Heat release kinetics in the reaction of decane with nitric acid

Yu. I. Rubtsov, A. I. Kazakov,* E. Yu. Rubtsova, L. P. Andrienko, and E. P. Kirpichev

*Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (095) 515 3588*

The kinetics of the reaction of decane with nitric acid (25.07—75.53 %) at 57.8 to 119 °C in an acid—decane—gas triphasic system was studied. The main contribution to the rate of heat release is made by the oxidation of decane with nitrogen dioxide in the organic phase proceeding *via* the mechanism of a degenerate branched-chain reaction. Nitration plays the role of a chain termination reaction. The acid phase is the source of NO_2, whose content increases with oxidation. The equilibrium of the nitrogen dioxide distribution in the triphasic system was analyzed. The kinetic law of the reaction, the dependences of the reaction constants of the initial and catalytic stages on temperature and the acid phase composition were determined. The results allow one to calculate the rate of heat release in the decane—HNO_3 system under any conditions of the process.

Key words: decane, nitric acid, nitrogen dioxide, oxidation, kinetics, mechanism.

Mixtures of aliphatic hydrocarbons with aqueous nitric acid are used rather often in modern technology, in particular, for the preparation of nitro compounds. A mixture of kerosene with tributyl phosphate is used for extraction of uranium and plutonium from solutions in nitric acid in regeneration of nuclear fuel.[1] In these mixtures, the exothermic oxidation reaction, which can pass into the regime of thermal self-ignition under certain conditions, is possible along with nitration. The calculation of critical parameters of self-ignition requires reliable kinetic data on the rate of heat release and its dependences on the main parameters of the process. The liquid-phase reactions of HNO_3 with alkanes were studied in detail to establish conditions for obtaining a maximum yield of nitroparaffins. It has been established that an increase in duration of the process and in the acid : hydrocarbon ratio favors a shift of the process toward oxidation products. When solutions of HNO_3 react with hydrocarbons, nitrogen dioxide serves as an active chemical reagent.[2] In a series of works on liquid-phase oxidation of the side chain of alkylarenes with solutions of HNO_3 in organic solvents,[3] NO_2 and its protonated form HNO_2^+ were suggested as particles leading the oxidation. It has been mentioned that in both the case of the slow gas-phase reaction of HNO_3 with alkanes and oxidation of alkylarenes in solutions, self-acceleration of the process associated with accumulation of NO_2 occurs. The reactions of alkanes with HNO_3 and with NO_2 in the gas phase obey the law of the degenerated branched-chain reaction, and the regimes of slow cool-flame reaction or the reaction with hot flame depending on temperature and pressure can be realized.[4] However, quantitative kinetic data on oxidation of alkanes with solutions of HNO_3 are lacking.

Experimental

The decane—aqueous nitric acid system was chosen as a model for the study. The rate of heat release was measured on differential automatic calorimeters of the DAK series.[5] The process was performed in sealed glass tubes kept totally at a constant temperature in the calorimeter cell, which made it possible to retain all components in the reaction zone and distinctly analyze phase equilibria and kinetic regularities of the process.

Results and Discussion

The system under study is heterogeneous and consists of three phases: acidic, organic, and gaseous; the reaction can occur in both liquid phases or at the interface between them.

The kinetic curves of heat release in the decane—aqueous nitric acid system were obtained in the temperature range from 57.8 to 119 °C, the concentration of HNO_3 varied from 25.07 to 75.53 %, and mixtures with 64.62 % HNO_3 were studied in the greatest detail. In the majority of experiments, a large excess of HNO_3 was used to neglect a change in its content during the process, but systems with a small excess of HNO_3 relative to the stoichiometry of the complete oxidation were also studied. At the beginning of the process, the reaction rate is below the sensitivity of a calorimeter, but it increases rapidly during the process and reaches a maximum at 35—40 % of the complete heat release. The rate of heat release ascribed to 1 mole of decane strongly depends on the value of free gas volume in the tube per mole of decane (V^g), while the dependence of the total number of moles of the acid and water per mole

