Kinetics of thermal decomposition of ammonium persulfate

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Kinetics of thermal decomposition of ammonium persulfate was studied by calorimetry and Raman spectroscopy. The values of activation energies of the overall reaction and its individual stages were estimated.

Key words: ammonium persulfate, kinetics of thermal decomposition, calorimetry, Raman spectroscopy.

Unlike alkaline metal persulfates,[1] the kinetics of thermal decomposition of ammonium persulfate (AP) is insufficiently studied. In this work, this reaction accompanied by the formation of pyrosulfate

$$(NH_4)_2S_2O_8 \longrightarrow (NH_4)_2S_2O_7 + 0.5\ O_2,$$

was studied by scanning calorimetry and Raman spectroscopy. Measurement of the temperature dependence of the heat flow upon decomposition of samples was used for estimation of the kinetic parameters: activation energy and frequency factor of the overall reaction. To estimate the activation energies of cleavage and formation of individual bonds, changes in chemical bonds were followed *in situ* by Raman spectroscopy in decomposing and forming substances, including intermediate products. This approach is oriented to development of informative methods of studying the kinetics of chemical reactions in solid states, which do not decompose substances.

Experimental

Powders of ammonium persulfate (reagent grade) with dispersity of 0.40 to 0.66 mm served as samples.

Calorimetric measurements were performed on a DSK-III calorimeter (Setaram, France) in scanning mode at a heating rate of 1, 3, 5, and 10 deg min^{-1} in air with ~100-mg weighted samples.

Raman spectra were recorded on a DFS-24 spectrometer with an ILA-120 I argon laser as the excitation source (λ = 488 nm, power at outlet ≤ 20 MW). Samples were heated in the 443 to 463 K temperature range in the isothermal regime on a special attachment,[2] which made it possible to record spectra during decomposition of the samples. The temperature was specified by a PIT-3 precision thermoregulator with accuracy of ±1 K.

Before the determination of kinetic dependences, the laser was held switched on for 2 h until the radiation power was stabilized. Then the temperature attachment with a Raman cell was adjusted until the maximum intensity of the line of the symmetric stretching vibration of the S—O—O—S bridge (ν_m) was obtained in the spectrum of the initial persulfate. Then the cell with the sample was taken from the temperature attachment, and heating of the attachment was switched on. After establishment of the specified temperature, the cell with the sample was placed in the attachment again, and the following kinetic dependences were recorded:

$$I = f(t),$$

where I is the relative intensity of the spectral line and t is time. These dependences were recorded by one of two methods: (1) scanning of the Raman spectrum of the sample at intervals of 2—4 min in the range of stretching (ν_s) or deformational (δ) vibrations of SO_3^- groups or S—O—O—S bridges (ν_m, δ_m) in persulfate and pyrosulfate anions, and (2) direct recording of intensity I as a time function at the constant frequency of one of the aforementioned vibrations. All kinetic dependences were recorded not less than three times at five values of temperature in the temperature range mentioned.

Results and Discussion

Only one intense exothermic peak is observed in the temperature dependence of the heat flow upon thermal decomposition of AP up to 480 K. The value of the heat effect referred to the amount of the reacted substance minus a portion of the heat released with the gaseous product (O_2) allows one to estimate the value of the reaction enthalpy: $\Delta H \approx 71\pm8$ kJ mol^{-1}.

The kinetic parameters were estimated from the dependence of the exothermic peak position (T_{max}) on the heating rate[3] by the Arrhenius equation in the following form:

$$e^{-E_a/K_B \cdot T_{max}} = \frac{\alpha}{A_0} \cdot \frac{E_a}{K_B \cdot T^2_{max}},$$

where E_a is the activation energy, K_B is Boltzmann's constant, α is the heating rate, and A_0 is the frequency

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Table 1. Parameters of thermal decomposition of AP

