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ON THE MECHANISM OF NONADDITIVE RADICAL FORMATION DURING RADIOLYSIS OF FROZEN SOLUTIONS OF $CCl_4 + CH_3OH$

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In a previous communication* it was shown that the radiolysis of frozen solutions of CCl_4 in methanol is associated with a substantial increase in the yield of stabilized radicals in comparison with the additive value. It was assumed that the process responsible for the formation of "superadditive" radicals at low concentrations of CCl_4 is the reaction of atomic hydrogen with CCl_4 molecules; this was confirmed by a decrease in the yield of hydrogen and the formation of Cl^- ions with a yield equal to the yield of the "superadditive" radicals. At the same time, Hamill and co-workers ($^{1-3}$), Shapoti and Aion (^{4}), Gordon, Hart (^{5}), and others showed the high effectiveness of haloalkyls as electron acceptors. In this case dissociative electron capture by a haloalkyl molecule takes place:

$$\mathrm{RHal} + e \rightarrow \mathrm{R} + \mathrm{Hal}^-.$$

This process may also lead to nonadditivity in the yield of radicals during radiolysis of the corresponding solutions.

The present work is devoted to elucidating the role of the reactions of electrons and hydrogen atoms with CCl_4 molecules in the formation of stabilized radicals during radiolysis of frozen solutions of CCl_4 in methanol. The difficulty of separating these processes lies in the fact that the products of dissociative electron capture by a CCl_4 molecule and of the reaction of hydrogen atoms with carbon tetrachloride are the same (CCl_3 radicals and Cl^- ions).

The methods of preparing the samples, γ-irradiation, recording e.p.r. spectra, and determining the radical yield have been described previously (^{6}). Pure methanol on freezing gives finely crystalline samples. To obtain amorphous samples, methanol containing 5% water was used. The iodine used for preparing some solutions was sublimed in vacuum. The irradiation dose was 1-2 Mrad.

The e.p.r. spectrum recorded immediately after γ-irradiation of an amorphous methanol sample is shown in Fig. 1a. It is a superposition of the spectra of three paramagnetic particles: the central triplet belongs to the $\dot{C}H_2OH$ radical; the broad asymmetric doublet with splitting $\simeq 130$ oersted belongs to the formyl

Fig. 1

Figure 1: Fig. 1

radical; and the central singlet ($\Delta H = 18$ oersted) belongs, as was shown in (^{4}), to the solvated electron. Approximate values of the yields of the primary paramagnetic particles are as follows: $G(\dot{C}H_2OH) = 2$, $G(e)_{\text{solv}} = 3$, $G(HCO) = 0.15$. Under the action of visible light the e.p.r. spectrum changes: the lines belonging to the formyl radical disappear; the singlet of the solvated electron also disappears, and the concentration of the triplet increases (Fig. 1b). At the same time the resolution of the spectrum improves and the initial coloration of the sample disappears. The total concentration of paramagnetic particles practically does not change under the action of visible light.

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In the EPR spectrum of γ-irradiated methanol samples with an addition of H_2SO_4 (ions H^+), a decrease is observed in the intensity of the singlet and of the coloration associated with the solvated electron, which leads to better resolution of the spectrum (Fig. 1). The concentration of the formyl radical remains unchanged. Figure 2 shows the dependence of the relative concentration of the solvated electron, characterized by the ratio of the amplitudes A_1/A_2 (Fig. 1), on the composition of the solution of H_2SO_4 in methanol. It is seen that already at an H_2SO_4 concentration of 0.2 N the yield of solvated electrons falls to zero. The total yield of paramagnetic particles does not change in acid methanol in comparison with neutral alcohol.

