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Decomposition and Oxidation Reactions of Aliphatic Nitro Compounds in Supercritical Water

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Abstract—The reaction kinetics of nitromethane, nitroethane, and 1-nitropropane decomposition and oxidation in supercritical water near the critical point was studied in a flow reactor. The reaction rate constants were calculated assuming first-order reaction. It was found that pressure has a considerable effect on the rates of decomposition of the above nitrogen-containing compounds in supercritical water over a wide pressure range. The reactivity of the above aliphatic nitro compounds in supercritical water in decomposition reactions decreased and in oxidation reactions increased with an increasing number of carbon atoms.

INTRODUCTION

The advantages of the use of supercritical solvents in performing chemical reactions, among which the reactions of nitrogen-containing organic compounds occupy a prominent place, have been extensively demonstrated in currently available publications [1–6]. This is likely due to the increased requirements imposed on the utilization of explosive components, rocket fuel components, rocket fuel wastes, metabolic wastes (products of human vital activity), and other compounds containing various groups such as C–NO_2, –O–NO_2, N–NO_2, and CH–N. At the same time, note that publications concerning the chemical transformations of nitrogen-containing compounds in supercritical water are scanty, although studies in this area are of considerable current interest.

In the conversion of various substances and wastes, including nitrogen-containing compounds in supercritical water, preference is given to oxidation reactions [3–5]. Air or pure oxygen is used as an oxidizing agent. As a rule, oxidation in supercritical water completely converts chemical compounds (99.9%) into nitrogen and carbon dioxide. At the same time, studies on the decomposition reactions of these compounds in supercritical water in the absence of oxidizing agents, that is, hydrothermal reactions, are of paramount importance not only for obtaining fundamental information on the kinetics and mechanism of these reactions under the specified conditions, but also for solving practical problems.

Nitromethane, nitroethane, and 1-nitropropane were chosen as nitro compounds that simulate the entire class of aliphatic nitrogen-containing explosives or explosive wastes. A few examples of studies concerning analogous hydrothermal reactions are known, such as the decomposition of 1-nitrobutane in “hot” water [7].

The aim of this work was to obtain experimental data in order to study the kinetics of decomposition and oxidation of the above aliphatic nitro compounds (RNO_2) in supercritical water: the dependence of the rate of reactions on reactant concentrations, pressure, and the nature of the starting reactants with different numbers of carbon atoms in RNO_2 molecules.

EXPERIMENTAL

Experiments on the conversion of the test compounds in supercritical water were performed in a flow-type tubular reactor. Figure 1 shows a schematic diagram of the experimental setup. The starting mixture was supplied to the reactor in two flows (*1* and *2*) with

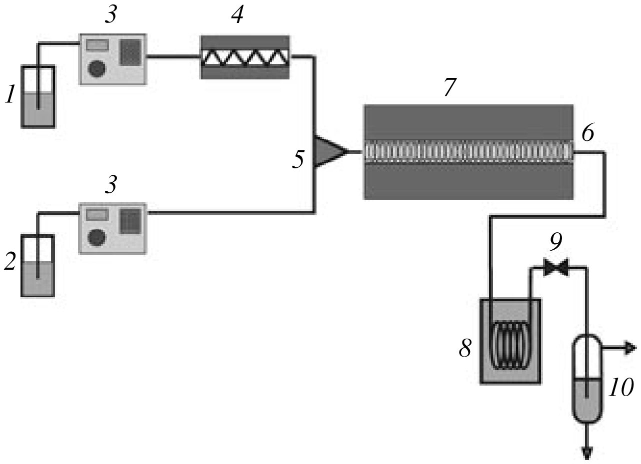

Fig. 1. Schematic diagram of the experimental setup: (*1*) source of water, (*2*) source of the reaction mixture, (*3*) high-pressure pumps, (*4*) heater (heat exchanger), (*5*) mixer, (*6*) reactor, (*7*) electric furnace, (*8*) cooler, (*9*) backpressure regulator, and (*10*) separator.

the use of JASCO-3 high-pressure plunger pumps. The first flow of pure water or a mixture of water and hydrogen peroxide for oxidation experiments was directed to heat exchanger *4*, heated, and supplied to mixer *5*. The second flow of a mixture of water with a nitrogen-containing compound was also supplied by pump *3* to mixer *5*. In the experiments, the ratio between these two flows was always maintained constant and equal to 4. This allowed us to keep a constant initial reactant concentration on varying flow rates. The reaction mixture (flow *2*) was prepared by adding 1 ml of a reagent to 100 ml of water with intense stirring. Note that, at the specified ratio in a mixture, 1-nitropropane was readily soluble in water at room temperature with intense stirring.