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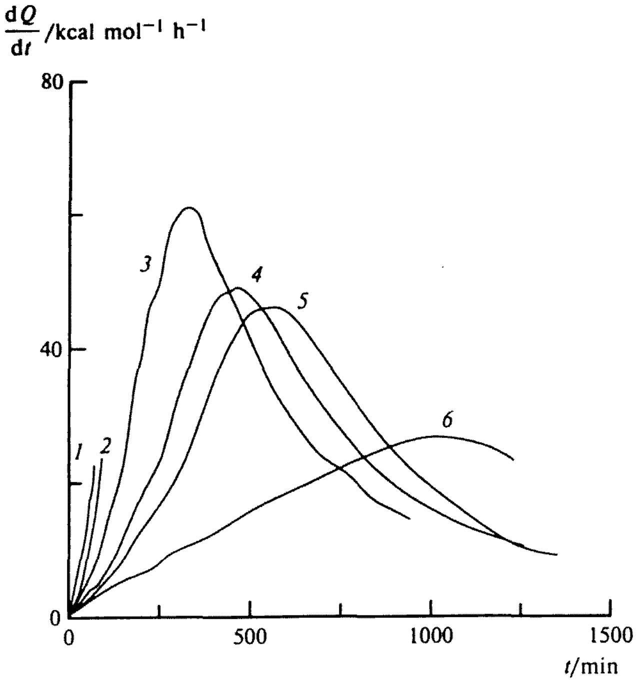

Fig. 1. Time dependences of rates of heat release in decane oxidation with 64.62 % HNO_3 at 92.8 °C at various V^g: 1.0 (*1*); 1.9 (*2*); 5.13 (*3*); 9.77 (*4*); 16.1 (*5*); and 39.1 (*6*) L mol^{-1}.

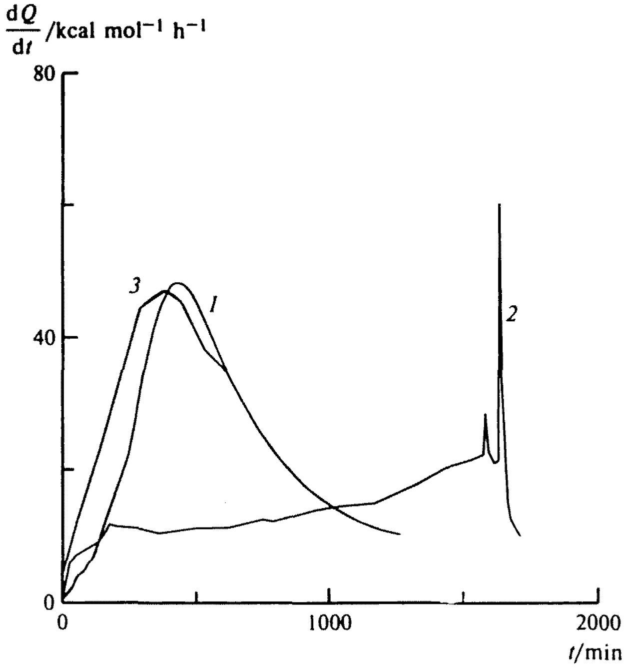

Fig. 2. Effects of additives (urea and NO_2) on the rate of the reaction of decane with 64.62 % HNO_3: *1*, without additives, V^g = 9.05 L mol^{-1}; n^{ac} = 140 mol per mol decane; *2*, in the presence of 3.03 mol urea per mol decane, V^g = 6.82; n^{ac} = 137; *3*, in the presence of 1.06 mol NO_2 per mol decane, V^g = 12.2; n^{ac} = 809.

