

Critical phenomena in acetone oxidation by nitric acid

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The kinetic regularities of acetone oxidation by aqueous nitric acid solutions (5.86–58.31 wt.%) were studied using a differential automatic microcalorimeter. The critical phenomena were discovered, which manifest themselves as a abrupt change in the initial heat release rate at a minor change in the temperature or acid concentration. The abrupt change in the oxidative activity of the reactant at a minor change in the system parameter was assumed to be related to changes in the structure of the solution and, as a consequence, in the solvation energy of the reactants at a certain acid/water ratio in the solution.

Key words: kinetics, mechanism, oxidation, acetone, nitric acid, critical phenomena.

The reactions of nitric acid with organic compounds, mainly nitration reactions, which are widely used for synthesis of dyes, drugs, explosives, gunpowders, *etc.*, are being intensively studied in the modern organic chemistry. Nitration is almost always accompanied by a parallel oxidation reaction, whose rate under normal conditions is much lower, but the thermal effect is substantially higher. The change in the parameters of the process may result in an abrupt increase in the heat release rate in the system and in the loss of the thermal stability of the process. According to the current knowledge, the kinetics and mechanism of liquid-phase oxidation of different classes of organic compounds including ketones with molecular oxygen can be described by the regularities of chain reactions with degenerate chain branching.¹ In turn, data on the kinetics and mechanism of ketone oxidation by bound oxygen, particularly, by the systems based on nitric acid solutions, are rather scarce, and the available works are mainly preparative. It was found^{2–6} in a series of studies on the liquid-phase oxidation of aliphatic hydrocarbons by nitric acid solutions that the process under study is classified as a reaction where acid-base equilibria play a substantial and in many aspects determining role along with the radical steps characteristic of oxidation. A combination of radical irreversible and ion-molecular reversible steps is the main specific feature of oxidation by systems based on nitric acid solutions. This opens new possibilities to control the rate of the overall process by shifting the acid-base equilibria.

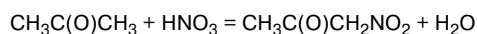
Experimental

Acetone (special purity grade) was used in experiments. Solutions of nitric acid were prepared from HNO₃ (reagent grade,

c 34.7 mol.%), and their concentrations were determined by acidometric volumetric titration. The heat release rate during oxidation was measured with a differential automatic calorimeter⁷ in glass sealed ampules without cold parts, which made it possible to retain all reaction components in the reaction bulk. The temperature interval studied was 17–99.4 °C, and the concentration of HNO₃ solutions expressed as a molar ratio of water to acid (*n*_{H₂O}/*n*_{HNO₃}) was 2.50–56.14. The investigated acetone–aqueous nitric acid system is homogeneous in the region of the studied concentrations of nitric acid solutions. A high HNO₃ excess with respect to acetone was used in order to neglect the change in its content during the process.

Results and Discussion

We studied the nature of critical phenomena in the acetone–aqueous nitric acid system. It was found by the integration of the time dependence of the experimental heat release rates that the thermal effect of acetone oxidation (*Q*_o) is ~770 kJ mol^{–1}, which corresponds to the oxidation mainly to carbon dioxide with a minor admixture of acetic acid. Acetone is oxidized to the same products during liquid-phase oxidation by molecular oxygen.¹ The fraction of nitration products among the reaction products should be insignificant, because the estimated heat of acetone nitration is ~120 kJ mol^{–1} of acetone.



If we assume that the decrease in the experimental heat compared to the theoretically possible value (800 kJ mol^{–1}) is related to the contribution of nitration, then at most 5 mol.% acetone should be consumed by this reaction to yield corresponding nitration products.

The experimental temperatures and concentrations of HNO₃ solutions expressed in the number of moles of

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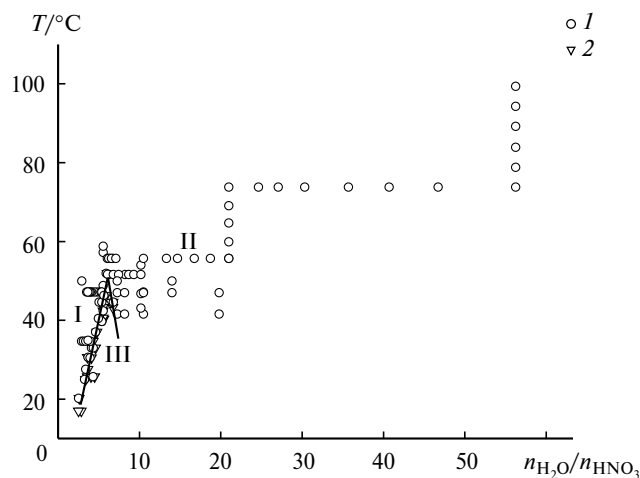


