

# Effect of supercritical water density on the rate constant of aliphatic nitrocompounds decomposition

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## Abstract

It was shown experimentally that the rate of aliphatic nitrocompounds decomposition in supercritical water (SCW) depends on pressure/density at constant temperature. The SCW density dependence of the apparent rate constant of decomposition for each of three compounds under consideration (nitromethane, nitroethane and 1-nitropropane) was found to correlate with the density dependence of the  $\text{H}_3\text{O}^+$  concentration in dissociated SCW. The rate constant of  $\text{RNO}_2$  decomposition in SCW decreased with increasing the length of hydrocarbon radical R.

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**Keywords:** Supercritical water; Chemical reaction; Decomposition; Pressure effect

## 1. Introduction

Aliphatic nitrocompounds are among the so-called energetic materials and can be both the explosives and the products of their manufacture. Chemistry of aliphatic nitrocompounds decomposition attracts recent attention mainly because it is necessary to develop efficient methods for their conversion to simple compounds, such as  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{H}_2\text{O}$ , etc. The most preferable is the method of decomposition and oxidation of these compounds in supercritical water (SCW) [1–4]. A feature of chemical reactions occurring in supercritical fluids is a strong dependence of their conversion rate on pressure/density [5–9]. This effect may be of great importance for developing the technology of energetic materials processing in supercritical solvents. Thus, the present work was aimed at experimental study of the effect of SCW pressure on the decomposition rate of selected aliphatic nitrocompounds  $\text{RNO}_2$  (nitromethane (NM), nitroethane (NE), and 1-nitropropane (NP)) and at

theoretical data processing for interpretation of the pressure effect on the reaction rate constant.

## 2. Experimental method and data processing technique

Experiments on conversion of the chosen  $\text{RNO}_2$  compounds in SCW were performed in a tubular flow reactor. The setup layout, experimental method, results and their primary processing are thoroughly described elsewhere [10].

The concentration of nitrocompounds in the initial mixture and in the reaction products was determined quantitatively with high accuracy, while the reaction products were identified only qualitatively. Gaseous products of  $\text{RNO}_2$  decomposition contained  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{NO}$ , and  $\text{N}_2\text{O}$  traces. Naturally, their ratio changed considerably with the type of nitrocompound. The presence of  $\text{H}_2$  and  $\text{CH}_4$  in the reaction products indicates the occurrence of the  $\text{RNO}_2$  thermal decomposition (pyrolysis) on the reactor metal wall, which was confirmed further.

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On this basis, the simplest reaction equation suitable for experimental data processing can be written as



It was found [10] that the overall rates of reaction (1) for all compounds under study obey the first-order equations with respect to  $\text{RNO}_2$ :

$$W_{\text{RNO}_2} = k_{\text{obs}}^{\text{RNO}_2} [\text{RNO}_2] \quad (2)$$

where  $k_{\text{obs}}^{\text{RNO}_2}$  is the apparent rate constant ( $\text{s}^{-1}$ ), and  $[\text{RNO}_2]$  is the concentration of nitrocompound in the solution ( $\text{mol/l}$ ). It was noted also that at a constant temperature 664 K, the  $k_{\text{obs}}^{\text{RNO}_2}$  values increase exponentially as the pressure rises. Data processing in the framework of the thermodynamic model [11]:

$$\frac{\partial \ln k_{\text{obs}}^{\text{RNO}_2}}{\partial P} = -\frac{\Delta V_{\text{RNO}_2}^{\#}}{RT} \quad (3)$$

allowed us to calculate the values of activation volumes  $\Delta V_{\text{RNO}_2}^{\#}$ . They proved to be  $-730 \pm 48 \text{ cm}^3/\text{mol}$  for each of three nitrocompounds. According to [12], the sign and value of the activation volume allow one to suggest the reaction mechanism. For example, homolytic reactions have positive activation volume of about  $5\text{--}40 \text{ cm}^3/\text{mol}$ , while the reactions that lead to electrical polarization either by bond formation or bond breaking have large negative activation volumes.

The present work considers a model explaining the effect of pressure on the reaction rate constant by the hypothesis that reaction (1) is catalyzed by  $\text{H}_3\text{O}^+$  ions formed in SCW due to dissociation of water. It is known [13] that the ionic product of water and hence the  $\text{H}_3\text{O}^+$  concentration are highly sensitive to changes in SCW density. The above hypothesis allowed us to describe in [5] the strong effect of SCW pressure/density on the rate constants of direct and reverse reactions of 2-propanol dehydration.

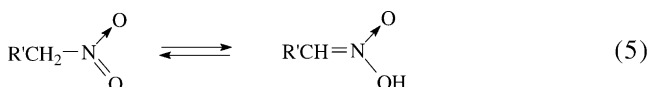
### 2.1. Assumption of the reaction mechanism

Taking into account strong dissociation of water in the critical region of its parameters and the suggested mechanism of acid catalysis, main reactions involved in the mechanism of aliphatic nitrocompounds hydrolysis in SCW can be presented as follows.

