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Transformations of Dichloromethane Radicals in Alkaline Water Solutions

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Abstract—Among transformation products of $\dot{C}HCl_2$ and $\dot{C}H_2Cl$ radicals generated by γ-irradiation of deaerated water solutions of dichloromethane oxygen-containing compounds (formic acid, formaldehyde, carbon monoxide) and chloride ions were found. The radicals $\dot{C}HCl_2$ suffer nucleophilic substitution by hydroxyl ions affording anion-radicals $H\dot{C}OO^{-2}$ that further transform into formic acid. At the growing concentration of alkali the frequency of chlorine substitution with hydroxyl ions in the dichloromethane radicals increases, and their transformation process becomes a chain reaction.

We formerly demonstrated that formaldehyde arose in the alkaline water solutions of dichloromethane under γ-irradiation by nucleophilic substitution of chlorine in $\dot{C}H_2Cl$ radicals with hydroxyl ion [1]. Here we report on more detailed investigation of reaction between dichloromethane radicals and nucleophilic species resulting in the other products of radicals transformation.

Deaerated water solutions of dichloromethane (0.1 mol l^{-1}) containing various quantities of alkali were subjected to ionizing irradiation. We observed increase in the radiation-chemical yield of chloride ions and decreased yield of dichloroethane. Radiation-chemical yields of transformation products originating from dichloromethane radicals are listed in the table. Typical kinetic curves of accumulation of identified radiolysis products are presented on Figs. 1, 2.

At γ-irradiation of water [reaction (1)] arise active species $HO^{\cdot}$, e^-_{aq}, $H^{\cdot}$, and H_2O_2 with radiation-chemical yields *G* 2.8, 2.8, 0.55 and 0.7 molecules per 100 eV respectively [2]. The radicals react further with dichloromethane molecules along reactions (2–5).

$$H_2O \xrightarrow{\gamma} HO^{\cdot},\ e^-_{aq},\ H^{\cdot},\ H_2O_2 \qquad (1)$$

$$CH_2Cl_2 + HO^{\cdot} \longrightarrow H_2O + \underset{\textbf{I}}{\dot{C}HCl_2} \qquad (2)$$

$$CH_2Cl_2 + e^-_{aq} \longrightarrow Cl^{\cdot} + \underset{\textbf{II}}{\dot{C}HCl_2} \qquad (3)$$

$$CH_2Cl_2 + H^{\cdot} \longrightarrow \begin{cases} H_2 + \textbf{I} & (4) \\ HCl + \textbf{II} & (5) \end{cases}$$

Dichloroethane forms along reaction (6).

$$2\ \textbf{II} \longrightarrow CH_2ClCH_2Cl \qquad (6)$$

Radiation-chemical yields *G* of products from radical transformations in water solutions of dichloromethane

[NaOH], mol l^{-1}	Yield, molecules per 100 eV					
	Cl^-	$C_2H_4Cl_2$	HCOOH	CH_2O	CO	Cl^- [a]
0	6.0 ± 1.0	1.20 ± 0.21	1.37 ± 0.48	0.21 ± 0.04	0.12 ± 0.02	44 ± 5
0.1	9.2 ± 1.2	1.05 ± 0.14	1.58 ± 0.79	0.56 ± 0.13	–	101 ± 17
0.3	12.4 ± 1.3	0.35 ± 0.10	4.33 ± 1.27	0.72 ± 0.21	–	–
0.5	13.6 ± 1.5	0.10 ± 0.02	4.91 ± 1.43	0.73 ± 0.22	–	110 ± 20

[a] Radiation-chemical yields of chloride ions obtained at absorbed dose power 0.18×10^{18} eV l^{-1} s^{-1}.

