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Abstract

Full Text

PHYSICAL CHEMISTRY

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THE INFLUENCE OF SOLIDS ON THE DECOMPOSITION PROCESS OF CCl_4 IN AQUEOUS SOLUTION UNDER THE ACTION OF GAMMA RADIATION

(Presented by Academician S. S. Medvedev, February 17, 1960)

In a number of works (¹⁻⁵) it was shown that the radiation yield of oxidation or reduction of inorganic substances in aqueous solution can be increased several-fold if a solid substance is present in the irradiated system. The solid substances used in these works were metals, oxides, and sulfides of metals. It could be expected that solid substances would exert an analogous effect under irradiation conditions on processes occurring in aqueous solutions of organic substances. However, there is no information on this question in the literature.

The present communication is devoted to a description of our experiments, in which we investigated conditions under which a solid substance accelerates the decomposition of an organic compound in aqueous solution under the action of γ -radiation. For this purpose a system was chosen consisting of CCl_4 and water (in the ratio 1 : 2) and a solid substance, the amount of which was varied from 1.4 to 20% by weight. Charcoal (Carbolen), silica gel, Al_2O_3 , Fe_2O_3 , and Cu_2O were used as the solid substances. The source of γ -radiation was Co^{60} with a dose rate of $4 \cdot 10^{16}$ eV/sec. Irradiation of the mixture was carried out in a glass vessel equipped with a bubbler for passing the corresponding gas (oxygen or nitrogen). The irradiation temperature was $8 \div 10^\circ\text{C}$.

After irradiation the reaction mixture was separated. The solid substance was washed with a 12% ammonia solution. The concentration of Cl^- ions, as a measure of the degree of decomposition of CCl_4 , was determined by potentiometric titration with an AgNO_3 solution. The total amount of Cl^- ions formed during irradiation was the sum of their content in the water and in 2-3 ammonia washings of the solid substance.

We investigated the dependences of the amount of Cl^- formed on the irradiation dose at different contents of solid substance in the irradiated mixture. The experimental results for silica gel are given in Fig. 1. Curve 1 in this figure refers to the mixture $\text{CCl}_4\text{-H}_2\text{O-O}_2$ without a solid substance; curves 2, 3, 4, and 5 refer to mixtures in which the silica-gel content was, respectively, 1.4; 7.7;

14.2; and 20% by weight. It is seen from Fig. 1 that the presence of silica gel in an amount of only 1.4% leads to an increase in the concentration of Cl^- ions in the irradiated mixture. Each subsequent increase in the percentage content of silica gel also promotes an increase in the concentration of Cl^- ions; however, the increase in the concentration of Cl^- is not proportional to the amount of added solid substance. Analogous dependences of the concentration of Cl^- ions on the irradiation dose are also observed for the other solid substances.

The influence of the nature of the solid substance on the process of radiation decomposition of CCl_4 in aqueous solution is clearly seen from Fig. 2, where curves are presented for the dependence of the amount of Cl^- formed on the irradiation dose for all the solid substances we investigated. The amount of solid substance in all cases was 7.7%.

All the solid substances, in terms of their ability to increase the yield of Cl^- ions, are arranged in the following sequence: Al_2O_3 , SiO_2 , Fe_2O_3 , carbon, Cu_2O . Each of the solid substances listed, without the simultaneous action of radiation, produces no chemical changes in the initial mixture, i.e., there is no dark catalytic effect. The catalytic activity of the solid substances, after preliminary irradiation, also does not change.

In order to determine what accounts for the acceleration of the decomposition of CCl_4 in the system with a solid phase—whether the presence of the solid substance or the presence of oxygen—experiments were carried out with nitrogen purging. The results of experiments for the system without a solid phase are given in Table 1. It was established that oxygen does not participate in the decomposition of CCl_4 , since replacing oxygen with nitrogen does not change the yield of Cl^- ions. The initial yield of H_2O_2 in the system $\text{CCl}_4\text{—H}_2\text{O—O}_2$ is approximately

Fig. 1. Dependence of the concentration of Cl^- ions on the irradiation dose. Dose rate $4.0 \cdot 10^{16}$ eV/sec. 1—system $\text{CCl}_4\text{—H}_2\text{O—O}_2$; the same in the presence of: 2—1.4; 3—7.7; 4—14.2; 5—20.0% silica gel.

Fig. 2. Dependence of the concentration of Cl^- ions on the irradiation dose: 1—system $\text{CCl}_4\text{—H}_2\text{O—O}_2$; the same in the presence of: 2— Al_2O_3 , 3—silica gel, 4— Fe_2O_3 , 5—carbon, 6— Cu_2O (7.7% by weight).

