Kinetics of vapor nitration of cellulose

1. Nitration with nitric anhydride under static conditions

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The kinetics of vapor nitration of cellulose with nitric anhydride at various pressures was studied under conditions of natural convection in the absence of air, using the nonisothermal kinetic method. The process rate was found to be proportional to the N_2O_5 pressure. The nitration is described by a law of the $d\eta/dt = k_1/(1+\beta\eta)$ type, where $k_1 = 10^{3.82\pm0.5}\exp[-(36000\pm3000)/(RT)]p_{N_2O_5}$ s^{-1}, $\beta = 10^{-7.33\pm1.4}\exp[(41300\pm8000)/(RT)]$ s^{-1}, within the extents of conversion from 0.04 to 0.4. At high levels of conversion, the nitration occurs with autoacceleration caused by the accumulation of the HNO_3 formed. The diffusion mechanism of vapor nitration of cellulose was suggested and discussed. The values of the effective diffusion constant for N_2O_5 in cellulose and the corresponding activation energy (38.4±2.8 kJ mol^{-1}) have been estimated.

Key words: vapor nitration, cellulose; nitric anhydride, kinetics, diffusion constant.

Regularities of nitration of cellulose with N_2O_5 vapor are almost unstudied at the quantitative level, despite the existence of many works on nitration of cellulose.[1–3] The specific features of this process is the absence of water in the products of nitration and its irreversibility. In vapor nitration, unlike the liquid-phase process, the analytic concentration of a nitrating agent is proportional to its activity, which facilitates the quantitative interpretation of experimental data obtained. The vapor-phase method of preparation of cellulose nitrate (CN) described in the literature[1,2] is of interest because of the possibility of using a lower nitrating agent : cellulose ratio compared to the liquid-phase method, and the content of nitrogen in the CN obtained is close to theoretical. In this work, the kinetics of nitration of cellulose with N_2O_5 vapor was studied, and the mechanism of the process was analyzed on the basis of the results obtained.

Experimental

Nitrogen(v) oxide was obtained by dehydration of anhydrous HNO_3 with phosphorus pentoxide. Anhydrous HNO_3 was obtained by distillation from fuming HNO_3 at reduced pressure. N_2O_5 was purified from N_2O_4 by evacuation and stored in sealed tubes in liquid nitrogen or at −18 °C. The nitration in samples taken from a reactor was stopped by immediate washing with a large amount of water until a neutral medium, determined by litmus, was achieved. The content of nitrogen in the samples was determined by potentiometric titration of CN solutions in 98 % H_2SO_4 with iron sulfate[4] or from the heat of combustion in oxygen[5] calculated for the dry mass of a sample. Cotton cellulose dried for 2 h at 110 °C and stored over P_2O_5 was used. The content of cellulose in the initial sample was 99.3 %.

Vapor nitration is retarded substantially in the presence of air.[2,6] Therefore, except particular experiments, the systems, from which air was preliminarily removed to achieve the residual pressure lower than 10^{-3} atm, were studied. Experiments were carried out on two different installations. In the first case, in order to decrease heating, a cellulose sample was preliminarily placed into a thermostated reactor to contact with its walls. Under such conditions ("isothermal" regime), cellulose was nitrated with a 1.5 to 1.75-fold excess of N_2O_5 calculated to the formation of trinitrate. N_2O_5 vapor was let in the evacuated reactor from a buffer vessel. The pressure in the reactor and the temperature of the sample were measured during the process. The temperature was measured by a thermocouple sealed into a thin glass capillary. The extent of nitration was determined both at different time intervals in samples taken from the reactor and by the calculation from a decrease in the pressure in the system, taking into account decomposition of N_2O_5 that was not higher than 5—8 %. In these experiments, the conditions close to isothermal were achieved after nitration of more than 40 % of OH groups of cellulose, which is due to the low heat conductivity of cellulose. At the same time, the thermographic method for studying the kinetics of heat release[7] is known. It was used in the absence of a noticeable temperature gradient over the mass of the sample, which was achieved due to a difficult heat exchange between the sample and the reactor wall and is characterized by values of the Bio criterion lower than unity. In experiments on the second installation, a sample of cellulose formed as a cylinder was hanged up freely on a thin-wall glass capillary in a thermostated reactor with a thermocouple inside it. The values of the Bio criterion in the system were from 0.6 to 0.8. The reaction vessel was constructed in such a way that the sample of cellulose was *in vacuo* ($p_{res} = 6 \cdot 10^{-4}$ atm) at the

