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Abstract

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TITANIUM AND TIN TETRACHLORIDES AS ACCEPTORS OF RADICALS IN THE RADIOLYSIS OF HYDROCARBONS

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In radiation-chemical processes occurring in the liquid phase, dissolved substances that react with primary radicals in ordinary stoichiometric ratios may be used to measure the yield of free radicals.

Thus, in the radiolysis of aqueous solutions, the action of H atoms is usually associated with the reduction of ions, for example,

$$Ce^{4+} \rightarrow Ce^{3+}, \quad Cr^{6+} \rightarrow Cr^{3+}, \quad Mn^{7+} \rightarrow Mn^{2+}, \quad NO_3^- \rightarrow NO_2.$$

([1–4]). Acidified iron serves as an acceptor of the oxidizing components of radiolysis in the presence of air ([5,6]), or deaerated aqueous solutions of divalent tin and trivalent titanium ([7,8]). Oxygen, iodine, diphenylpicrylhydrazyl, and vinyl compounds are commonly used as radical acceptors in the radiolysis of hydrocarbons. New possibilities are opened by the use, for this purpose, of compounds of metals of variable valence. Acceptance of radicals formed during radiolysis in organic media by salts of metals of variable valence leads to reduction of the latter. Collinson and Chernyak showed this for ferric chloride dissolved in methanol, acetone, and tetrahydrofuran ([9,10]). In this case ferric chloride is reduced according to the reaction:

$$FeCl_3 + R\cdot \rightarrow FeCl_2 + RCl.$$

In the present work we studied the reaction of radiation-chemical reduction of titanium tetrachloride and tin chloride in hydrocarbon solutions under the action of γ-radiation from Co^{60}, and the possibility of using these reactions to initiate polymerization. Mixtures of $TiCl_4$—*n*-octane, $TiCl_4$—benzene, $SnCl_4$—*n*-octane, and $SnCl_4$—octamethylcyclotetrasiloxane were irradiated in glass ampoules. Octamethylcyclotetrasiloxane was dried with $CaCl_2$. Distillation of $TiCl_4$ was carried out in the presence of copper powder. Deaeration of the solutions was carried out by the usual freezing–thawing operations in vacuum, after which the ampoules were evacuated and sealed. Analysis of the subchloride precipitates,

after removal of the liquid radiolysis products and drying of the precipitates in vacuum at 120°, was carried out by potentiometric titration with silver chloride and platinum electrodes.

The amount of absorbed energy was determined by ferrosulfate dosimetry. The reaction yield was taken to be 15.6 molecules per 100 eV. The design of the radiation-chemical apparatus with a Co^{60} source, with an activity of 1440 g-eq Ra, has been described previously ([11]). Upon irradiation of $TiCl_4$–hydrocarbon mixtures, a loose brown precipitate, gradually becoming denser, is formed. The radiation-chemical yield of disappearance of $TiCl_4$, $G(-TiCl_4)$, in *n*-octane solutions as a function of the $TiCl_4$ concentration is shown in Figs. 1 and 2. In the case of benzene solutions, $G(-TiCl_4)$ is an order of magnitude lower, and the maximum ···

its value reaches 0.75, in good agreement with the known data of other authors ([9]) on the radiation-chemical yield of radicals formed upon irradiation of benzene.

According to elemental-analysis data, the composition of the precipitates formed corresponds to $TiCl_3$. They are completely soluble in dry N,N-dimethylformamide.

The brown modification of β-$TiCl_3$ obtained was used as a component of a complex Ziegler-type catalyst, β-$TiCl_3$ (iso-$C_4H_9)_2AlCl$, and exhibited normal catalytic activity in the polymerization reaction of diolefins.

Fig. 1. Radiation-chemical yield of the reduction of $SnCl_4$ (1) and $TiCl_4$ (2) in solutions of *n*-octane

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Trivalent titanium evidently gives rise to the electron-paramagnetic-resonance (e.p.r.) spectrum in *n*-octane–$TiCl_4$ mixtures irradiated at 77° K. The spectrum of Ti^{3+}, detected alongside the hydrocarbon spectrum and stable at this temperature, is shown in Fig. 2. The line width, measured between the maxima of the first derivative of the signal, was 22 oersteds. The *g*-factor of the center of the signal is 1.91. The sensitivity in this case corresponded to $\sim 5 \cdot 10^{-12}$ *M* diphenylpicrylhydrazyl. It is important to note that the intensity of the spectrum increases linearly with increasing $TiCl_4$ concentration. At the same time, the presence of the e.p.r. spectrum of an H atom stabilized on the surface of quartz was confirmed ([12]).