Fig. 1. Temperatures and concentrations of HNO_3 at which acetone oxidation was studied: I, self-accelerating reaction, the presence of NO_2 in the products (1); II, self-accelerating reaction, NO_2 is not visually observed in the products (1); III, the heat release rate is lower than the microcalorimeter sensitivity (~ 0.01 mW) during the observation time up to several days (2).

water per mole of the acid at which the oxidation experiments were carried out are shown in Fig. 1. The whole interval of experimental temperatures and concentrations of nitric acid solutions can be divided into three regions depending on the observed regularities. In region I of relatively high concentrations of HNO_3 solutions with $n_{\text{H}_2\text{O}}/n_{\text{HNO}_3} < 4$ and low temperatures ($T < 40$ °C), the reaction occurs with self-acceleration, the curve of the heat release rate is characterized by an induction period followed by the evolution of the maximum amount of heat in a narrow time interval. The reaction rate depends monotonically on the temperature and concentration of HNO_3 solutions, and the accumulation of NO_2 is visually observed during the reaction.

In region II of relatively low concentrations of HNO_3 solutions ($n_{\text{H}_2\text{O}}/n_{\text{HNO}_3} > 10$) and relatively high temperatures ($T > 60$ °C), the oxidation also occurs with self-acceleration, the maximum rate is achieved within several hours, but the release of the maximum amount of heat occurs in a larger time interval than that for the process in region I. The heat release curves of the oxidation process in region II are shown, as an example, in Fig. 2. As in region I, the reaction rate varies regularly with temperature and concentration of HNO_3 solutions, and no accumulation of NO_2 in the reaction products is visually observed.

When the concentration of an HNO_3 solution decreases with an increment of 1–2 wt.% in region I at a constant temperature, the reaction rate decreases smoothly, but at some next insignificant change in the concentration of an HNO_3 solution the process rate decreases jumpwise to the value that is not detected by a microcalo-

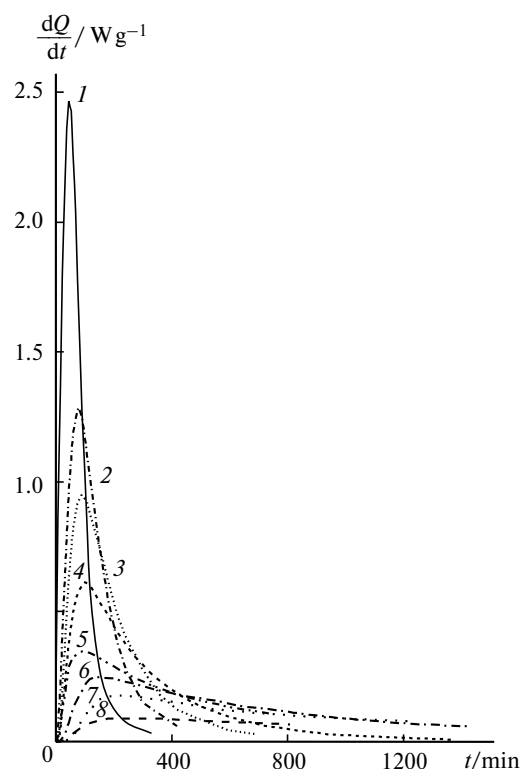


Fig. 2. Plots of the heat release rate vs time during acetone oxidation by HNO_3 solutions of different concentrations at 73.8 °C, $n_{\text{H}_2\text{O}}/n_{\text{HNO}_3}$: 20.98 (1), 24.61 (2), 27.06 (3), 30.31 (4), 35.69 (5), 40.69 (6), 46.72 (7), and 56.23 (8).

rimeter during several days. The corresponding region in Fig 1 is designated as region III. For example, at $T = 34.7$ °C and the nitric acid concentration $n_{\text{H}_2\text{O}}/n_{\text{HNO}_3} = 3.97$ (region I) the maximum oxidation rate is achieved for ~ 250 min, whereas at $n_{\text{H}_2\text{O}}/n_{\text{HNO}_3} = 4.31$ (region III) no heat release is observed during 38 days (Fig. 3). Upon further decrease in the initial concentration of the nitric acid solution (at a constant temperature) at the next increment corresponding to the transition from region III to region II, the oxidation process can be detected again with the times of achievement of the maximum rate about several hours. Such critical phenomena as two abrupt changes in the time of achievement of the maximum rate (from hours to days and then again from days to hours) with the consecutive decrease in the initial concentration of the nitric acid solution were observed at 47.2, 51.6, and 55.7 °C. The heat release curves obtained at 55.7 °C are shown in Fig. 4.