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initial moment, and the bottom outlet contained N_2O_5 cooled to the temperature of liquid nitrogen. Then the bottom outlet with frozen N_2O_5 was placed into a thermostat with the specified temperature. In these experiments, the nitrating agent : cellulose ratio was several tens. In the course of the process, the pressure in the reactor was measured continuously by a capacity detector, and the temperature of the sample was detected continuously by the thermocouple. The vapor nitration of freely hanged samples results in their volume expansion. Therefore, thermophysical measurements were carried out taking into account both a growth of the sample surface, assuming that the ratio of the length to the diameter of the cellulose bunch was unchanged, and an increase in the mass of the sample due to etherification. Accepting that at the N_2O_5 pressures used the coefficient of heat transfer is proportional to the pressure (*i.e.*, $\alpha = \alpha_0 p/p_0$, where α_0 is the coefficient of heat transfer at $p_0 = 1$ atm), the dependence of the $\alpha S/m$ ratio on the extent of nitration (η) under the aforementioned assumptions is obtained in the form

$$\alpha S/m = (\alpha_0/p_0)(S_0/m_0)p/[(1+a\eta)^{1/3}(1+b\eta)^{2/3}], \tag{1}$$

where S and S_0 are the values of the current and initial surfaces of the sample, through which the heat transfer with the reactor wall occurs, respectively; m_0 is the initial mass of the cellulose sample; $a = 3(\mu_{NO_2} - \mu_H)/\mu_c = 0.83$; $b = \rho_{CN}/\rho_c - 1$; μ_{NO_2}, μ_H, and μ_c are the molecular masses of NO_2 groups, H atoms, and a cellulose unit, respectively; and ρ_{CN} and ρ_c are the volume densities of CN and the cellulose bunch, respectively.

Since $b \ll 1$, the product $(1+a\eta)^{1/3}(1+b\eta)^{2/3}$ in Eq. (1) can be substituted by the expression $[1+(a+2b)\eta]^{1/3}$; and the error of the calculation of this product will not exceed tenth fractions of percent. Using function (1) and the approximation mentioned, the expression for the nonisothermal rate[7] of nitration of the freely hanged cellulose bunch with a vaporous nitrating agent can be presented in the following form:

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

where $d\eta/dt$ is the nonisothermal nitration rate; c is the specific heat of CN; and Q is the heat of the nitration reaction.

After multiplying the both parts of Eq. (2) by the $[1 + (a + 2b)\eta]^{1/3}$ value and integrating under the initial conditions $t = 0$, $\eta = 0$, and $T = T_0$, taking into account that $[1 + (a + 2b)\eta]^{1/3} \approx 1$ at low reaction extents, we obtain the following expression for the calculation of the extent of nitration:

$$\eta \approx \frac{1}{a+2b}\{[\frac{c(T - T_0)}{Q} + \frac{\alpha_0 S_0}{p_0 Q m_0}\int_0^t p(T - T_0)dt] \times \\ \times \frac{4}{3}(a + 2b) + 1\}^{3/4} - \frac{1}{a + 2b}. \tag{3}$$

When experimental data were calculated by Eqs. (2) and (3), the value of the specific heat of CN was taken as 1.25 J $(\text{g deg})^{-1}$ (see Ref. 8) and the Q value was taken as ~1250 J g^{-1}. The Q value was estimated from the heats of formation of cellulose and CN,[9] N_2O_5, and HNO_3[10] using the stoichiometric equation

$$C_6H_7O_2(OH)_3 + \gamma N_2O_5(g) \rightarrow C_6H_7O_2(OH)_{3-\gamma}(ONO_2)_\gamma + \\ + \gamma[(1-x)HNO_3(g) + xHNO_3(l)] \tag{4}$$

taking into account the extent of nitration γ achieved in experiments and the amounts (x) of HNO_3 (40—60 %) retained by a CN sample to the end of nitration. The average values of parameters b (0.089) and $\alpha_0/(P_0 Q)$ ($3.24 \cdot 10^{-6}$ g cm^{-2} $(\text{atm deg s})^{-1}$) were estimated from particular experiments that proceeded to completion without changing the form of the cellulose sample (as a rule, a cellulose bunch becomes "open" until the end of the reaction, and the law of change in the surface value becomes indefinite). The S_0/m_0 values were determined experimentally in each case before the beginning of nitration. To calculate $d\eta/dt$ and η from Eqs. (2) and (3), the values of the constants presented above and the p and $(T - T_0)$ values measured experimentally, from which the values of $\int p(T - T_0)dt$ and dT/dt, respectively, were determined by numerical integration, were used. The isothermal reaction rate for vapor nitration, for example, at $T = T_0$, was calculated from the equation[7]

$$\left.\frac{d\eta}{dt}\right|_{T = T_0} = \left.\frac{d\eta}{dt}\right|_T \exp[E_{eff}(1/T - 1/T_0)/R]. \tag{5}$$

The values of effective activation energy E_{eff} at various extents of the process were determined from the series of experiments carried out at various temperatures.

