

Effect of Pressure on the Reaction Rate Constant at the Decomposition of Aliphatic Nitrocompounds in Supercritical Water

V.I. Anikeev, A. Yermakova

Boreskov Institute of Catalysis, SB RAS, Novosibirsk, Russia
e-mail: anik@catalysis.nsk.su, Fax: +7 383 239 74 47

It was shown experimentally that the rate of aliphatic nitrocompounds (nitromethane, nitroethane and 1-nitropropane) decomposition in supercritical water (SCW) depends on pressure/density at constant temperature. The rate constant of RNO_2 decomposition in SCW decreased with increasing length of hydrocarbon radical R. The SCW density dependence of the apparent rate constant of decomposition of each of three compounds under consideration was found to correlate with the density dependence of the H_3O^+ concentration in dissociated SCW. The transition state theory has been applied to simulate the effect of pressure on the rate constants. The calculated values of activation volumes in the decomposition reactions of nitromethane, nitroethane and 1-nitropropane in SCW were similar that suggested the same nature of the activation complex in all three cases.

INTRODUCTION

Aliphatic nitrocompounds are among the so-called energetic materials and attract particular attention because of strict requirements for utilization of explosives, rocket fuel components and their production wastes, municipal wastes and other substances containing C-NO₂, -O-NO₂, N-NO₂, CH-N and some other groups. Decomposition and oxidation in supercritical water (SCW) is the most preferable (promising) method for the utilization these compounds [1,2]. Specific feature of chemical reactions occurring in supercritical fluids is a strong dependence of a conversion rate on pressure/density [3,4]. This effect may be of great importance for developing the technology of energetic materials processing in supercritical solvents.

1. EXPERIMENTAL METHOD AND DATA PROCESSING TECHNIQUE

Experiments on the conversion of the chosen RNO_2 compounds in SCW were performed in a tubular flow reactor. On this basis, the simplest reaction equation suitable for experimental data processing can be written as



It was found that the overall rate of reaction (1) for all compounds under study obeys the first-order equation with respect to RNO_2 :

$$W_{RNO_2} = k_{obs}^{RNO_2} [RNO_2], \quad (2)$$

where $k_{obs}^{RNO_2}$ is the apparent rate constant, 1/s; $[RNO_2]$ is the concentration of a nitrocompound in the solution, mol/l. It was noted also that at constant temperature of 664 K, the $k_{obs}^{RNO_2}$ values increased exponentially with increasing pressure. Data processing in the framework of thermodynamic model:

$$\frac{\partial \ln k_{\text{obs}}}{\partial P} = \left(\frac{\partial \ln \Phi_{\text{RNO}_2}}{\partial P} - \frac{\partial \ln \Phi_{\text{TS}}}{\partial P} \right) = \frac{-\Delta \bar{V}^\ddagger}{RT} \quad (3)$$

allowed us to calculate the values of activation volumes $\Delta \bar{V}_{\text{RNO}_2}^\ddagger$. Integration of equation (3) reduces to:

$$k_{\text{obs}} = k_0 \exp\left(\frac{-\Delta \bar{V}^\ddagger P}{RT}\right) \quad (4)$$

Unknown parameters k_0 and $\Delta \bar{V}^\ddagger$ in eq. (4) were calculated by the least-squares method. Calculation showed that the studied nitrocompounds had similar values of activation volume $\Delta \bar{V}^\ddagger$ within the confidence interval: $-730 \pm 48 \text{ cm}^3/\text{mol}$.

2. PRESSURE EFFECT IN THE FRAME OF ACID-CATALYZED MECHANISM

The present paragraph considers a model explaining the effect of pressure on the reaction rate constant on the assumption that reaction (1) is catalyzed by H_3O^+ ions formed in SCW due to dissociation of water. It is known that the ionic product of water and hence the H_3O^+ concentration are highly sensitive to SCW density alteration.

