Kinetic regularities of the heat release during the reactions of aliphatic hydrocarbons with aqueous HNO_3

Yu. I. Rubtsov, A. I. Kazakov,* E. Yu. Rubtsova, L. P. Andrienko, and G. B. Manelis

Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588

The kinetics of the heat release during the reactions of aqueous HNO_3 with *n*-heptane and *n*-octadecane was studied. The kinetic regularities of the reactions of hydrocarbons C_7H_{16}—$C_{18}H_{38}$ with HNO_3 and the heats of the reactions were described. At all stages, except initial, the hydrocarbon reacts with NO_2 and nitric acid reproduces NO_2 in the reaction with NO. The accumulation of NO_2 results in the acceleration of the process. When the pressure of the hydrocarbon vapor is equilibrium, its reaction with NO_2 can also proceed in the gas phase. The contribution of this reaction to the total heat release was estimated. The additives of aromatic and unsaturated hydrocarbons to aliphatic hydrocarbons increase strongly the initial rate of the heat release and changes slightly the subsequent stages of the process. Naphthenic hydrocarbons have almost no effect on the kinetic parameters of the process.

Key words: hydrocarbons, reaction with nitric acid, heat release, kinetics; nitrogen dioxide, oxidation, mechanism.

We have previously studied[1] the kinetics of the heat release during the reaction of aqueous HNO_3 with *n*-decane and established the quantitative regularities of the process. They are mainly determined by the oxidation of *n*-decane by nitrogen dioxide, the dimerization of NO_2, its distribution between the phases of the system, and the reaction of HNO_3 with NO to form additional amounts of NO_2. The kinetic regularities of the reaction of NO_2 with *n*-decane were also studied.[2] The results obtained confirm the reaction mechanism suggested previously.[1]

Since various hydrocarbons are used for syntheses of nitroparaffins, and a mixture of kerosene with tributyl phosphate is used in the nuclear-power industry for extracting uranium and plutonium from nitric solutions,[3] it would be useful to reveal whether the regularities obtained for *n*-decane are valid for other hydrocarbons and their mixtures. For this purpose, we studied the kinetics of the heat release during the reactions of *n*-heptane and *n*-octadecane with solutions of HNO_3 and determined the generalized dependences, which make it possible to calculate the rates of the reactions of HNO_3 with different linear hydrocarbons. Since technical lots of kerosene contain other components capable of changing substantially the overall kinetics of the heat release, we studied their effect on the rate of the process. In addition, the kinetics of the reaction of *n*-heptane with NO_2 in the gas phase was studied to evaluate a possible contribution of this reaction to the overall rate of the process. This reaction was not taken into account in the study of the oxidation of *n*-decane, because the equilibrium pressure of the *n*-decane vapor was low.

Experimental

The kinetics of the heat release during the reactions of *n*-heptane, *n*-octadecane, and kerosene with aqueous HNO_3 (25.07—75.53 wt.%), including the effect of additives of unsaturated, cyclic, and aromatic hydrocarbons on these processes, and the kinetics of the reaction of *n*-heptane with NO_2 in the gas phase were studied on a differential automated microcalorimeter[4] by a procedure similar to that used previously for mixtures of HNO_3 with *n*-decane.[1] The reactions of HNO_3 with *n*-heptane and *n*-octadecane were studied in the 57.8—115.8 °C and 72—115.8 °C temperature ranges, respectively. The effect of additives on the kinetics of the reaction of *n*-octadecane with a solution of HNO_3 was studied at 92.8 °C. The gas-phase reaction of *n*-heptane with NO_2 was studied at 115.8 °C.

n-Heptane, *n*-octadecane, cyclohexane, 1-decene, benzene, and toluene were purified and stored according to the known procedures.[5] Nitrogen dioxide was obtained, stored, and dosed as described previously.[6] The used kerosene lot consisted of a 98% mixture of aliphatic hydrocarbons. Solutions of HNO_3 were prepared by the weighing method, and their concentrations were established by potentiometric titration.

