with the light of the DRSh-500 lamp using a transmission monochromator separating the light of the wavelength 313 nm for the measurement of the quantum yield. The actinometry was performed utilizing a modified ferrioxalate actinometer [8]; the quantum yield of the actinometer was 1.1 at 313 nm. The work utilized a Jeol FX90Q NMR spectrometer (the working frequency of 89.55 MHz) and a Specord M40 spectrophotometer from Carl Zeiss.

The PMR spectrum of (I) (δ, ppm) was as follows: 3.98 s (6H, 2CH$_3$), 4.51 s (2H, CH$_2$), 7.72 d and 7.91 d (4H, p-C$_6$H$_4$, J = 9.1 Hz).

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A STUDY BY PULSE RADIOLYSIS OF THE RADIATION-CHEMICAL
TRANSFORMATION OF AQUEOUS SOLUTIONS OF HYDRAZINE
IN THE PRESENCE OF OXYGEN

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It is shown by pulse radiolysis that in aqueous solutions of hydrazine containing oxygen the radical N$_2$H$_3$ reduces oxygen to O$_2^-$ at pH > 7 (k $\geq$ 3$\cdot$10^9 dm$^3\cdot$mole$^{-1}\cdot$sec^{-1}), while this reaction does not occur for the protonated form N$_2$H$_4^+$ at pH < 7 (k $\leq$ 5$\cdot$10^6 dm$^3\cdot$mole$^{-1}\cdot$sec^{-1}). The rate constants for the disappearance of O$_2^-$ have been determined in the pH range from 4 to 12. Rate constants have been calculated for the reaction of O$^-$ with N$_2$H$_4$ [k = (1.6 $\pm$ 0.2)$\cdot$10^9 dm$^3\cdot$mole$^{-1}\cdot$sec^{-1}] and of O$_3^-$ with N$_2$H$_4$ [k = (1.2 $\pm$ 0.2)$\cdot$10^6 dm$^3\cdot$mole$^{-1}\cdot$sec^{-1}].

The use of hydrazine in atomic energy for optimizing the aqueous chemical regime lends importance to the problem of determining the mechanism of its radiation-chemical transformation. It has been shown [1-3] that γ-irradiation of deaerated solutions of hydrazine decomposes it efficiently into ammonia, nitrogen, and hydrogen. The following relations have been established between the yields of the main products: G($-$N$_2$H$_4$) = G(NH$_3$) = 2G(N$_2$, H$_2$) = 5.2-5.5. Pulse radiolysis has been used to determine the rate constants for the reaction of the primary radiolysis products of water (e$_{aq}^-$ and the OH radical) with hydrazine in deaerated solutions, and to investigate the nature of the radical products formed [4]. In the presence of oxygen the decomposition of hydrazine under the influence of radiation involves a chain mechanism [2, 5]. Increasing the pH of the solutions stimulates this process.

In the present study we have used pulse radiolysis to investigate the short-lived ion-radical products and the mechanism of the radiation-chemical transformation of hydrazine in solutions containing oxygen.


EXPERIMENTAL

The source of radiation was a linear U-12 electron accelerator [energy of electrons 5 MeV, duration of pulse 2.3 μsec, dose per impulse $(1-5) \cdot 10^{17}$ eV·cm^{-1}). The short-lived radiolysis products were monitored spectrophotometrically. The results were processed on an Iskra-226 computer.

The solutions were prepared with triply distilled water. The experiments were carried out with hydrazine hydrate prepared from the hydrochloride or the sulfate; commercial 30% hydrazine hydrate was redistilled [6]. Buffer solutions were prepared from perchloric acid and potassium hydroxide. The hydrazine concentration varied from 10^{-5} to 10^{-1} mole·dm^{-3} and was measured spectrophotometrically with p-dimethylaminobenzaldehyde at 465 nm. The pH was measured on an ÉV-74 pH meter with an ÉSL-63-07 glass indicator electrode and an ÉVL-1M3 silver chloride electrode. In the absence of irradiation the concentration of hydrazine in freshly prepared solutions in the pH range 4-12 remained constant for the duration of an experiment.