Results and Discussion

Vapor nitration of cellulose under "isothermal" conditions was carried out at the temperature of the reactor wall equal to 19.9 °C. At the initial stages, the main portion of HNO_3 formed due to the nitration (Eq. (4)) is sorbed by nitrocellulose, and the total pressure in the reactor decreases during the process. The values of the extents of nitration obtained by direct measurements and those calculated from the pressure in the reactor (assuming that the vapor phase contains no HNO_3) agree satisfactorily (Fig. 1). First several minutes of nitration are accompanied by the maximum warming-up (10—18 °C). At a nitration time of 5—18 min (*i.e.*, at extents of nitration from 0.03 to ~0.1), the warming-up of the sample remains approximately constant (3—5 °C, see Fig. 1). The process rate is also constant, which corresponds to the linear character of the time dependence of the reaction extent in this region (see Fig. 1); hence, the values of the rates obtained by graphic differentiation of the time dependence of η are unchanged in this region. The process occurs with autoacceleration from extents of nitration from 0.15 to 0.2. The shape of the time dependence of η is S-like. Heating of the sample in this region is not higher than 5 °C, in contrast to the region characterized by a constant rate of nitration (see Fig. 1). The maximum nitration rate is observed at $\eta = 0.35 \div 0.4$, and the rate of change in the extent of nitration increases ~3-fold compared to that for the initial regions, reaching $5 \cdot 10^{-4}$ s^{-1} (T~30 °C).

Nitration of cellulose by the thermographic method was studied in the range of the N_2O_5 pressure from 0.171 to 0.355 atm at the initial temperatures of the sample $T_0 = 10.7 \div 23.6$ °C. The change in the temperature of the sample during the nitration is characterized by two

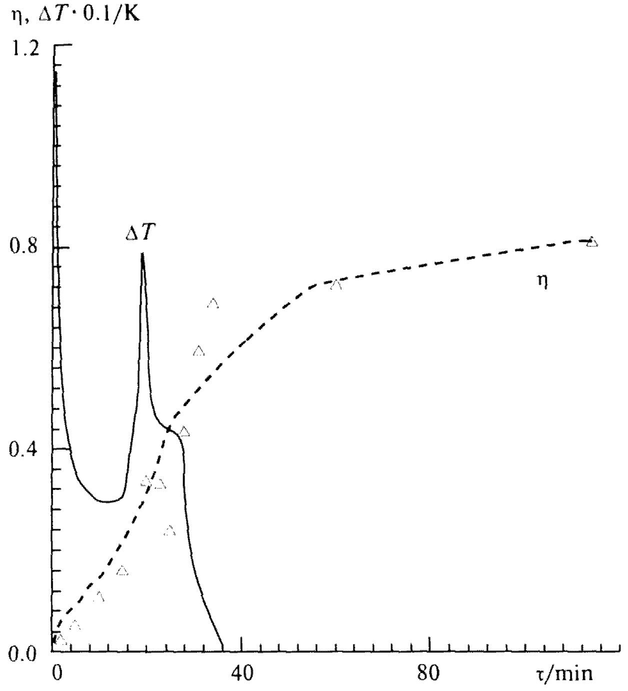

Fig. 1. Time dependence of the extent of nitration (η) and warming-up of the sample (Δ*T*, solid line) upon vapor nitration of cellulose with N_2O_5 under conditions of easy heat removal at the nitration module from 1.5 to 1.75 (T_0 = 19.9 °C). Experimental data are indicated by points, and the dotted line shows the calculation of η from the decrease in N_2O_5 pressure in one of the experiments.