α K/min	α K/s	$\log\alpha$	$\ln\alpha$	$\log T_{max}$	T_{max}	$\ln T_{max}$	$2\ln T_{max} - \ln\alpha$	$(1/T_{max}\cdot 10^3)$ K^{-1}
1	0.0166	−1.780	−4.094	2.634	430	6.058	16.21	2.32
3	0.0500	−1.301	−2.992	2.639	435	6.070	15.31	2.30
5	0.0833	−1.079	−2.482	2.648	445	6.090	14.66	2.24
10	0.1670	−0.777	−1.787	2.650	447	6.095	13.98	2.23

factor. This equation can be transformed to the form convenient for determination of the kinetic parameters from the experimental data:

$$y = m\cdot x + b,$$

where $y = 2\ln T_{max} - \ln\alpha$, $m = E_a/K_B$, $x = E_a/K_B$, and $b = \ln(E_a/K_B) - \ln A_0$.

The T_{max} and α values were used for calculation of the left part of the equation, and the E_a and A_0 values were determined from slope m and intercept b on the Y axis. Some results are presented in Table 1. The following values of the kinetic parameters were calculated: activation energy $E_a = 205\pm10$ kJ mol^{-1}, frequency factor $A_0 \sim 10^{22}$ s^{-1}. Such a high value of A_0 is normal for solid-phase reactions.[4a]

The main lines of the Raman spectra of AP and the product of its thermal decomposition (Fig. 1) were assigned in Ref. 5. The kinetic dependences for the main lines of the Raman spectra of AP and pyrosulfate obtained upon decomposition of AP at 443 K are presented in Fig. 2. In order to estimate the activation

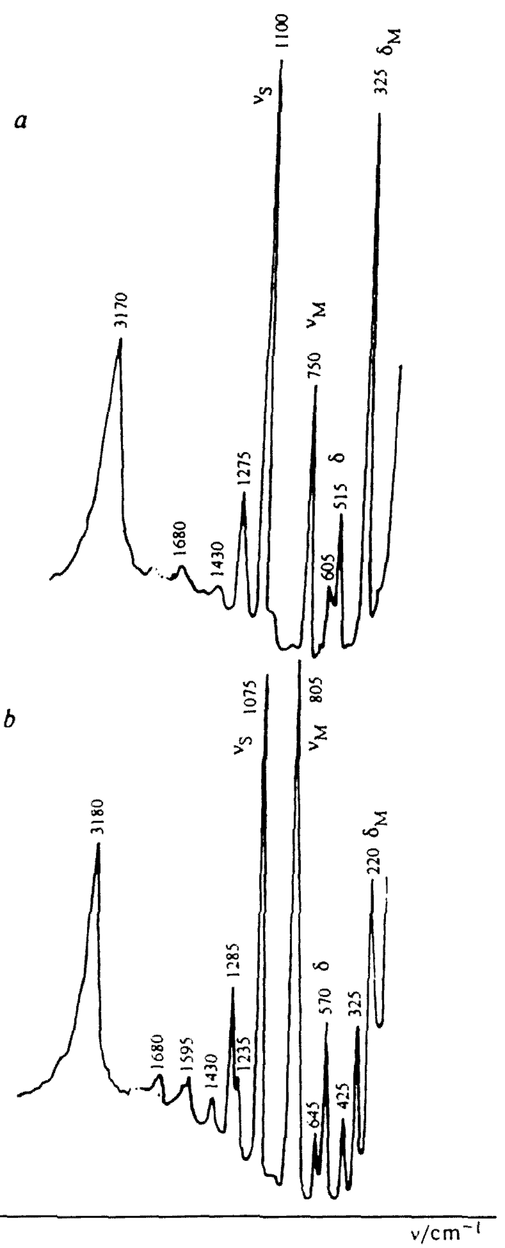


Fig. 1. Raman spectra of ammonium pyrosulfate (*a*) and persulfate (*b*).

