

REACTIONS OF DECOMPOSITION AND OXIDATION OF ALIPHATIC NITROCOMPOUNDS IN SUPERCRITICAL WATER

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The kinetics of nitromethane, nitroethane and 1-nitropropane decomposition and oxidation in supercritical water near the critical point has been studied in a flow reactor. The reaction rate constants have been calculated on the assumption of the first order reaction. The pressure varied over a wide range produced strong effect on the rate of the nitrocompounds decomposition in supercritical water. The rate of aliphatic nitrocompounds oxidation in supercritical water increased with increasing number of carbon atoms.

INTRODUCTION

Numerous literature data are available now devoted to the advantages of supercritical solvents-fluids for the performance of a wide range of chemical reactions, especially for the conversion of organic nitrocompounds [1-4]. The latter attracts particular attention because of strict requirements for utilization of explosives, rocket fuel components and their production wastes, municipal wastes and other substances containing the C-NO₂, -O-NO₂, N-NO₂, CH-N and some other groups. However, notwithstanding the urgency of studies in this field, analysis of available literature reveals the deficit of works on the conversion of nitrocompounds in supercritical water (SCW).

The oxidation reactions are preferred for the processing of various substances and wastes, including organic nitrocompounds, in SCW [1-4]. Air or oxygen is used as an oxidant. Oxidation in supercritical water provides complete and rapid conversion of chemical substances (99.99%) into nitrogen and carbon dioxide. However, the studies on the decomposition of these compounds in SCW without an oxidizer (i.e., hydrothermal reactions) are very important both for understanding fundamental regularities of reaction mechanism and kinetics, and for solving practical tasks.

Nitromethane (NM), nitroethane (NE) and 1-nitropropane (NP) were selected as the models for aliphatic nitrogenated explosives and their production wastes. We found in literature only few works studying hydrothermal decomposition of 1-nitrobutane in SCW [4].

The aim of the present work was to study experimentally the decomposition and oxidation of the named aliphatic nitrocompounds RNO₂ in SCW and elucidate the main kinetic regularities of the reactions, namely, to determine how reaction rate depended on the concentration, pressure and nature of nitrocompounds RNO₂ differing by the number of C atoms.

EXPERIMENTAL METHODS

Experiments on RNO_2 conversion in SCW were carried out in a tubular flow reactor. Fig. 1 shows the setup layout. Initial mixture (flows 1 and 2) was fed into reactor by two high-pressure piston pumps JASCO, 3. Flow 1 consisted of pure water (or contained hydrogen peroxide in oxidation experiments). The water was heated under pressure in heat exchanger 4 and fed to mixer 5. Flow 2, consisting of a mixture of water and nitrocompound, was fed by pump 3 into mixer 5. The flows' ratio was kept constant and equal to 4 that allowed retaining constant initial concentration of reagents at varying flow rates. Mixture for flow 2 was prepared by adding 1 ml of reagent to 100 ml of water under intensive stirring.