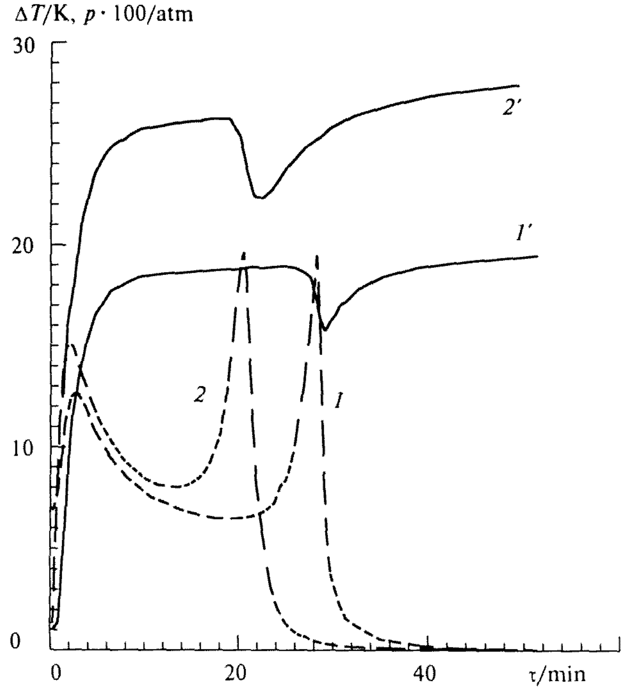

Fig. 2. Change in warming-up of the cellulose sample (*1*, *2*) and in the pressure (*1'*, *2'*) upon nitration of cellulose with N_2O_5 vapor under conditions of restricted heat removal: *1*, $p^0_{N_2O_5}$ = 0.171 atm, T_0 = 12.4 °C; *2*, $p^0_{N_2O_5}$ = 0.240 atm, T_0 = 19.9 °C.

Table 1. Parameters of nitration of cellulose with N_2O_5 vapor under conditions of restricted heat removal

Experiment	$p^0_{N_2O_5}$ /atm	p_{exp} /atm	T_0 /°C	τ_f /min	N_f (mass. %)	τ^* /min	ΔT_{max} /°C	η^*
1[a]	0.171	0.239	10.7	41.0	14.14	26.0	19.0	0.917
2[b]	0.171	0.329	10.7	79.4	14.06	57.4	15.8	0.915
3	0.171	0.188	12.4	51.3	14.03	28.3	19.5	0.905
4	0.171	0.184	14.5	52.5	14.10	34.3	20.5	0.910
5	0.171	0.197	16.7	42.5	14.14	21.8	24.2	0.906
6	0.171	0.184	18.9	62.4	14.14	32.1	21.2	0.849
7	0.171	0.187	20.6	38.3	9.41	—	—	—
8	0.203	0.216	13.5	43.0	14.08	22.9	17.5	0.892
9	0.203	0.209	13.5	45.5	14.14	23.8	15.5	0.877
10[a]	0.203	0.237	17.7	41.6	14.07	27.2	25.1	0.895
11	0.203	0.226	23.6	46.0	14.14	25.3	15.7	—
12[a]	0.240	0.299	20.1	44.7	14.14	21.8	30.5	0.921
13	0.240	0.260	19.9	49.4	14.12	20.5	19.7	0.857
14	0.258	0.268	16.1	48.7	14.00	22.4	21.2	0.782
15[a]	0.258	0.314	16.1	33.8	14.14	16.7	31.0	0.886
16[b]	0.258	0.382	16.1	52.4	14.14	29.7	29.3	0.875
17[a]	0.258	0.291	18.4	36.8	14.14	16.8	18.5	0.687
18	0.258	0.284	21.0	38.6	14.14	21.8	22.2	0.882
19	0.297	0.303	19.9	64.7	14.11	18.0	26.2	0.828
20	0.353	0.375	21.7	36.5	13.89	13.3	22.3	0.830

[a] N_2O_5 contained noticeable amounts of an N_2O_4 admixture. [b] The residual air pressure in the reactor was ~0.132 atm.

maxima: at the initial stage and in 20—30 min after the beginning of the process (Fig. 2).

The values of the following parameters are presented in Table 1: $p^0_{N_2O_5}$, the equilibrium pressure of N_2O_5 over the condensed phase calculated by the equation[11]

$$\log p^0_{N_2O_5} = -3161.2/T + 1.75\lg T - 0.00606T + 10.679$$

and p_{exp}, the experimentally measured equilibrium pressure established in the system in 5—8 min (see Fig. 2), which in some cases is noticeably higher than $p^0_{N_2O_5}$ due to an admixture of N_2O_4 present in the N_2O_5 used; τ_f, the duration of the experiment (usually until a decrease in the temperature of the sample to lower than the sensitivity of the thermocouple); N_f, the final content of nitrogen, determined by potentiometric titration, in the sample of CN obtained at time τ_f; ΔT_{max}, the value of the maximum heating at this late stage; $\tau^\star$, the time of reaching ΔT_{max}; and $\eta^\star$, the reaction extent when ΔT_{max} is reached (calculated by Eq. (9)).