Table 1

System $\text{CCl}_4\text{—H}_2\text{O}$

No.	O ₂	O ₂	O ₂	N ₂	N ₂	N ₂
	purging: dose ×10 ⁻²¹ eV/36 g	purging: conc. Cl ⁻ ×10 ² equiv/L	purging: yield of Cl ⁻ ions/100 eV	purging: dose ×10 ⁻²¹ eV/36 g	purging: conc. Cl ⁻ ×10 ² equiv/L	purging: yield of Cl ⁻ ions/100 eV
1	1.38	1.24	10.8	1.25	1.15	11.0
2	2.76	2.08	9.0	2.52	2.32	11.0
3	5.52	4.12	9.0	5.04	4.24	10.0
4	8.28	5.27	7.6	7.56	6.05	9.65

3 times lower (0.07 molecule/100 eV) than in the experiments with nitrogen purging. It is characteristic that, both in experiments with nitrogen purging and in experiments with oxygen purging, the concentration of H₂O₂ decreases with increasing irradiation dose.

As can be seen from Table 2, introduction of a solid substance (Al₂O₃, SiO₂, Fe₂O₃, carbon) into the system for irradiation increases the concentration of Cl⁻ ions only in the presence of oxygen.

When the system CCl₄—H₂O—solid substance is irradiated with nitrogen purging, the concentration of Cl⁻ ions practically does not differ from the concentration

Table 2

System CCl₄—H₂O—1 g of solid substance

No.	Solid substance	Dose	Cl ⁻	Yield	Solid substance	Dose	Cl ⁻	Yield
		×10 ⁻²¹ eV/37 g	con- centra- tion ×10 ² equiv/l	of Cl ⁻ ions/100 eV		×10 ⁻²¹ eV/37 g	con- centra- tion ×10 ² equiv/l	of Cl ⁻ ions/100 eV
1	Al ₂ O ₃	1.33	1.62	14.6	Al ₂ O ₃	1.33	1.12	10.2
2	Al ₂ O ₃	2.66	2.90	13.0	Al ₂ O ₃	2.66	2.28	10.3
3	Al ₂ O ₃	5.32	5.33	12.0	Al ₂ O ₃	5.32	4.18	9.5
4	Al ₂ O ₃	7.98	6.37	9.6	Al ₂ O ₃	7.98	7.15	10.7
5	Charcoal	1.33	1.95	17.6	Charcoal	1.33	1.3	11.7
6	Charcoal	2.66	3.95	17.6	Charcoal	2.66	2.64	11.9
7	Charcoal	5.32	6.66	15.0	Charcoal	5.32	4.52	10.9
8	Charcoal	7.98	9.70	15.0	Charcoal	7.98	6.54	9.9
9	Cu ₂ O	1.33	3.62	32.7	Cu ₂ O	1.33	2.6	23.5
10	Cu ₂ O	2.66	4.46	20.1	Cu ₂ O	2.66	4.2	19.0
11	Cu ₂ O	5.32	7.87	18.0	Cu ₂ O	5.32	7.00	15.8
12	Cu ₂ O	7.98	12.00	18.0	Cu ₂ O	7.98	7.85	11.8

No.	Solid substance	Dose $\times 10^{-21}$ eV/37 g	Cl ⁻ concentration $\times 10^2$ equiv/l	Yield of Cl ⁻ ions/100 eV	Solid substance	Dose $\times 10^{-21}$ eV/37 g	Cl ⁻ concentration $\times 10^2$ equiv/l	Yield of Cl ⁻ ions/100 eV
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ions Cl⁻ in the system without a solid phase. In this case the solid substance is a ballast absorbing the energy of the γ -radiation but not transferring this energy to the components of the mixture. In all the systems investigated, the yield of hydrogen peroxide both in the presence of nitrogen and in the presence of oxygen is very small, but, in contrast to the system without a solid substance, the concentration of H₂O₂ in the solution increases with increasing irradiation dose. In contrast to the solid substances cited above, Cu₂O increases the concentration of Cl⁻ ions even when the system is irradiated with nitrogen bubbling. The yield of H₂O₂ reaches 2 molecules/100 eV.

The experimental data obtained show that a necessary condition for increasing the radiation yield of decomposition of an organic substance in aqueous solution, for most of the systems studied, is the simultaneous presence in the irradiated system of oxygen and a solid substance—a catalyst. It is possible that on the surface of the solid body oxygen is converted into a more active form capable of reacting with adsorbed molecules of the components of the mixture. Reactions on the surface are apparently specific for each solid substance and will be determined by its electrical and adsorption properties.

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