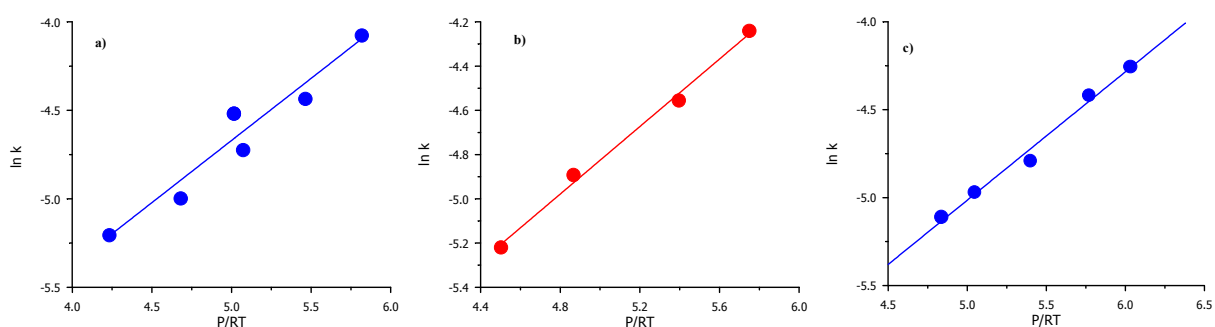


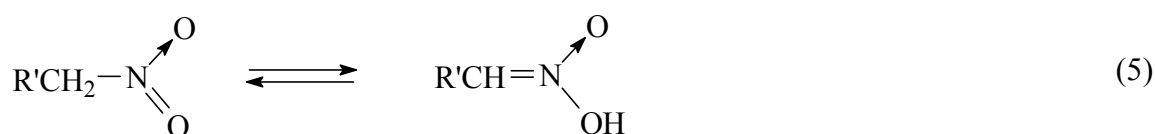
Figure 1. Pressure dependence of apparent rate constants for the decomposition of aliphatic nitrocompounds in SCW: a) NM, b) NE, c) NP

Taking into account strong dissociation of water in the critical region of its parameters and the suggested mechanism of acid catalysis, the 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 C_2H_5) to nitronic acid:



Protonation of nitronic acid:



Assuming stage (5) to be the limiting stage of the process and other stages being in thermodynamic equilibrium, the rate equation can be presented as

$$W_{\text{RNO}_2} = k^{\text{RNO}_2} K_1 [\text{RNO}_2] [\text{H}_3\text{O}^+] = k_{\text{obs}}^{\text{RNO}_2} [\text{RNO}_2], \quad (6)$$

where K_1 is the equilibrium constant of stage (4), and k^{RNO_2} is the rate constant of stage (5). Therefore, according to this mechanism, the apparent rate constant can be presented as a direct ratio of the H_3O^+ ion concentration:

$$[\text{H}_3\text{O}^+] = \sqrt{K_w} = 10^{-4.30735} \times \rho_w^{6.999}, \text{ g ion/kg}$$

The dependencies of apparent rate constant $k_{\text{obs}}^{\text{RNO}_2}$ on the concentration of $[\text{H}_3\text{O}^+]$ ions are presented in Figs. 2 for NM, NE and NP. The dependencies prove the straight-line relationship between $k_{\text{obs}}^{\text{RNO}_2}$ and $[\text{H}_3\text{O}^+]$; however, the lines do not pass through the origin. This fact allows suggestion that together with the reactions in supercritical solvent, the reactions of thermal pyrolysis of RNO_2 occur on metal walls of the reactor, their rate being independent on the $[\text{H}_3\text{O}^+]$ concentration.

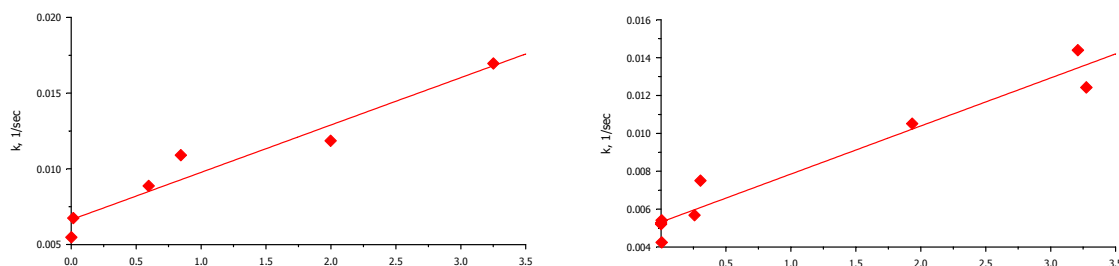
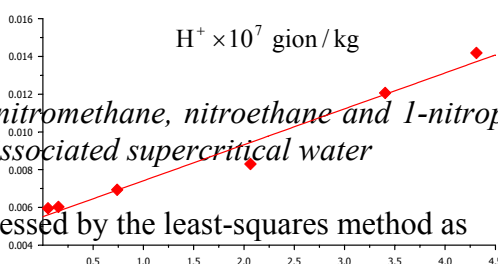


Figure 2. Rate constant of nitromethane, nitroethane and 1-nitropropane decomposition vs. the H_3O^+ concentration in dissociated supercritical water

Experimental data were processed by the least-squares method as



$$k_{\text{obs}}^{\text{RNO}_2} = k_0^{\text{RNO}_2} + k_1^{\text{RNO}_2} [\text{H}_3\text{O}^+] \quad (7)$$

Results of statistical processing are presented in Table 1.