In region III, as in region II, no NO_2 is visually observed among the products. The boundary between regions I and III, determining the critical concentration and temperature values, can be approximated by a linear equation (Fig. 1)

$$T_{\text{cr}} = 13.3 \cdot (n_{\text{H}_2\text{O}}/n_{\text{HNO}_3})_{\text{cr}} - 18.8.$$

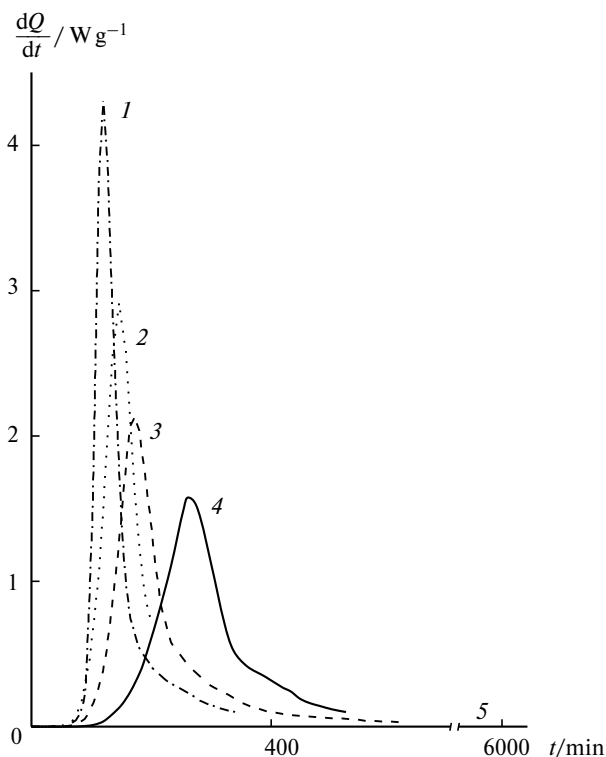


Fig. 3. Plots of the heat release rate vs time during acetone oxidation by HNO_3 solutions of different concentrations at 34.7°C , $n_{\text{H}_2\text{O}}/n_{\text{HNO}_3}$: 2.88 (1), 3.11 (2), 3.38 (3), 3.97 (4), and 4.31 (5); the heat release rate is lower than the microcalorimeter sensitivity.

The processing of the experimental curves by the Origin program showed that the oxidation rate in regions I and II is described by the empirical equation

$$d\eta/dt = k_1(1 - \eta)^n + k_2(1 - \eta)^m \cdot \eta^m,$$

where $\eta = \int_0^t \frac{dQ}{dt} dt / \int_0^\infty \frac{dQ}{dt} dt$ is the conversion of the reaction, $d\eta/dt = 1/Q_0 \cdot (dQ/dt)$ is the process rate, dQ/dt is the heat release rate, and $\int_0^\infty \frac{dQ}{dt} dt = Q_0$ is the total oxidation heat.

The values of the k_2 rate constant and the reaction orders were determined by the processing. It was found that in region I $n_{\text{av}} = 2$ and $m_{\text{av}} = 1$, and in region II the corresponding values are 2 and 0.5. The k_1 rate constants are too low to be determined with the Origin program. They were found by the comparison of the experimental kinetic curves $\eta(t)$ with the curves calculated using specified values of k_1 , k_2 , n , and m by a numerical calculation procedure developed at the Institute of Problems of Chemical Physics (Russian Academy of Sciences). The program is based on an implicit first-order difference scheme with Newton iterations. The dependences of the reaction rate constants k_1 and k_2 on the temperature and