of decane (n^{ac}) is relatively weak. The experiment was performed in ranges of V^g from 1.0 to 39.1 and n^c from 15.4 to 2864. Some rate curves of heat release are shown in Fig. 1. The kinetic curves of the autocatalytic reaction are not described by a simple equation of the first or higher orders, and the degree of autoacceleration decreases during the process. It is established that considerable amounts of NO_2 are accumulated in the system. On going from a 25.07 to 75.53 % solution of HNO_3, the number of moles of NO_2 formed per mole of hydrocarbon, in the case of decane oxidation, increases from 1 to 3.8 as determined by the spectral method.[6] We studied a role of NO_2 that was preliminarily added to the tube with a decane—aqueous HNO_3 mixture. When NO_2 is added, the initial rate of heat release increases strongly: it increases 13 times when 1.3 mol NO_2 per mole of decane is added, but it is lower than that in the case of accumulation of the same amount of NO_2 during the process. Nitrogen dioxide continues to be accumulated after the addition of NO_2, and the degree of self-acceleration and the maximum rate are close to respective values observed without an addition of nitrogen dioxide. Binding of NO_2 by a urea pellet placed in the tube, which has no direct contact with the decane phase, almost eliminates the self-acceleration of the reaction (Fig. 2).

To determine the amount of nitrogen dioxide in the organic phase, which is in equilibrium with the gas and acid phases, we measured the equilibrium pressure of the $NO_2 + N_2O_4$ mixture above the decane—64.62 % HNO_3 system in the temperature range from 0 to 25 °C (Table 1) by the static method in the Bourdon flask.

The study of the effect of dilution of nitric acid on the kinetics of decane oxidation was performed in a range of HNO_3 concentrations from 25.07 to 75.53 % at 92.8 °C. The reaction was found to have an autocatalytic character. When the concentration of HNO_3 decreases, the initial and maximum rates of the processes decrease (Fig. 3), the maximum rate is achieved at the earlier depths of the reaction, and the thermal effect decreases insignificantly.

Table 1. Pressures of NO_2 and N_2O_4 (p/Torr) in the decane (0.305 g)—aqueous HNO_3 (64.62 %, 1.395 g)—mixture of NO_2 and N_2O_4 system

T/°C	m_{NO_2}/g					
	0.005		0.009		0.0132	
	p_{tot}	$p_{\Sigma NO_2}$	p_{tot}	$p_{\Sigma NO_2}$	p_{tot}	$p_{\Sigma NO_2}$
0	33.1	31.7	61.5	60.1	95	93.6
15	51.1	47.1	94	90	117	113
20	59.6	53.2	108	101.6	142	135.6
25	71.5	61.5	122	112	162	152

Note. p_{tot} is the total pressure over the system, $p_{\Sigma NO_2}$ is the sum of partial pressures of NO_2 and N_2O_4. Pressures of vapor of decane, HNO_3, and H_2O were calculated using published data.[7,8]

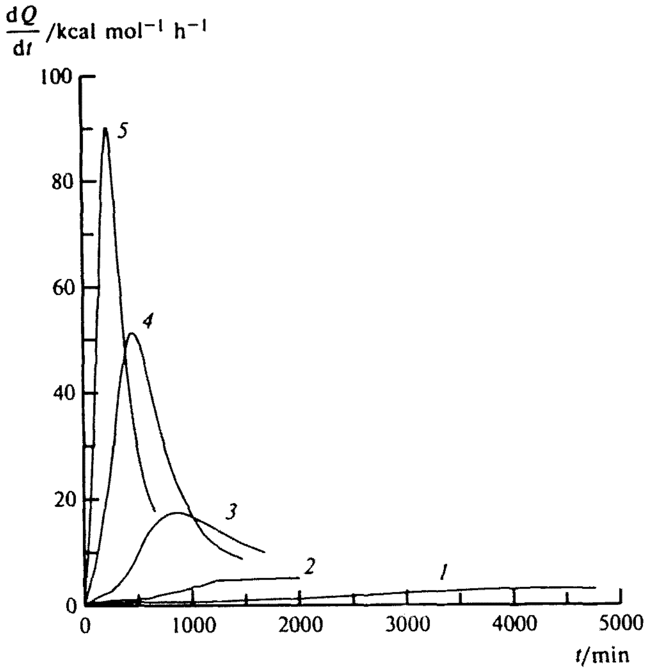

Fig. 3. Time dependences of rates of heat release in decane oxidation with solutions with various concentrations of HNO_3 at 92.8 °C and V^g ≈ 5.0 L mol^{-1}: 25.07 (*1*); 34.09 (*2*); 44.06 (*3*); 64.66 (*4*); and 75.33 (*5*) %.