Table 1. Constants of equation (7) and confidence intervals

Reagent	$k_0^{\text{RNO}_2} \pm \Delta k_0$, 1/s	$k_1^{\text{RNO}_2} \pm \Delta k_1$, kg/g ion/s	σ^* , %
CH_3NO_2	$6.6363 \cdot 10^{-3} \pm 6.4548 \cdot 10^{-4}$	$3.1290 \cdot 10^{+4} \pm 3.9989 \cdot 10^{+3}$	13.80
$\text{C}_2\text{H}_5\text{NO}_2$	$5.3108 \cdot 10^{-3} \pm 3.7586 \cdot 10^{-4}$	$2.5395 \cdot 10^{+4} \pm 2.2586 \cdot 10^{+3}$	13.04
$\text{C}_3\text{H}_7\text{NO}_2$	$5.5051 \cdot 10^{-3} \pm 3.9640 \cdot 10^{-4}$	$1.9054 \cdot 10^{+4} \pm 1.6409 \cdot 10^{+3}$	7.90

* σ is the root-mean square relative deviation of experimental and calculated data

One may see from Table 1 that the model fits experimental data well and constants of equation (7) were determined reliably. Therefore, the hypothesis of joint occurrence of thermal and acid catalytic decomposition of nitrocompounds in SCW does not contradict the experimental data.

The first item $k_0^{\text{RNO}_2}$ in equation (7) is the rate constant of the first order reaction of RNO_2 thermal decomposition:

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

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:

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

One may see from Table 1 that the rate constant of thermal decomposition “on the wall” remains approximately constant with increasing length of hydrocarbon radical in the RNO_2 molecule. At the same time, the rate constant of RNO_2 decomposition in SCW decreases considerably with increasing length of hydrocarbon radical. Evidently, this is caused by decreasing value of equilibrium constant in the $\text{R}'\text{CH}_2\text{NO}_2$ series ($\text{R}' = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5$) due to strengthening of the electron-donor properties of R' substituents.

3. PRESSURE EFFECT IN THE FRAME OF TRANSITION STATE THEORY

It is important to understand the pressure effect on the reaction rate with the use of thermodynamic models. In the framework of transition state theory, the main stage of RNO_2 decomposition is the formation of TS, which exists in equilibrium with the initial RNO_2 :



Then TS irreversibly decomposes to the reaction products:



The rate of RNO_2 decomposition by scheme (2)-(3) in a plug-flow reactor is described by equation:

$$\frac{dy_{\text{RNO}_2}}{d\tau} = -k^{\#} y^{\#} = -k_{\text{obs}} y_{\text{RNO}_2}, \quad k_{\text{obs}} = k^{\#} K^{\#} \frac{\Phi_{\text{RNO}_2}}{\Phi_{\text{TS}}} \quad (4)$$

where y_{RNO_2} is the reagent mole fraction; $k^\#$ denotes the rate constant of limiting stage (3), $y^\#$ is the mole fraction of TS; $K^\#$ is the equilibrium constant; $\Phi_i = \Phi_i(y, T, P)$ is fugacity coefficient.

The partial derivative of fugacity coefficient with respect to pressure at constant temperature and mixture composition is equal to partial molar volume (\bar{V}_i) of a component:

$$\left(\frac{\partial \ln \Phi_i}{\partial P} \right)_T = \frac{\bar{V}_i}{RT} \quad (10)$$

Finding the logarithm of second equation of (4) with its following differentiation and inserting eq. (10) gives (3). $\Delta\bar{V}^\# = \bar{V}_{\text{TS}} - \bar{V}_{\text{RNO}_2}$, i.e., the difference between the partial molar volumes of TS and reagent is the activation volume of the reaction. In the critical region the $\Delta\bar{V}^\#$ value may be either negative or positive. As a rule, so extreme values of $\Delta\bar{V}^\#$ mean that even insignificant pressure variation in the critical region causes profound alteration of the fluid density.

According to eq. (3), at pressure-independent $\Delta\bar{V}^\# < 0$, the apparent reaction rate constant increases exponentially with increasing pressure. Exactly this effect is observed at the decomposition of NM, NE and NP in SCW. Note that $\Delta\bar{V}_{\text{NM}}^\#$, $\Delta\bar{V}_{\text{NE}}^\#$, and $\Delta\bar{V}_{\text{NP}}^\#$ are negative values and independent of pressure in the interval of 22.7-32.0 MPa at a temperature of 664 K.

The experimental data showed that the activation volumes in the studied reactions were independent of pressure. However, partial molar volumes of reagents and TS must be pressure-dependent. So, in order to verify the validity of using the transition state theory for modeling of the studied reactions, it is necessary to demonstrate that, although partial molar volumes of reagents vary with pressure, their difference remains constant.