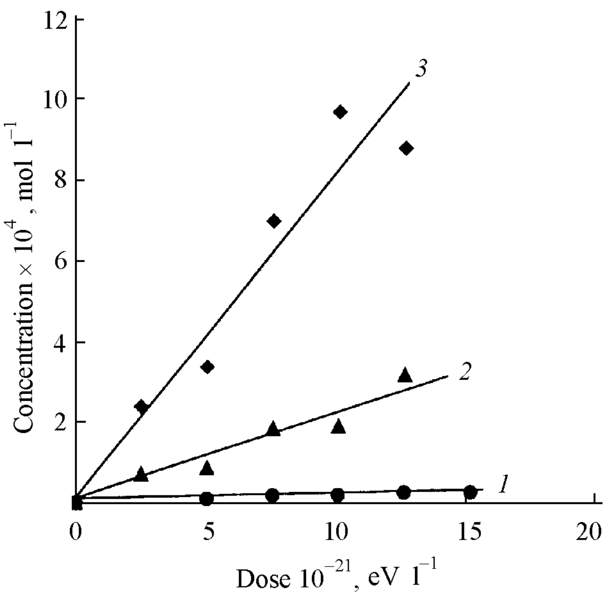

Fig. 1. Concentration of carbon monoxide (*1*) and formic acid (*2, 3*) in dichloromethane water solutions as a function of radiation dose. [NaOH], mol l^{-1}: 0.5 (*1*), 0 (*2, 3*).

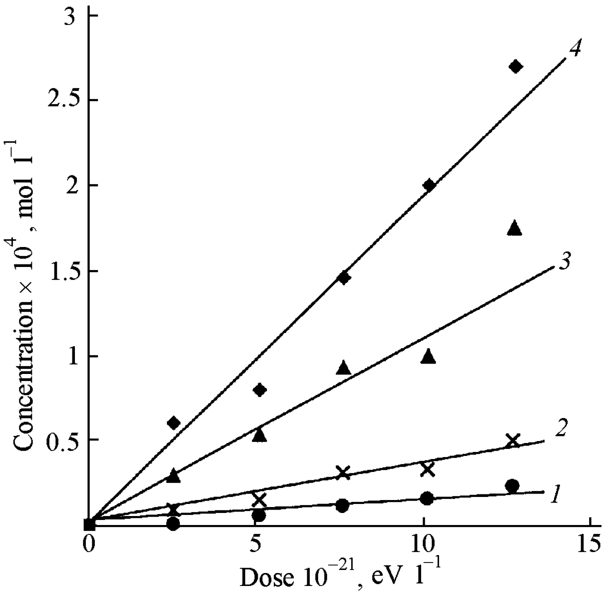

Fig. 2. Concentration of dichloroethane (*1, 4*) and formaldehyde (*2, 3*) as a function of radiation dose. [NaOH], mol l^{-1}: 0 (*1, 3*), 0.5 (*2, 4*).

The radiation-chemical yield of chloride ions (see table) suggests that chloride ions form not only in reactions (3) and (5). They might arise in reaction of hydrogen peroxide that forms by water radiolysis with radicals **I** and **II** along reactions (7) and (8).

$$H_2O_2 + H_2O + \mathbf{I} \rightarrow HO^{\cdot} + HCOOH + 2HCl \quad (7)$$

$$H_2O_2 + \mathrm{II} \rightarrow HO^{\cdot} + H_2CO + H_2CO + HCl \quad (8)$$

Taking into account reactions (3, 5, 7, 8) the radiation-chemical yield of chloride ions amounts to $G_{Cl^-} \le G_{e\text{-aq}} + G_H + 2G_{H_2O_2} \le 4.8$ ion per 100 eV, that is by 1.2 ion per 100 eV less than shows the experiment. Therefore radicals **I** and **II** react also with water molecules by reactions (9) and (10).

$$2H_2O + \mathbf{I} \rightarrow \underset{\mathbf{III}}{H\dot{C}(OH)_2} + 2HCl \quad (9)$$

$$H_2O + \mathbf{II} \rightarrow \underset{\mathbf{IV}}{\dot{C}H_2OH} + HCl \quad (10)$$

Radicals **III** and **IV** further can transform into formic acid and formaldehyde by reactions (11, 12) and to lesser extent by reactions (13, 14).

