3. Geminal recombination of low-molecular-weight radicals in polyvinyl chloride films is characterized by polychromatic kinetics and makes a marked contribution with a concentration of plasticizer ≤60%.

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RADIOLYSIS OF AQUEOUS SOLUTIONS OF TETRAZOLIUM SALTS

Z. K. Kriminskaya, A. A. Konarev, K. M. Dyumaev,
B. V. Tolkachev, and A. K. Pikaev

UDC 541.15:547.796.1-145.2

Reducing agents act on colorless tetrazolium salts to form intensely colored formazanes, which has practical utility [1, 2]. We have previously [3] used pulse radiolysis to study the intermediate products of radiolysis of aqueous solutions of tetrazolium salts and proposed a mechanism for their radiolytic transformations. The aim of the present work was to study both final and intermediate products of radiolysis of aqueous solutions of tetrazolium salts with various chemical additives.

EXPERIMENTAL

The aqueous solutions of the tetrazolium salts were irradiated on cobalt gamma-apparatus "Issledovatel'" [Researcher] using a dose of 1.64 Gy/sec on a GUG-120 isotopic hydraulic gamma-apparatus, using a dose of 0.52 Gy/sec. The dosimetry of the γ-radiation was carried out by the ferrosulfate method.

To determine the amount of formazine formed during the radiolysis and separating as a precipitate, the latter was dissolved by adding isopropanol to the irradiated aqueous solution in a per-volume ratio of 1:1. The molar extinction coefficient of formazine in this aqueous—alcoholic mixture is equal to its molar extinction coefficient in isopropanol: $(1.6 \pm 0.1)\cdot 10^4$ liter/(mole·cm) at 485 nm for 1,3,5-triphenylformazane, $(1.9 \pm 0.2)\cdot 10^4$ liter/(mole·cm) at 480 nm for 1-nitrophenyl-3,5-diphenylformazane and $(1.2 = 0.1)\cdot 10^4$ liter/(mole·cm) at 480 nm for 1,5-diphenyl-3-nitrophenylformazane.

In studies on pulse radiolysis, we used a rapid-acting spectrophotometric apparatus with a microsecond time resolution, functioning on a base of a U-12 linear electronic accelerator [4]. The methods of irradiation, preparation of the samples and carrying out the dosimetry, as well as the statistical treatment of the experimental results are described in [5].

The polarograms were recorded by means of a PU-1 polarograph in a Britton—Robinson buffer solution at pH 9.8. The concentration of the solutions was $1.15\cdot 10^4$ M. A mercury

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Institute of Physical Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1746-1750, August, 1988. Original article submitted April 3, 1987.

0568-5230/88/3708-1555 $12.50

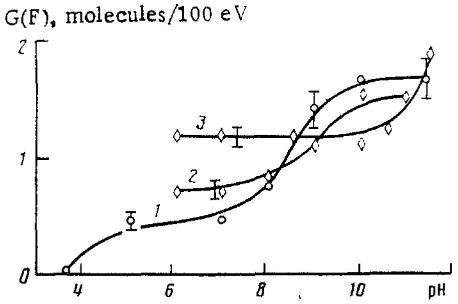


Fig. 1

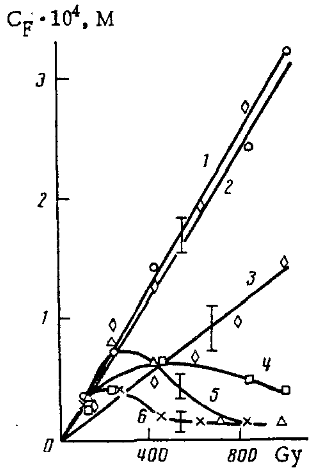


Fig. 2

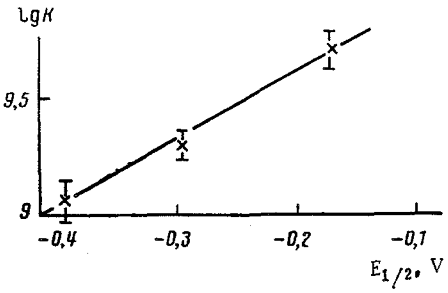


Fig. 3

Fig. 1. Dependence of G(F) on pH of a 10^{-3} M solution of TTC (1), 10^{-3} M p-NTC (2), and $5 \cdot 10^{-4}$ M of p-NTB (3).

Fig. 2. Dependence of the concentration of formazane on the dose in a 10^{-3} M aqueous solution of TTC (pH 10.3) in the presence of a 0.2 mole/liter formate (1) or EDTA (2) and in the absence of additives (3), in a 10^{-3} aqueous–ethanol (1:1 by volume) solution of TTC in the absence of additives (4), and in the presence of 0.2 mole/liter formate (5) or EDTA (6).

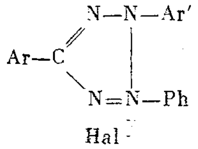
Fig. 3. Dependence of log K on the first half-wave potential of the reduction of tetrazolium salt.

dropping electrode with forced separation of the drop with an open circuit and a height of the mercury column of 50 cm in 0.1 M KCl had the following characteristics: $m = 1.0$ mg·sec^{-1}, τ 0.65 sec. Calomel half cells served as reference and auxiliary electrodes. The potentials were measured relative to a calomel cell.

