

The kinetics of vapor-phase nitration of cellulose

2.* Nitration with nitric acid under static conditions

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The regularities of vapor-phase nitration of cellulose with HNO_3 under conditions of natural convection and hindered heat removal in the absence of air were studied using the nonisothermal kinetic method. It was established that the nitration rate at the depth of conversion of 0.08 to 0.7 is described by the kinetic law $d\eta/dt = k_1 p / (1 + \beta\eta)$, where $k_1 = 10^{4.49 \pm 0.6} \exp(-A/RT) \text{ s}^{-1} \text{ atm}^{-1}$, $\beta = 10^{-35.5 \pm 15.7} \exp(B/RT)$, $A = 36.6 \pm 3.8 \text{ kJ mol}^{-1}$, and $B = 203 \pm 88 \text{ kJ mol}^{-1}$. The diffusion mechanism of vapor-phase nitration of cellulose, which explains the high value of activation energies, is discussed. The effective diffusion coefficient of HNO_3 in cellulose at 25°C ($3.7 \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) and the activation energy of diffusion ($38.3 \pm 4.2 \text{ kJ mol}^{-1}$) were estimated.

Key words: cellulose, nitration, nitric acid, kinetics, diffusion coefficient.

The regularities of nitration of cellulose (C) with HNO_3 vapor were studied in several works,^{2–4} because this process of the preparation of cellulose nitrate (CN) is one of the simplest methods; however, its kinetics has not yet been described. The vapor-phase nitration of C with such nitrating agents as N_2O_5 and HNO_3 is accompanied by substantial warming of a sample due to the low heat conductivity of the reacting system, which makes the application of classic methods difficult for the quantitative study of the kinetic regularities of the process. As shown previously using the vapor-phase titration of C with nitric anhydride¹ as an example, the thermographic nonisothermal procedure,⁵ which makes it possible to obtain quantitative results at an insignificant temperature gradient over the mass of the sample, can be used for this purpose. This work continues the study of the kinetic regularities of the vapor-phase nitration of C. Nitric acid was used as a nitrating agent.

Experimental

Cellulose was nitrated with the HNO_3 vapor, which was in an equilibrium with a 98–99 % solution of HNO_3 obtained by distillation of fuming HNO_3 at low pressure. It is undesirable to use more concentrated HNO_3 , because the appearance of N_2O_5 molecules in the vapor is possible due to the equilibrium



When the acid contains even 1 % H_2O , the equilibrium concentration of N_2O_5 is not greater than 0.01 mol. %. According to the estimations from the linear interpolation of partial pressures over solutions of 90 and 100 % HNO_3 ,⁶ the

partial pressure of H_2O over 98 % HNO_3 at $20\text{--}30^\circ\text{C}$ is 0.4 to 0.7 % of the total value. The nitration process in the samples taken from the reactor was stopped by intermediate washing with a large amount of water to neutral reaction (by the litmus probe). Samples of C for the study, their preparation, storage, methods for analysis of the content of nitrogen in CN, and an installation for thermographic studies were the same as those for the vapor-phase nitration with nitric anhydride.¹ All mentioned kinetic data on the nitration of C with N_2O_5 were taken from the same work.

The kinetics of the vapor-phase nitration of C was studied in the absence of air with continuous monitoring of the pressure in the reactor and temperature of the sample. The ratio of the total mass of vapor and liquid HNO_3 to the mass of the C sample was several tens. The rate of the nonisothermal reaction ($d\eta/dt$) and the depth of conversion (η) were determined from the dependences¹:

$$\frac{d\eta}{dt} = \frac{c}{Q} \cdot \frac{dT}{dt} + \frac{\alpha_0 S_0}{p_0 Q m_0} \cdot \frac{p(T - T_0)}{[1 + (a + 2b)\eta]^{1/3}}, \quad (1)$$

$$\eta = \frac{1}{a + 2b} \cdot \left\{ \left[c(T - T_0)/Q + \frac{\alpha_0 S_0}{p_0 Q m_0} \int_0^t p(T - T_0) dt \right] (4/3)(a + 2b) + 1 \right\}^{3/4} - \frac{1}{a + 2b} \quad (2)$$

where c is the heat capacity of C, $\text{cal g}^{-1} \text{ K}^{-1}$; Q is the heat effect of the nitration, cal g^{-1} ; α_0 is the heat-transfer coefficient at $p_0 = 1 \text{ atm}$, $\text{cal cm}^{-2} \text{ s}^{-1} \text{ K}^{-1}$; S_0 is the value of the initial surface of the sample through which the heat exchange with the reactor wall occurs, cm^2 ; m_0 is the initial mass of the C sample, g; p is the pressure of HNO_3 vapor, atm; $a = 3(\mu_{\text{NO}_2} - \mu_{\text{H}})/\mu_{\text{C}} = 0.83$; $b = p_{\text{CN}}/p_{\text{C}} - 1$; μ_{NO_2} , μ_{H} , and μ_{C} are the molar weights of the NO_2 and H groups and