Fig. 1. EPR spectra of γ-irradiated CH_3OH and CH_3OH with additions. $-CH_3OH$ immediately after γ-irradiation; $-CH_3OH$ after exposure to visible light; -0.2 N H_2SO_4 in CH_3OH; -0.2 M CCl_4 in CH_3OH; -2 N H_2SO_4 + $0.2\,M$ CCl_4 in CH_3OH

The addition of CCl_4 to methanol also suppresses the yield of solvated electrons, as is indicated by the disappearance of the coloration and the absence of any effect of visible light on the resolution of the EPR spectrum. At the same time, an increase occurs in the total concentration of radicals (Fig. 3, 1). The EPR spectrum in this case (Fig. 1) is a superposition of the spectra of the radicals $\dot{C}H_2OH$ and $\dot{C}Cl_3$.* The concentration of the individual radicals in spectrum 1 was determined by comparing the ratios of the characteristic amplitudes A_3/A_4 with analogous ratios in model spectra obtained by superposing the spectra of the separate radicals with allowance for the difference in g-factors. Figure 3 gives the dependences of the yields of trichloromethyl radicals (curve 2) and $\dot{C}H_2OH$ radicals (curve 3) on the composition of the solution. The yield of $\dot{C}H_2OH$ radicals decreases, reaching a constant value $G = 2$ at a CCl_4 concentration of 0.2 M (at this concentration of CCl_4 the coloration also completely disappears); the yield of trichloromethyl radicals continues to increase. It may be assumed that the decrease in the yield of CH_2OH radicals is associated with electron capture by CCl_4 molecules. The $G(CH_2OH)$ that cannot be suppressed in the presence of CCl_4 is evidently due to processes not connected with the participation of electrons.

The fact that the increase in the yield of trichloromethyl radicals exceeds the decrease in the yield of $CH_2^{\cdot}OH$ radicals makes it necessary to suppose that trichloromethyl radicals are formed not only as a result of dissociative electron capture by CCl_4 molecules, but also as a result of the reaction of hydrogen atoms with CCl_4. This assumption was tested in experiments on irradiation of acid (0.2 N H_2SO_4) solutions of CCl_4 in methanol. The data obtained are presented in Fig. 3. It is seen that the total concentration radicals (curve 1b) does not differ from this value for neutral solutions, although the relative fraction of $\dot{C}Cl_3$ radicals decreases somewhat compared with neutral solutions. The formation of $\dot{C}Cl_3$ radicals is observed even in the presence of 2 N H_2SO_4 (Fig. 1b).

Consideration of the possible reactions occurring during the radiolysis of CCl_4+CH_3OH solutions shows that dissociative electron capture by CCl_4 molecules cannot lead to an increase in the total yield of stabilized radicals in comparison with the additive value. This conclusion is confirmed by the constancy of the total concentration of paramagnetic particles in the presence of H^+ ions, although the yield of solvated electrons is suppressed in this case. The facts presented make it possible to propose the following sequence of reactions leading to the formation of paramagnetic particles during the radiolysis of pure methanol and methanol with the additives studied. Upon γ-irradiation of amorphous methanol at 77°K, the following processes occur:

Fig. 2. Dependence of the ratio A_1/A_2 and of the total yield of paramagnetic particles on the concentration of H_2SO_4 in methanol. 1 –immediately after γ-irradiation, 2 –after exposure to visible light, 3 –yield of paramagnetic particles.

Fig. 3. Dependence of the radical yield in a CCl_4+CH_3OH solution on the composition of the solution. 1 –total concentration, 2 –$G(\dot{C}Cl_3)$, 3 –$G(CH_2^{\cdot}OH)$. a –neutral solution, b –solution containing 0.2 N H_2SO_4.

$$CH_3OH \rightsquigarrow CH_2OH^+ + H + e, \qquad (1)$$

$$CH_3OH \rightsquigarrow CH_2^{\cdot}OH + H, \qquad (2)$$

$$H + H \rightarrow H_2, \qquad (3)$$

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* It should be noted that the EPR spectrum of the trichloromethyl radical described by us earlier (see the note on p. 1) practically coincides with the spectrum of this radical obtained chemically in Ref. (7).