The initial period of nitration covering the extents up to ~0.04 occurs under the conditions of the substantial change in the N_2O_5 pressure (from 0 to the pressure close to p_{exp}) and is accompanied by a sharp increase in the temperature (see Fig. 2). Since the initial region of nitration is characterized by the pronounced nonstationarity of thermophysical processes, the data were processed quantitatively from the nitration extents >0.04. When the extents of nitration exceeded 0.4, no quantitative description of the process was performed due to the "opening" of the cellulose bunches in the overwhelming majority of experiments and indefinite regularity of the change in the sample surface and heat transfer. The values of the effective activation energy of the process E_{eff} at different nitration extents used in the calculation of the isothermal nitration rate by Eq. (5) were determined from the experiments performed at the N_2O_5 pressure equal to 0.171 atm and different initial temperatures of the sample. The values of E_{eff} were determined in the range of η from 0.04 to 0.4 from the series of *5—7* experiments at each η value. The dependence of E_{eff} on η has an extreme character and is described by the parabolic law, and the maximum E_{eff} value (~46 kJ mol^{-1}) is reached at η = 0.3. In the mentioned range of η from T_0 to the temperatures observed experimentally, the isothermal rate of vapor nitration decreases monotonically as the extent of nitration decreases and is described satisfactorily by the following kinetic law

$$0.04 < \eta < 0.4 \qquad \left.\frac{d\eta}{dt}\right|_{T=\mathrm{const}} = \frac{k_1}{1+\beta\eta}. \qquad (6)$$

At high nitration extents, the process occurs with autoacceleration, and the time dependence of heating characterizes qualitatively a change in the reaction rate (see Fig. 2), because the E_{eff} values are not greater than 10 kJ mol^{-1} at high nitration extents, as follows from the

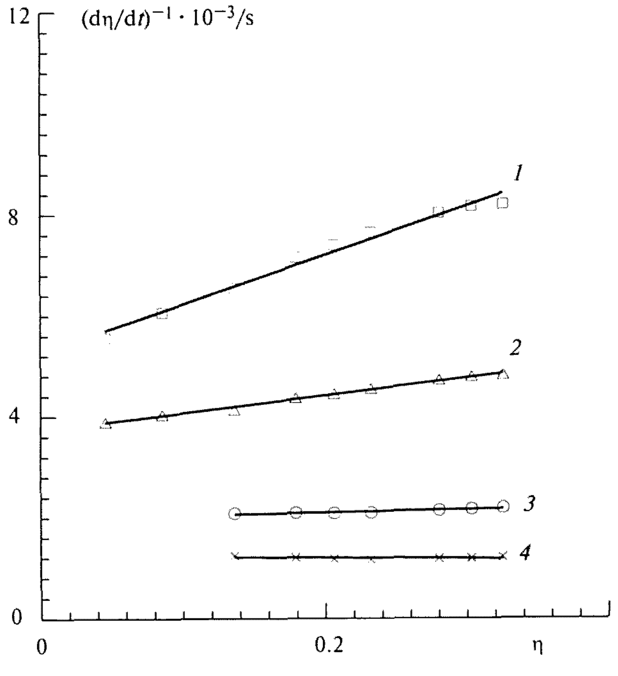

Fig. 3. Typical dependence of the inverse rate of vapor nitration of cellulose on the extent of nitration under isothermal conditions ($p^0_{N_2O_5}$ = 0.171 atm) at T_0/°C: 6.8 (*1*); 14.5 (*2*); 26.8 (*3*); 36.8 (*4*).

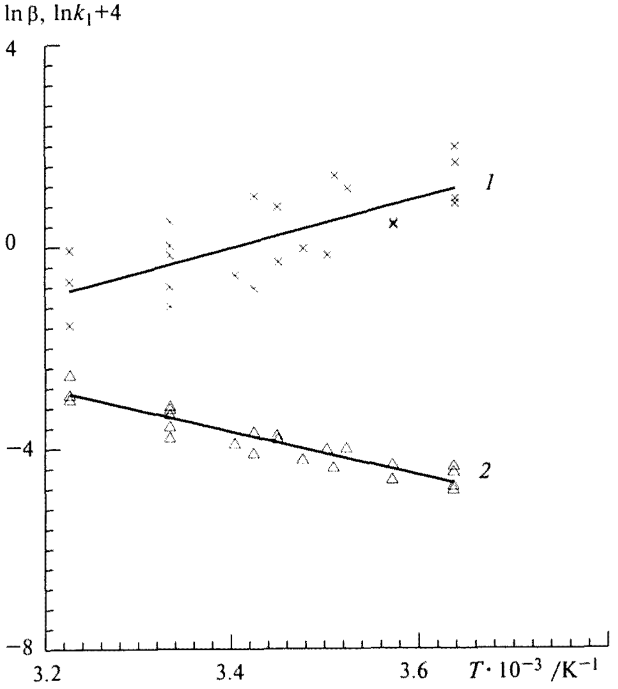

Fig. 4. Dependence of logarithms of β (*1*) and k_1 (*2*) on the inverse temperature.

form of the dependence E_{eff} *vs.* η obtained and the estimations performed.