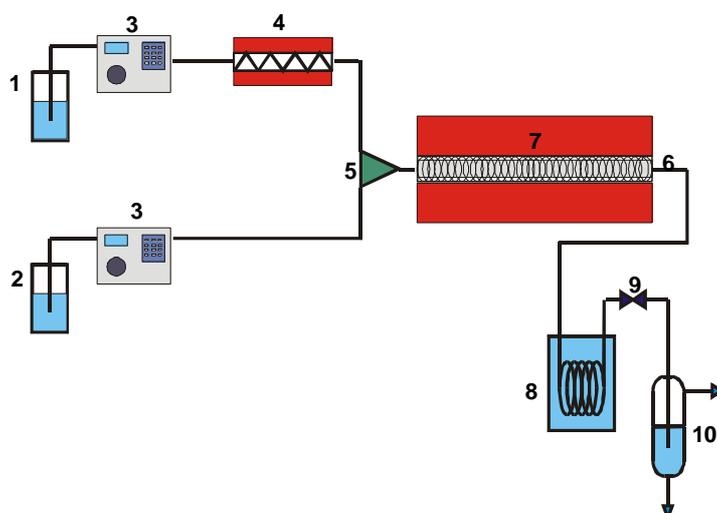


Fig.1. Schematic of the continuous flow reactor system

The selection of mixer volume and flows' ratio was determined by the following factors: the mixer must be considerably smaller than the reactor, but provide efficient flows mixing; the flows' ratio must provide efficient heating of flow 2 up to the reactor temperature. This approach allowed preventing reagent conversion prior reactor, feeding reactor with low-concentrated reagent flow, and fast mixing and heating of the flows up to reaction conditions.

Reactor 6 was a spiral stainless steel capillary (i.d. 1.0 x 1.6 mm, length 7 m) placed in electric furnace 7. Total volume of the reactor and mixer was equal to 5.66 cm^3 . This allowed variation of contact time from 0.5 to 8 min.

The outlet mixture was cooled in heat exchanger 8. The pressure in the reactor was controlled by back pressure regulator Tescom-9. The samples of gaseous and liquid phases were taken in separator 10. The rest reagent concentration in the liquid phase was measured by a Hewlett Packard 6890 chromatograph equipped with a 30m capillary column. Some gaseous samples were analyzed by gas chromatograph with Unibeads C packed column.

RESULTS AND DISCUSSION

Destruction of NM, NE and NP in SCW

Primary experimental data represented the change of a reagent content (expressed as molar fractions) in reaction products depending on contact time. Here, molar fraction means the ratio of current concentration of a reagent to inlet concentration of this reagent. Decomposition conditions were as follows: $T = 663.5-664\text{K}$, $P = 272 \text{ atm}$, reagent inlet concentration 0.037 mole/l ; contact time varied within $50-500 \text{ s}$ that provided variation of reagent conversion within $0.2 - 0.8$.

The reagent conversion depending on contact time was determined by equation:

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

where X – conversion of RNO_2 ; C_0 – inlet concentration of RNO_2 , mole/l; n – apparent reaction order; $\tau \equiv V_R/Q$, s; V_R – reactor's volume; Q – flow rate, cm^3/s .

Integration of eq. (1) from 0 to τ gives:

$$F(X) = \frac{1}{1-n} [1 - (1-X)^{1-n}] - kC_0^{n-1}\tau = 0 \quad \text{by } n \neq 1, \quad (2)$$

$$F(X) = \ln(1-X) + k\tau = 0 \quad \text{by } n=1 \quad (3)$$

Comparison of the calculated and experimental dependencies showed that kinetic equations of the first order with respect to RNO_2 (i.e., $n=1$) described the reagent conversion as a function of contact time most adequately in all cases.

Fig. 2 illustrates the dependencies of $\ln(1-X)$ from τ for NM, NE and NP. Slope angle of these lines gives the apparent constants of the 1st order reactions, which equal 0.0102 , 0.0053 , 0.0044 1/s for NM, NE and NP, respectively, at $T = 663.5-664 \text{ K}$, $P = 272 \text{ atm}$.