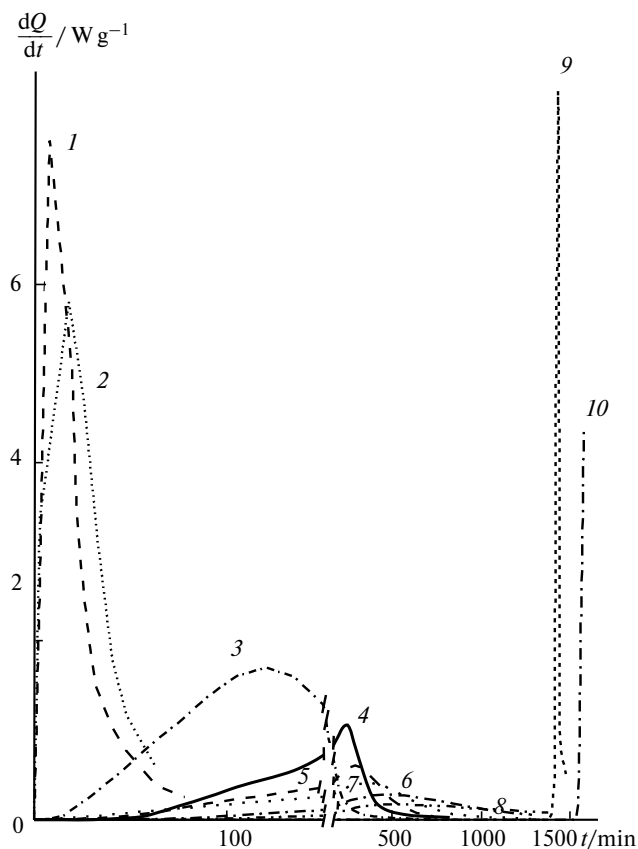


Fig. 4. Plots of the heat release rate vs time during acetone oxidation by HNO_3 solutions of different concentrations at 51.7°C , $n_{\text{H}_2\text{O}}/n_{\text{HNO}_3}$: 6.05 (1), 7.09 (2), 10.48 (3), 13.22 (4), 14.68 (5), 16.73 (6), 18.71 (7), 20.98 (8), 6.74 (9), and 6.74 (10).

concentration of undissociated and unbound nitric acid in aqueous solutions⁸ are presented in Figs 5 and 6.

The abrupt jumpwise change in the apparent rate constant in the initial step at a consecutive transition from region I to region III and then from region III to region II (see Figs 5 and 6) corresponds to the critical phenomena. In region I at different $n_{\text{H}_2\text{O}}/n_{\text{HNO}_3}$ ratios the apparent activation energy for the initial step is approximately the same ($\sim 200 \text{ kJ mol}^{-1}$) and the pre-exponential factors increase with increasing acid concentration as follows:

$n_{\text{H}_2\text{O}}/n_{\text{HNO}_3}$	Pre-exponential factor (min^{-1})
56.22	$6.6 \cdot 10^{22}$
20.98	$3.1 \cdot 10^{27}$
10.48	$7.2 \cdot 10^{29}$

The apparent rate constants k_2 in the region of increasing rates are characterized by smooth (no jumps) dependences on the temperature and nitric acid concentration in the entire interval of external parameters. The apparent activation energy for this stage is approximately the same for the oxidation by solutions of different con-