* For Part 1, see Ref. 1.

the C unit, respectively; ρ_{CN} and ρ_{C} are the volume density of the CN and C samples, respectively, g cm^{-3} ; and T_0 and T are the temperatures of the reactor wall and sample, respectively, K.

The heat effect of the nitration calculated from the values of standard enthalpies of formation of C and CN,⁷ H_2O and HNO_3 ⁸ for the achieved depth of nitration and from the experimentally measured amounts of HNO_3 retained to the end of the nitration (40–60 %), which were accepted in the liquid state in the thermodynamic calculations, was estimated as equal to 840 J g^{-1} . The heat capacity of C was taken equal to $1.25 \text{ J g}^{-1} \text{ deg}^{-1}$.⁹ The calculations of the η and $d\eta/dt$ values from Eqs. (1) and (2) used the values of $\int p(T - T_0)dt$ and dT/dt , which were obtained by the numerical integration and differentiation of the experimental time dependences of p and $T - T_0$; the constant $b = 0.089$ was accepted the same as in the nitration of C with the N_2O_5 vapor; and the value of the $\alpha_0/(p_0Q)$ parameter was estimated from the experimental data. The values of S_0 and m_0 were measured before the beginning of the nitration in each case.

Results and Discussion

The regularities of the vapor-phase nitration of C were studied in a range of HNO_3 pressures from 0.0329 to 0.0829 atm at the initial temperatures of the sample $T_0 = 12.6$ – 29.3°C . The maximum warming of the sample (12– 30°C) is achieved in the first min of the nitration, and in the course of the process the warming monotonically decreases approaching T_0 (Fig. 1). Some parameters of the experiments performed are presented in Table 1; the reduced values of the pressure of the HNO_3 vapor (p_s) characterize the almost stationary values achieved in 15 to 20 min after the beginning of the experiment.

The establishment of the heat and sorption equilibria and probably the nitration of the surface layers faster than that of the main mass of C occur during the first 1

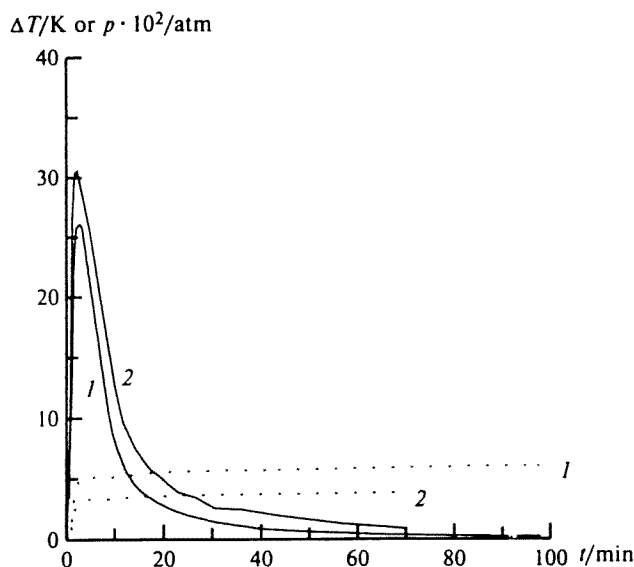


Fig. 1. Characteristic dependences of warming of the C sample (solid curves) and pressure of the HNO_3 vapor (dotted curves) in vapor-phase nitration under static conditions at T_0 equal to 22.9 (1) and 12.6 (2) $^\circ\text{C}$.

Table 1. Conditions of nitration of C with the HNO_3 vapor and parameters of CN formed to the termination of the reaction

Sample	T_0 $^\circ\text{C}$	$p_s \cdot 10^3$ /atm	t /min	Content of N (%) in CN
1	12.6	32.9	158	13.9
2	15.3	32.9	76	13.4
3	19.0	46.0	57	13.7
4	22.9	52.6	98	13.8
5	26.4	52.6	75	13.4
6	26.6	72.4	160	13.5
7	29.3	82.9	14	13.3

to 2 min after the beginning of the reaction.¹ Therefore, these initial regions are excluded from further kinetic considerations. According to the calculations, the depth of nitration is 0.05 to 0.1 for 1 to 2 min. The dependences of the rates of nonisothermal nitration on the depth of nitration beginning from the initial moments are presented for some experiments in Fig. 2. It is seen that the change in the nitration rate, which can be described by one kinetic law (the discussion of this law is presented below) shown by solid lines in Fig. 2, begins from the depths of nitration of 0.05 to 0.08.