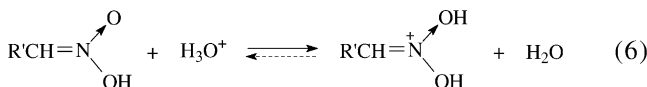
Dissociation of water:



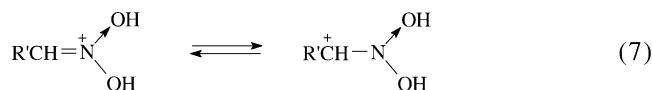
Isomerization of nitrocompound  $\text{R}'\text{CH}_2\text{NO}_2$  (where  $\text{R}' = \text{H}$ ,  $\text{CH}_3$  or  $\text{C}_2\text{H}_5$ ) to nitronic acid:



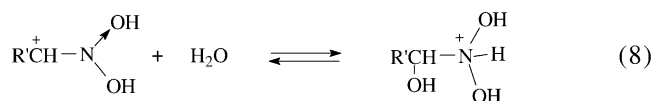
Protonation of nitronic acid:



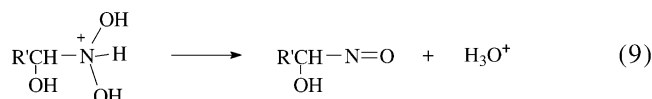
Charge redistribution:



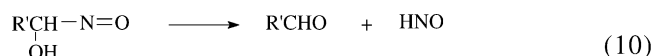
Addition of water to protonated species of nitronic acid:



Separation of oxonium ion ( $\text{H}_3\text{O}^+$ ):



Formation of carbonyl compounds and nitrous oxides:



Note that many intermediate compounds in reactions (7)–(10) may further decompose to give nitrous oxides, light hydrocarbons and other gases.

Assuming stage (6) to be the limiting stage of the process and other stages being in thermodynamic equilibrium, the rate equation can be presented as

$$W_{\text{RNO}_2} = k^{\text{RNO}_2} K_1 [\text{RNO}_2] [\text{H}_3\text{O}^+] = k_{\text{obs}}^{\text{RNO}_2} [\text{RNO}_2] \quad (11)$$

where  $K_1$  is the equilibrium constant of stage (4), and  $k^{\text{RNO}_2}$  is the rate constant of stage (6). Therefore, according to this mechanism, the apparent rate constants can be presented as a direct ratio of the  $\text{H}_3\text{O}^+$  ion concentration.

### 2.2. Ionic product of water in SCW

Ionic product of water near the critical point differs sharply from the value obtained under the normal conditions. In [13],  $K_w$  is calculated by an empirical equation integrating numerous experimental data of various authors. This equation is suitable for calculations in the critical region:

$$\log K_w = Q_1(T) + Q_2(T) \log \rho \quad (12)$$

$$Q_1(T) = A + \frac{B}{T} + \frac{C}{T^2} + \frac{D}{T^3} \quad Q_2(T) = E + \frac{F}{T} + \frac{G}{T^2} \quad (13)$$

Dimensions of  $K_w$  are determined by formula (12) in  $(\text{mol/kg})^2$ . Water density ( $\rho$ ) is substituted into formula (12) in  $\text{g/cm}^3$  units. According to [13], Eq. (13) has the following coefficients depending on temperature:  $A = -4.098$ ;  $B = -3245.2 \text{ K}$ ;  $C = 2.2362 \times 10^5 \text{ K}^2$ ;  $D = -3.984 \times 10^7 \text{ K}^3$ ;  $E = 13.957$ ;  $F = -1262.3 \text{ K}$ ;  $G = 8.5641 \times 10^5 \text{ K}^2$ .

Eq. (12) holds true within the temperature range of 273–1273 K and the pressure range of 0.1–1000.0 MPa. It is easy to verify that at  $T = 298 \text{ K}$  and  $\rho_w = 1 \text{ g/cm}^3$  formula (12) gives the known value  $K_w$  equal to 13.995. For the temperature used in the present studies,  $T = 664 \text{ K}$ , it gives

$$Q_1(T) = -8.6147 \quad Q_2(T) = 13.9983 \quad (14)$$

Then the pressure dependence of  $[H_3O^+]$  is expressed by equation:

$$[H_3O^+] \text{ (mol/kg)} = \sqrt{K_w} = 10^{-4.30735} \times \rho_w^{6.999} \quad (15)$$

SCW density is unambiguously related to pressure and was recalculated with NIST data [14] at  $T = 663\text{--}664$  K and varying pressure. The density values calculated for the measured pressure were used to find  $[H_3O^+]$  by formula (15).