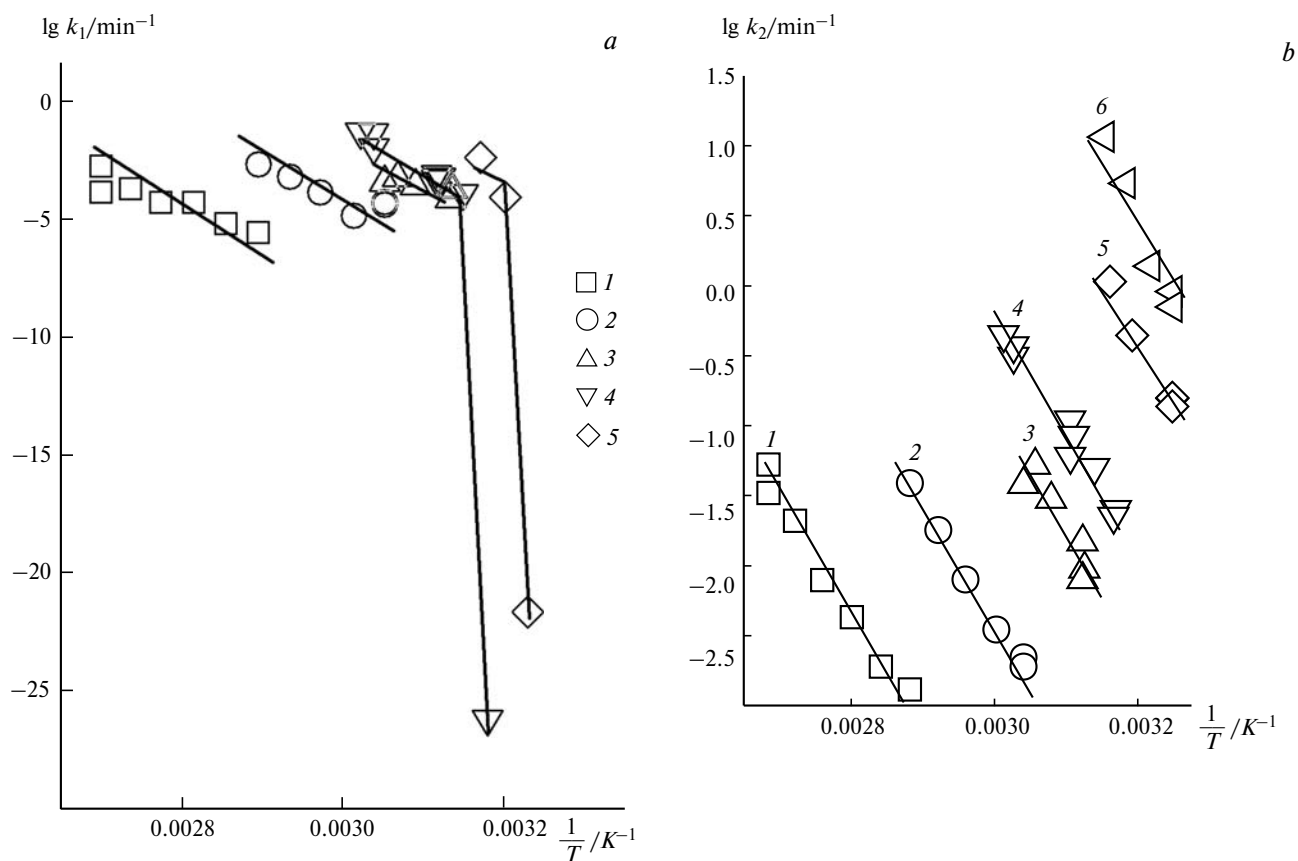


Fig. 5. Plots of $\lg k_1$ (a) and $\lg k_2$ (b) vs $1/T$ during acetone oxidation by nitric acid solutions of different concentrations, $n_{\text{H}_2\text{O}}/n_{\text{HNO}_3}$: 56.22 (1), 20.98 (2), 10.48 (3), 5.54 (4), and 3.68 (5).