Nitric acid in the liquid phase is a less reactive nitrating agent of alcohols compared to N_2O_5 .¹⁰ Meanwhile, the rates of the vapor-phase nitration referred to the pressure of the nitrating agent at the same temperature differ only by several times, and the specific rate of the nitration with the HNO_3 vapor is even higher. The closeness of the observed rates of the vapor-phase nitra-

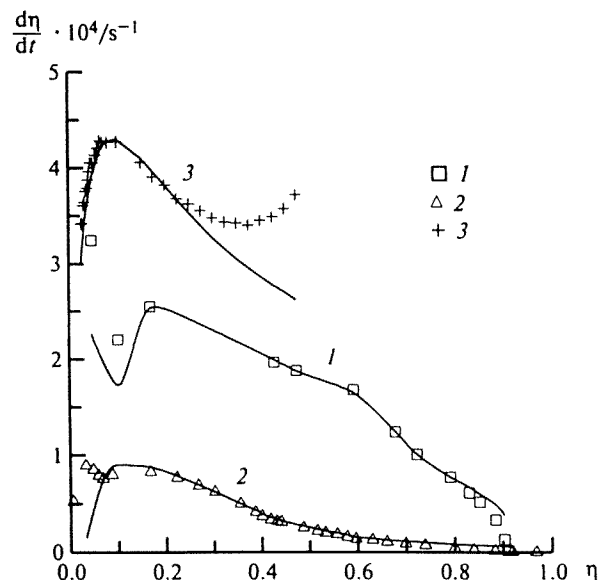


Fig. 2. Dependences of the rate of nonisothermal titration of C with HNO_3 and N_2O_5 vapor on the depth of nitration (signs show the experiment, solid curves show the calculation from Eq. (3) with parameters determined by the numerical processing of experimental data): 1, $p_{s,\text{HNO}_3} = 0.0526 \text{ atm}$, $T_0 = 22.9^\circ\text{C}$; 2, $p_{s,\text{HNO}_3} = 0.0329 \text{ atm}$, $T_0 = 12.6^\circ\text{C}$; 3, $p_{s,\text{N}_2\text{O}_5} = 0.171 \text{ atm}$, $T_0 = 12.4^\circ\text{C}$.

tion with nitric acid and nitric anhydride can be explained only by the fact that these reactions are limited by the diffusion transfer of HNO_3 and N_2O_5 molecules. The nitration of C with the N_2O_5 vapor in the range $0.04 < \eta < 0.4$ is described by the kinetic law in the form

$$\frac{d\eta}{dt} = \frac{k_1 p}{1 + \beta \eta} \quad (3)$$

and there is such a temperature dependence of β that the rate is independent of the nitration depth above 30°C . It is established from the experiments carried out at various pressures of HNO_3 that above 30°C the rate of the nonisothermal nitration of C with the HNO_3 vapor at the same temperatures is proportional to the pressure of the HNO_3 vapor to the power of 0.8–1.6, i.e., it is close to 1 on the average. At the same time, at these temperatures the logarithm of the rate of the nonisothermal nitration referred to the pressure of the HNO_3 vapor depends linearly on the inverse temperature of the sample (Fig. 3; signs connected by dotted lines). This means that at relatively high temperatures the nitration rate is independent of the nitration depth as well as for N_2O_5 . It is evident that the nitration of C with the HNO_3 vapor obeys the same kinetic regularities as in the case of the nitration with the N_2O_5 vapor. It is established using the method of subsequent approximations and the principle of the least square deviation in the computation of the temperature dependences of parameters k_1 and β that the experimental data are described with a satisfactory accuracy by the kinetic law (3) in a range of nitration depths from 0.08 to ~0.7. The calcu-

lated values of $d\eta/dt$ and $\ln(d\eta/dt)$ are presented in Figs. 2 and 3 by solid lines. The averaged temperature dependences of k_1 and β are determined in the form

$$k_1 = 10^{4.49 \pm 0.6} \exp(A/RT), \text{ s}^{-1} \text{ atm}^{-1}, \\ A = (-3.66 \pm 3.8) \text{ kJ mol}^{-1}, \quad (4)$$

$$\beta = 10^{-35.5 \pm 16} \exp(B/RT), \\ B = (203 \pm 88) \text{ kJ mol}^{-1}. \quad (5)$$