A change in the obtained values of the inverse isothermal rate at different extents of the reaction are presented in Fig. 3. According to Eq. (6), this change is represented by a straight line. The dependences of the logarithms of k_1 and β on the inverse temperature characterizing the nitration of cellulose at the N_2O_5 pressure equal to 0.171 atm are presented in Fig. 4. The analytic form of the temperature dependences of these parameters is the following

$$k_1 = 10^{3.05\pm0.5}\exp[-(36000\pm3000)/RT]\ \mathrm{s}^{-1}, \qquad (7)$$

$$\beta = 10^{-7.33\pm1.4}\exp[(41300\pm8000)/RT]\ \mathrm{s}^{-1}. \qquad (8)$$

When the temperature is higher than 30 °C, the process rate is independent of the extent of nitration up to the extents of ~0.4 (see Fig. 3). A similar dependence is observed qualitatively, when cellulose is nitrated under "isothermal" conditions at nitration modules from 1.5 to 1.7 (see Fig. 1).

To the moment of reaching the second maximum, ~90 % of the reaction heat is released. Therefore, the extent of nitration, when $\Delta T_{\max}$ is achieved, can be determined with an accuracy of several percent by the dependence:

$$\eta^\star = \int_0^{\tau^\star} p(T-T_0)\mathrm{d}t \Big/ \int_0^{\tau_f} p(T-T_0)\mathrm{d}t. \qquad (9)$$

Processing of the experimental results shows that close values of $\Delta T_{\max}$ are achieved to moment $\tau^\star$ at close initial temperatures, and vapor nitration occurs to the same extent of $\eta^\star$ with an accuracy up to ±5 % (see Table 1). Assuming that the nitration rate depends on the pressure of the N_2O_5 vapor to the power n for an arbitrary form of its dependence on the nitration rate, *i.e.*,

$$\mathrm{d}\eta/\mathrm{d}t = k_{02}\exp(-E_2/RT)p^n f(\eta), \qquad (10)$$

owing to the aforementioned specific features of the process in the range of $\Delta T_{\max}$, and considering the E_2 value to be low, the n value was estimated from the experimental data using a plot of the dependence of $\ln(\eta^\star/\tau^\star)$ on $\ln p^0_{N_2O_5}$ (Fig. 5). The estimation shows that the reaction order with respect to the N_2O_5 pressure is 1.08. Thus, in the absence of an inert gas, the rate of nitration of cellulose with N_2O_5 vapor under conditions of natural convection is proportional to the pressure of the N_2O_5 vapor. Therefore, the value of the effective rate constant k_1 (s^{-1}) determined for $p_{N_2O_5} = 0.171$ atm (Eq. (7)) at an arbitrary pressure of the N_2O_5 vapor can be presented in the form

$$k_1 = 10^{3.82\pm0.5}\exp[-(36000\pm3000)/RT]p_{N_2O_5}. \qquad (11)$$

Vapor nitration of cellulose under conditions of restricted heat removal can be considered if three arbitrary regions are distinguished: from the beginning of thawing out N_2O_5 to achieving a pressure of its vapor close to equilibrium; nitration under conditions of an approximately constant equilibrium pressure of N_2O_5 described by kinetic law (6); and nitration accompanied by autoacceleration ($\eta > 0.4$).

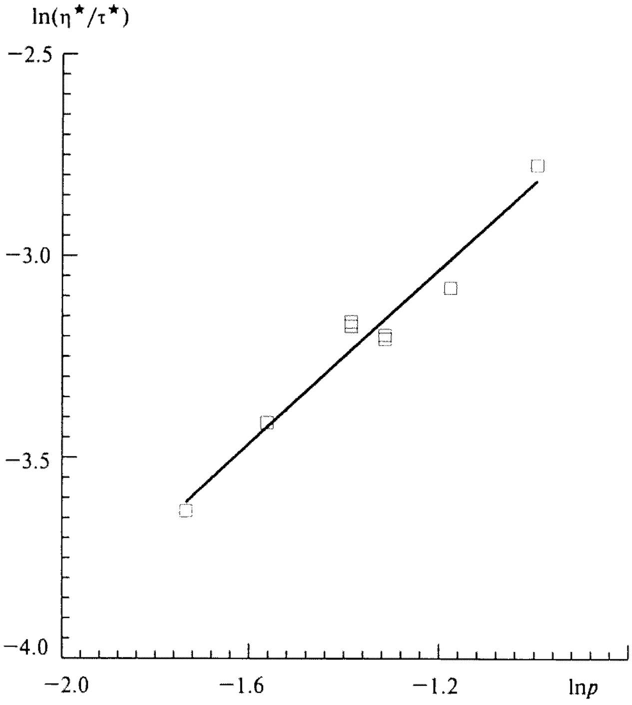

Fig. 5. Dependence of the $\eta^\star/\tau^\star$ parameter on the N_2O_5 pressure in logarithmic coordinates.