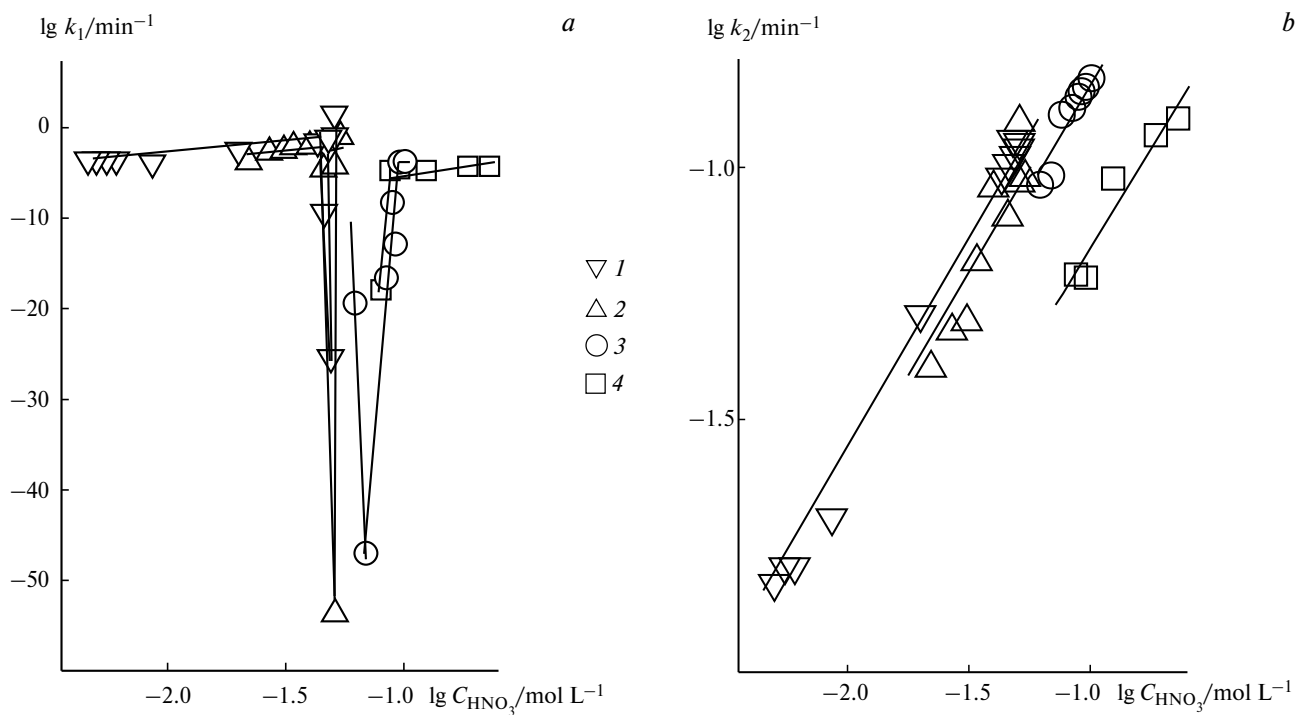


Fig. 6. Plots of $\lg k_1$ (a) and $\lg k_2$ (b) vs $\lg C_{\text{HNO}_3}$ during acetone oxidation by nitric acid solutions at different temperatures, $T/^\circ\text{C}$: 55.7 (1), 51.6 (2), 47.2 (3), and 34.7 (4).

centrations ($\sim 120 \text{ kJ mol}^{-1}$), while the pre-exponential factors change as follows:

$n_{\text{H}_2\text{O}}/n_{\text{HNO}_3}$	Pre-exponential factor (min^{-1})
56.22	$1.7 \cdot 10^{14}$
20.98	$1.3 \cdot 10^{15}$
10.48	$1.9 \cdot 10^{17}$
5.54	$9.0 \cdot 10^{17}$
3.68	$2.9 \cdot 10^{19}$
2.92	$2.2 \cdot 10^{20}$

As follows from the slope ratios of the straight lines, the apparent rate constant for the initial stage k_1 is proportional to the concentration C of undissociated and unbound nitric acid, and the apparent rate constant k_2 in the self-acceleration stage is proportional to $C^{0.75}$ (see Fig. 6).

The influence of sodium nitrite additives on the rate of acetone oxidation was studied at a fixed concentration of HNO_3 ($n_{\text{H}_2\text{O}}/n_{\text{HNO}_3} = 10.17$, region III) and 33.5°C . The added amount of nitrite ranged from 0.05 to 0.9 mole per mole of acetone. The sodium nitrite additives substantially increase the initial rate. The initial rate was found to be proportional to the initial concentration of sodium nitrite $C_0\text{NO}_2^-$ to the 0.5 power

$C_0\text{NO}_2^- \cdot 10^6$ /mol L^{-1}	$(dQ/dt)_{t=0} \cdot 10^{-1} / (C_0\text{NO}_2^-)^{0.5}$ /W $\cdot \text{L}^{0.5} \cdot \text{g}^{-1} \cdot \text{mol}^{-0.5}$
111	6.5
100	6.3
19	6.5
17	6.4
8.1	6.5

The k_1 and k_2 values were determined at a fixed sodium nitrite additive in an amount of $1.15 \cdot 10^{-4} \text{ mol L}^{-1}$ in HNO_3 with $n_{\text{H}_2\text{O}}/n_{\text{HNO}_3} = 10.17$ in the temperature interval from 33.5 to 54°C

$T/^\circ\text{C}$	$k_1 \cdot 10^3 / \text{min}^{-1}$	$k_2 \cdot 10^3 / \text{min}^{-1}$
33.5	0.2	0.5
38.3	1.3	1.3
39.3	1.6	1.7
43.3	1.9	2.9
44.5	1.4	2.3
48.8	3.6	5.0
54.0	7.8	10.8

The temperature dependence of k_1 can be presented as $4.5 \cdot 10^{17} \exp(-124 \cdot 10^3/RT) \text{ min}^{-1}$. The activation energies in the equations for k_1 and k_2 are equal to each other within the limits of experimental error, while the rate constants k_2 are on the average 1.5 times higher than k_1 .

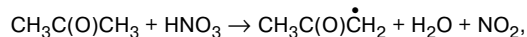
The oxidation with a sodium nitrite additive proceeds with a substantially lower rate constant k_2 compared to the systems without additives.