The nitration of C with the N_2O_5 vapor is limited by the diffusion transfer of N_2O_5 over micropores with the activation barrier close to the evaporation heat of N_2O_5 , i.e., the diffusion transfer occurs *via* the Knudsen mechanism. It is likely that the diffusion of HNO_3 molecules upon the vapor-phase nitration of C with nitric acid occurs *via* a similar mechanism and, since the initial C is the same in both processes, the nitration rate can be expressed by the dependence¹

$$d\eta/dt = K_* D_{\text{HNO}_3} p_{\text{HNO}_3} / T, \quad (6)$$

where $K_* \approx 10^7 \text{ deg cm}^{-2} \text{ atm}^{-1}$ and D_{HNO_3} is the effective diffusion coefficient.

The dependences of $\ln(D_{\text{HNO}_3})$ calculated from Eq. (6) on the inverse temperature for some experiments are presented in Fig. 4. The temperature dependence of D_{HNO_3} averaged over all experiments is determined in the form

$$D_{\text{HNO}_3} = 10^{0.28 \pm 0.7} \exp(C/RT), \text{ cm}^2 \text{ s}^{-1}, \\ C = (-38.3 \pm 4.2) \text{ kJ mol}^{-1}. \quad (7)$$

The resulting value of the effective activation energy of diffusion ($38.3 \pm 4.2 \text{ kJ mol}^{-1}$) coincides with the evaporation heat of HNO_3 (38.2 kJ mol^{-1} ⁸), which confirms, as in the case of N_2O_5 , the limiting role of

$\ln(d\eta/dt)$ or $\ln(d\eta/dt/p)$

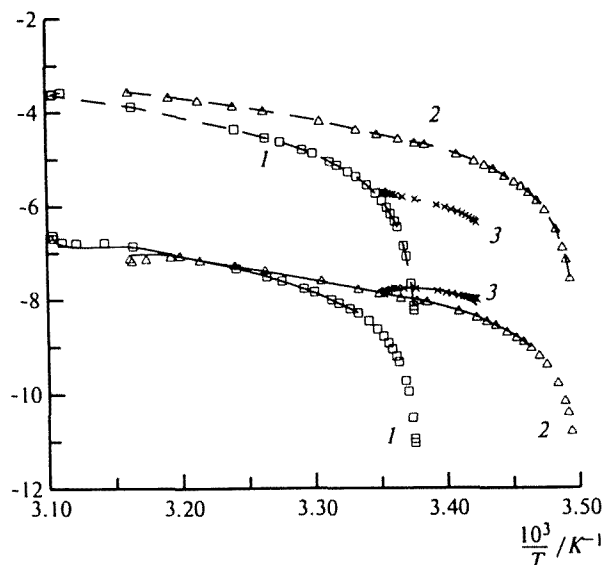


Fig. 3. Dependences of the logarithm of the rate of nonisothermal nitration (signs with solid curves) and logarithm of its ratios to the pressure of HNO_3 and N_2O_5 vapor (signs with dotted curves) on the inverse temperature at $p_{s,\text{HNO}_3} = 0.0526$ (1); $p_{s,\text{HNO}_3} = 0.0329$ (2); and $p_{s,\text{N}_2\text{O}_5} = 0.171$ (3) atm.

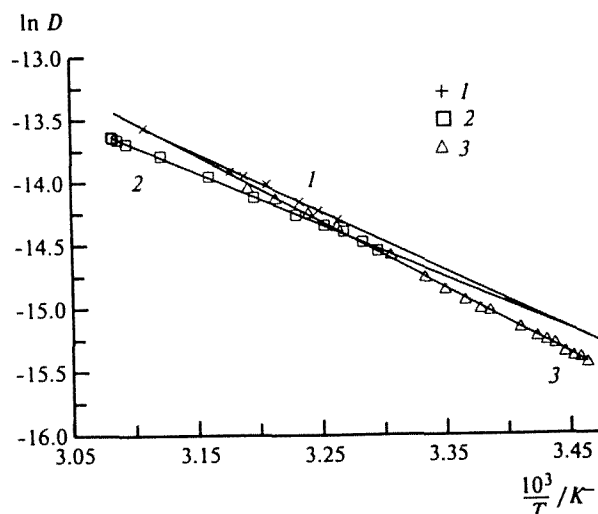


Fig. 4. Dependences of the values (calculated from the experimental data) of logarithms of the diffusion coefficient of HNO_3 on the inverse temperature at: $p_{s,\text{HNO}_3} = 0.0829$ (1); 0.0526 (2); and 0.0329 (3) atm.