Taken together, the kinetic data (the effects of the V^g and n^{ac} values, and the addition of NO_2 and urea on the reaction rate) show that the oxidation of decane with nitric acid proceeds *via* its oxidation with an NO_2 molecule in the organic phase; the rate of oxidation with HNO_3 is considerably lower and determines only the initial oxidation rate when NO_2 is absent in the system. It can be supposed that the initial act of oxidation is the energetically unfavorable detachment of an H atom from a hydrocarbon molecule by an electron-saturated HNO_3 molecule accompanied by the simultaneous decomposition of the H_2NO_3 radical to H_2O and NO_2.

$$RH + HNO_3 = R^{\cdot} + NO_2 + H_2O \text{ (slow)} \qquad (1)$$
$$\Delta H = +27.7 \text{ kcal mol}^{-1}$$

$$RH + NO_2 = R^{\cdot} + HNO_2 \text{ (fast)} \qquad (2)$$
$$\Delta H = +20.3 \text{ kcal mol}^{-1}$$

$$2HNO_2 \rightleftharpoons NO_2 + NO + H_2O$$
$$\Delta H = -1.0 \text{ kcal mol}^{-1}$$

The sum of the two latter equations gives:

$$2RH + NO_2 = 2R^{\cdot} + H_2O + NO.$$

The endothermic barrier for reaction (1) is considerably higher than that for reaction (2).

The values of heats of formation of the reagents for the calculation of reaction heats have been determined previously,[9,10] and the decyl radical is designated by the symbol $R^{\cdot}$. The values of heats of formation of HNO_2, NO, and NO_2 for the gas phase were used; the ΔH values are tentative, because the reactions considered in the scheme occur in the liquid phase.

In addition to the formation of NO_2 in reaction (1), its consumption occurs in reaction (2) to form NO. Three NO_2 molecules are regenerated upon the reaction of NO with HNO_3, which is the main reason for an increase in the content of NO_2.

$$NO + 2HNO_3 \rightleftharpoons 3NO_2 + H_2O \qquad (3)$$
$$\Delta H = +16.8 \text{ kcal mol}^{-1}$$

The rate of reaction (3) is rather high, and pressures of NO and NO_2 are close to equilibrium.

The reactions of chain propagation

$$R^{\cdot} + NO_2 = RO^{\cdot} + NO \qquad (4)$$
$$\Delta H = -17.0 \text{ kcal mol}^{-1},$$

$$RO^{\cdot} + RH = ROH + R^{\cdot} \qquad (5)$$
$$\Delta H = -6.0 \text{ kcal mol}^{-1},$$

and chain termination

$$R^{\cdot} + NO_2 = RNO_2 \qquad (6)$$
$$\Delta H = -60.0 \text{ kcal mol}^{-1}.$$

are also substantial for the development of the process.[10]

These are radical exothermic reactions that occur with high rates. Reaction (6) makes a very substantial contribution to the overall process, and the yield of nitro compounds is usually[2] 30—50 % in reactions of aliphatic hydrocarbons with aqueous nitric acid. The other termination reactions, for example, $2R^{\cdot} \rightarrow R_2$, are considerably less important due to the low concentration of these radicals. The mechanism of chain branching typical of high-temperature reactions of alkanes with NO_2 followed by the substitution of the low-reactive NO_2 radical for the aldehyde radical are not realized at these temperatures due to the low value of the branching constant.[11] However, the process under study is the branched-chain reaction, which occurs *via* low-reactive NO_2 radicals, two equivalents of which are formed in the cycle, and with the efficient termination by reaction (6).