The critical phenomena are an important feature of the acetone oxidation by nitric acid solutions. They appear as a sharp change in the heat release rate at an insignificant change in the temperature or acid concentration. The critical phenomena observed in chain branched reactions at an insignificant change in the parameter of the system are related to the abrupt change in the apparent rate constant in the self-acceleration step due to the difference in the rate constants and orders of the chain branching and termination reactions.⁹ In the case of acetone oxidation in solutions by bound oxygen of nitric acid, the critical phenomena, probably, have another nature. The smooth change in the parameters of the system (temperature or concentration) is accompanied by a jumpwise change in the initial rate of the process, which can be associated to the same kind of changes in the concentration of the oxidized compound or the oxidizing reagent in the initial step. For acetone oxidation by nitric acid solutions, the apparent rate constant for the self-acceleration step exhibits a smooth dependence on the temperature and HNO_3 concentration in the entire interval of concentrations of HNO_3 solutions, including the initial parameters at which critical phenomena are observed (see Figs 3 and 5). This is the basic difference between the nature of critical phenomena observed previously in the branched chain reactions and in the present study.

Throughout studied interval of solution concentrations, except for region II, the initial rate of acetone oxidation is proportional to the concentration of undissociated and unbound acid. It can be assumed that, as for the earlier studied reaction of hydrocarbon oxidation by nitric acid,¹ the reaction rate is controlled by the rate constant and equilibrium concentration of molecular HNO_3 . The concentrations of other potential oxidants present in the equilibrium system (nitric acid anhydride N_2O_5 and the product of its ionization NO^{2+}) are substantially lower than the concentration of molecular HNO_3 . Initially, there is no nitrogen dioxide in the system, because the relatively dilute solutions of nitric acid used are stable at the experimental temperatures.¹⁰ It can be assumed that the observed jumpwise changes in the initial rate of acetone oxidation on going to region II are associated with an abrupt change in the solvation energy of acetone or oxidizing agent at a certain water/acid ratio in solution at a given temperature. There exist dynamic equilibria between diffusion-averaged supramolecular structures of hydrated proton and anion in nitric acid solutions, with singularities at particular temperatures and concentrations.¹¹ The specific features of the supermolecular structure and specificity of incorporation of an acetone molecule into these structures in a certain interval of concentrations and temperatures can result in a lesser accessibility of the acetone molecule to the attacking nitric acid molecule and, correspondingly, in an abrupt

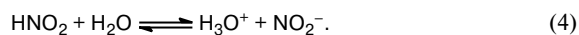
decrease in the initial oxidation rate. Interrelations between the structure of nitric acid solutions and kinetic phenomena will be a subject of future studies.

The initial step of acetone oxidation can be either the abstraction of an H atom from the methyl group of the ketone form of acetone by the HNO_3 molecule



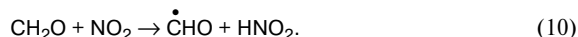
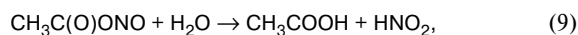
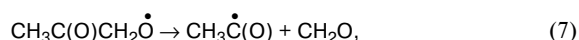
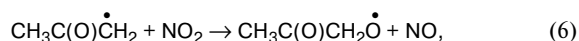
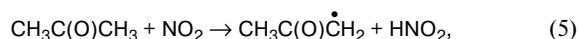
or the addition of the HNO_3 molecule to the double bond in the enolic form of acetone followed by the reduction of nitric acid to nitrous acid and acetone oxidation to the α -oxy compound.¹² The oxidation rate by HNO_3 molecules is low and controls only the initial rate of oxidation.

Nitrogen-containing molecules with the oxidation state of lower than +5 (NO_2 , N_2O_4 , N_2O_3 , HNO_2) formed upon the reduction of HNO_3 are stronger oxidants than molecular HNO_3 . In HNO_3 solutions, their concentrations are determined by mobile equilibria. On going from concentrated HNO_3 solutions ($n_{\text{H}_2\text{O}}/n_{\text{HNO}_3} = 2.3$) to dilute solutions with increasing the water content the equilibrium shifts from NO_2 to N_2O_3 , then to HNO_2 and, finally, to NO_2^- according to the equations¹³

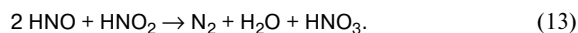
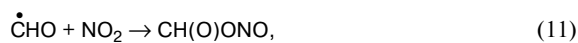


As the process develops and these reduced nitrogen-containing molecules appear in the system, the oxidation rate in the developed process is controlled by the reaction with that oxidant whose oxidative activity, determined by the oxidation rate constant and the equilibrium concentration, is the highest in the studied interval of HNO_3 concentrations. In region I, where the accumulation of NO_2 is visually observed, the rate of the developed acetone oxidation of acetone is determined by its reaction with NO_2 and increases with increasing the equilibrium concentration of the latter.

