
RADIATION CHEMISTRY

Radiation-Induced Decomposition of Cyclotrimethylenetrinitramine in Aqueous Solutions

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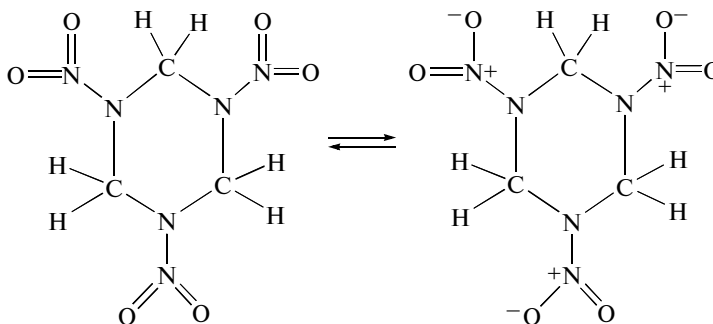
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Abstract—Radiation-induced decomposition of cyclotrimethylenetrinitramine, a representative of heterocyclic nitramines, in dilute aqueous solutions saturated with argon, air, and N_2O has been investigated. Dose dependence curves have been obtained, and the initial yields of formation of nitrite ions and hydrogen peroxide have been measured, making up 0.122 and 0.049 in deaerated solutions, 0.050 and 0.065 in aerated solutions, and 0 and 0.074 $\mu\text{mol/J}$ in N_2O -saturated solutions, respectively. The main radiolysis initial steps involve the reaction of dissociative electron capture with nitro-group elimination in the form of nitrite ion and the reaction of hydrogen atom abstraction from the methylene group by hydroxyl radicals and atomic hydrogen.

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The denitration of organic nitro compounds, initiated by ionizing radiation, is of considerable interest for radiation chemistry and physical chemistry of organic compounds. The mechanism of this process is not completely clear; in particular, it has not been established to which extent the electron dissociative capture is responsible for the total denitration yield. Nitramines compose a special group of organic nitro compounds having the nitro group attached to a nitro-

gen atom. The radiation chemistry of these compounds in solutions so far has not been studied. The object of this study was cyclotrimethylenetrinitramine (CTT) (other chemical names: hexahydro-1,3,5-trinitro-1,3,5-triazine, 1,3,5-triaza-1,3,5-trinitrocyclohexane; commercial names: cyclonite, hexogen, hexalite, RDX, PBX) a representative of the class of heterocyclic nitramines, having the following chemical structure:



Published data on the radiolysis of this compound are fragmentary and refer only to its solid state [1–3]; however, the mechanism of radiation-chemical processes in the solid phase considerably differs from that in solutions. In this work, we studied the initial stages of the continuous radiolysis of cyclotrimethylenetrinitramine and determined the main stable products of its radiolytic transformations.

EXPERIMENTAL

The test solutions were irradiated carried on a linear electron accelerator operating in the quasi-continuous mode with an average dose rate of about 12 Gy/s. A Specord M-40 recording spectrophotometer was used for optical measurements. Concentrations of hydrogen peroxide and nitrite ions were determined by chemical analysis using iodometry method [4] and the Shinn method [5], respectively. Aqueous CTT solu-