$$\mathbf{III} + CH_2Cl_2 \rightarrow HCOOH + \mathbf{II} + Cl^- \quad (11)$$

$$\mathbf{IV} + CH_2Cl_2 \rightarrow CH_2O + \mathbf{II} + Cl^- \quad (12)$$

$$\mathbf{III} + H_2O_2 \rightarrow HCOOH + HO^- + HO^{\cdot} \quad (13)$$

$$\mathbf{IV} + H_2O_2 \rightarrow CH_2O + HO^- + HO^{\cdot} \quad (14)$$

Reaction (9) also helps to understand the formation of carbon monoxide [reactions (15) and (16)] that is present in the products of dichloromethane radicals transformation in neutral solution.

$$\mathbf{III} \rightarrow H_2O + H\dot{C}O \quad (15)$$

The rate constant of a similar dehydration process for $CH_3\dot{C}(OH)_2$ radical is $k\ 3 \times 10^4\ s^{-1}$ [3].

$$\mathbf{V} \rightarrow CO + H^{\cdot} \quad (16)$$

The CO formation directly indicates the nucleophilic substitution reaction between radicals **I** and water molecule to occur [reaction (9)].

On addition of sodium hydroxide to the dichloromethane solution the yield of chloride ions grows up to 13.6 ions per 100 eV. Under these conditions the yield of formic acid and formaldehyde also increases. The radiation-chemical yield of dichloroethane decreased with growing alkali concentration (see table). The yield of CO decreased to $G <$ 0.001 molecule per 100 eV (sensitivity level of the analytical procedure) already at alkali concentration of 0.1 M. These data show that hydoxyls more efficiently react with radicals **I, II** [reactions (17, 18)] than water molecules.

$$\textbf{I} + 2HO^{\cdot} \rightarrow \textbf{III} + 2Cl^{\cdot} \qquad (17)$$

$$\textbf{II} + HO^{\cdot} \rightarrow \textbf{IV} + Cl^{\cdot} \qquad (18)$$

Radicals **III, IV** in alkaline medium turn to radical-anions [reactions (19, 20)] and transforming along reactions (21, 22) end up as formate anion and formaldehyde.

$$\textbf{IV} + HO^{\cdot} \rightarrow \underset{\textbf{IV}}{\dot{C}H_2O^{-}} + H_2O \qquad (19)$$

$$\textbf{III} + HO^{-} \rightarrow \underset{\textbf{VII}}{HCOO^{\cdot}} + 2H_2O \qquad (20)$$

$$\textbf{VII} + CH_2Cl_2 \rightarrow HCOO^{-} + \textbf{II} + Cl^{-} \qquad (21)$$

$$\textbf{VI} + CH_2Cl_2 \rightarrow CH_2O + \textbf{II} + Cl^{-} \qquad (22)$$

The sharp decrease in CO yield in alkaline solution may be rationalized by reaction (20). The low yield of dichloroethane that forms by second-order reaction (6) is due to diminishing of radicals **II** stationary concentration for in alkaline solutions they are involved in reaction (18). The described reactions in total provide a possibility of chain process of chlorine substitution in the dichloromethane radicals whose efficiency would be greater at lower power of the absorbed radiation dose. Under conditions of lower dose power the concentration of dichloromethane radicals and the frequency of reactions of second-order chain termination would be considerably less. We measured radiation-chemical yields of chloride ions at 10-fold reduced dose power in the solution containing various alkali concentrations (see table). The yield of chloride ions at NaOH concentration 0.5 M amounted to 110 ions per 100 eV and significantly exceeded the overall yield of radical species in water radiolysis equal to 6 species per 100 eV. This fact confirms the chain character of chlorine ions formation process.

The short-lived intermediate products of dichloromethane radicals transformation were studied by means of ESR.

As seen from Fig. 3, at rising temperature the ESR spectrum of the dichloromethane water solution gets simpler. The intensity of the absorption band in the right-hand part of the spectrum sharply decreased, and that of three bands in the left part increased. Their maximum intensity is reached at –63°C. The final pattern of the spectrum is also attained at –63°C.