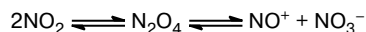
When equilibria (1)–(4) shift to the left, NO_2 is formed, and these reactions result in chain branching. The chain propagation reactions,¹⁴ in which NO_2 is consumed to form the product of acetone oxidation (MeCOOH), are presented below



The oxidation by HNO_3 solutions differs from the oxidation by molecular oxygen, in that the concentration of NO_2 leading the process can increase following the acid-base equilibrium reaction (1). For two NO_2 molecules consumed in reactions (5) and (6), three NO_2 molecules are regenerated *via* equilibrium (1). The NO_2 molecules formed can again enter into the oxidation reaction to form NO and HNO_2 . This process can formally be considered as a branched chain reaction. Thus, when nitrogen oxide is accumulated in the system, reaction (1) can be one of the main sources of the fast increase in the NO_2 content and of strong self-acceleration of the oxidation of organic compounds by nitric acid. According to equilibrium (1), the NO_2 concentration in the system should be proportional to the concentration of free nitric acid molecules to the 0.66 power, which is close to the experimentally observed order of the apparent rate constant k_2 with respect to the concentration of free nitric acid molecules. The role of chain termination reactions is played by the oxidation by NO_2 with the formation of N_2



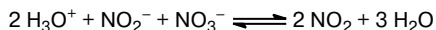
During acetone oxidation by HNO_3 solutions, the recombination of NO_2 with $\text{CH}_3\text{C}(\text{O})\text{C}^*\text{H}_2$ and $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}^*$ radicals can probably lead to the formation of the nitration product. The reactions of formation of the nitro derivatives and nitric acid esters and the equilibria (1)–(4) along with the equilibrium



shifted to HNO_2 , N_2O_3 , N_2O_4 , NO^+ , and NO_2^- are also chain termination reactions when the oxidation is led by nitrogen dioxide.

As in region I, in region II (HNO_3 solutions with $n_{\text{H}_2\text{O}}/n_{\text{HNO}_3} > 10$ and relatively high temperatures), the reaction rate shows a smooth dependence on the temperature, concentration of the HNO_3 solutions, and conversion with no critical jumps. It was established for this region of HNO_3 concentrations that the initial oxidation rate is proportional to the concentration of sodium nitrite added ($C_0^{\text{NO}_2^-}$). This means that NO_2 is the leading oxidizing agent in region II both in the initial step in the presence of the nitrite ion and for the developed process

without nitrite additives, as in region I. The initial oxidation rate in the presence of nitrite ion with the leading role of nitrogen dioxide according to the equilibrium



should be proportional to the square root of the nitrite ion concentration, which is observed in the experiment. The same mechanism of NO_2 -mediated oxidation in the initial step and in the acceleration step in the presence of sodium nitrate in HNO_3 at $n_{\text{H}_2\text{O}}/n_{\text{HNO}_3} = 10.17$ is also indicated by similar temperature dependences of the rate constants k_1 and k_2 .

It may be assumed that with the further dilution of the starting HNO_3 solutions with water, the leading role in the oxidation at the stage of the developed process will transfer from NO_2 to N_2O_3 and then to HNO_2 .

The presence of the carbonyl group increases the reactivity of acetone compared to hydrocarbons. A comparison of the oxidation rates of acetone and decane² shows that the maximum rate of acetone oxidation at 92.8 °C and $n_{\text{H}_2\text{O}}/n_{\text{HNO}_3} = 2.92$ is 350 times higher than that of decane oxidation.

Thus, the critical phenomena were observed in the oxidation of acetone by nitric acid solutions. They manifest themselves as an abrupt change in the apparent rate constant for the initial oxidation step upon an insignificant change in the temperature or acid concentration. The nature of these phenomena differs from that of the known critical phenomena in the branched chain reactions of oxidation by molecular oxygen, which are related to the dramatic change in the apparent rate constant in the self-acceleration step due to the difference in the rate constants and orders of the chain branching and termination reactions. It seems important to study the nature of the critical phenomena in the oxidation by bound oxygen. It is assumed that they are due to changes in the structure of an acid solution and, as a consequence, its solvating ability with respect to the oxidizing agent or acetone molecule at a certain acid/water ratio in the solution.

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