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Abstract

Full Text

PHYSICAL CHEMISTRY

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FORMATION OF AEROSOLS DURING THE RADIOLYSIS OF GASEOUS HYDROCARBONS

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The formation and destruction of aerosols produced during the radiolysis of gaseous hydrocarbons was studied by an optical method and by the method of weight concentrations. These methods were described in a previous paper (1), in which aerosols formed during the radiolysis of methane were investigated. Irradiation was carried out with fast electrons with a mean energy of 112 keV. For comparison with works (2–7) on the study of radiation-chemical reactions, experiments with ethane, propane, *n*-butane, ethylene, propylene, and a mixture of methane with oxygen were carried out in a brass reactor; experiments with acetylene—in an iron reactor; and experiments with a mixture of ethylene with oxygen—in an aluminum reactor. The volume of each reactor was 2 liters.

In Fig. 1 are shown the dependences of the attenuation of light with time (with absorbed energy) for aerosols arising upon irradiation of ethane, propane, and *n*-butane, at $t = 20^\circ$, $p = 1$ atm, electron-beam intensities $I = 10$ μa and $I = 100$ μa, and an irradiation time of 30 min. From Fig. 1 it is seen that the greatest attenuation of light occurs in the experiment with *n*-butane, the smallest—in the experiment with propane, and at 100 μa all the aerosol-formation curves have minima dividing them into two parts. At short times (doses) a nearly linear dependence of the attenuation of light on absorbed energy is observed; then the processes of coagulation and sedimentation lead to the result that, although the process of aerosol formation continues, the attenuation of light decreases markedly. After irradiation is stopped, the aerosols are destroyed rather rapidly. Reducing the intensity of the electron beam from 100 μa to 10 μa reduces the attenuation of light by approximately a factor of two.

Fig. 1. Change in light flux with time for aerosols arising during radiolysis: *a* —propane, *b*—ethane, *c*—*n*-butane.

In Fig. 2 are shown the dependences of the attenuation of light with time for aerosols arising upon irradiation of mixtures of methane with oxygen (composition 4 : 1) and ethylene with oxygen (1 : 1) at $p = 1$ atm, $I = 100$ μa, and at $t = -10^{\circ}$ (curves 1, 2) and $t = 20^{\circ}$ (curves 3, 4), as well as the curve for an aerosol formed upon irradiation of propylene at $p = 1$ atm, $t = 20^{\circ}$, and $I = 10$ μa (curve 5) and $I = 100$ μa (curve 6). The irradiation time in all cases was 30 min, with the exception of curve 6, where it was 10 min. All

the curves in Fig. 2 have the same characteristic form as the curves in Fig. 1, i.e., after absorption of a certain amount of energy, a maximum attenuation of light is observed.

The temperature dependence is most sharply expressed in the case of the mixture $CH_4 + O_2$. In the case of the mixture $C_2H_4 + O_2$, however, a change in temperature within the indicated limits has little effect on the attenuation of light. This is evidently connected with the fact that the aerosols arising upon irradiation of the mixture $CH_4 + O_2$ are aqueous solutions of formic acid, formaldehyde, and peroxides, whereas the aerosols arising upon irradiation of the mixture $C_2H_4 + O_2$ consist mainly of high-boiling products ([5]). The sharp increase in the aerosol phase when the temperature is lowered from 20 to -10° in the case of $CH_4 + O_2$ is evidently the cause of the similarly sharp change in the qualitative composition of the oxidation products observed precisely in this narrow temperature interval in work ([6]). In the case of the mixture $C_2H_4 + O_2$, the small changes in the aerosol phase with temperature correspond to the fact that the composition of the products in this temperature interval remains practically unchanged ([5]).

Fig. 2. Change in luminous flux with time for aerosols arising during radiolysis: **a**—mixture of methane with oxygen, **b**—ethylene with oxygen, **v**—propylene

Consequently, changes in the aerosol phase can influence the course of radiation-chemical reactions. As for the aerosol formed upon irradiation of propylene, almost complete attenuation of light occurs already by the 4th min at $I = 10\,\mu$a. At $100\,\mu$a, the curve has no minimum, i.e., the processes destroying the aerosol did not, in this experiment, lead to a decrease in the attenuation of light.

In Fig. 3, the change in weight concentration with time (with absorbed energy) is given for aerosols formed during the radiolysis of ethane, propane, normal butane, and the mixtures $CH_4 + O_2$ (4 : 1) and $C_2H_4 + O_2$ (1 : 1) at $t = 20^{\circ}$, $p =$ 1 atm, and electron-beam intensities $I = 10\,\mu$a and $I = 100\,\mu$a. The irradiation time is 30 min. The largest values of weight concentration in the case of the saturated hydrocarbons, as well as the greatest attenuation of light, are observed for *n*-butane, and the smallest for propane. The maximum concentration values are shifted toward higher doses in comparison with the maximum attenuation of light, since the latter depends not only on the weight concentration of the aerosol, but also on the size of its particles.

Fig. 3. Change in weight concentration with time for aerosols formed during radiolysis: **a**—mixture of methane with oxygen, **b**—ethylene with oxygen, **v**—

ethane, **g**—propane, **d**—butane

The maximum weight concentration for the mixture $C_2H_4 + O_2$ is reached considerably faster than for the mixture $CH_4 + O_2$ and exceeds it in magnitude.

