Macrokinetics of initial stages of liquid-phase oxidation of hydrocarbons by nitric acid

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The influence of mass transfer on the rate of initial stages of liquid-phase oxidation of hydrocarbons by nitric acid was analyzed. The parameters of the diffusion-controlled near-surface regime were determined.

Key words: hydrocarbons, liquid-phase oxidation, nitric acid, macrokinetics.

This work is devoted to the theoretical analysis of the influence of mass transfer processes on the regularities of liquid-phase oxidation in the hydrocarbon—nitric acid system. This reaction accompanying important technological processes[1] is characterized by a great thermal effect and a high temperature sensitivity and can become uncontrollable under certain conditions. The specific feature of the system is that nitric acid and hydrocarbons form immiscible phases with a restricted solubility of the acid in the organic phase.

Calculation procedure

The simplest mathematical model of two layers of stationary liquid phases is considered. The changes in concentrations of reagents in these phases are described by equations of the form

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial z}\left(D_i \frac{\partial C_i}{\partial z}\right) - \Phi_i, \qquad \Phi_i = \sum_{\nu} \chi_{i\nu}\varphi_\nu ,$$

where t is time, z is the distance from the contact surface to a given point ($z > 0$ is the organic phase, $z < 0$ is the acidic phase), C_i are the concentrations of reagents, Φ_i are the overall rates of their consumption, φ_ν are the rates of individual reactions, $\chi_{i\nu}$ are the stoichiometric coefficients of the corresponding reagents, and D_i are the diffusion coefficients. In different phases, the parameters and properties of the substance differ. Changes in volumes are not taken into account.

According to the data of thermokinetic studies,[2] this is not nitric acid itself that participates directly in hydrocarbon oxidation, but nitrogen dioxide (NO_2) that is formed slowly from the acid and reacts with hydrocarbon to be transformed into nitrogen monoxide NO. The total amount of nitrogen oxides remains unchanged, because NO reacts rapidly with nitric acid according to the overall stoichiometric equation

$$2\ HNO_3 + NO = 3\ NO_2 + H_2O,$$

and the oxidation kinetics gains, as a result, the characteristic features inherent in autocatalytic processes.

According to the aforesaid, the overall rates of consumption of reagents can be expressed as follows:

$$\Phi_{HNO_3} = \varphi_I + 2\varphi_A,$$

$$\Phi_{NO_2} = \varphi_{Ox} - \varphi_I - 3\varphi_A + \varphi_N,$$

$$\Phi_{NO} = \varphi_A - \varphi_{Ox},$$

where φ_{Ox} is the oxidation rate, φ_I is the initiation rate, φ_A is the rate of NO consumption in the reaction with HNO_3, and φ_N is the nitration rate.

According to the published data,[2] the following equations are accepted for oxidation and initiation rates

$$\varphi_{Ox} = k_{Ox}C_{NO_2}(1 - \eta), \qquad \varphi_I = k_I C_{HNO_3}(1 - \eta),$$

where k_{Ox} and k_I are the temperature-dependent rate constants of the corresponding reactions, and η is the conversion taking into account a change in the hydrocarbon concentration during oxidation. Restricting our consideration by the initial stages of the process, we can assume that $\eta = 0$ and the temperature is constant.

As for the reaction of nitrogen monoxide with the acid, this reaction is assumed to proceed so rapidly that the oxide formed is immediately consumed in the presence of the acid and, hence, $\varphi_A = \varphi_{Ox}$. Then

$$\Phi_{NO_2} = \varphi_N - 2\varphi_{Ox} - \varphi_I.$$

The scheme also includes the nitration reaction, and the expression for its rate (φ_N) was accepted similar to that for the oxidation rate, but with the corresponding constant k_N. The autocatalytic character of the oxidation process is manifested at $\varphi_N/\varphi_{Ox} = k_N/k_{Ox} < 2$, and when 1 mole of NO_2 reacts with hydrocarbon, the total number of moles of NO_2 increases by the value $g = (2k_{Ox} - k_N)/(k_{Ox} + k_N)$.