The rate constant for the reaction of N_2O_5 with methanol in the homogeneous liquid phase is ~10^6 L mol^{-1} s.[12] There are no reasons to expect that the reactivity of both primary and secondary hydroxyl groups of cellulose and the hydroxyl group of methanol can differ by several orders of magnitude. Therefore, in the case when the reaction occurs in the kinetic regime at an N_2O_5 pressure of ~0.1 atm, an extent of nitration equal to 0.98 should be achieved in thousandths or hundredths of a second. It is evident that the nitration of the main mass of cellulose is limited by diffusion. At the initial moments, N_2O_5 vapor reacts only with easily accessible surface layers of cellulose, which corresponds to sharp warming-up of the sample at the initial region (see Fig. 2). The microscopic study of fibers of the initial cellulose shows that they are spiral rectangular ribbons with an average width (H) of 15 μm and average thickness (h) of 5 μm. Accepting the density of cellulose in fiber equal to 1.4 g cm^{-3}, the specific external surface of fibers can be estimated as the value of $\cong 8 \cdot 10^3$ cm^2 g^{-1}. According to the modern views, a cellobiose fragment of a cellulose molecule is 10.3 Å in length and 2.4 Å in width.[13] On the basis of these data, one can draw the conclusion that the monomolecular layer located on the external surface of fibers contains ~0.2 % of glucopyranose fragments of their total number. These glucopyranose fragments as well as probably several deeper monolayers adjacent to the external surface of fibers are nitrated at the initial stage without diffusion restrictions. It also follows from the estimation of the value of the monolayer that the extent of nitration, which comprises ~0.04 and is inaccessible for quantitative measurements by the thermographic procedure due to the nonsteady-state character of the process, covers approximately 20 molecular layers adjacent to the external surface of the cellulose fibers.

At the next stage of vapor nitration of cellulose, which occurs at the approximately constant pressure of N_2O_5 vapor and is described by kinetic law Eq. (6), the N_2O_5 pressure near the surface of the cellulose sample in the absence of an inert gas is equal to the equilibrium pressure in the volume of the reactor. The N_2O_5 flow reaches the fibers localized inside the sample in the regime of viscous flow, overcoming the hydrodynamic resistance that depends on the degree of porosity of the sample. In the case when the stage of the N_2O_5 transfer to the fiber surface limits the process in the viscous flow regime, the temperature dependence of the rate of vapor nitration should be close to the temperature dependence of the reverse value of the gas viscosity, and the activation energy of this process should comprise 8—17 kJ mol^{-1}.[14] The value of the activation energy (36.0 kJ mol^{-1}, dependence (7)) observed in the experiment testifies that the transfer of the nitrating agent to the surface of cellulose fiber is not the limiting stage.

Thus, N_2O_5 transfered rapidly to the surface of fiber is likely adsorbed partially on their external surface, while its another portion penetrates inside fibers through micropores. It is known[15] that the internal specific surface of various celluloses is close to $2 \cdot 10^6$ cm^2 g^{-1}, and a mean radius of micropores is 40 Å.[16] It can be asserted on the basis of the estimated value of the external surface of fibers ($8 \cdot 10^3$ cm^2 g^{-1}) that the surface of micropores exceeds this value by several hundreds times, therefore, the predominant portion of N_2O_5 is transfered into cellulose fibers through micropores. When the pressure is of an order of 0.1 atm, the gas flow over micropores with the radius not less than 100 Å is described by the molecular (Knudsen) diffusion, because collisions of molecules with capillary walls becomes predominant instead of collisions between molecules.[14] Therefore, movement of sorbed gases, in particular, N_2O_5, within a micropore should be accompanied by overcoming adsorption forces, *i.e.*, it should have an activation barrier equal to the heat of adsorption. In this case, the diffusion activation barrier is close, as a rule, to the heat of evaporation of the diffusing gas.[14] Assuming that N_2O_5 and N_2O_4 have equal values of melting heat (14.6 kJ mol^{-1})[17] and taking into account the heat of sublimation of N_2O_5 (54 kJ mol^{-1}),[10] the heat of evaporation of N_2O_5 is 39.4 kJ mol,$^{-1}$ which coincides satisfactorily (within the determination accuracy) with the value of the activation energy of nitration (36.0±3 kJ mol^{-1}, Eq. (7)). Then N_2O_5 molecules adsorbed on the external surface of fibers and on the surface of micropores diffuse inside fiber through the layer of NC formed and react with OH groups of glucopyranose fragments. The form of kinetic law (6) is close to that often occurred in heterogeneous reactions, when the process rate is limited by the diffusion through the layer of the product formed.[18] It is likely that this also takes place upon nitration of cellulose with N_2O_5 vapor. Thus, the kinetic regularities of nitration of cellulose with N_2O_5 vapor observed at the extents of 0.04—0.4 can be explained by the fact that the process occurs in the diffusion regime, in which the diffusional transfer of N_2O_5 over micropores inside cellulose fibers followed by diffusion of N_2O_5 over the layer of NC formed plays a controlling role. At high temperatures, the rate of diffusion over the NC layer becomes substantially higher due to the difference in the dependences of these processes on the temperature, and the process becomes limited by the diffusion rate N_2O_5 in micropores. The gradient of the N_2O_5 pressure along the length of micropores is constant at these extents of nitration, and therefore, no dependence of $d\eta/dt$ on the extent of nitration is observed. In this case, according to the first Fick law, the N_2O_5 flow transfered to fibers can be presented in the form