In order to calculate TS PMV, it is necessary to select the TS model and determine its physical parameters. It is reasonable to suggest to a first approximation that critical parameters of TS considered as the polarized RNO_2 molecule with loose bonds remain equal to critical parameters of the initial molecule [5], whereas the coefficients of binary interaction k_{ij} and c_{ij} change [6].

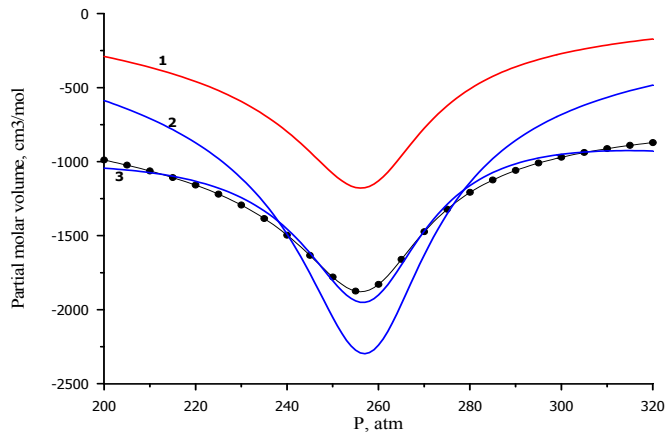


Figure 3. The pressure dependence of PMV: curve 1 — NM-SCW at $k_{ij} = -0.3$, $c_{ij} = 0.3$; curve 2 — TS, “experimental”; curve 3 — TS, calculation at $k_{ij} = -0.5346$, $c_{ij} = 0.5240$; curve 4 — TS, calculation at variable k_{ij} u c_{ij} . $T = 665$ K.

Figure 3 illustrates the results of the TS PMV calculations. Curve 1 represents the pressure dependence of NM PMV in water (\bar{V}_{RNO_2}) calculated at $k_{12} = -0.3$, $c_{12} = 0.3$. Curve 2 represents “experimental” pressure dependence of TS PMV calculated by equation $\bar{V}_{\text{TS}}^{\text{exp}} = \Delta\bar{V}^{\#} + \bar{V}_{\text{RNO}_2}$ assuming $\Delta\bar{V}^{\#} = -700$ cm³/mol. Curve 3 is the calculated pressure dependence of TS PMV obtained using constant values $k_{ij} = -0.53$ and $c_{ij} = 0.52$ resulting from the solution of eq. (13). Curve 4 represents the pressure dependence of TS PMV calculated with variable k_{ij} and c_{ij} determined by eq. (14) with coefficients (15). Figure 3 shows that the pressure dependence of TS PMV calculated using variable k_{ij} and c_{ij} agrees well with the “experimental” dependence.

CONCLUSION

It was shown experimentally that the rate of NM, NE and NP decomposition in SCW strongly depended on pressure at constant temperature. The effect of pressure on the rate constants at the decomposition of NM, NE and NP in SCW was explained on the basis of two different models. One of the models based on transition state theory, another – on acid-catalyzed mechanism involving H_3O^+ ions formed in SCW due to dissociation of water.

Application of transition state theory allowed proving the experimental fact on the independence of the reaction activation volume of pressure. The natures of initial nitrocompounds and TS differ only in the character of solvent-reagent interactions. The studied nitrocompounds showed similar values of TS activation volumes that allow suggestion on the same TS nature in all three cases.

Modeling of this phenomenon on the basis on the acid-catalyzed mechanism 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_3O^+ concentration in dissociated SCW. Processing of experimental data showed that together with the reactions in SCW, decomposition of these compounds proceeds on metal walls of the tubular flow reactor.

REFERENCES

1. Savage P.E., Gopalan S., Mizan T.I. *AIChE Journal*, Vol. 41, **1995**, p.1723-1778.
2. Cocero M.J., Alonso E., Torio R., Vallelado D., Fdz-Polanco F. *Ind. Eng. Chem. Res.*, Vol. 39, **2000**, p. 3007-3016.
3. Naud D.L., Brower K.R. *J. Org. Chem.*, Vol. 57, **1992**, p. 3303-3308.
4. Anikeev V.I., Yermakova A. *Russian J. Physical Chemistry*, Vol. 77, **2003**, p.265-268.
5. Glasstone S., Laidler K., Eyring H., *The theory of rate processes*. Frick Chemical Laboratory, Princeton University, New York and London, **1941**.
6. Anikeev. V.I., Yermakova A. *Theoretical Fundamentals of Chemical Engineering (in Russian)*, Vol. 32, **1998**, p. 508-214.