Equilibrium correlations between concentrations of reagents should be specified at both sides from the interface, in particular, for the acid and nitrogen dioxide. However, the

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value of the equilibrium ratio for the acid remains, in essence, unknown. This difficulty can be avoided as follows. Taking into account the poor solubility of HNO_3 in the organic phase, we can assume that the amount of the acid in the organic phase is insufficient for achievement of a noticeable conversion of hydrocarbons, which could affect the reaction rate.

Results and Discussion

If the organic phase contained acid in the initial moment, assuming its initial concentration equal to the equilibrium value $C^{\circ}_{HNO_3}$ near the interface surface, we have the following equation for a time change in the concentration of NO_2 in the absence of spatial distribution:

$$C_{NO_2}(t) = C^{*}\exp\left(t\,\frac{gk-k_l}{2}\right)\cdot \mathrm{sh}\left(\frac{t}{2}\sqrt{(gk-k_l)^2-4k_lk_N}\right),$$

where

$$C^{*} = C^{\circ}_{HNO_3}\cdot 4k_l\Big/\sqrt{(gk-k_l)^2-4k_Nk_l}\,, \qquad k = k_{Ox}+k_N.$$

According to this equation, at low k_l, the amount of nitrogen dioxide increases almost exponentially with the increment $\Omega^{\circ} \equiv 2k_{Ox} - k_N = gk$. Then, as the acid is consumed, the amount of NO_2 accumulated previously decreases exponentially down to zero. In both stages, the initial concentration of the acid acts as the normalizing factor and determines the amplitude only rather than the dynamics of the process and, hence, the specific value of HNO_3 concentration is insignificant in this case.

Diffusional transfer provides the presence of the acid near the interface, and the formation of nitrogen dioxide continuing near the interface results again in an increase in its total amount (Fig. 1, curve *2*). Note that since the increase in the total amount of NO_2 is related to processes in the organic phase layers adjacent to the interface, and the first stage described above is associated with bulk reactions, the broader the width of the organic phase layer (h), the deeper the well on the curve of total amount of nitrogen dioxide (see Fig. 1).

If at first the organic phase contains no acid, the accumulation of NO_2 occurs monotonically (see Fig. 1, curve *1*). When the acid penetrates into the organic phase, NO_2 begins to accumulate, and NO formed during oxidation of hydrocarbon is immediately consumed along with the acid, and an increase in the NO_2 concentration is accelerated in the presence of the acid. However, the increase in the oxidation rate and related increase in the rate of acid consumption during the reaction with NO result in the appearance (at some distance from the interface surface) of a region in which the rate $\varphi_A = 0$ due to the complete consumption of the acid. The NO accumulated there then diffuses to the boundary of the region where it reacts with the acid.

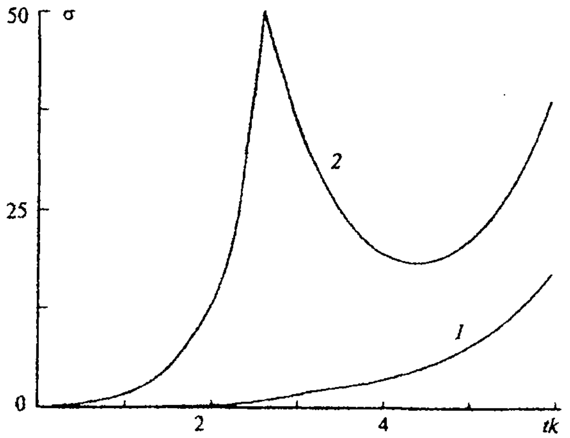

Fig. 1. Changes in integral amounts of nitrogen dioxide ($\sigma = \int C_{NO_2}dz/C^{\circ}_{HNO_3}h$) in the hydrocarbon—$HNO_3$ system in the case where in the initial moment the acid is absent (*1*) or present (*2*) in the organic phase ($h/h^{\circ} = 50$, $k_l/k = 0.01$, $g = 2$).