$$dn_{N_2O_5}/dt = -SD_{N_2O_5}(C_{N_2O_5} - C^{\star}_{N_2O_5})/\Delta l, \qquad (12)$$

where S is the value of the external surface of fibers; $D_{N_2O_5}$ is the effective diffusion constant; and C and $C^{\star}$ are the concentrations of N_2O_5 near the surface of fibers and at the depth of Δl from the fiber surface, respectively.

Assuming that $C^{\star}_{N_2O_5} \approx 0$, $C_{N_2O_5} = p_{N_2O_5}/(RT)$, and the Δl value is 0.5 h, we obtain for the nitration rate

$$d\eta/dt = K^{\star} D_{N_2O_5} p_{N_2O_5}/T, \qquad (13)$$

where $K^{\star} = 4/3(\mu_c/\rho_{cf})(h+H)/(h^2HR1000) \approx 10^7$ deg (cm^2 atm)$^{-1}$; (μ_c and ρ_{cf} are the molecular mass of one cellulose unit (162.14 g mol^{-1}) and the density of cellulose fiber (1.4 g cm^{-3}); and R is the universal gas constant).

It follows from Eq. (13) that the experimentally determined k_1 constant from Eq. (6) represents $K^{\star} D_{N_2O_5} p_{N_2O_5}/T$, which agrees with the experimentally observed linear dependence of k_1 on $p_{N_2O_5}$ (Eq. (11)). On the basis of the experimental data of vapor nitration of cellulose at a pressure of N_2O_5 vapor equal to 0.171 atm, we determine (cm^2 s^{-1}):

$$D_{N_2O_5} = 10^{-0.28\pm0.5}\exp[-(38400\pm2800)/RT]. \qquad (14)$$

According to Eq. (14), the effective constant of diffusion of N_2O_5 over cellulose fiber is $1.27 \cdot 10^{-7}$ cm^2 s^{-1} at 30 °C, and the activation energy of this process nearly coincides with the heat of evaporation of N_2O_5 (39.4 kJ mol^{-1}), which confirms the limiting role of molecular

(Knudsen) diffusion of N_2O_5 molecules in the vapor nitration of cellulose.

The calculations show that at the stage of autoacceleration of vapor nitration of cellulose ($\eta > 0.4$) the maximum rate corresponds to the moment of reaching the pressure of saturated HNO_3 vapor formed in the nitration in the reactor. The condensation of HNO_3 on the walls of the reactor and fibers of cellulose is observed visually. Inherent autoacceleration of nitration of cellulose by phosphorus pentoxide is ceased, when the constant pressure of HNO_3 equal to the pressure of saturated vapor is achieved.

It is likely that in the presence of air the nitration can be controlled by the extradiffusional transfer of N_2O_5 to the surface of cellulose fibers. For example, when the residual air pressure in the reactor is about 0.13 atm, the maximum warming-up of the cellulose is observed later, and the duration of the reaction increases (see Table 1, experiments Nos. *2* and *16*). It is likely that the process changes to the extradiffusional regime due to the accumulation of O_2 and NO_2 formed in the thermal decomposition of N_2O_5 only at higher temperatures than in the experiments performed, because at the temperatures used, taking into account the value of the rate constant of decomposition of N_2O_5 vapor,[19] the pressure of O_2 and NO_2 at the end of nitration did not exceed 10 % of the pressure of N_2O_5.

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