Analytically pure brand 2,3,5-triphenyltetrazolium chloride (TTC) was recrystallized from ethanol; 2-p-nitrophenyl-3,5-diphenyl tetrazolium chloride (p-NTC) from the firm "Reanal" was used without further purification; 5-p-nitrophenyl-2,3-diphenyltetrazolium bromide (p-NTB) was obtained by a method similar to that used in [6]. The pH values of the solution were adjusted by adding NaOH or HCl solutions.

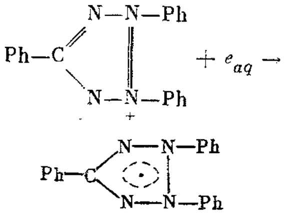
RESULTS AND DISCUSSION

During irradiation of Ar-saturated aqueous solutions of all the tetrazolium salts studied, a precipitate is formed, which, after filtration and dissolution in alcohol, gives an electronic absorption spectrum characteristic of the corresponding formazane. It is known [7] that in alkaline aqueous solutions of TTC, the yield of formazane G(F) is higher than in neutral solutions. We studied the dependence of G(F) on pH (Fig. 1) for aqueous solution of TTC, p-NTC and p-NTB having the following structural formulas:



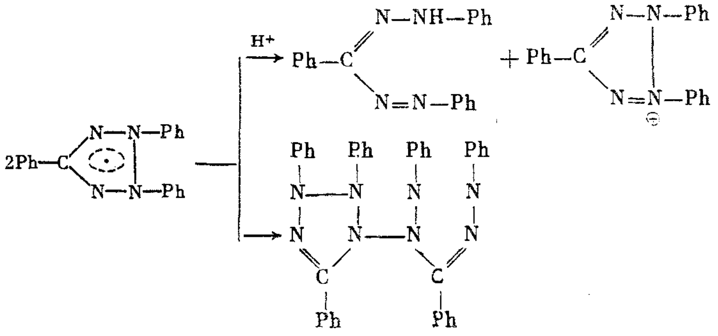
Ar = Ar′ = Ph, Hal = Cl (TTC), Ar = Ph, Ar′ = $C_6H_4NO_2$-*p*, Hal = Cl (p-NTC); Ar = = $C_6H_4NO_2$-*p*, Ar′ = Ph, Hal = Br (p-NTB).

In neutral media and at low pH values, $G(F) < 1/2\ G_{e_{aq}}$. Since the reduction of the tetrazolium salt to formazane is a two-electron process, and taking into account the high value ($>10^{10}$ liter/(mole·sec) [3]) of the rate constant of the reaction of the salt with e_{aq}, leading to the formation of a tetrazolium radical



(1)

it can be concluded that under these conditions, in aqueous solutions, as in isopropanol solutions, not only a disproportionation of the tetrazolium radicals takes place, leading to the formation of formazane, but also their dimerization



(2)

(3)

Since the H atoms do not reduce the tetrazolium salt (3), the ratio of the disproportionation and dimerization rate constants is in this case equal to:

$$\frac{K_{dia}}{K_{dim}} = \frac{2G(F)}{G_{e_{aq}} - 2G(F)} \tag{4}$$

It was calculated that for neutral solutions of TTC, this ratio is equal to 0.5, while for solutions of p-NTC, it is equal to unity. These values are much lower than the corresponding values for isopropanol solutions. In aqueous solutions of p-NTB, the G(F) is close to $G_{e_{aq}}$. As follows from the value of G(F) in isopropanol [6], for the tetrazolium radicals of this salt, dimerization is not characteristic, and the radicals formed during radiolysis preferentially undergo disproportionation with the formation of formazane.

Increase in G(F) with increase in pH can occur as a result of an increase in K_{dis}/K_{dim}. This ratio can increase as a result of a change in the structure of the tetrazolium radical in alkaline medium, which leads to a lower probability of dimerization because of steric hindrances.

The radical OH formed during radiolysis of water is an oxidant and does not participate in the reduction of tetrazolium salts [3]. However, if an OH radical acceptor which produces through reaction with the radical an active reducing particle, capable of reducing the tetrazolium salt, is introduced into the solution, then, in principle, G(F) can be increased. Formate, $i\text{-}C_3H_7OH$ and EDTA were used as such acceptors. The following reactions proceed effectively in these solutions:

$$HCOO^- + OH(H) \rightarrow CO_2^- + H_2O(H_2) \tag{5}$$

$$R'RNCH_2COO^- + OH(H) \rightarrow R'RN\dot{C}HCOO^- + H_2O(H_2) \tag{6}$$

TABLE 1. Values of G(F) in 10^{-3} M Aqueous Solutions of TTC (at pH 10.3) in the Presence of Acceptors