The oxidation is not stopped at the formation of alcohol ROH, which is indicated by a considerably higher experimental thermal effect of the process compared to the effect possible in the case of oxidation to alcohol. The rate of oxidation of alcohols with nitric acid is much higher than that of hydrocarbons,[12] and this results in the formation of a large set of oxidation and nitration products. The heat of the reaction (575—600 kcal per mole of decane) is only 60 % less than the maximum possible heat of its oxidation to CO_2 and H_2O. This heat corresponds to the involvement of 7—8 moles HNO_3 per mole of decane in the reaction. Heat release in the nitration reaction $RH + HNO_3 = RNO_2 + H_2O$ is only 32 kcal mol^{-1}.

The rate of heat release in the decane oxidation with NO_2 in the organic phase in an assumption of the first-order reaction with respect to the reagents is described by the equation

$$\mathrm{d}Q/\mathrm{d}t = \gamma k' Q C_{NO_2}^{org}(1 - \eta),$$

where $\mathrm{d}Q/\mathrm{d}t$ is the rate of heat release referred to 1 mole of decane, kcal mol^{-1} s^{-1}; k' is the rate constant of the reaction of decane with NO_2, L mol^{-1} s^{-1}; Q is the heat of oxidation per mole HNO_3; $C_{NO_2}^{org}$ is the concentration of NO_2 in the organic phase, mol L^{-1}; γ is the stoichiometric coefficient of HNO_3 in the equation of oxidation; η is the dimensionless depth of conversion in the reaction.

Introducing the designations $\gamma \cdot k' \cdot C_d{}^{org} = k$ and $C_{NO_2}^{org}/C_d{}^{org} = n_{NO_2}^{org}$, we obtain

$$\mathrm{d}Q/\mathrm{d}t = kQ(1 - \eta)n_{NO_2}^{org}, \tag{7}$$

where k is the effective constant of the reaction of decane with NO_2, s^{-1}, $n_{NO_2}^{org}$ is the number of moles of NO_2 in the organic phase per mole decane, and $C_d{}^{org}$ is the concentration of decane.

All NO_2 existing in the system at the given moment is distributed between the gas, organic, and acid phases, and the equilibrium $2NO_2 \rightleftharpoons N_2O_4$ takes place in each of the phases. The system of equations for these equilibria has the following form.

$$\left.\begin{aligned}
p_{NO_2} &= K_g^{org}(NO_2) \cdot N_{NO_2}^{org} \\
p_{N_2O_4} &= K_g^{org}(N_2O_4) \cdot N_{N_2O_4}^{org} \\
p_{NO_2} &= K_g^{ac}(NO_2) \cdot N_{NO_2}^{ac} \\
p_{N_2O_4} &= K_g^{ac}(N_2O_4) \cdot N_{N_2O_4}^{ac} \\
K_N^{org} &= (N_{NO_2}^{org})^2/N_{N_2O_4}^{org} \\
n_{NO_2(N_2O_4)}^{g} &= p_{NO_2(N_2O_4)} \cdot V^g/RT \\
n_{NO_2(N_2O_4)}^{ac} &= \left(\frac{K_g^{org}}{K_g^{ac}}\right)_{NO_2(N_2O_4)} \frac{n_{NO_2(N_2O_4)}^{org} n^{ac}}{\sum n^{org}}
\end{aligned}\right\} \tag{8}$$

Here $K_g{}^{org(ac)}$ are Henry's constants of the equilibrium of the gas phase and the corresponding liquid phase, atm; $N^{org(ac)}{}_{NO_2(N_2O_4)}$ are the molar fractions of components in the corresponding phases; $K_N{}^{org}$ is the constant of the equilibrium $2NO_2 \rightleftharpoons N_2O_4$ in the organic phase; Σn^{org} is the sum of the number of moles of the components in the organic phase (for the initial stages of the process, $\Sigma n^{org} = 1$ can be accepted, because the amount of decane in the organic phase is much greater than those of the other components); p_{NO_2} and $p_{N_2O_4}$ are the pressures of nitrogen oxides, atm.

The mass balance with respect of NO_2 is the following:

$$n_{NO_2}{}^g + 2n_{N_2O_4}{}^g + n_{NO_2}{}^{org} + 2n_{N_2O_4}{}^{org} + n_{NO_2}{}^{ac} + 2n_{N_2O_4}{}^{ac} = \alpha\eta, \tag{9}$$

where α is the stoichiometric coefficient of accumulation of NO_2 per mole of reacted decane.