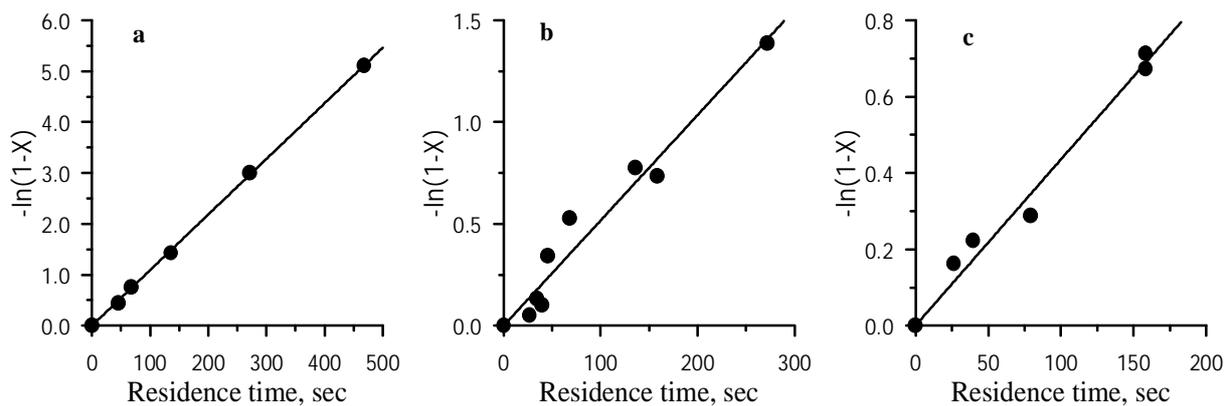


Fig.2. A plot of $\ln(1-X)$ against residence time. a)-NM, b)- NE, c)- NP

Analysis of the above data proves that as the number of C atoms in RNO_2 increases, the rate of RNO_2 destruction in SCW decreases. Besides, the rate of NM destruction in SCW considerably exceeds the decomposition rates of both NE and NP.

Some suggestions on the mechanism of reagent destruction can be concluded from the analysis of the gaseous reaction products. Unfortunately, in the present experiments we didn't sampled the gaseous products for analysis depending on contact time; the samples were taken at the same contact time, at which the reagent conversion was high. Note again that we were able to detect with appropriate accuracy only the inlet reagent in the liquid samples.

Analysis showed that the gaseous products of NM decomposition at its degree of conversion more than 50-70% contained about 11-25% H₂, 18-21% N₂, 13-24% CO, 11-23% NO, 0.6-1.2% CH₄, 3-12%CO₂ and N₂O traces.

The gaseous products of NE decomposition contained about 0.7-3% H₂, 24-35% N₂, 9-18% CO, 2.5% CH₄, 1.5-2.5% CO₂ and N₂O traces.

Gaseous products of NP destruction contained about 1% H₂, 27-32%N₂, 12-39%CO, 1%CH₄, 2-7%CO₂ and N₂O traces. Note, that NO is present at the separate samples in amount 7-20%.

Obviously, the outlet compositions differ by both quantitative and qualitative characteristics. The most considerable difference is observed in the case of NM destruction products. Most likely, destruction of NM in SCW is accompanied by thermal decomposition on the reactor walls.

Effect of SCW pressure/density

In earlier work [5] we discussed some peculiarities and disadvantages of flow reactors for the studying of pressure/density effects. Nevertheless, the present experiments on NM, NE and NP decomposition in SCW in the flow reactor showed unambiguously that in all three cases increasing pressure caused the increase of the reagent conversion.

Experiments on pressure effect were carried out at T = 664 K and constant contact time. The data obtained on the dependence of reagent conversion from pressure were used to calculate the rate constant of the first order reaction. Fig. 3 presents the dependencies of reaction rate constants on pressure for the three studied compounds. It is seen that the reaction rate constant increases exponentially with increasing pressure: $k = A \exp(BP/RT)$, where A and B are characteristic constants for each reagent.

Exponential dependence of reaction rate constant on pressure allows suggesting a hypothesis about the reaction mechanism based on the "transition state" theory.

Oxidation reactions

The studied nitrocompounds were oxidized in situ by oxygen evolved by hydrogen peroxide dissolved in flow 1 (see Fig. 1). Fig. 4 presents the change of molar fraction of NM, NE and NP upon their oxidation in SCW depending on residence time. Besides, we performed additional experiments to compare the reactivity of NM, NE and NP oxidized under the same conditions (P = 242 atm, T = 410K, inlet concentration of O₂ = 0.084 mole/l, τ = 89 s) (Table 1).