The volume of mixer *5* and the ratio between flows *1* and *2* were chosen so that, on the one hand, the mixer volume was much smaller than the reactor volume but, on the other hand, it provided efficient mixing of the flows, and the ratio between flows provided rapid heating of flow *2* to the reactor temperature.

This procedure and the chosen ratio between flows allowed us, first, to avoid chemical transformations of the reagent before its supply to the reactor, second, to supply small reagent concentrations to the reactor with a high accuracy, and, third, to mix and heat the flows to reaction conditions in a short time.

Reactor *6* was a capillary as a stainless-steel coil 1.0×1.6 mm in diameter and 7 m in length placed in electric furnace *7*. The volume of the reactor with the mixer was 5.66 cm^3, which allowed us to vary the contact time of the reaction mixture over a range from 0.5 to 8 min.

The reaction mixture from the reactor was cooled in heat exchanger *8*. The reactor pressure was maintained and regulated with a Tescom-9 backpressure reducer. Gas and liquid samples were taken from separator *10*.

The composition of a liquid phase was analyzed using a Hewlett-Packard 6890 chromatograph equipped with a mass-spectrometric detector and a 30-m capillary column. Liquid-phase microsamples, which were taken from separator *10* at different contact times, were introduced into the sampler of the chromatograph. The conditions of analysis allowed us to determine quantitatively the residual concentrations of parent reagents in reaction products with an adequate accuracy. For the analysis of the composition of individual gas-phase samples, a Shimadzu gas chromatograph with a thermal conductivity detector and a 3-m column packed with the sorbent Unibeads C was used. Gas products were sampled from separator *10* and injected into the sampler of the chromatograph with a microsyringe. Helium used as a carrier gas and column temperature programming allowed us to separate H_2, O_2, N_2, CO, NO, CH_4, CO_2, N_2O, and C_2H_6.

RESULTS AND DISCUSSION

CH_3NO_2, $C_2H_5NO_2$, and 1-$C_3H_7NO_2$ Decomposition in Supercritical Water

Primary experimental data were obtained as the dependence of the dimensionless concentration of a reagent in reaction products on contact time. Here, the dimensionless concentration is the ratio between the current and the initial concentrations of the reagent. The decomposition of nitromethane, nitroethane, and 1-nitropropane was performed at 663.5–703 K, 222–320 atm, and initial reactant concentrations of 0.037 (nitromethane), 0.028 (nitroethane), and 0.022 mol/l (1-nitropropane). The contact time was varied over the range 50–500 s to change the conversion of the reactants over a range from 0.2 to 0.8.

To find the dependence of the rate of reaction on contact time, we used an equation of the form

$$\frac{dX}{d\tau} = kC_0^{n-1}(1-X)^n; \quad \tau = 0, \quad X = 0, \qquad (1)$$

where X is the degree of RNO_2 conversion; C_0 is the initial concentration of RNO_2, mol/l; n is the apparent order of reaction; $\tau \equiv V_R/Q$, s; V_R is the reactor volume, cm^3; and Q is the flow rate, cm^3/s. A comparison between experimental data and calculated functions demonstrated that, in all cases, the dependence of reactant conversion on contact time was best described by a first-order rate equation with respect to RNO_2, that is, at $n = 1$.

As an illustration, Fig. 2 shows the dependence of $\ln(1 - X)$ on τ for nitromethane, nitroethane, and 1-nitropropane. The slopes of these straight lines give the apparent first-order constants at $T = 663.5$–664 K and $P = 272$ atm. They are equal to 0.0102, 0.0053, and 0.0044 s^{-1} for nitromethane, nitroethane, and 1-nitropropane, respectively. Moreover, the analysis of these data indicates that the reaction rate of RNO_2 decomposition in supercritical water decreased with an increasing number of carbon atoms in the RNO_2 molecule. In this case, the rate of the decomposition of nitromethane in supercritical water was much higher than the rates of decomposition of both nitroethane and 1-nitropropane.

Some idea of the reaction mechanism can be gained from an analysis of the composition of gaseous decomposition products of the test compounds. Unfortunately, in our experiments, gaseous reaction products were sampled for analysis only selectively, that is, regardless of contact time and under reaction conditions at which the reactant conversion was sufficiently high.