The combined solution of Eqs. (7)—(9) gives the dependences of the rate on all external parameters of the system:

$$\frac{\mathrm{d}Q}{\mathrm{d}T} = \frac{2\alpha k Q_{HNO_3}\eta(1-\eta)}{B_1} \Bigg/ \left(1 + \sqrt{1 + \frac{8\alpha\eta B_2}{B_1^2}}\right), \tag{10}$$

$$B_1 = 1 + \frac{K_g^{org}(NO_2)}{RT}V^g + \frac{K_g^{org}(NO_2)}{K_g^{ac}(NO_2)}n^{ac},$$

$$B_2 = \frac{1}{K_N^{org}} + \frac{K_g^{org}(N_2O_4)}{K_N^{org}RT}V^g + \frac{K_g^{org}(N_2O_4)}{K_N^{org}K_g^{ac}(N_2O_4)}n^{ac}.$$

The initial reaction rate is not taken into account in Eqs. (10); it will be considered below. Its contribution to the overall rate of the process can be neglected throughout except for the very beginning of the reaction. These equations describe the dependence of the rate of heat release on the main parameters of the process. Using the equilibrium pressures of NO_2 and N_2O_4 above the triple system, the known[8] value of the equilibrium constant for $2NO_2 \rightleftharpoons N_2O_4$,

$$\log K_N^g = -\frac{2962}{T} + 1.75\log T + 0.00484T - 7.144 \cdot 10^{-6}\,T^2 + 3.062,$$

and performing measurements with various relative amounts of NO_2 added to the system, we calculated the values of the corresponding constants:

$$\begin{aligned}
K_N{}^{org} &= 0.53\exp(-172/T), \\
K_g{}^{org}(NO_2) &= 2.1 \cdot 10^5 \exp(-3440/T), \\
K_g{}^{org}(N_2O_4) &= 24.6\exp(-346/T).
\end{aligned} \tag{11}$$

The closest description of the experimental dependences of the rate on the temperature, V^g, and n^{ac} can be obtained with the following values of the parameters:

$$k = 3.8 \cdot 10^{18} \exp(-35 \cdot 10^3/RT),\ s^{-1},$$
$$Q = 80 \text{ kcal (mol } HNO_3)^{-1},$$

$$\begin{aligned}
K_g{}^{ac}(NO_2) &= 2 \cdot 10^3 K_g{}^{org}(NO_2), \\
K_g{}^{ac}(N_2O_4) &= 2 \cdot 10^3 K_g{}^{org}(N_2O_4).
\end{aligned} \tag{12}$$

The ratio between Henry's constants of nitrogen oxides in the organic and acid phases was estimated in the analysis of the effect of the n^{ac} value on the oxidation rate at a constant value of V^g.

The values $K_N{}^{org}$, $K_g{}^{org}(NO_2)$, and $K_g{}^{org}(N_2O_4)$ differ from those for the decane—NO_2 system presented in Ref. 13. This is likely associated with a change in the composition of the hydrocarbon phase due to dissolution of HNO_3 and H_2O from the acid phase, which can substantially change the solubility of NO_2 and N_2O_4 and the equilibrium between them.

When the pressure in the system increases, the equilibrium pressure of NO grows rapidly and, hence, the degree of conversion of NO into NO_2 decreases. When the values $p_{NO_2} > 3$—4 atm are achieved, equilibrium (3), whose constant was analyzed previously,[14] should be taken into account in the balance of NO_2. The following term should be added to the left part of Eq. (9)

$$n^{g}_{NO} = K_{eq}[K^{org}_{g}(NO_2)]^3 \cdot (n^{org}_{NO_2})^3 \frac{V^g}{RT}, \qquad (13)$$

then Eq. (9) becomes cubic, its analytical solution is too complicated, and numerical methods should be applied for its solution. However, the contribution of term (13) can be neglected under the conditions used in this work.