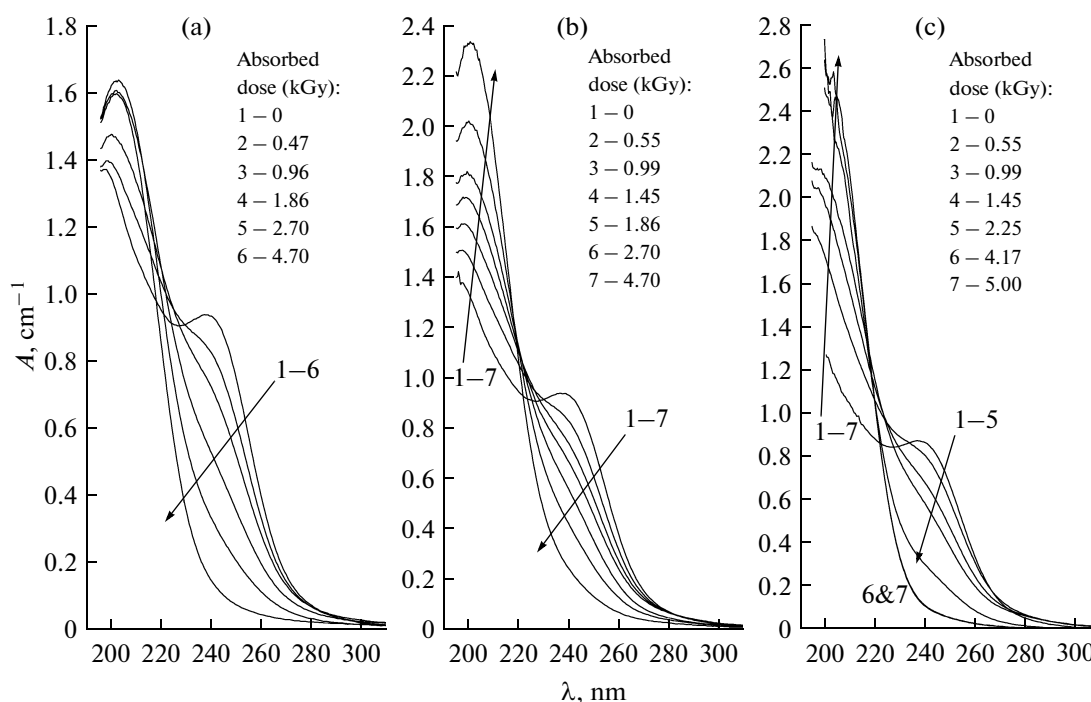


Fig. 1. Changes in the spectra of cyclotrimethylenetrinitramine in aqueous solutions with an initial concentration of 1.786×10^{-4} mol/l saturated with (a) argon, (b) air, and (c) N_2O during irradiation.

tions were prepared from a CTT solution in acetonitrile (1 ml), a commercial reagent, by evaporation to dryness on a water bath and the subsequent dilution with doubly distilled water. The CTT concentration was determined by the chemical analysis based on the decomposition of this compound with sulfuric acid [6] followed by the determination of the decomposition product formaldehyde via its reaction with chromotropic acid [7]. Due to the low solubility of CTT in water (38.2 mg/l at 20.2°C and pH 6.2 [8]), the concentration of the prepared solutions was less than 2×10^{-4} mol/l. In most cases, the solutions had a concentration of 1.786×10^{-4} mol/l.

RESULTS AND DISCUSSION

Since there is a lack of data in the literature on the optical absorption spectra of CTT in aqueous solutions (only its UV spectra in organic solvents, in particular, ethanol and methanol, exhibiting a maximum at 202–206 nm and a shoulder at 234–236 nm have been reported [9]), we studied optical absorption of CTT in the UV and visible range in aqueous solutions of different concentrations. The shape of the spectrum having a maximum at 195 ± 1 nm and a shoulder at 237 ± 1 nm does not change when the concentration is varied in the range of 1×10^{-5} – 2×10^{-4} mol/l. The molar absorption coefficient measured at 237 nm is $\epsilon_{237} = (1.05 \pm 0.05) \times 10^3 \text{ m}^2/\text{mol}$.

The irradiation of the solutions results in a decrease of absorption in the shoulder area and an increase in the area of the main peak (Fig. 1). The shape of the absorption curve in the range of $\lambda > 230$ nm does not change during the irradiation, thereby indicating that radiolysis products do not absorb in this range. Thus, it becomes possible to use direct spectrophotometric measurements at 237 nm for the determination of the CTT concentration. The increase of absorption in the short-wavelength region during the irradiation is apparently due to the accumulation of radiolysis products. The greatest increment is observed in the N_2O -saturated solutions, and the smallest one is in the deaerated solutions (saturated with Ar). The aerated solutions occupy an intermediate position in this respect.

Figure 2 shows the relative decrease in the CTT concentration during the irradiation of solutions saturated with argon, air, and N_2O (by absorbance at 237 nm). One can see that the saturating gas has a little effect on the initial yield of decomposition of the starting material, which is $0.032 \mu\text{mol/J}$ for the aerated solutions and $0.039 \mu\text{mol/J}$ for the solutions saturated with Ar or N_2O .