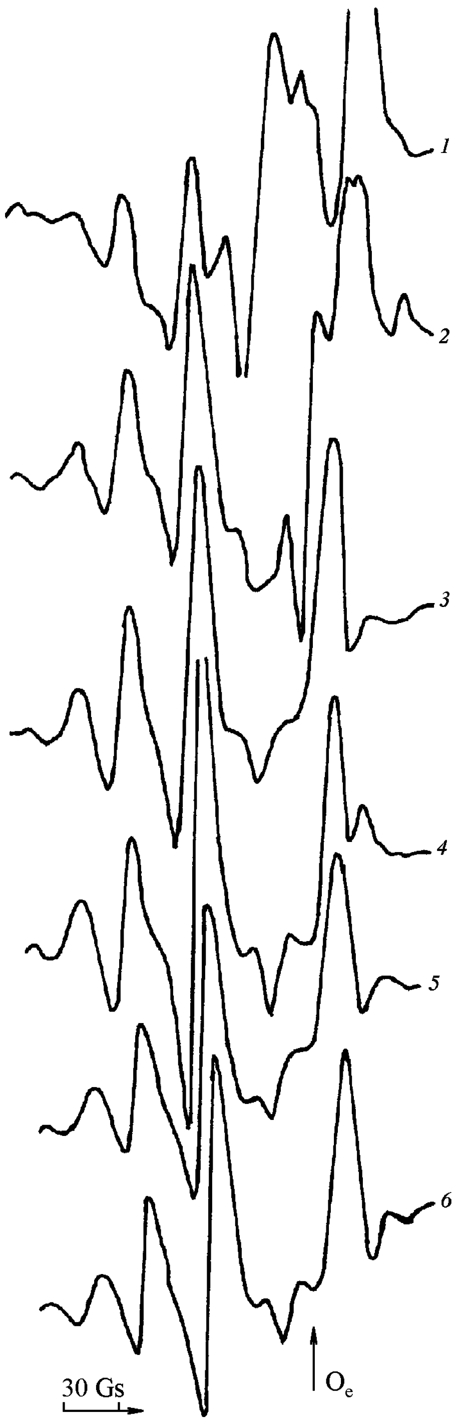

Fig. 3. ESR spectrum of dichloromethane water solution irradiated at –196°C (*1*) with a dose of $2.5–10^{21}$ eV l^{-1}, and changes thereof at temperature risen to the following values: –80 (*3*), –63 (*4*), –20 (*5*), 0°C (*6*); g_e 2.0055; [NaOH] 0.5 M.

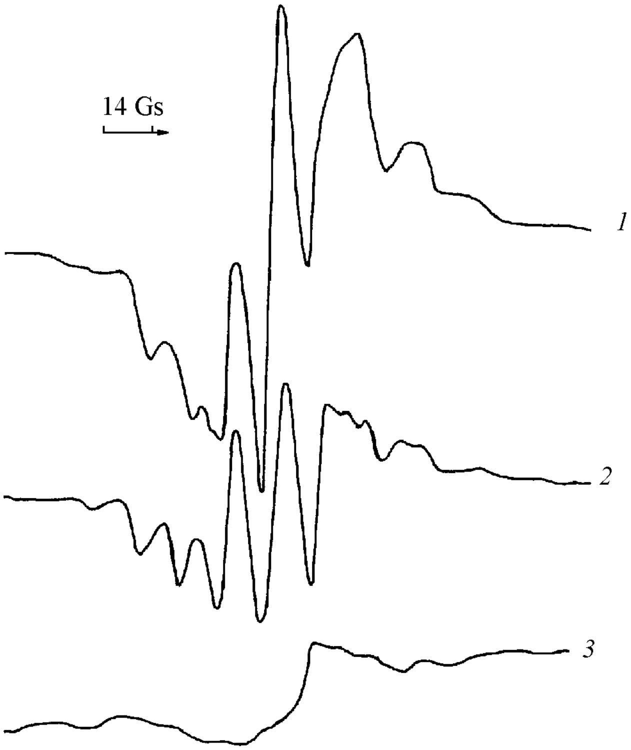

Fig. 4. ESR spectrum of pure dichloromethane irradiated with a dose 3.2×10^{21} eV l^{-1} at following temperatures: –196 (*1*), –102 (*2*), –86°C (*3*).