A particular analysis is necessary for the initial rates of the process, which are determined by a different mechanism. Nitrogen dioxide is absent at the beginning of the process, and decane can react only with HNO_3 molecules or components existing in equilibrium with HNO_3, such as N_2O_5, NO_2^+, NO_3^-, *etc.* The reaction rate is low and cannot be measured directly; its values can be obtained from the analysis of time of achievement of certain depths of conversion η. Kinetic law (10) is very complicated, but at $\eta \leq 0.01$ the degree of dimerization of NO_2 is low and, with consideration of the initial rate, we can write for these η

$$\frac{dQ}{dt} = k_1(1-\eta) + k_2\eta(1-\eta). \qquad (14)$$

Here k_1 is the rate constant of the initial stage of the reaction, $k_2 = \alpha k Q_{NO_2}/B_1$.

Solving this equation, we obtain

$$\ln\frac{\eta + k_1/k_2}{(k_1/k_2)(1-\eta)} = k_2t.$$

Using experimental values of k_2, η, and t for $\eta \leq 0.01$, we calculated k_1 (Table 2). The k_1 values are independent of the weight of decane, V^g, and n^{ac}. Therefore, the reaction occurs in the bulk of the hydrocarbon phase with dilute HNO_3 or other products. When the reaction occurs at the interface, the k_1 value should decrease as the mass of decane increases, because the interface in a tube is independent of the mass of decane. The k_1 values are 500—2000 times lower than k_2, and their temperature dependences have the form

$$k_1 = 10^{8.15}e^{-\frac{19500}{RT}} \text{ kcal mol}^{-1}\text{ s}^{-1}. \qquad (15)$$

The resulting rate constants are presented in Table 2.

In the analysis of the effect of the concentration of nitric acid on the rate of heat release, changes in the initial rate (k_1) and degree of self-acceleration, which is determined first of all by k, α, and B_1 values, should be considered separately. The k_1 value increases by an order of magnitude as the concentration of HNO_3 increases from 25.07 to 75.53 %. The dependence of k_1 on the molar fraction of HNO_3 in the acid phase (N) is described by the empirical formula $k_1 = 1.58 \cdot 10^{-3}N^{1.44}$ kcal mol^{-1} s^{-1}. The dependence of k_1 on C_{HNO_3} in the acid phase was analyzed using the published data on the equilibrium concentration of HNO_3 in solutions containing 40 % of HNO_3 and more.[15] It is established that the effective reaction order with respect to HNO_3 ranges from 0.4 to 0.5. Such a low reaction order can be explained by an increase in the coefficient of distribution of HNO_3 between the organic and acid phases as the concentration of HNO_3 in the acid phase decreases. However, it is evident that the initial rate is determined by the reaction of decane with HNO_3 molecules; if N_2O_5 or NO_2^+ were the reagents, the order should be much higher, probably higher than 2.

The comparison of the initial rates of decane oxidation and thermal decomposition of solutions of HNO_3 [16] makes it possible to establish that the oxidation rate is approximately two orders of magnitude higher than the rate of thermal decomposition over the whole concentration range. Therefore, despite a large difference in rate constants of oxidation with NO_2 and HNO_3, the reaction of decomposition of HNO_3 does not provide the system with such an amount of NO_2 that the oxidation with NO_2 would determine the overall initial rate. As