Knudsen diffusion of HNO_3 over micropores of cellulose upon the vapor-phase nitration under the conditions of natural convection.

There is a qualitative difference between the nitration of C with the N_2O_5 vapor and the vapor-phase nitration with nitric acid, which is that the reaction with N_2O_5 occurs with a self-acceleration at nitration depths higher than ~ 0.4 (see Fig. 2). In terms of the diffusion model suggested, this self-acceleration is explained by the accumulation of HNO_3 with a higher diffusion mobility. It can be estimated from Eq. (7) and the previously obtained data¹ that at 25 °C the values of the effective diffusion coefficients for HNO_3 and N_2O_5 molecules are $3.7 \cdot 10^{-7}$ and $9.8 \cdot 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, respectively, i.e., their ratio is equal to 3.8.

According to the theoretical views, at constant temperature the diffusion coefficient of gas in polymer (D) should depend on the molecular weight of the diffusing gas. The studies of films of cellulose nitrate show that only the tendency of this dependence is manifested.¹¹ In particular, for NH_3 , H_2O , O_2 , CO_2 , and SO_2 , the D values at 25 °C were determined to be equal to $0.79 \cdot 10^{-8}$, $2.6 \cdot 10^{-8}$, $15 \cdot 10^{-8}$, $2.2 \cdot 10^{-8}$, and $0.18 \cdot 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, respectively. At similar values of molecular weights of the gases (for example, NH_3 and H_2O , CO_2 and SO_2), the D values can differ several times. It is evident that the physicochemical nature of the diffusing gas plays a substantial role in the diffusion in CN. Based on these concepts, the obtained difference in the D values for HNO_3 and N_2O_5 seems quite appropriate.

It has been established¹² in the study of the diffusion properties of the water vapor in C and CN that the D value at the equal contents of sorbed water changes from $1 \cdot 10^{-7}$ for pure C to $1 \cdot 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ for CN containing 13.2 % N. In the case of the Knudsen mechanism of diffusion of the water vapor both in C and CN, a strong decrease (by 2 orders of magnitude) in D on going from C to CN due only to the difference in the chemical composition of these compounds seems highly improbable. It is likely that the decrease in the effective D value can be caused by a decrease in the average pore size (and, as a consequence, by a decrease in the value of the specific internal surface observed previously¹³ as the duration of the nitration increases) due to an increase in the volume of C molecules in its micellar packing during the nitration. The specific weight of the dense C is 1.514 g cm^{-3} , while that of CN containing 13.2 % nitrogen is 1.643 g cm^{-3} .¹² The molecular weights of C and CN units are 162.1 and 281.5, respectively. It can be estimated from these data that g-moles of C and CN in the densest packing occupy 107.1 and 171.3 cm^3 , respectively. Therefore, the volume of the elementary (dense) structures in C micelles increases by 60 % due to esterification, which should result in a decrease in the average pore sizes in the macrostructure formed. Probably, the factor of a decrease in the average pore size along with diffusion hindrances associated with the formation of the layer of denser packed CN compared to that of C finally results in the kinetic law (3), according

to which the nitration rate is inversely proportional to the depth of nitration. The physical meaning of the expression $(1+\beta\eta)$ in the kinetic law (3) likely reflects a decrease in the effective diffusion constant during nitration due to these two factors.

According to the published data,¹⁴ the diffusion coefficient of H_2SO_4 in CN at 95 °C is $2.1 \cdot 10^{-9} \text{ cm}^2 \text{ s}^{-1}$. It can be estimated from Eq. (7) that at this temperature the D value for HNO_3 is equal to $7.0 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, i.e., it is more than three orders of magnitude higher than that for H_2SO_4 molecules. It follows from these estimations that H_2SO_4 molecules can get inside cellulose micropores only due to capillary forces of wettability in the nitration of C with nitrating mixtures containing H_2SO_4 at durations of the nitration on the order of several tens of minutes. It is difficult to wash off H_2SO_4 with water from CN compared to HNO_3 ,⁴ which is associated with a substantial difference in D values for these molecules rather than with the formation of sulfo esters of cellulose.

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