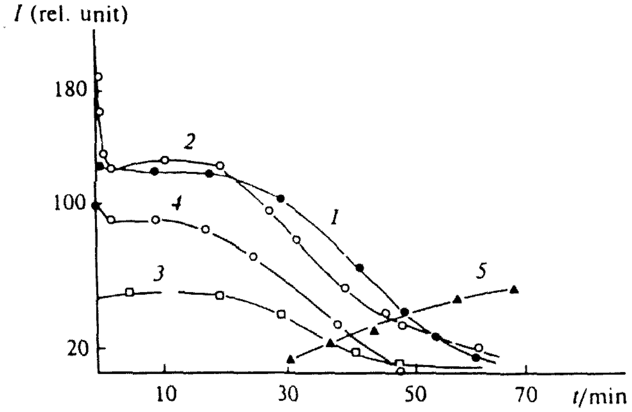


Fig. 2. Kinetic dependences of thermal decomposition of ammonium persulfate at 443 K corresponding to vibrations of the persulfate anion (*1—4*): *1*, ν_s(S—O), *2*, ν_m(S—O—O—S), *3*, $\delta(SO_3^-)$, *4*, δ_m(S—O—O—S); and the pyrosulfate anion (*5*): ν_s(S—O).

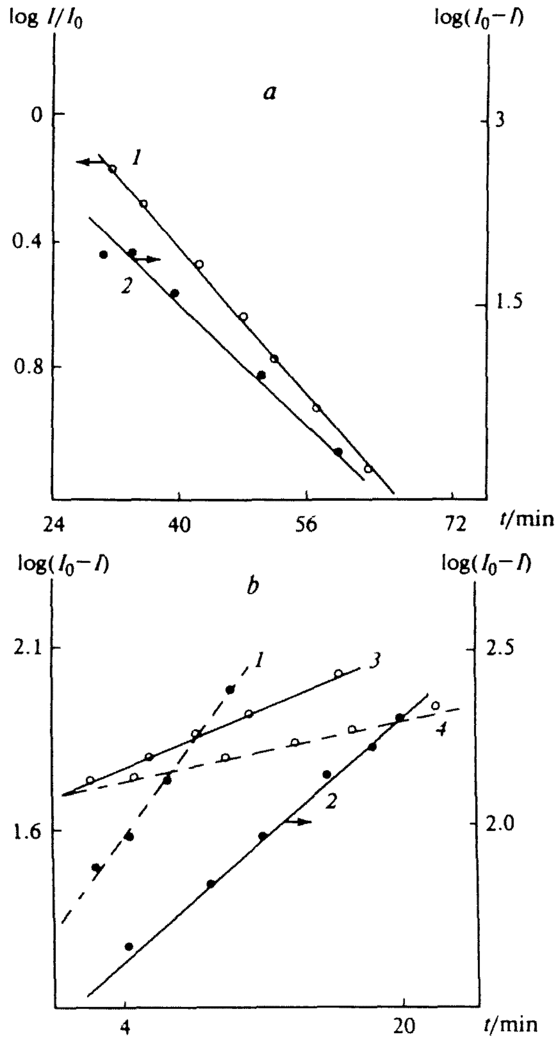


Fig. 3. Time dependences: (*a*) $\log(I/I_0)$ *vs.* t for the stretching vibration (ν_s) of the S—O bonds of persulfate (*1*) and pyrosulfate (*2*) anions; (*b*) $\log(I_0 - I)$ *vs.* t for deformational (δ_m) (*1*, *2*) and stretching (ν_s) (*3*, *4*) vibrations of the persulfate anion at 444 (*1*, *3*, *4*) and 447 K (*2*); *4* for the sample after activation.

energies, the experimental data were kinetically processed using the functions

$$I = I_0e^{-Kt}, \qquad I = I_0(1 - e^{-Kt})$$

for the decomposition of persulfate and formation of pyrosulfate, respectively, used for reactions in dispersed media. The experimental dependences $\log(I/I_0)$ *vs.* t and $\log(I_0 - I)$ *vs.* t are presented in Fig. 3 (*a*). The corresponding experimental data are presented in Fig. 2. The linear character of these dependences indicates a first-order reaction with respect of reagents as in the case of thermal decomposition of rubidium and cesium persulfates.[1] The values of activation energies were calculated by the graphic method from the Arrhenius dependences. For the induction period, E_a was calculated from the initial regions of the kinetic dependences of the decrease in the intensity of the line of symmetric stretching vibrations of peroxide bonds nm (805 cm^{-1}). The results of the calculation are presented in Table 2 (upper line), and some typical dependences log$K$ *vs.* $1/T\cdot10^3$ are presented in Fig. 4. The values of the constants necessary for calculation of E_a were also determined by the graphic method. Some dependences $\log(I - I_0)$ *vs.* t for the lines of symmetric stretching (ν_s) vibrations of the S—O bonds of the SO_3^- groups of the persulfate anions (1075 cm^{-1}) and deformational vibrations (δ_m) of the S—O—O—S bridges (220 cm^{-1}) at two temperatures are presented in Fig. 3 (*b*).