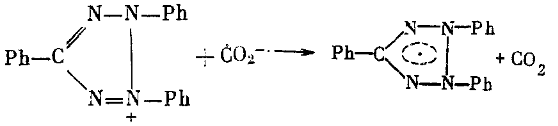
Acceptor and its concentration, M	Dose rate, Gy/sec	G(F), molecules/100 eV
–	0,52	1,2±0,1
2.2. $(CH_3)_2CHOH$	0,52	3.5±0.1
0,2, HCOONa	1,64	3,0±0,5
0,2, EDTA	1,64	3,1±0,3

TABLE 2. Rate Constants K of Reactions of CO_2^- with Tetrazolium Salts and Half-Wave Potentials of Their Reduction

Tetrazolium salt	K, liter/(mole·sec)·10^{-9}	$E_{1/2}$, V
TTC	1,1±0,3	−0,40±0,01
p-NTC	5,0±0,4	−0.17±0,01
p-NTB	1,9±0,1	−0,30±0,01

$$(CH_3)_2CHOH + OH(H) \rightarrow (CH_3)_2\dot{C}OH + H_2O(H_2). \tag{7}$$

The active particles formed in reactions (5)-(7) reduce the tetrazolium salt to tetrazolium radical, for example



(8)

Hence it follows, that in alkaline solutions at fairly high concentrations of the acceptors, G(F) should be equal to

$$G(F) = {}^1/_2 (G_{e_{aq}} + G_H + G_{OH}) \tag{9}$$

Figure 2 and Table 1 show the data on the γ-radiolysis of alkaline 10^{-3} M aqueous solutions of TTC in the presence of the above enumerated acceptors. It is seen that introduction of acceptors leads, in accordance with Eq. (9), to increase in the G(F) to a value of 3.3-3.5 molecules/100 eV. The deviation of the dose dependences from the linearity in aqueous alcoholic solutions is due to a further reduction of formazane itself; in this system it is soluble, while in aqueous solutions it precipitates, which hinders its reduction. The differences in the form of curves (4)-(6) in Fig. 2 are due to differences in the ratios between the rate constants of the reactions of radicals CO_2^-, $R'RN\dot{C}HCOO^-$ and $(CH_3)_2\cdot\dot{C}OH$ with the tetrazolium salt and those with formazane. Since the rate constants of the reactions of the OH radicals and H atoms with the tetrazolium salts have high values (for example, for p-NTC they are equal to $1.0 \cdot 10^{10}$ and $5.7 \cdot 10^9$ liter/(mole·sec), respectively [3]), for complete suppression of the reactions relatively large concentrations of the acceptors have to be used.

Increase in G(F) when the above acceptors are introduced shows that the radicals formed in reactions (5)-(7) in fact reduce the tetrazolium salts. A similar conclusion was reached previously in [8], where the rate constant of the reaction of CO_2^- with nitrotetrazolium Blue was measured. This conclusion is also confirmed by our data on pulse radiolysis of aqueous tetrazolium solutions containing formate and saturated with nitrous oxide. In these solutions, after the process

$$e_{aq} + N_2O + H_2O \rightarrow OH^- + OH + N_2 \tag{10}$$

reaction (5) takes place, and only radical CO_2^- is formed in the solution. It was found that by the action of an electron pulse in aqueous TTC, p-NTC and p-NTB solutions (pH 10.0) containing formate and saturated with N_2O, an absorption belonging to tetrazolium radicals is observed. The rate constants of the reaction of CO_2^- with tetrazolium salts were measured in a 10^{-4} M solution of TTC and $5 \cdot 10^{-5}$ M solution of p-NTB, containing 0.2 M of $HCOO^-$ (pH 10.0) and saturated with nitrous oxide.

The constants were calculated by a method described in [5]. The linearity of the dependence of the optical absorption of the tetrazolium radical on the dose per pulse was particularly verified from the calculations. When this dependence is linear, the reaction

$$CO_2^- - CO_2^- \rightarrow \text{Products} \tag{11}$$

does not proceed, and all the CO_2^- radicals participate in the reduction of the tetrazolium salts. The values of the constants obtained are listed in Table 2.

The rate constants of these reactions are lower than the diffusional limit, which is equal to $\geq 10^{10}$ liters/(mole·sec) [3]). In this case, there may be a correlation between the rate constants of these reactions and the half-wave potentials of the reduction of the tetrazolium salts, and the measure of the ability of these salts to be reduced to tetrazolium radicals can be the half-wave potential corresponding to a one-electron process. The measured values of these potentials are given in Table 2. Figure 3 shows the dependence of the logarithm of the rate constants on the half-wave potential. It is seen that this dependence is linear.

Thus, the above data confirm the mechanism that we proposed for radiolytic transformations of the tetrazolium salts in aqueous solutions, consisting in their reduction to formazanes via the stage of formation of tetrazolium radicals.

CONCLUSIONS

1. In γ-radiolysis of aqueous solutions of nitrotetrazolium salts, the yield of formazane in a neutral medium is higher than that for 2,3,5-triphenyltetrazolium chloride. The yields of formazanes increase in alkaline medium and in the presence of OH radical acceptors.

2. A correlation between the values of the rate constants of the reactions of the CO_2^- radicals with tetrazolium salts and the half-wave potentials of the reduction of these salts was established.

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