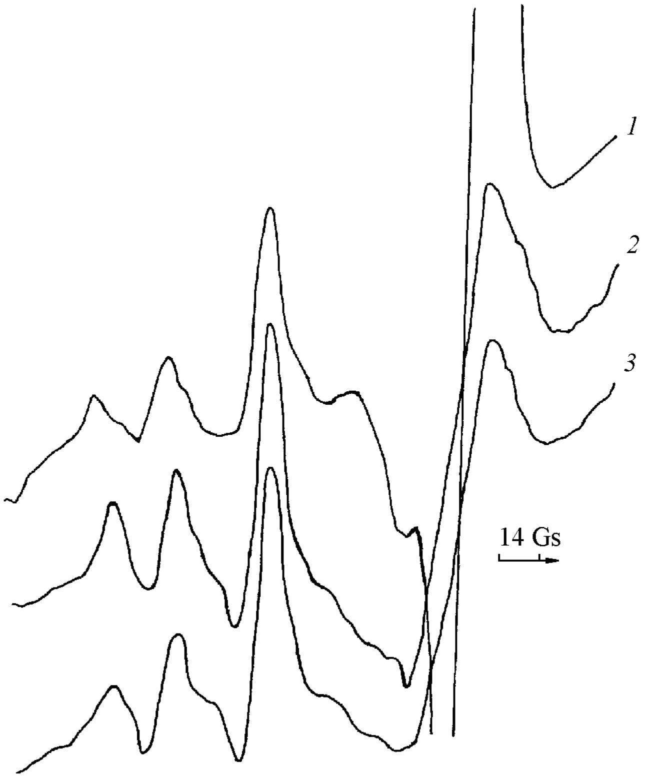

Fig. 5. ESR spectrum of water solution containing 0.1 M HCOOH and 0.6 M NaOH after irradiation with a dose 11.4×10^{21} eV l^{-1} at –63 (*1*), –20 (*2*), and 0°C (*3*).

Further heating does not change the qualitative pattern of the spectrum up to 0°C (without phase transition).

The loss of intensity of the right spectrum band is due to disappearance of $HO^{\cdot}$ radicals [4]. Therefore the spectrum in Fig. 3 corresponding to –80°C belongs to radicals arising from dichloromethane as a result of its reactions with $HO^{\cdot}$, $H^{\cdot}$ and e^{-}_{aq} species, and also probably to radical products formed at replacement of chlorine with HO^{-} ions. In the pure dichloromethane all radical species (also radicals **I** and **II**) are terminated by recombination already at –86°C. It is clearly shown on Fig. 4 where is presented the ESR spectrum obtained at irradiation of pure dichloromethane.

Consequently, in the ESR spectrum of the alkaline solution of dichloromethane (Fig. 3) at –63°C all the absorption bands originate from species formed in reaction of radicals **I** and **II** with hydroxyls. The existence of ESR spectrum at –20°C and 0°C shows that the radical species corresponding to this spectrum difficultly undergo recombination. This fact suggests that the ESR signal originates from radical-anions **VII** that form by reactions (17) and (20). The large negative charge of these radicals prevents their recombination.

At –63°C the ESR spectrum of water solution containing formic acid in 0.1 M concentration and NaOH is 0.6 M concentration obtained after irradiation with a dose 11.4×10^{21} eV l^{-1} (Fig. 5) is similar to the spectrum from the irradiated alkaline dichloromethane solutions (Fig. 3). Both spectra in the left-hand part contain three bands of unequal intensity that remain till 0°C. The irradiation of the alkaline solution of formic acid may give rise to radical-anions **VII** under the action of hydrated electrons. The rate constant of this reaction is 1×10^{4} l mol^{-1} s^{-1}) [5]. Therefore it is possible to state that three absorption bands in the left part of the ESR spectra of the irradiated alkaline dichloromethane solutions (Fig. 3) originate from radical-anion **VII**. The band in the right part of the spectrum belongs presumably to radical-anion **VI** that forms by reactions (18, 19). The charge hampers its disappearance by the second-order processes. On the other hand, the destruction of radical-anions **VII** provides radical-anions **VI** [by reaction sequence (21), (18), (19)].

The formation of radical-anion **VII** [by reactions (17) and (20)] already at –80°C evidences that activation energy of reaction (17) is very small as follows also from results of calculation performed in [1].