In dilute solutions whose concentration is determined by the low CTT solubility limit, the only factor initiating the decomposition of the substrate is the

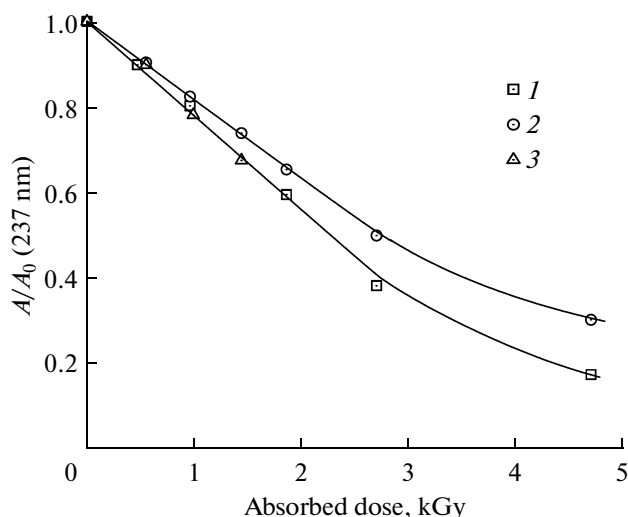


Fig. 2. Changes in the relative amount of cyclotrimethylenetrinitramine during the irradiation of its aqueous solutions with an initial concentration of 1.786×10^{-4} mol/l saturated with (1) argon, (2) air, and (3) N_2O .

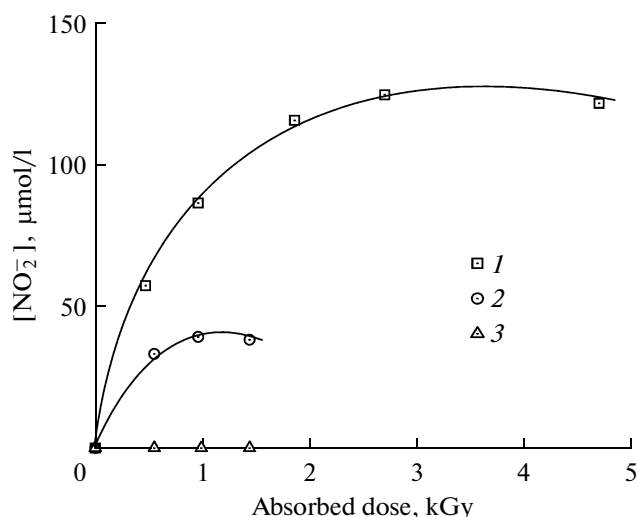
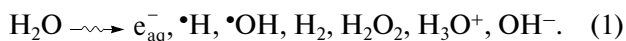


Fig. 3. Accumulation of nitrite ions in irradiated cyclotrimethylenetrinitramine aqueous solutions with an initial concentration of 1.786×10^{-4} mol/l saturated with (1) argon, (2) air, and (3) N_2O .

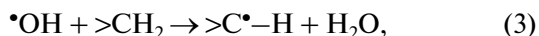
interaction with water radiolysis products, which arise in accordance with the general equation:



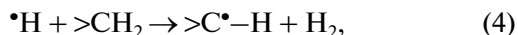
Since hydrogen peroxide does not react with CTT, the main products of the interaction with the solute are the hydrated electron, the atomic hydrogen, and the hydroxyl radical. The structure of the CTT molecule is such that there is only one position for the e_{aq}^- attack, one of the three equivalent nitro groups:



which leads to the formation of the radical anion, and the only position for the OH radicals attack is one of the three equivalent methylene groups:



which is accompanied by the abstraction of a hydrogen atom and the formation of the carbon-centered radical. Hydrogen atoms generally react in a similar way to OH radicals:



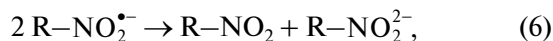
however, they may participate in the reaction of nitrate radical anion formation:



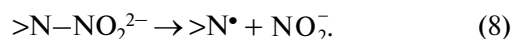
The rate constants for the reactions of e_{aq}^- and $\cdot OH$ with CTT in aqueous solutions are $(1.4 \pm 0.3) \times 10^{10}$ and $(7.4 \pm 0.7) \times 10^9$ l mol⁻¹ s⁻¹, respectively, as determined by the pulse radiolysis technique [10].