RESULTS AND DISCUSSION

In aqueous solution hydrazine exists in two forms in equilibrium with one another [4, 7, 8]:

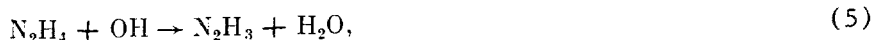$$N_2H_4 + H_2O \rightleftarrows N_2H_5^+ + OH^-, \quad pK_a = 8,1 \pm 0,1. \tag{1}$$
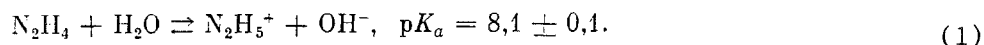
After irradiation with accelerated electron pulses of 2.3 μsec duration the absorption of e_{aq}^- with $\lambda_{max} = 720$ nm is observed in hydrazine solutions of concentrations 10^{-5}-10^{-1} mole·dm^{-3} saturated with argon. According to [4], e_{aq}^- is destroyed in the following reactions:

$$N_2H_4 + e_{aq}^- \rightarrow N_2H_4^-, \tag{2}$$

$$N_2H_5^+ + e_{aq}^- \overset{\longrightarrow N_2H_4 + H}{\underset{\longrightarrow N_2H_3 + H_2}{\big|}} \tag{3}$$

In solutions saturated with nitrous oxide e_{aq}^- is mainly destroyed in the reaction

$$N_2O + e_{aq}^- \overset{H_2O}{\longrightarrow} OH(O^-) + OH^- \tag{4}$$

Absorption is then observed with $\lambda_{max} = 230$ nm at pH ≥ 8.0 ($\varepsilon = 3.5 \cdot 10^3$ dm^3·mole^{-1}·cm^{-1}) and at $\lambda < 225$ nm at pH < 8.0, attributed, respectively, to N_2H_3 and $N_2H_4^+$, formed in the reactions [5-8]

$$N_2H_4 + OH \rightarrow N_2H_3 + H_2O, \tag{5}$$

$$N_2H_5^+ + OH \rightarrow N_2H_4^+ + H_2O, \tag{6}$$

$$N_2H_5^+ + H \rightarrow N_2H_4^+ + H_2. \tag{7}$$

According to [4], the following equilibrium is set up:

$$N_2H_3 + H_2O \rightleftarrows N_2H_4^+ + OH^-, \quad pK_a = 7.1 \pm 0.1. \tag{8}$$
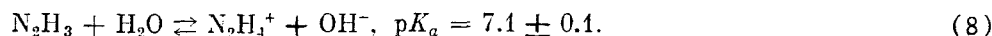
In solutions saturated with O_2, after the electron pulse an absorption band is observed at the position ($\lambda = 245$ nm) and having the shape corresponding to the ion-radical O_2^- (Fig. 1). Since there is a considerable amount of luminescence in this part of the spectrum, induced by the irradiation, this absorption could be reliably observed only 15 μsec after the pulse. At pH > 8.0, which, according to reaction (8), corresponds to the range of existence of N_2H_3, the intensity of the 245-nm band increases with increasing content of hydrazine and reaches constant values at concentrations above 10^{-3} mole·dm^{-3} (Fig. 2). At pH < 6.0, i.e., in the range of existence of $N_2H_4^+$, the intensity of the O_2^- signal is almost independent of the concentration of N_2H_4.

Figure 3 shows the pH dependence of $G \cdot \varepsilon_{250}$ for this band; it increases at pH ≥ 6.0, but reaches a constant value at pH > 8.0, the point of inflection being at 7.0-7.5. The form of this dependence correlates with the changes in the concentration of N_2H_3 radicals due to the electrolytic dissociation of $N_2H_4^+$ by reaction (8) [4, 8] (Fig. 3).
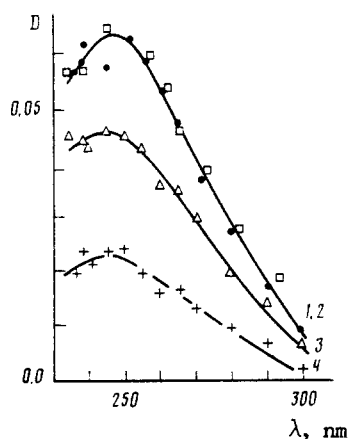
Fig. 1   Fig. 2

Fig. 1. Absorption spectrum of O_2^- in a 10^{-3} M solution of N_2H_4 saturated with O_2, pH 9.3. The times elapsed after the pulse were: 1) 20 μsec; 2) 10 msec; 3) 80 msec; 4) 280 msec.
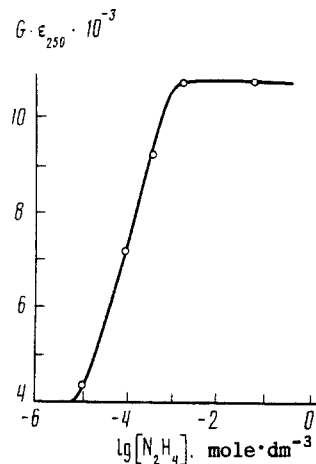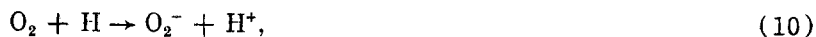
Fig. 2. Dependence on the concentration of N_2H_4 of $G \cdot \varepsilon_{250}$ for the O_2^- band (λ_{max} = 250 nm) in a solution of N_2H_4 saturated with O_2.

