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RADIATION AND QUANTUM YIELDS OF Cl^- IONS IN CHLOROBENZENE, CARBON TETRACHLORIDE AND WATER TWO-PHASE SYSTEMS

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ABSTRACT

The γ-radiolysis of unstirred two-phases systems of water-carbon tetrachloride and water-chlorobenzene and the dependence of total radiation-chemical yields of Cl^- ions from the partial volume of phase II (organic phase) has been examined. From this dependence, the partial yields $_{I}G(Cl-)$ and $_{II}G(Cl^-)$ for water and organic phase has been calculated, respectively. The photolysis of two-phases systems has been investigated under the conditions similar to irradiation experiments and the quantum yields were compared.

KEYWORDS

Radiolysis; gamma radiation; radiation-chemical yields; photolysis; quantum yields; carbon tetrachloride; chlorobenzene; water; chloride ion.

INTRODUCTION

A production of aggressive products is very important in liquid-liquid extraction of radionuclides. Previous studies on the radiolysis (Čech 1984) and the photolysis (Kuruc 1983, 1984) of nitrobenzene-carbon tetrachloride mixture have shown that, chlorobenzene and chlorine were produced. The question is how will an aqueous phase influence on radiation and quantum yields?
For the dependence of total radiation-chemical yield from the partial volume of organic phase Macášek and Čech (1984) proposed expression:

$$_{T}G = w_{I} \; . \; _{I}G + z \; . \; w_{II} \; . \; _{II}G \qquad (1)$$

where $w_I = V_I / V_T$; $w_{II} = V_{II} / V_T$ and

$$z = e_{II} \; .\rho_{II} \; / \; e_{I} \; . \; \rho_{I} \qquad (2)$$

where V_I and V_{II} are volumes of phase I and II, V_T - total volume; w_I and w_{II} are partial volumes; e_I and e_{II} are electron densities of phase I and phase II, respectively; ρ_I and ρ_{II} are volume densities; $_{I}G$ and $_{II}G$ are partial yield for the phase I and phase II, respectively, and G is a total yield.

EXPERIMENTAL

Samples were irradiated in a glass vials with I.D. 13.7 mm with total volume 6 cm^3. The ^{60}Co radiation unit was used for irradiation of samples with dose rate 0.67 Gy/s and temperature 32±3°C. The total energy absorbed in the cell was determined by ferrosulphate dosimetry (Pikayev 1975). The mercury lamp Osram HQE 40 W (Germany) was excited with high frequency field 20 MHz. The lamp was immersed in a photoreactor with total volume 70-80 cm^3. Intensity or monochromatic light (95 % 254 nm) established actinometrically by potassium ferrioxalate (Calvert, Pitts 1968) was I_0 = (2.17 + 0.039 . 10^{16} quant/s.

RESULTS AND DISCUSSION

The dependence of total radiation-chemical yields of Cl^- ions from the partial volume of phase II (organic phase) in the γ-radiolysis of unstirred two-phases systems has been investigated. The partial yields $_{I}G(Cl^-)$ for water phase and $_{II}G(Cl^-)$ for organic phase have been calculated according to equation (1). The dependence of total radiation-chemical yield for water-carbon tetrachloride system and water-chlorobenzene system on a partial volume of phase II is shown in fig. 1. The radiation yields $_{I}G(Cl^-)$ = 10.5 ± 0.5 (ions/100 eV) and $_{II}G(Cl^-)$ = 7.0 ± 0.6 have been calculated according to formula (1); in the case of water-chlorobene system radlo1ysis, both phases were approximate equally reactive: $_{I}G(Cl^-)$ = 1.02 ± 0.02 and $_{II}G(Cl^-)$ = 1.28 + 0.05. The linearity of dependences enables to assume that radiolytical processes in the investigated two--phases systems under given irradiation condition, follows a kinetic regime.

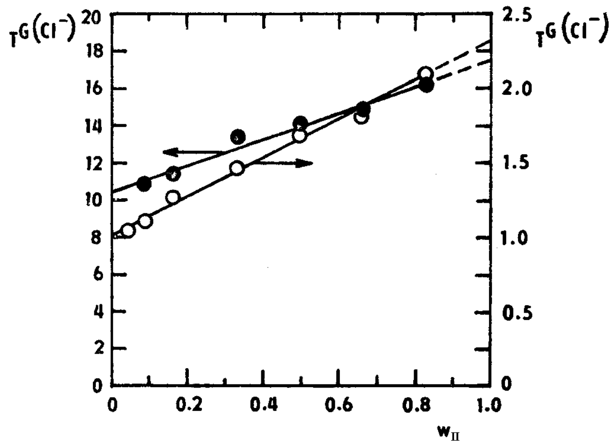

Fig. 1. Relationship between total radiation yields of chloride ions and partial volume of phase II for radiolysis of two-phase • - water--carbon tetrachloride system; o - water-chlorobenzene system.

We have also examined UV photolysis of these systems. In the photolysis of two-phase system under irradiation of organic phase only the average quantum yield of formation Cl^- ions were $\varnothing(Cl^-)$ = = 0.89 ± 0.04 while at photolysis of saturated solution of carbon tetrachloride in the water $\varnothing(Cl^-)$ = 18.9 ± 5.6. Similarly, in the photolysis of water-chlorobenzene system the quantum yields under irradiation of organic phase were $\varnothing(Cl^-)$ = 0.14 ± 0.01 and for the saturated water chlorobenzene solution $\varnothing(Cl^-)$ = 0.56 ± 0.03.

Table 1. The comparision of energy efficiency of Cl^- production

System	$_IG(Cl^-)$	$_{II}G(Cl^-)$	$_I\varnothing(Cl-)$	$_{II}\varnothing(Cl^-)$
	[ions/100 eV]		[ions/100 eV]*	
H_2O-CCl_4	10.5	7.0	387	18.2
H_2O-PhCl	1.02	1.28	11.5	2.87

* 1 quant of light of 254 nm = 4.882 eV.

The comparison of energy efficiency of Cl^- production in the radiation and photochemical initiated decomposition of carbon tetrachloride or of chlorobenzene in the presence of water is shown in tab. 1. The efficiency of arising Cl^- differs very much in the case of aqueous phase or saturated aqueous solutions. As seen the table 1, the Cl^- yield in aqueous solution saturated with carbon tetrachloride has value typical for a chain reaction mechanism.

REFERENCES

Calvert, J., and J. Pitts (1968). Photochemistry, Mir Publishers, Moscow, p.625.
Čech, R., H. Chrenčíková, V. Širáňová, J. Kuruc, and F. Macášek (1984). J. Radioanal. Nucl. Chem., 86, 337-346.
Kuruc, J., and R. Čech (1983). Radiochem. Radioanal. Lett., 57, 169-176.
Kuruc, J. (1984). J. Radioanal. Nucl. Chem., 82, 93-100.
Macášek, F., and R. Čech (1984). Radiat. Phys. Chem., 23, 473-479.
Macášek, F. (1984). Radiat. Phys. Chem., 23, 481-484.
Pikayev, A. K. (1975). Dozimetriya v radiyacionnoy khimiyi, Nauka Publishers, Moscow, p.135.