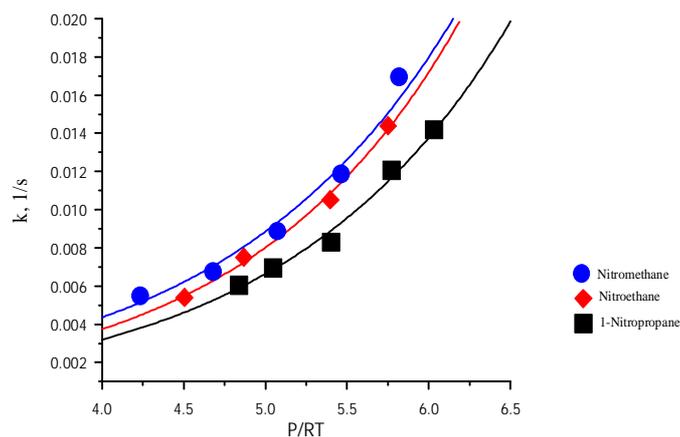


Fig.3. Dependence of reaction rate constant on the pressure

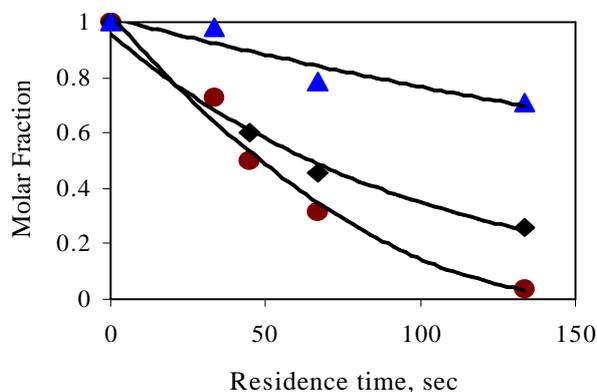


Fig. 4. Dependence of molar fraction on the residence time.

Table 1. Reactivity of aliphatic nitrocompounds

Reagent	Initial concentration, mole/l	Degree of conversion
CH ₃ NO ₂	0.037	0.35
C ₂ H ₅ NO ₂	0.029	0.71
1-C ₃ H ₇ NO ₂	0.0224	0.79

Since we didn't determine how the oxygen content in the reaction products changed depending on contact time, experimental dependencies of reagent conversion on contact time were processed on the assumption of the first order reaction regarding RNO₂ and zero order with regard to O₂. The latter assumption seems to be quite correct, since the most of works devoted to the oxidation of organic compounds in supercritical fluids (for example, [6]) report experimentally determined reaction orders with regard to oxygen to be well below unit. The dependence of $-\ln(1-X)$ on τ for the oxidation of NP at $P = 273$ atm, $T = 663.5$ K proves well the suggestion on the first order

reaction regarding the initial reagent and zero order – regarding oxygen. The first order constant in this case is equal to 0.0052 l/s.

Rectilinear dependence of the rate constant, calculated from the data of Table 1, is shown that the oxidation rate of aliphatic nitrocompounds in SCW increases linearly with increasing number of C atoms in RNO₂. It is seen in principal, this observation confirms suggestion that as the number of CH-groups in aliphatic nitrocompounds increases, the energy of bond R-NO₂ (*decreases*), and, consequently, reactivity changes (*increases*) [7]. However, it remains unclear why the same compounds decomposing in SCW without oxygen demonstrate “reverse” reactive behavior.

CONCLUSION

Kinetics of nitrocompounds (NM, NE, NP) decomposition and oxidation in SCW was studied using a flow reactor. Reaction rate constants were calculated on the assumption of the first order reaction. It was shown that the rate of NM, NE and NP decomposition strongly depended on the pressure varied over a wide range. Analysis of the results obtained showed that the oxidation rate of aliphatic nitrocompounds in SCW linearly increased with increasing number of C atoms in the compound.

The data obtained are promising for the studies of the mechanism of nitrocompounds destruction and oxidation in SCW. The effect of pressure on the rate constant of the first order reaction can be explained on the base of thermodynamic model in the framework of transition state theory, or basing on the theory of acid-base catalysis by HO⁻ and H₃O⁺ ions resulted from water dissociation in supercritical region.

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