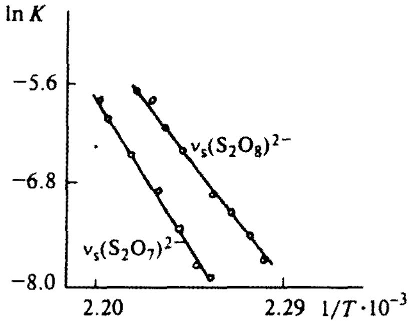


Fig. 4. Arrhenius dependences for reaction rate constants of isothermal decomposition of ammonium persulfate based on the kinetic dependences for stretching vibrations (ν_s) of S—O bonds of persulfate (*1*) and pyrosulfate (*2*) anions.

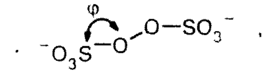
Table 2. Values of activation energy of thermal decomposition of AP from data of Raman spectroscopy

No.	E_a at induction period kJ mol^{-1}	E_a at acceleration period kJ mol^{-1}			
	(ν_m)	$\nu_s(S_2O_8{}^{2-})$	$\delta(S_2O_8{}^{2-})$	$\delta_m(S_2O_8{}^{2-})$	$\nu_s(S_2O_7{}^{2-})$
1	125±10	206±8	210±15	235±21	251±21
2*	115±8	191±15	—	140±13	145±11

* After mechanical activation.

For comparison, several measurements were performed on AP samples subjected to mechanical activation by static compression in a mold for 1 h at 10 kbar. The activation resulted in no noticeable changes in the Raman spectrum of AP; however, the E_a values of cleavage of chemical bonds decreased noticeably (Table 2, bottom line).

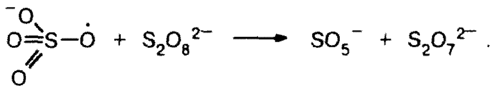
Let us consider the kinetic peculiarities of thermal decomposition of ammonium persulfate. The E_a value at the induction period ($t \approx 20$ min) coincides with the energy of the peroxide bond in persulfates.[6] The cleavage of the bond, which is the weakest in the anion



$$^{-}O_3S{-}O{-}O{-}SO_3^{-},$$

is accompanied by the formation of two SO_4^- radical ions retaining positional symmetry of the initial anion. Since the intensity of the ν_s line does not substantially change at this stage, the angle between the bonds likely remains unchanged as well. This stage is primary and corresponds to the formation of the metastable state.[7]

The E_a value at the acceleration period of the reaction is determined by calorimetry (205±10 kJ mol^{-1}) and is the closest to the activation energy of decomposition of the persulfate anion calculated from a decrease in the intensity of the line of the stretching vibration (ν_s) of the S—O bonds in the persulfate anion (206+8 kJ mol^{-1}). Therefore, it cannot be excluded that E_a of the overall reaction is determined by the cleavage of the S—O bonds in the persulfate ion. The acceleration period can be associated with a growth of rotation of radical ions formed upon cleavage of peroxide bonds, which also provides the necessary frequency of approach of particles to the activation barrier and orientation of radial ions relative to the adjacent persulfate ion followed by the reaction



Perhaps, this is the reason for the weak effect of the mechanical activation on processes associated with cleavage of peroxide S—O—O—S bonds at the induction period and S—O bonds of SO_3^- groups in persulfate anions at the acceleration period and for a considerable decrease in E_a at the acceleration period due to facilitation of rotation of radical ions (vibration δ_m in pyrosulfate anions). This results in a decrease in E_a during the formation of pyrosulfate anions.

The results of this work supplement our previous data[2,5] on thermal decomposition of ammonium persulfate.

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