Fig. 2. E.p.r. spectrum of $TiCl_4$ solutions in *n*-octane irradiated at 77° K. Component of the hydrogen-atom doublet (1) and spectrum of Ti^{3+} (2). Dose –3.5 million r.

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Irradiation of $SnCl_4$–hydrocarbon mixtures leads to precipitation of stannous chloride. The radiation-chemical yield of $SnCl_4$ consumption ($G(-SnCl_4)$) for the *n*-octane–$SnCl_4$ system as a function of the mixture composition is shown in Fig. 1, 1. Of particular interest was the system stannous chloride–octamethylcyclotetrasiloxane. As was shown by Andrianov ([13]), stannous chloride at temperatures of 120-150° is a catalyst for the polymerization of octamethylcyclotetrasiloxane, accompanied by ring opening.

In this connection, it seemed possible to carry out the indicated reaction under the action of ionizing radiation at room temperature, with simultaneous chlorination of the polymer formed through the reduction reaction of stannic chloride. We established that irradiation of a mixture of octamethylcyclotetrasiloxane and stannic chloride at room temperature does indeed lead to polymerization of octamethylcyclotetrasiloxane.

At the same time, the reduction reaction $Sn^{4+} \rightarrow Sn^{2+}$ proceeds, accompanied by chlorination of the polymer. The chlorine content in the polymer reaches 3 mole % at irradiation doses of about 30 million r.

With increasing concentration of $SnCl_4$, an increase is observed in the molecular weight of the polymer isolated after filtering off the stannous chloride precipitate in an atmosphere of dry nitrogen and then removing the unreacted stannic chloride (Fig. 3). The methane/hydrogen ratio in the gases evolved upon irradiation of individual octamethylcyclotetrasiloxane over a wide dose range up to 45 million r remains constant. In the same dose range, the addition of stannic chloride leads to an increase in this ratio (Fig. 4).

Fig. 3. Characteristic viscosity of benzene solutions of polymer in the system SnCl4–octamethylcyclotetrasiloxane. Irradiation dose: 1–6.4 • 10^6; 2–2 • 10^7; 3–2.9 • 10^7 r

Fig. 3. Characteristic viscosity of benzene solutions of polymer in the system $SnCl_4$–octamethylcyclotetrasiloxane. Irradiation dose: 1–$6.4 \cdot 10^6$; 2–$2 \cdot 10^7$; 3 –$2.9 \cdot 10^7$ r.

Fig. 4. Gas evolution upon irradiation of mixtures of SnCl4–octamethylcyclotetrasiloxane. Irradiation dose–29.6 million r

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This circumstance indicates the greater activity of the hydrogen atom, compared with the methyl radical, in the reduction reaction of stannic chloride under the action of radiation.

On the basis of the experimental data presented above and known concepts concerning the character of radiation-chemical reactions occurring in hydrocarbons ([14]), the following possible types of initial reactions may be outlined:

$$\mathrm{RH} \rightsquigarrow \mathrm{RH}^* \longrightarrow \begin{cases} \mathrm{R} + \mathrm{H} & (1) \\ \mathrm{R}_n + \mathrm{R}_m & (2) \\ \mathrm{H}_2 + \mathrm{C}_n\mathrm{H}_{2n} & (3) \\ 2\mathrm{H}_2 + \mathrm{C}_n\mathrm{H}_{2n-2} & (4) \end{cases}$$

Free radicals formed by reactions 1 and 2 may interact with $TiCl_4$ or $SnCl_4$:

$$\mathrm{TiCl_4} + \mathrm{H} \rightarrow \mathrm{TiCl_3} + \mathrm{HCl},$$

$$\mathrm{TiCl_4} + \mathrm{R} \rightarrow \mathrm{TiCl_3} + \mathrm{RCl}.$$

In addition, the possibility of redistribution of the absorbed energy in this two-component system with increasing concentration of the tetrachlorides of the elements under consideration cannot be ruled out.

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