We suggest that in solutions of N_2H_4 the ion radical O_2^- is formed not only by the reactions

$$O_2 + e_{aq}^- \rightarrow O_2^-. \tag{9}$$

$$O_2 + H \rightarrow O_2^- + H^+, \tag{10}$$

but also by the reaction of N_2H_3 radicals with oxygen

$$N_2H_3 + O_2 \xrightarrow{OH^-} O_2^- + N_2H_2 + H_2O. \tag{11}$$

Allowing for the fact that 15 μsec after the pulse all the N_2H_3 radicals have been captured by oxygen, we estimate that the rate constant for reaction (11) is $\geq 3 \cdot 10^9$ dm³·mole⁻¹·sec⁻¹ at pH > 8.0. At the same time, at pH ≤ 6.0 the ion radical $N_2H_4^+$ either does not react with O_2, or the rate constant for this reaction is considerably smaller than for reaction (11). It therefore follows that, at the end of the pulse, the optical density of O_2^- should be approximately doubled on going from pH < 6.0 to pH > 8.0, since it is formed not only from e_{aq}^- and H but also from N_2H_3. However, after the elapse of 15 μsec corresponding to the conditions under which absorption by O_2^- was observed in our experiments, the difference between the intensities is considerably greater. This is presumably because at pH < 6.0 the greater part of the O_2^- disappears by the reaction

$$N_2H_4^+ + O_2^- \rightarrow \text{products} \tag{12}$$

which must have a rate constant $\geq 7 \cdot 10^9$ dm³·mole⁻¹·sec⁻¹. The calculated value of $G \cdot \varepsilon_{250}$ at the end of the pulse of electrons is shown in Fig. 3 by a broken line. If the radical $N_2H_4^+$ also reacts with O_2, the rate constant must be less than $5 \cdot 10^6$ dm³·mole⁻¹·sec⁻¹. The N_2H_3 radicals are converted into O_2^- by reaction (11). The concentration of the latter will change inappreciably more than 15 μsec after the pulse, since the rate constant for their recombination is low. The observed value of $G \cdot \varepsilon_{250}$ in the range pH > 8.0 is therefore approximately twice as great as the calculated value for pH < 6.0. Taking these facts into account shows that the initial yield of O_2^- radicals at pH > 8.0 is equal to the sum $G_{e_{aq}^-}$ + G_H + G_{OH}. The value of ε_{250} calculated from the data in Fig. 3 on the basis of this assumption is $1.75 \cdot 10^3$ dm³·mole⁻¹·cm⁻¹, close to the accepted value of $1.95 \cdot 10^3$ dm³·mole⁻¹·cm⁻¹ [9, 10].

At the end of the pulse reactions (5)-(10) lead mainly to the formation of pH 4-6 of $N_2H_4^+$, O_2^-, HO_2, which react with one another. According to our results, in this pH range the fall in the absorption due to the radical O_2^- (HO_2) more than 15 μsec after the pulse obeys second-order kinetics with rate constants which are in good agreement with published
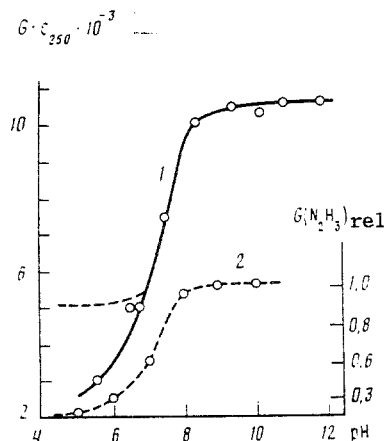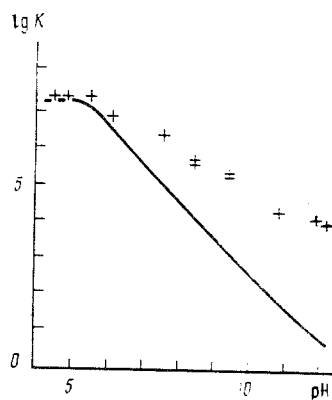
Fig. 3

Fig. 4

Fig. 3. Dependence on pH of $G \cdot \varepsilon_{250}$ for the O_2^- band ($\lambda_{max} = 250$ nm) in a 10^{-3} M solution of N_2H_4 saturated with O_2 (1); dependence on pH of the relative concentration of N_2H_3 radicals according to [4] (2).

Fig. 4. Dependence on pH of the rate constant for the disappearance O_2^- ($\lambda_{max} = 250$ nm) in a 10^{-3} M solution of N_2H_4 saturated with O_2. The curve represents published data [9, 10, 13] and the points are experimental.

values for the recombination of O_2^- with HO_2 (Fig. 4) [9-12].