Fig. 4. Change in the yield of stabilized radicals upon addition of J_2. 1—neutral CH_3OH, 2—CH_3OH with addition of 0.4 N H_2SO_4, 3—cyclohexane

Figure 2: Fig. 4. Change in the yield of stabilized radicals upon addition of J_2. 1—neutral CH_3OH, 2—CH_3OH with addition of 0.4 N H_2SO_4, 3—cyclohexane

$$\mathrm{e} \rightarrow (\mathrm{e})_{\mathrm{solv}}. \tag{4}$$

Under the action of visible light, the electrons are ejected from the traps and enter into the reaction:

$$\mathrm{e} + CH_2OH^+ \rightarrow C\dot{H}_2OH. \tag{5}$$

In the presence of H^+ ions, as also in crystalline methanol (^{4}), reaction (4) is suppressed, apparently owing to the unfavorable influence of the matrix on electron solvation, and reaction (5) proceeds directly in the course of irradiation. The total value of the yield of paramagnetic particles then remains unchanged. In the presence of CCl_4 one must additionally consider the reactions:

$$\mathrm{e} + CCl_4 \rightarrow \dot{C}Cl_3 + Cl^-, \tag{6}$$

$$H + CCl_4 \rightarrow \dot{C}Cl_3 + HCl. \tag{7}$$

Reaction (6), like reaction (5), does not change the total yield of radicals. The only process responsible for the increase in the total yield of stabilized radicals is reaction (7). When H_2SO_4 is added to solutions of CCl_4 in methanol, competition of reactions (5) and (6) leads-

leads to a decrease in the fraction of $\dot{C}Cl_3$ radicals, but the magnitude of the deviation of the total yield of stabilized radicals from the additive value, determined by the probability of reaction (7), remains unchanged.

The proposed mechanism also explains certain features of the radiolysis of frozen solutions of $CCl_4 + CH_3OH$ in the amorphous and crystalline phases that were noted earlier.* If in the crystalline phase the yield of Cl^- is equal to the yield of "superadditive" radicals, then in the amorphous phase the yield of Cl^- substantially exceeds the yield of "superadditive" radicals, but coincides with the yield of trichloromethyl radicals. These differences are associated with a change in the conditions of electron solvation upon transition from the crystalline to the amorphous phase.

Fig. 4. Change in the yield of stabilized radicals upon addition of J_2. 1—neutral CH_3OH, 2—CH_3OH with addition of 0.4 N H_2SO_4, 3—cyclohexane.

The formation of solvated electrons with $G = 3$ means that, in γ-irradiated methanol, positive ions are simultaneously stabilized with an equal yield. Such an ion may be $\dot{C}H_2OH^+$—the principal ion in the mass spectrum of methanol (8), since the other possible ion CH_3OH^+ is paramagnetic and should be observed in the EPR spectrum. The formation of CH_2OH radicals with $G = 2$ is evidently connected with the decomposition of excited methanol molecules, or the radicals are formed through ions with lifetimes shorter than the electron solvation time.

Additional data confirming the proposed mechanism of radical formation in the radiolysis of methanol were also obtained in a study of the radiolysis of frozen iodine solutions in methanol. In this case the yield of solvated electrons is suppressed at an J_2 concentration equal to $\sim 3 \cdot 10^{-2}$ mol/liter, while the concentration of $\dot{C}H_2OH$ radicals decreases (Fig. 4). Iodine atoms, which may be formed as a result of dissociative electron capture by the J_2 molecule, cannot be observed in the EPR spectrum (9). In the radiolysis of solutions in acidified methanol (0.4 N H_2SO_4), the yield of $\dot{C}H_2OH$ radicals is practically independent of the composition of the solution over the investigated range of J_2 concentrations. Hence it may be concluded that the decrease in the radical yield is associated with the acceptance of electrons by iodine and the consequent decrease in the probability of reaction (5). It is interesting that J_2 has no effect on the yield of stabilized radicals in solid cyclohexane; the latter is apparently due to the fact that the probability of capture of slow electrons by positive ions in a hydrocarbon is considerably greater than in alcohols and other polar matrices (10).

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* See the note on p. 1.

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