Increasing the intensity of the electron beam from 10 to 100 μa increases the mass concentration by a factor of 5–8.

Figure 4 shows the dependence of the mass concentrations on time for aerosols formed during the radiolysis of ethylene, propylene, and acetylene at 20°, $p = 1$ atm, $I = 100$ μa (for propylene also at $I = 10$ μa). The irradiation time for propylene and acetylene at 100 μa is 10 min, and for ethylene and propylene at 10 μa it is 30 min. The maximum mass concentration attained, equal to 40 mg/l, is observed in the experiment with propylene at the 5th min, with absorption of $1.75 \cdot 10^{22}$ eV of energy. Decreasing the intensity to 10 μa reduces the mass concentration of the aerosol in the experiment with propylene by approximately a factor of two. The maximum aerosol concentration obtained in the experiments with ethylene is approximately the same as in the experiment with propylene, but is reached with absorption of a larger amount of energy ($2.8 \cdot 10^{22}$ eV). In all cases, the mass concentration, having reached its maximum value, begins to decrease with further absorption of energy, owing to processes that destroy the aerosol. The maximum concentration for the aerosol obtained by irradiating acetylene and consisting of solid particles of cuprene was found to be 27 mg/l.

Fig. 4. Change in mass concentration with time for aerosols formed during radiolysis: *a*—propylene, *b*—ethylene, *c*—acetylene.

Thus, in the reaction zone, as the dose increases, there first occurs an accumulation of the aerosol phase at different rates and up to different concentrations depending on the reactants, and then a decrease in it owing to processes of aerosol destruction. After irradiation is stopped, the systems obtained continue to exist for some time: from several minutes (experiments with acetylene) to several tens of minutes (experiments with a mixture of $CH_4 + O_2$).

Table 1 gives the values of the yields of the aerosol phase G_a (the number of transformed molecules of the initial hydrocarbon found in the aerosol phase upon absorption of 100 eV of energy) as a function of time (dose), at an electron-beam intensity equal to 100 μa, $p = 1$ atm and $t = 20°$. For comparison, values of G are given (the number of transformed molecules of the initial hydrocarbon found in liquid or solid products) ([2–7]).

Table 1

Substance	Absorbed energy, eV/min $\cdot 10^{-21}$	G	G_a, irradiation time, min: 3	5	10	20	30
CH_4	1.45	2.5			0.10	0.13	0.20
C_2H_6	2.63	4.1			0.85	0.90	0.60
C_3H_8	3.68	6.7			0.37	0.40	0.20
C_4H_{10}	3.68	11.0			0.42	0.30	0.27
C_2H_4	2.32	8.8		5.9	5.9	2.6	1.5
C_3H_6	3.49	20	7.8	6.5	2.8		
$CH_4 + O_2$	1.62	3.6			2.8	2.2	1.7
$C_2H_4 + O_2$	2.32	9.4	4.3	3.5	2.6	1.1	0.4
C_2H_2	2.04	56.6	18.7	11.8	6.1		

As is evident from the data in Table 1, a considerable amount of the liquid products formed in radiation-chemical reactions passes through the aerosol state. The yields G_a vary over wide limits, depending both on the initial hydrocarbon and on the amount of absorbed energy. The highest yield was found for acetylene and the lowest for methane; moreover, as a rule, the aerosol yield decreases as the absorbed energy increases. Thus, when the irradiation time is increased by a factor of 10, the yield for the mixture $C_2H_4 + O_2$ decreases by more than a factor of 12, while the yield for *n*-butane, when the irradiation time is increased by a factor of 3, decreases by a factor of 1.5. The yields in the case of unsaturated hydrocarbons and mixtures of CH_4 and C_2H_4 with O_2 are an order of magnitude greater than the yields in the case of saturated hydrocarbons. It should be noted that the maximum yield G_a does not correspond to the maximum concentrations: thus, for acetylene $G_a = 18.7$ and the concentration is 27 mg/liter, whereas for propylene $G_a = 7.8$ and the concentration is 40 mg/liter.

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REFERENCES

1. V. S. Bogdanov, *ZhFKh*, **34**, no. 5, 1050 (1960).

2. B. M. Mikhailov, L. V. Tarasova, V. S. Bogdanov, *The Action of Ionizing Radiations on Organic and Inorganic Systems*, Publishing House of the Academy of Sciences of the USSR, 1958, p. 218.

3. B. M. Mikhailov, M. E. Kuimova, V. S. Bogdanov, ibid., p. 223.

4. B. M. Mikhailov, L. V. Tarasova, V. G. Kiselev, V. S. Bogdanov, *Proceedings of the First All-Union Conference on Radiation Chemistry*, Publishing House of the Academy of Sciences of the USSR, 1958.

5. B. M. Mikhailov, V. G. Kiselev, *Izv. AN SSSR, OKhN*, no. 9, 1619 (1960).

6. B. M. Mikhailov, M. E. Kuimova, V. S. Bogdanov, *Proceedings of the First All-Union Conference on Radiation Chemistry*, Publishing House of the Academy of Sciences of the USSR, 1958.

7. L. M. Dorfman, F. J. Shipko, *J. Am. Chem. Soc.*, **77**, 4723 (1955).

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