Table 2. Rate constants of the reaction of decane with HNO_3

Concentration of HNO_3 (%)	T/°C	V^g /L mol^{-1}	n^{ac} /mol mol^{-1}	k_1 /kcal mol^{-1} s^{-1}	k/s^{-1}
64.62	57.8	1.8	100	$2.05 \cdot 10^{-5}$	$1.97 \cdot 10^{-5}$
64.62	73.0	5.19	370	$5.66 \cdot 10^{-5}$	$2.28 \cdot 10^{-4}$
64.62	92.8	1.9	132	$3.5 \cdot 10^{-4}$	$2.96 \cdot 10^{-3}$
55.92	92.8	3.93	340	$2.5 \cdot 10^{-4}$	$1.63 \cdot 10^{-3}$
44.06	92.8	4.26	330	$1.23 \cdot 10^{-4}$	$1.2 \cdot 10^{-3}$
34.09	92.8	4.79	376	$7.2 \cdot 10^{-5}$	$8.18 \cdot 10^{-4}$
64.62	92.8	5.15	118	$3.21 \cdot 10^{-4}$	$2.78 \cdot 10^{-3}$
75.33	92.8	5.67	269	$5.84 \cdot 10^{-4}$	$2.94 \cdot 10^{-3}$
25.04	92.8	5.10	409	$4.7 \cdot 10^{-5}$	$5.28 \cdot 10^{-4}$
64.62	92.8	9.8	489	$2.81 \cdot 10^{-4}$	$3.27 \cdot 10^{-3}$
64.62	92.8	15.8	850	$2.72 \cdot 10^{-4}$	$3.05 \cdot 10^{-3}$
64.62	92.8	39.1	2864	$2.4 \cdot 10^{-4}$	$3.21 \cdot 10^{-3}$
64.62	119	13.9	814	$3.03 \cdot 10^{-3}$	$6.0 \cdot 10^{-2}$

the temperature increases, the rate of thermal decomposition of solutions of HNO_3 increases more rapidly than the rate of oxidation with HNO_3 due to the difference in activation energies, and the contribution of the oxidation with NO_2 to the overall initial rate can become determining when temperatures higher than 180 °C are achieved.

The ratio of the maximum rate to the initial rate (degree of self-acceleration) is determined by k, α, B_1, and B_2 parameters. On going from 75.53 to 25.07 % HNO_3, the α value decreases by 74 %, while the degree of self-acceleration decreases by 94 %. This ratio of the values corresponds to the effective decrease in the rate constant k upon dilution of HNO_3 solutions. Since the rate constant should retain the unchanged value in solutions with various concentrations of HNO_3, it is necessary to suppose that dilution of HNO_3 solution results in a decrease in the equilibrium concentration of NO_2 due to additional equilibria that are not included in the equilibrium (8). Their contribution increases as the concentration of water and dielectric permeability of the medium increase. These equilibria are reaction (3) and

$$NO + NO_2 + H_2O \rightleftharpoons 2HNO_2 \rightleftharpoons H_3O^+ + NO_2^-, \qquad (16)$$

$$NO + NO_2 \rightleftharpoons N_2O_3 \rightleftharpoons NO^+ + NO_2^-, \qquad (17)$$

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-. \qquad (18)$$

For practical calculations of rates of decane oxidation with solutions of HNO_3 of various concentrations the dependence of k on the molar fraction of HNO_3 in the acid phase (N) can be presented in the form $k = 4.89 \cdot 10^{-3} \cdot N^{0.92}$.

Equations (10)—(13) and (15) allow one to calculate the rate of heat release per mole of decane in the decane—aqueous HNO_3 system under nearly any conditions of the process.

Since a possible loss of control of the process under study is determined first of all by an increase in the rate of heat release, it is important to analyze the probable reasons for an increase in this rate. The main process is the reaction of hydrocarbon and intermediate products of its oxidation with NO_2. This is the degenerate branched-chain reaction, and all sources of free radicals can increase this rate. Nevertheless, there are no additional sources of radicals under ordinary conditions of the process.

The presence of any admixtures that can be sufficiently rapidly oxidized with nitric acid, in particular, unsaturated hydrocarbons, alcohols, aldehydes, *etc.*, in the organic phase results in an increase in the initial rate of heat release. The presence of such admixtures in technical mixtures is undesirable. One of the possible reasons for an increase in the rate is an increase in the content of NO_2 in hydrocarbon. This can be caused, for example, by a sharp decrease in the gas volume V^g. The content of NO_2 in the gas, especially at higher temperatures, can be much higher than in hydrocarbon. A decrease in V^g will result in the passage of NO_2 to the organic phase accompanied by an increase in the rate of heat release. This increase can be calculated with a known change in V^g by Eq. (10).

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