoron, and actinon—there are also Xe^{133}, Kr^{85}, and Ar^{41}. The latter three radioactive isotopes can be obtained from the corresponding inert unreactive gases by the (n, γ)-reaction. In addition, Xe^{133} and Kr^{85} are fission products of U^{235} and Pu^{239} and are released during the purification of nuclear-fuel blocks contaminated with fission products.

The use of inert radioactive gases makes it possible, for initiation purposes, to employ all types of radiation: α, β, and γ, at different values of radiation energy. Moreover, the α- and β-particles emitted by the corresponding radioactive atoms enter the reacting system directly and exert their action uniformly throughout the entire mass of the liquid. This is very important, since the introduction of these particles into the reaction vessel from external sources is associated with enormous difficulties or is altogether impossible because of their strong absorption by the vessel wall or by the window material.

The use of radiation from radioactive gases for initiation purposes should be highly effective not only in the case of slow chain liquid-phase reactions. There is also no doubt that the use of radioactive gases will make it possible to carry out interesting experiments with gas-phase chain reactions.

In the present work, as the object of study we chose the reaction of oxidation of isodecane (2,7-dimethyloctane) under the action of α-particles of radon. We proceeded from the fact that the processes of hydrocarbon oxidation in the liquid phase are strongly branched chain reactions. This means that stimulation of such processes can be carried out only in the initial period of the development of the process.

The action of radon radiation leads to the appearance in the system of active

Fig. 1. Diagram of the experimental setup

Figure 1: Fig. 1. Diagram of the experimental setup

particles—free radicals and atoms, i.e., to an increase in the initial rate of chain initiation w_0. In the case of exposure to radioactive gases, the magnitude of w_0 can easily be calculated from the energy of the ionizing radiation and the energy of the bond broken in the original hydrocarbon. This circumstance is one of the advantages of using radioactive inert gases as initiators in comparison with chemically active gases.

The experiments were carried out on a glass apparatus (Fig. 1), including an oxidation cell of the type adopted in our work on liquid-phase oxidation (ˆ3).

The mixture of radon with oxygen was prepared in flask *1*, equipped with a test tube with openings and with a double ground joint; the upper joint is intended for turning rod *R*, which breaks the ampoule with radon placed in the test tube, and the lower one for fastening the test tube in the flask.

To avoid losses of radon into the surrounding atmosphere, the system operated under a slight vacuum (700 mm Hg). Oxygen containing radon was pumped by a water-jet pump from flask *1* through an oxidation cell placed in an air thermostat at a temperature of 120° and was led out through three U-shaped traps connected in series, filled with activated charcoal and cooled to a temperature of −80°. The unreacted oxygen, freed from radon by adsorption of the latter on the charcoal, was discharged into the atmosphere.

Fig. 1. Diagram of the experimental setup

After the initiating action of radon had ended (one hour after the beginning of the experiment), the flask was disconnected and oxidation was carried out with pure oxygen from a cylinder. Under the conditions of our experiments, the reaction is affected by the radiation of radon bubbling through the liquid, by dissolved radon, and by radon present in the gas phase above the surface of the liquid. In addition, the daughter products of Rn decay play a substantial role. In calculating the integral dose we took into account all these sources of radioactive effects on isodecane. With an initial radon activity in the ampoule of 12 mCi, the total dose received by the system during one hour of initiation proved to be 615 rad. It is interesting to note that, under the conditions of our experiments, the principal action is exerted by radon dissolved in isodecane (165 rad) and by the daughter radioactive decay products (437 rad). The action of the radioactive decay products, which constitutes a considerable part of the total radiation dose, continues for some time after the initiation period, i.e., after the radon has been completely blown out of the liquid by a stream of pure oxygen. However, this aftereffect period of the active deposit does not exceed 1-1.5 hours, and during this time the activity of the deposit falls sharply (after 20 min only 30% of the activity at the end of the initiation period remains). Thus, under the conditions of our experiments (with an initial radon activity of

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

12 mCi), the initiating action of radon continued for at most 2.5 hours.

It should be noted that when chemically active gaseous initiators of liquid-phase oxidation of hydrocarbons (NO_2, Cl_2, O_3, etc.) are used, we restrict—

were initiated with significantly shorter initiation times. However, with respect to the oxidation reaction of isodecane at 120°, an irradiation exposure time of 2.5 hours is not excessively long, since the noninitiated reaction of acid formation under these conditions has an induction period on the order of 20 hours.

Fig. 2. Kinetic curves of the accumulation of hydroperoxides in the course of oxidation of isodecane at 120°. **1** —noninitiated reaction, **2** —exposure to Rn (initial activity 12 mCu) for 1 hour, **3** —change in the total activity in the course of the reaction (right-hand scale)

Fig. 3. Kinetic curves of the accumulation of acids in the course of oxidation of isodecane at 120°. **1** —noninitiated oxidation, **2** —oxidation under the action of Rn (initial activity 7 mCu) for 1 hour, **3** —the same at an initial activity of 12 mCu, **4** —change in the total activity in the course of the reaction

The kinetic curves of the accumulation of peroxides and acids during the oxidation of isodecane initiated by the α-radiation of radon (as well as by the α- and β-radiation of the decay products of Rn) are presented in Fig. 2 and Fig. 3. In the same figures, the dotted curves show the change in total activity with time at an initial radon activity in the ampoule of 12 mCu.

Fig. 2 shows that the short-term stimulating action of radon radiation is sufficient for a significant reduction in the induction period in the formation of hydroperoxides. The maximum yield of peroxide compounds also increases.

From a comparison of the kinetic curves of acid accumulation (**2** and **3**) with curve **1** for noninitiated oxidation (Fig. 3), the effect of a short-term stimulating action is also very clearly apparent. If, under ordinary conditions, in autoxidation, the process of acid formation begins only 20 hours after the supply of oxygen, then, when 12 mCu of Rn is added to the oxygen and this gas is passed through isodecane at 120° for 1 hour (curve **3**), noticeable amounts of acids appear in the reacting mixture already after 5-6 hours; i.e., the induction period of oxidation is shortened by more than a factor of three. This result is consistent with the change in the initial rate of chain initiation under the action of ionizing radiation. The value w_0 for the noninitiated reaction, calculated on the assumption of a thermal reaction of the hydrocarbon with an O_2 molecule, is 10^2–10^3 radicals/cm$^3 \cdot$ sec. In the case of the initiating action of 12 mCu Rn, however, w_0 is 10^{12} radicals/cm$^3 \cdot$ sec.

Such a strong increase in the rate of formation of active centers should have led to a substantial shortening of the induction period, which is indeed observed experimentally.

An even greater effect is exerted by the action of the α-radiation of Rn on the reaction rate after the end of the induction period. Noninitiated oxidation of isodecane after the end of the induction period proceeds at a relatively low rate, which remains practically constant up to large depths of conversion (32 mol. %). The kinetic curve of acid formation under

under the action of 12 mCu of Rn is a curve with a sharply expressed autocatalytic character. The oxidation rate in this case, after the end of the induction period, increases sharply, and its maximum value exceeds the rate of non-initiated oxidation by more than 10 times. Experiments with other activities (different from 12 mCu) were only of an approximate character. It was shown that an increase in dose (above 615 rad) does not lead to additional effects in increasing the reaction rate.

From the data on the initiating action of 7 mCu of radon (Fig. 3), it is seen that doses of less than 615 rad can also cause distinct accelerations of the oxidation process. The total dose when 7 mCu of radon was used was approximately 400 rad, and the acceleration effect obtained was practically the same as when 12 mCu of radioactive emanation was used.

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CITED LITERATURE

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