The analysis of the gaseous decomposition products of nitromethane (depending on the conversion of nitromethane (60–80%), pressure, and temperature) demonstrated the presence of the following components: ~11–25% H_2, 10–14% N_2, 12–25% CO, 17–23% NO, 0.7–1.5% CH_4, 5–12% CO_2, and 2–5% N_2O (henceforth, the gas composition is specified in mol %).

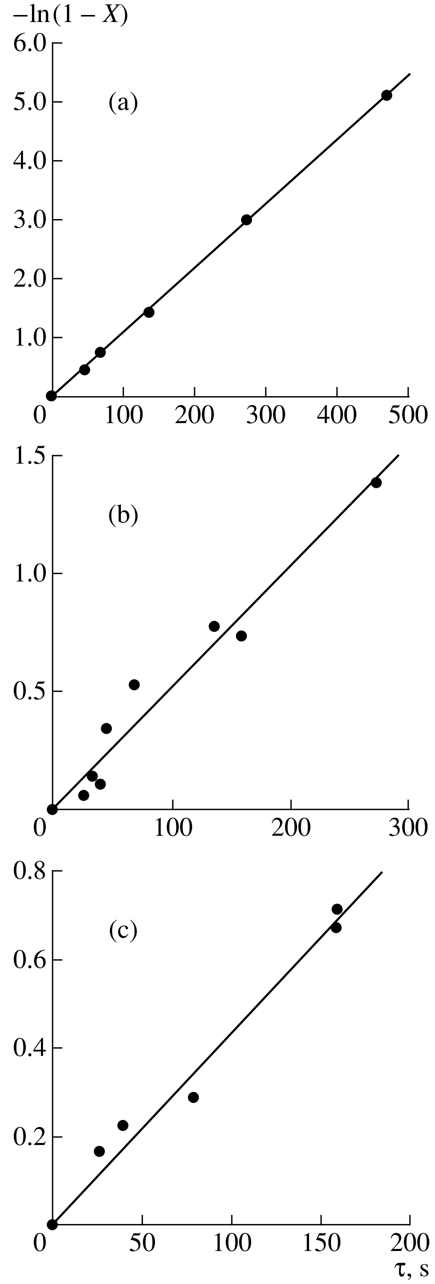

Fig. 2. Dependence of ln (1 – X) on contact time: (a) nitromethane, (b) nitroethane, and (c) 1-nitropropane.

In the decomposition of nitroethane in supercritical water, the following products were detected: 0.7–3.5% H_2, 24–27% N_2, 9–18% CO, 2.5% CH_4, 1.5–2.5% CO_2, and trace N_2O and C_2H_6. The reaction products did not contain NO in detectable amounts.

The composition of the gaseous decomposition products of 1-nitropropane was the following: 1–1.5% H_2, 26–32% N_2, 12–39% CO, 1–1.3% CH_4, 2–7% CO_2, and trace N_2O.

Even a cursory comparison between product compositions shows considerable quantitative and qualitative differences. The most significant difference was observed between the decomposition products of nitromethane and nitroethane or 1-nitropropane. It is reasonable to assume that, in the decomposition of nitromethane in supercritical water, the thermal decomposition (pyrolysis) of nitromethane at the metal wall of the tubular reactor can occur simultaneously with reactions in the bulk of the solvent (supercritical water). This assumption can explain the high hydrogen content of nitromethane decomposition products.

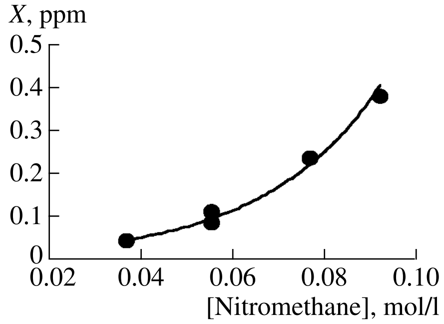

Fig. 3. Conversion of nitromethane in supercritical water as a function of initial concentration.

Effect of Initial Concentration

The effect of initial reactant concentration was studied in the course of nitromethane decomposition at $T = 662$ K and $P = 266$ atm; the initial concentration of nitromethane was varied over the range of $C_0 = 0.037$–0.09 mol/l. We found (Fig. 3) that the conversion of nitromethane significantly increased as the initial concentration was increased, all other factors being the same. This dependence of X on C_0 is characteristic of a chemical reaction with the order $n > 1$. However, as demonstrated above, the experimental data on nitromethane decomposition in supercritical water, which were represented as the dependence of X on τ, are adequately described by first-order Eq. (1) (Fig. 2). Thus, on the assumption that the reaction is of first order, the reaction rate constant can be plotted as a function of initial concentration (Fig. 4). Figure 4 indicates that this function is clearly exponential and falls outside the limits of ordinary kinetic laws. This effect, which was found for the first time in the reaction of nitromethane decomposition in supercritical water, allows us to hypothesize that the reaction mechanism can vary with changes in the initial nitromethane concentration in the starting mixture.