At pH 6-10, the disappearance of O_2^- during any time interval is not well represented by the equations for first- or second-order reactions. It is known [9, 12] that in this range of pH the disappearance of O_2^- in water containing oxygen is of a mixed kinetic order, which is attributed to the presence of indeterminate amounts of impurities, in particular metal ions of variable valency. In the range pH 10-12 the rate of disappearance of O_2^- falls sharply and agrees well with second-order kinetic equations. As will be seen from Fig. 4, the rate constant calculated from a second-order kinetic equation at pH > 7 is greater than that obtained for water containing O_2 [9, 10, 12].

The chain decomposition of hydrazine in solutions containing O_2 involves reaction (11) and the reaction

$$N_2H_4 + O_2^- \rightarrow N_2H_3 + HO_2^-. \tag{13}$$

It was assumed that chain breaking occurs by recombination of the ion radicals O_2^- (HO_2)
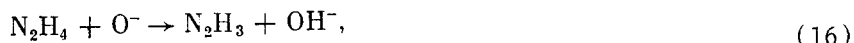
$$O_2^- + O_2^- \rightarrow \text{products} \tag{14}$$

The observed increase in the yield in the decomposition of hydrazine with increase in pH is in accordance with the fact that there is then a considerable decrease in the rate constant of reaction (14) [12]. However, our rate constant for the disappearance of O_2^- in hydrazine solutions at pH > 7.0, although decreasing with increase in pH, is considerably greater than the known constant for water (see Fig. 4), and the kinetics are of a mixed order: this shows that under these conditions there must be other reactions which remove O_2^-. These might be the reaction of O_2^- with chance impurities in the hydrazine (metals, oxidation products of hydrazine, etc.). The relative contribution of these reactions increases with increasing pH, owing to the decrease in the rate constant of reaction (14), thus leading to an increased deviation of the effective constants for the disappearance of O_2^- from the constants in water (cf. Fig. 4).

We shall consider separately features of the pulse radiolysis of aqueous solutions of hydrazine at pH $\geq$ 12. Under these conditions the radical OH dissociates:

$$OH + OH^- \rightleftharpoons O^- + H_2O, \quad pK_a = 11.85 \tag{15}$$
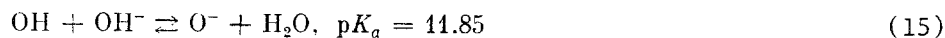
The ion radical O^- takes part in the reactions

$$N_2H_4 + O^- \rightarrow N_2H_3 + OH^-, \tag{16}$$

$$O_2 + O^- \rightarrow O_3^-. \tag{17}$$

The ion radical O_3^- formed in the last reaction absorbs with $\lambda_{max} = 430$ nm ($\varepsilon_{-3:} = 1900$ $dm^3 \cdot mole^{-1} \cdot cm^{-1}$). By varying the concentration of hydrazine it is possible to use the changes in the intensity of the band of the ozonide ion and the known value $k_{17} = 3.4 \cdot 10^9$ $dm^3 \cdot mole^{-1} \cdot sec^{-1}$ [13] to determine the rate constant of reaction (16), which is found to be $(1.6 \pm 0.2) \cdot 10^9$ $dm^3 \cdot mole^{-1} \cdot sec^{-1}$. It appears that the reaction

$$N_2H_4 + O_3^- \rightarrow \text{products} \tag{18}$$

takes place, having a measured rate constant of $(1.2 \pm 0.2) \cdot 10^6$ $dm^3 \cdot mole^{-1} \cdot sec^{-1}$. In strongly alkaline solutions of hydrazine saturated with oxygen the O_2 is completely consumed after one or more electron pulses, owing to the reaction of hydrazine with oxygen by a chain mechanism. As a result of this, subsequent pulses lead to the appearance in the optical spectrum of absorption by hydrated electrons.

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AUTOCATALYTIC REACTIONS IN POLYMER FILMS AND
SOLUTIONS CONTAINING FERROCENE AND CARBON TETRABROMIDE

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547.1'13:546.72:547.412.134

The effective rate constants of autocatalytic reactions taking place in the system $Fc-CBr_4$-aromatic amine are not decreased on passing from a liquid solution to a polymer film in the absence of oxygen. When films containing the above components are covered on both sides with poly(vinyl alcohol) their oxygen content is reduced to a level at which it has no effect on the autocatalytic reactions which produce colored products in the films.

The kinetics of radical reactions in solid polymers has recently become an independent branch of chemical kinetics. Passing from the liquid phase to a solid polymers involves a decrease in molecular mobility and thus lowers the rate constants of reactions [1]. In solid polymer films containing ferrocene (Fc) and carbon tetrabromide (CBr_4) there occurs at 60-90°C an autocatalytic reaction induced by light which leads to the accumulation of Fe^{3+} salts and to discoloration of the film; a mechanism has been proposed [2]. The low