EXPERIMENTAL

In the studies was used dichloromethane of “pure” grade after distillation. Before irradiation the solutions were deaerated by successive dilution procedure [6] with the use of argon of high purity. The NaOH used was of “chemically pure” grade. The irradiation was carried out in sealed ampules on an installation LMB-γ-1M. The power of the absorbed dose as measured with ferrosulfate dosimeter was 2.12×10^{18} eV l^{-1} s^{-1}, the range of doses used was $(2.5–15.3) \times 10^{21}$ eV l^{-1}. The radiation-chemical yields were calculated from the curves of yields as a function of dose with the use of least-squares procedure. The analysis for formaldehyde was spectrophotometric with the use of chromotropic acid [7]; as reference served the initial nonirradiated solution. The molar extinction factor determined with calibrating solutions was close to that in [7] $(1.56 \pm 0.19) \times 10^4$ l mol^{-1} cm^{-1}). The formic acid was determined by procedure from [8]. To the samples under study was added the appropriate amount of fine magnesium turnings and hydrochloric acid, and after reduction of the acid to formaldehyde its content was measured by spectrophotometric procedure. As reference here was used the initial solution that was not subjected to reduction. The molar extinction factor for the formic acid was determined by calibration with standard formic acid solutions that were subjected to all stages of treatment perscribed for the sample under investigation. The value of molar extinction factor thus obtained was $(1.15 \pm 0.3) \times 10^4$ l mol^{-1} cm^{-1}). Dichloroethane analysis was carried out by GLC on chromatograph LKhM-8MD equipped with flame-ionization detector, column 2 m long, stationary phase PEG-600 (10%) on Chromosorb W, carrier gas argon. Carbon monoxide was analyzed on chromatograph LKhM-8MD equipped with katharometer, column 1 m long packed with activated carbon [9], carrier gas helium. Chloride ions were analyzed by potentiometric titration with silver nitrate solution calibrated against a standard sodium chloride solution. The samples before titration were neutralized and acidified with nitric acid.

The ESR spectra of radical species were recorded on spectrometer ESR220 at –196°C. The magnetic field was calibrated with the use of magnetometer MJ-110R by the hyperfine structure lines of a standard sample of Mn^{2+}/MgO. Variable temperature measurements were performed with the use of standard cooling baths from liquid nitrogen with methanol, methyl ethyl ketone, ethyl acetate, chloroform, and tetrachloromethane [10]. The sample before measurement was maintained at a given temperature for 10 min.

REFERENCES

1. Kosobutskii, V.S. and Petryaev, E.P., *Zh. Org. Khim.*, 1993, vol. 29, no. 2, pp. 235–241.
2. Khenli, E. and Dzhonson, E., *Radiatsionnaya khimiya*, Moscow: Atomizdat, 1974.
3. Von Sonntag, C., *J. Am. Chem. Soc.*, 1988, vol. 110, no. 7, pp. 5698–5701.
4. Pshezhetskii, S.Ya. and Kotov, A.G., *EPR svobodnykh radikalov v radiotsionnoi khimii)*, (ESR of free Radicals in Radiochemistry), Moscow: Khimiya, 1972.
5. Pikaev, A.K. and Kabakchi, S.A., *Reaktsionnaya sposobnost' pervichnykh produktov radioliza vody* (Reactivity of Primary Products of Water Radiolysis), Moscow: Energoizdat, 1982.
6. Khart, E. and Anbar, M., *Gidratirovannyi elektron* (Hydrated Electron), Moscow: Atomizdat, 1974.
7. Korenman, I.M., *Fotometricheskii analiz* (), Moscow: Khimiya, 1970.
8. Lur'e, Yu.Yu., *Analiticheskaya khimiya promyshlennykh stochnykh vod* (Analytical Chemistry of Industrial Waste Water), Moscow: Khimiya, 1984.
9. Petryaev, E.P., Kosobutskii, V.S., and Shadyro, O.I., *Khim. Vys. Energ.*, 1982, vol. 16, no. 6, pp. 516–519.
10. Gordon, A.J. and Ford, R.A., *The Chemist's Companion*, New York: Wiley–Interscience, 1972; Translated under the title *Sputnik khimika*, Moscow: Mir, 1976, p. 319.