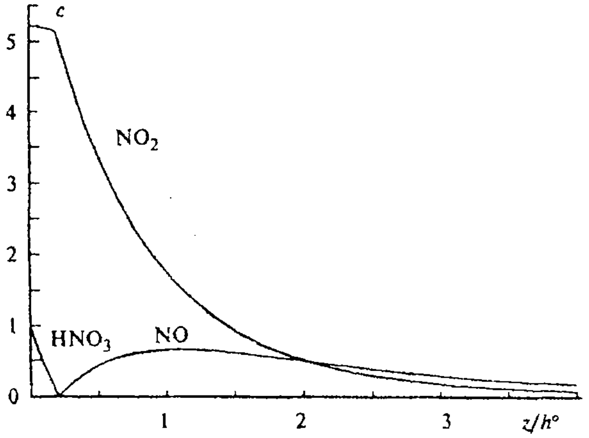

Fig. 2. Typical distributions of dimensionless concentrations ($c = C/C^{\circ}_{HNO_3}$) of reagents ($tk = 45$, $k_l/k = 0.01$, $g = 2$).

The typical distributions of dimensionless concentrations referred to the equilibrium value of acid concentration ($C^{\circ}_{HNO_3}$) near the interface surface are presented in Fig. 2. The formation of NO_2 is possible only near the interface where the acid exists, and the consumption of NO_2 occurs in a wider region, and NO before reacting should diffuse to the near-surface layers containing the acid. Since the total amount of NO increases, the diffusion flow also increases, the region occupied by the acid is more and more localized near the interface, and it can be considered in the limit that NO and acid interact at the interface.

The parameters of the establishing regime of the oxidation process can be determined assuming exponential time dependences of NO_2 and NO concentrations: $C \sim \exp(\Omega t)$. Then we have the following equations for their spatial distributions:

$$C_{NO_2}(t,z) = C_{NO_2}(t,0) \cdot \exp\left(-z\sqrt{\frac{\Omega + k}{D_{NO_2}}}\right),$$

$$C_{NO}(t,z) = \frac{k_{Ox}}{(k+\Omega)(D_{NO}/D_{NO_2}) - \Omega} \times$$
$$\times\left[C_{NO_2}(t,0)\cdot\exp\left(-z\sqrt{\frac{\Omega}{D_{NO}}}\right) - C_{NO_2}(t,z)\right].$$

For the ratio of integral amounts of the components in the organic phase, we can write

$$\int C_{NO}dz\Big/\int C_{NO_2}dz = k_{Ox}\Big/\left(\Omega + \sqrt{(k+\Omega)\Omega D_{NO}/D_{NO_2}}\right),$$

and taking into account that the NO_2 flow from the interface is threefold higher than the NO flow to the interface, we obtain an equation that allows one to determine the value of increment of increasing the NO_2 amount (Ω):

$$D_{NO_2}\sqrt{\frac{k+\Omega}{D_{NO_2}}} + b\sqrt{D^{a}_{NO_2}\Omega} = 3k_{Ox}\Big/\left(\sqrt{\frac{\Omega}{D_{NO}}} + \sqrt{\frac{k+\Omega}{D_{NO_2}}}\right),$$

where $D^{a}_{NO_2}$ is the value of diffusion coefficient of NO_2 in the acidic phase, and b is the value of equilibrium ratio of its concentrations near the contact surface. The b values are low,[2] and assuming $b = 0$ and neglecting the differences between the diffusion coefficients, we find $\Omega = kg^2/(g + 1)$.

Checking the calculations, we assumed that the thickness of the organic phase layer exceeds considerably the characteristic size $h^{\circ} = \sqrt{D/k}$. According to the published data,[2] this size for decane at, *e.g.*, 70 °C is equal to 0.1 cm at the values usual for liquids $D = 3 \cdot 10^{-6}$ cm^2 s^{-1}.

It should be noted in conclusion that the exponential increase in the amount of NO_2 will be finally stopped due to the complete consumption of hydrocarbon. But earlier, due to the high volatility of nitrogen dioxide, its concentration in the layer adjacent to the interface achieves the value to which the equilibrium pressure of NO_2 vapor equal to the atmospheric pressure corresponds. This fact gives important supplements to the picture described above for the diffusion-controlled near-surface regime of the reactions by changing the mechanism of the spatial distribution of NO_2. "Excess" amounts of NO_2 appearing near the surface of phase contact do not go out directly to the gas phase, but move up to enrich the layers that they pass through to the corresponding limiting concentration. As a result, a sharply pronounced layer uniform in NO_2 concentration is formed (its external boundary is blurred by slower diffusion processes). The thickness of this layer determines the current value of the overall oxidation rate.

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