Arising in reactions (2) and (5) as in the case of other organic nitro compounds [10], the radical anion

$R-NO_2^{\bullet-}$ can either disproportionate to form the parent compound and the nitroso compound



or eliminate the nitro group yielding a nitrogen-centered radical and the nitrite ion:



The latter reaction is dominant, as evidenced by the accumulation of nitrite ions observed both in deaerated and aerated solutions (Fig. 3). In the solutions saturated with N_2O , the formation of nitrite ions was not detected. This indicates that the source of their formation is hydrated electrons, via the reactions (2) and (8), since all e_{aq}^- are converted into OH radicals by the following reaction in the presence of N_2O :



In the aerated and deaerated solutions, the initial yields of nitrite ions are 0.050 and 0.122 μmol/J, respectively. An appreciable yield of nitrite ions in the aerated solutions, in spite of the reaction



is due to the fact that at rate constants of 1.9×10^{10} and 1.4×10^{10} l mol⁻¹ s⁻¹ for reactions (10) and (2), respectively, and initial O_2 and CTT concentrations of 2.7×10^{-4} and 1.8×10^{-4} mol/l, respectively, about 1/3 of the total amount of the e_{aq}^- formed is involved in the reaction (2).

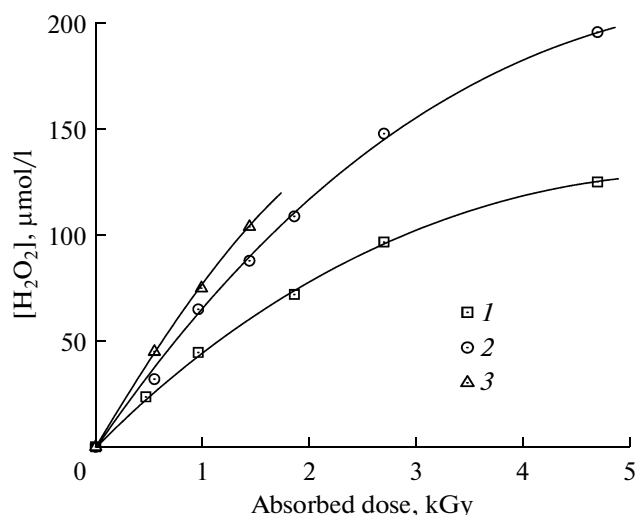


Fig. 4. Accumulation of hydrogen peroxide in irradiated cyclotrimethylenetrinitramine aqueous solutions with an initial concentration of 1.786×10^{-4} mol/l saturated with (1) argon, (2) air, and (3) N_2O .

The formation of hydrogen peroxide in CTT solutions during irradiation was also examined. Figure 4 shows dose dependence curves for H_2O_2 buildup in the solutions saturated with argon, oxygen, and N_2O . In all cases, a monotonic increase in the concentration and a gradual decrease in the formation yield are observed. The $G(H_2O_2)$ values calculated from the initial portions of the curves are 0.049, 0.065, and 0.074 $\mu\text{mol/J}$ for the solutions saturated with argon, air, and N_2O , respectively. The latter value is close to the initial yield of hydrogen peroxide $G_{H_2O_2}$, corresponding to the completion of the reactions in spurs. The values of $G(H_2O_2)$ in the solutions saturated with air or argon are smaller, apparently, because of the reaction of the formed hydrogen peroxide with organic radicals that are generated via the reactions of the hydrated electron.

A characteristic feature of the radiolytic transformation of CTT in aqueous solutions is an extremely high rate constant for the detachment of the H atom from the methylene group, which is almost an order of magnitude higher than the corresponding constants for other organic compounds. This may be due to the low C–H bond energy in the CTT molecule, which probably facilitates the involvement of the peroxide radicals, produced in the aerated solutions via reaction (10), in the hydrogen-atom abstraction reaction. The consequence of such a reaction are close values of CTT decomposition yields in the aerated and deaerated solutions, as well as the absence of significant anomalies in the CTT degradation curves and H_2O_2 buildup curves associated with the consumption of dissolved oxygen in the irradiated aerated solutions.

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