### 3. Results of experimental data processing

The primary data used in further processing are listed in Tables 1–3.

One may see from Tables 1–3 that the concentration of  $[H_3O^+]$  ions increases considerably with increasing density.

The dependencies of apparent rate constants  $k_{obs}^{RNO_2}$  on the concentration of  $[H_3O^+]$  ions are presented in Figs. 1–3, respectively, for NM, NE and NP. From these figures follows a straight-line relationship between  $k_{obs}^{RNO_2}$  and  $[H_3O^+]$ ; however, the lines do not pass through the origin. From this it can be assumed that, alongside the reactions in supercritical

Table 1  
Decomposition of nitromethane in SCW,  $T = 664$  K

$P$ (MPa)	$P_r = P/P_c$	$\rho$ (g/cm <sup>3</sup> )	$[H_3O^+]$ (mol/kg)	$k_{obs}$ (s <sup>-1</sup> )
22.7	1.043	0.1515	$9.0452 \times 10^{-11}$	0.0055
25.1	1.153	0.2286	$1.6104 \times 10^{-9}$	0.0067
27.2	1.250	0.3830	$5.9649 \times 10^{-8}$	0.0089
27.6	1.268	0.4025	$8.4441 \times 10^{-8}$	0.0109
29.3	1.347	0.4552	$1.9979 \times 10^{-7}$	0.0119
31.2	1.434	0.4880	$3.2514 \times 10^{-7}$	0.0169

Here  $P_c$  is the critical pressure, and  $P_r$  is the reduced pressure.

Table 2  
Decomposition of nitroethane in SCW,  $T = 663.5$  K

$P$ (MPa)	$P_r = P/P_c$	$\rho$ (g/cm <sup>3</sup> )	$[H_3O^+]$ (mol/kg)	$k_{obs}$ (s <sup>-1</sup> )
22.0	1.011	0.1397	$5.1278 \times 10^{-11}$	0.0052
22.2	1.020	0.1432	$6.0975 \times 10^{-11}$	0.0053
24.2	1.112	0.1930	$4.9244 \times 10^{-10}$	0.0054
24.2	1.112	0.1930	$4.9244 \times 10^{-10}$	0.0042
26.4	1.213	0.3397	$2.5759 \times 10^{-8}$	0.0057
26.5	1.218	0.3477	$3.0316 \times 10^{-8}$	0.0075
29.0	1.333	0.4531	$1.9342 \times 10^{-7}$	0.0105
30.9	1.420	0.4871	$3.2096 \times 10^{-7}$	0.0144
31.0	1.425	0.4885	$3.2748 \times 10^{-7}$	0.0124

Table 3  
Decomposition of 1-nitropropane in SCW,  $T = 663$  K

$P$ (MPa)	$P_r = P/P_c$	$\rho$ (g/cm <sup>3</sup> )	$[H_3O^+]$ (mol/kg)	$k_{obs}$ (s <sup>-1</sup> )
22.9	1.052	0.1585	$1.2283 \times 10^{-10}$	
24.1	1.107	0.1925	$4.7881 \times 10^{-10}$	
25.5	1.172	0.2702	$5.1410 \times 10^{-9}$	0.0059
26.0	1.195	0.3161	$1.5420 \times 10^{-8}$	0.0060
27.1	1.245	0.3954	$7.3897 \times 10^{-8}$	0.0069
29.0	1.333	0.4579	$2.0645 \times 10^{-7}$	0.0083
31.0	1.425	0.4918	$3.4037 \times 10^{-7}$	0.0121
32.4	1.489	0.5087	$4.3120 \times 10^{-7}$	0.0142

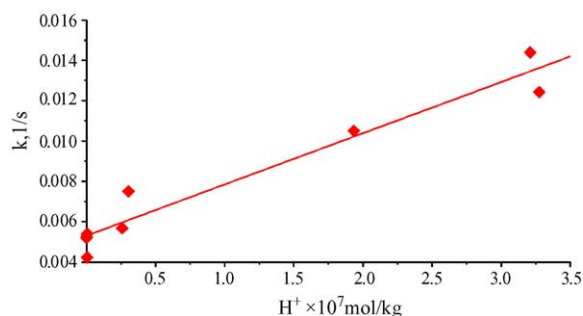


Fig. 1. Rate constant of nitromethane decomposition vs. the  $H_3O^+$  concentration in dissociated supercritical water.