Effect of the Pressure/Density of Supercritical Water

The experimental studies of the effect of pressure on the rates of chemical reactions were performed in a flow reactor at 664 K and contact times that were constant for each particular substance. With the use of data on the pressure dependence of the conversions of reac-

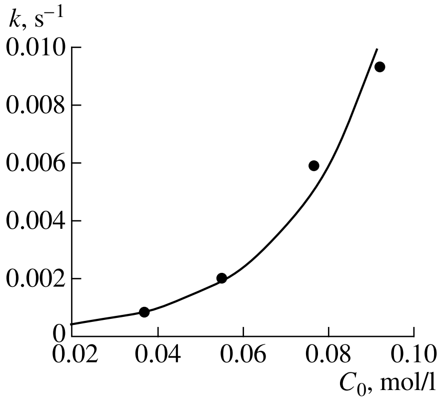

Fig. 4. Dependence of the apparent reaction rate constant of nitromethane decomposition in supercritical water on initial nitromethane concentration.

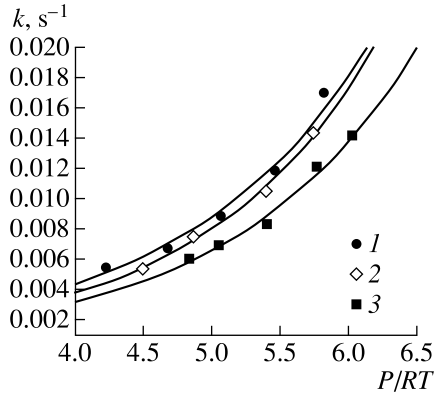

Fig. 5. Dependence of the reaction rate constants of (*1*) nitromethane, (*2*) nitroethane, and (*3*) 1-nitropropane decomposition on pressure (in P/RT units) at $T = 390°C$.

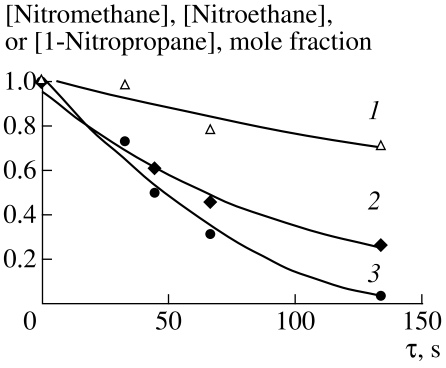

Fig. 6. Dimensionless concentrations of nitro compounds in oxidation products as functions of contact time: (*1*) nitromethane, (*2*) nitroethane, and (*3*) 1-nitropropane.

tants, the first-order reaction rate constants (k) were calculated. Figure 5 shows the pressure dependence of k for all of the three test substances. It can be seen in Fig. 5 that the reaction rate constant increases with pressure. This increase obeys an exponential law, which is described by the equation

$$k = A\exp(BP/RT),$$

where A and B are constants characteristic of each particular reactant.

This pressure dependence of reaction rate constant is mainly typical of supercritical conditions, and it results from specific interactions between a supercritical solvent and a reactant. In actual practice, the activated complex or transition state theory is most commonly used for describing this effect [8].

Oxidation Reactions

The test nitro compounds were oxidized by oxygen in supercritical water. Oxygen was formed in heat exchanger *4* by the decomposition of hydrogen peroxide, which was predissolved in water in flow *1* (see Fig. 1). Figure 6 shows changes in the dimensionless concentrations of nitromethane, nitroethane, and 1-nitropropane in supercritical water in the course of oxidation as functions of contact time. It can be seen that the reactivity of an aliphatic nitro compound in the oxidation reaction in supercritical water increases with the number of carbon atoms in its molecule. To support this relationship, we performed additional experiments for comparing the rates of oxidation of CH_3NO_2, $C_2H_5NO_2$, and 1-$C_3H_7NO_2$ under almost identical conditions ($P = 242$ atm; $T = 710$ K; initial O_2 concentration of 0.084 mol/l; contact time of 89 s); these experiments provided support for the above relationships:

Substance	Initial concentration, mol/l	Degree of conversion
CH_3NO_2	0.037	0.35
$C_2H_5NO_2$	0.029	0.71
1-$C_3H_7NO_2$	0.022	0.79

Figure 7 shows the experimental conversion of 1-nitropropane in supercritical water oxidation at $P = 273$ atm and $T = 663.5$ K in the $-\ln(1 - X) - \tau$ coordinates. It can be seen that experimental points lie along a straight line within the limits of experimental error. If the overall order of reaction were other than first, this function would be nonlinear; therefore, it is believed that the overall reaction of 1-nitropropane oxidation is also of first order. Then, on the assumption that the reaction is of first order with respect to the starting reactant, that is, 1-nitropropane, the reaction is of zero order with respect to oxygen. Note that our assumption is not far from the truth because the order of reaction with respect to an organic compound was taken first in all known publications on the supercritical water oxidation of organic compounds (for example, [9]) and the order of reaction with respect to oxygen was no higher than 0.2.

The consistency of the above assumption was supported by the treatment of experimental data using rate

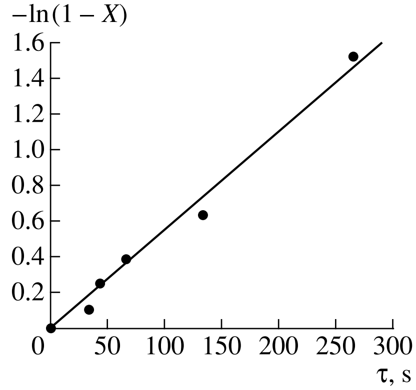

Fig. 7. Dependence of ln (1 – X) on contact time in the reaction of 1-nitropropane oxidation in supercritical water.

equations for first-order and zero-order reactions with respect to RNO_2 and oxygen, respectively, because the calculated straight line in Fig. 7 describes the experimental data with an adequate accuracy. Under the specified conditions, the experimentally found first-order reaction rate constant of 1-nitropropane oxidation was equal to 0.0052 s^{-1}.

From an analysis of the results, it follows that the reactivity of an aliphatic nitro compound in supercritical water oxidation linearly increases with the number of carbon atoms. In principle, this fact supports the hypothesis that the $R–NO_2$ bond energy [10] and, consequently, the reactivity change with increasing number of CH_n groups in the molecules of aliphatic compounds. Nevertheless, it remains to be explained why the reactivity of this series of aliphatic compounds in decomposition reactions in supercritical water in the absence of oxygen changes in an “opposite manner.”

As in the case of decomposition reactions, samples for the analysis of gaseous products in the oxidation reactions of the test nitro compounds were taken only selectively. Unfortunately, in this work, quantitative analytical data can be presented only for the supercritical water oxidation of 1-nitropropane. Thus, the gaseous products of 1-$C_3H_7NO_2$ oxidation contained 12–20% N_2, more than 38% CO, 10–13% NO, 1.5–3% CH_4, 20–28% CO_2, and 0.8–1.5% N_2O. Moreover, the oxidation products of nitro compounds can contain unreacted oxygen obtained by the decomposition of hydrogen peroxide; the amount of unreacted oxygen depends on the excess of oxygen in the initial mixture, as compared with a stoichiometric amount.

In the gaseous products of $C_2H_5NO_2$ oxidation, the same components as in 1-nitropropane oxidation were determined in approximately the same amounts. It was beyond the scope of these experiments to choose conditions for the complete oxidation of nitro compounds. Nevertheless, the results demonstrate that the oxidation of these aliphatic nitro compounds in supercritical water increased the amounts of N_2, CO, CO_2, and NO in reaction products, as compared with decomposition reactions.

CONCLUSIONS

The reaction kinetics of decomposition and oxidation of aliphatic nitro compounds (nitromethane, nitroethane, and 1-nitropropane) in supercritical water was studied in a flow-type reactor. The rate constants of the reactions were evaluated on the assumption of first-order reactions. It was found that pressure significantly affects the reaction rate of decomposition of the test nitrogen-containing compounds in supercritical water over a wide range of pressure changes.

An analysis of the results demonstrated a linear increase in the reactivity of aliphatic nitro compounds in supercritical water oxidation with an increasing number of carbon atoms. The experimental results can be considered as a basis suitable for studying the reaction mechanisms of decomposition and oxidation of the test compounds in supercritical water. The effect of pressure on the rate constant of a first-order reaction can be explained later on based on both a “thermodynamic” model in terms of the transition state theory and the theory of acid and base catalysis by OH^- and H_3O^+ ions formed by water dissociation in the critical region.

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