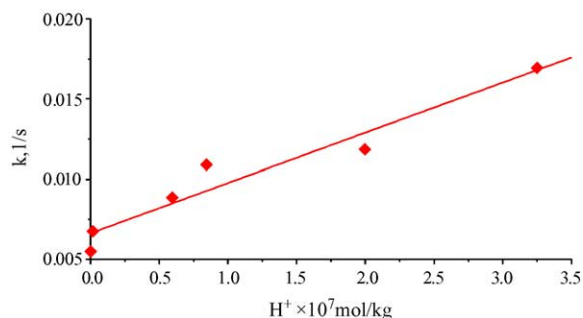


Fig. 2. Rate constant of nitroethane decomposition vs. the  $H_3O^+$  concentration in dissociated supercritical water.

solvent, the reactions of thermal pyrolysis of  $RNO_2$  occur on metal walls of the reactor, with their rate being independent of the  $[H_3O^+]$  concentration. This explanation has been supported experimentally in many works [15,16].

Experimental data of Tables 1–3 were processed by the least-squares method as

$$k_{obs}^{RNO_2} = k_0^{RNO_2} + k_1^{RNO_2} [H_3O^+] \quad (16)$$

Results of statistical processing are presented in Table 4.

One may see from Table 4 that model (16) fits experimental data well and constants of Eq. (16) were determined reliably. Therefore, the hypothesis of joint occurrence of thermal and catalytic decomposition of nitrocompounds in SCW does not contradict the experimental data.

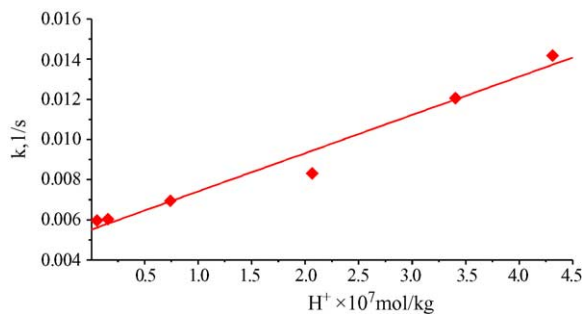


Fig. 3. Rate constant of 1-nitropropane decomposition vs. the  $H_3O^+$  concentration in dissociated supercritical water.

Table 4  
 Constants of Eq. (16) and confidence intervals

Reagent	$k_0^{\text{RNO}_2} \pm \Delta k_0$ (s <sup>-1</sup> )	$k_1^{\text{RNO}_2} \pm \Delta k_1$ (kg/mol/s)	$\sigma^a$ (%)
CH <sub>3</sub> NO <sub>2</sub>	$6.6363 \times 10^{-3} \pm 6.4548 \times 10^{-4}$	$3.1290 \times 10^{+4} \pm 3.9989 \times 10^{+3}$	13.80
C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>	$5.3108 \times 10^{-3} \pm 3.7586 \times 10^{-4}$	$2.5395 \times 10^{+4} \pm 2.2586 \times 10^{+3}$	13.04
C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub>	$5.5051 \times 10^{-3} \pm 3.9640 \times 10^{-4}$	$1.9054 \times 10^{+4} \pm 1.6409 \times 10^{+3}$	7.90

<sup>a</sup>  $\sigma$  is the root-mean square relative deviation of experimental and calculated data.

The first item  $k_0^{\text{RNO}_2}$  in Eq. (16) is the rate constant of the first-order reaction of RNO<sub>2</sub> thermal decomposition:

$$W_0^{\text{RNO}_2} (\text{mol/l/s}) = k_0^{\text{RNO}_2} [\text{RNO}_2] \quad (17)$$

The addend containing the  $k_1^{\text{RNO}_2}$  constant is responsible for contribution of the rate described by the acid-catalyzed mechanism presented above:

$$W_1^{\text{RNO}_2} (\text{mol/l/s}) = k_1^{\text{RNO}_2} [\text{H}_3\text{O}^+] [\text{RNO}_2] \quad (18)$$

One may see from Table 4 that the rate constant of thermal decomposition “on the wall” remains approximately constant with increasing the length of hydrocarbon radical in the RNO<sub>2</sub> molecule. At the same time, the rate constant of RNO<sub>2</sub> decomposition in SCW decreases considerably with increasing the length of hydrocarbon radical. Evidently, this is caused by decreasing the value of equilibrium constant in the R'CH<sub>2</sub>NO<sub>2</sub> series (R' = H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>) due to strengthening the electron-donor properties of R' substituents.

#### 4. Conclusion

It was shown experimentally that the rate of nitromethane, nitroethane and 1-nitropropane decomposition in SCW strongly depends on pressure at constant temperature. Modeling of this phenomenon demonstrated that the effect of SCW pressure on the apparent rate constant of decomposition of aliphatic nitrocompounds under consideration is adequately explained by the dependence of the limiting stage rate on the H<sub>3</sub>O<sup>+</sup> concentration in dissociated SCW. Processing of experimental data showed that alongside the reactions in SCW, there occurs the decomposition of these compounds on metal walls of the tubular flow reactor.

#### Acknowledgements

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