The accumulation of NO_2 during the oxidation of *n*-heptane and *n*-octadecane by solutions of HNO_3 with different concentrations were monitored by the Griess reagent.[7]

Results and Discussion

n-Heptane and *n*-octadecane are typical representatives of the light and heavy fractions of kerosene, respectively, and in combination with *n*-decane, make it possible to describe the kinetics of the reactions of

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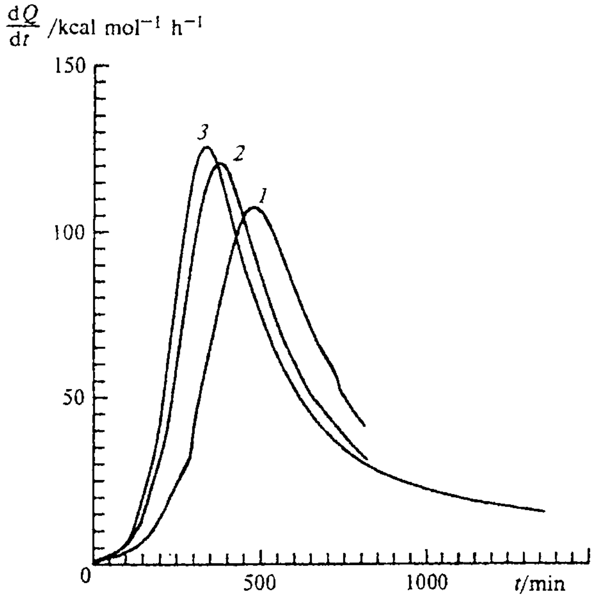

Fig. 1. Dependence of the rate of the heat release (dQ/dt) on the duration (t) of the reaction of *n*-octadecane with 64.62% HNO$_3$ at 92.8 °C and different V^g. Curves: *1*, entry *26*; *2*, entry *24*; *3*, entry *23* (see Table 1).

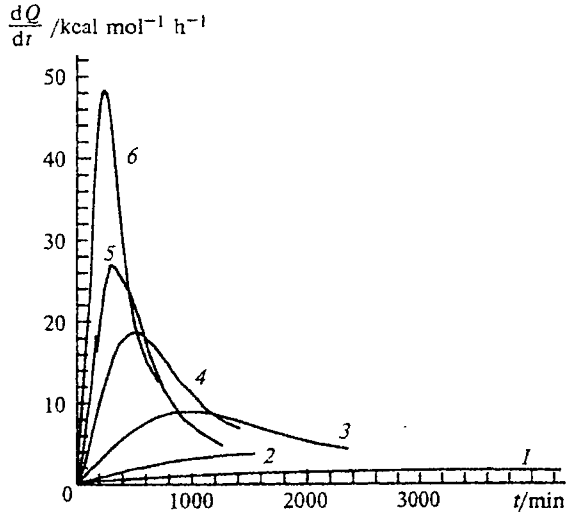

Fig. 2. Dependence of the rate of the heat release on the duration of the reaction of *n*-heptane with aqueous HNO$_3$ with different concentrations at 92.8 °C. Curves: *1*, entry *3*; *2*, entry *4*; *3*, entry *5*; *4*, entry *6*; *5*, entry *7*; *6*, entry *9* (see Table 1).

HNO$_3$ with linear hydrocarbons C_7H_{16}—$C_{18}H_{38}$ and their mixture, kerosene, in sufficient detail.

The curves of the rate of the heat release for the HNO$_3$—*n*-heptane and HNO$_3$—*n*-octadecane mixtures are presented in Figs. 1 and 2, respectively.

The main kinetic regularities observed for the oxidation of *n*-decane by nitric acid remain true for other hydrocarbons with different chain lengths. When hydrocarbons react with a solution of HNO$_3$, the system consists of three phases: acid, organic, and gaseous. The process proceeds with strong acceleration; the rate of the heat release per mole of hydrocarbon depends strongly on the free gas volume (V^g), and the dependence on the total number of moles of the acid and water per mole of hydrocarbon (n^{ac}) is less pronounced; the maximum of the rate is achieved at conversions of 30—40%. At the same time, the values of the initial rates, degrees of acceleration, and heats of oxidation differ for different hydrocarbons.

The analysis of the kinetic curves of the heat release shows that the mechanism of the oxidation of *n*-heptane and *n*-octadecane by aqueous HNO$_3$ is the same as that for the oxidation of *n*-decane. The heat release is mainly determined by the rate of the interaction of the hydrocarbon molecules with nitrogen dioxide dissolved in the organic phase. An increase in this rate is related to the accumulation of NO$_2$ formed in the reaction of NO with the starting HNO$_3$:

$$RH + NO_2 = ROH + NO,$$

$$NO + 2\,HNO_3 \rightleftharpoons H_2O + 3\,NO_2.$$

All NO$_2$ in the system is distributed between three phases and dimerized to N_2O_4.

The initial rate of the process in the absence of NO$_2$ is determined by the interaction of the hydrocarbon with HNO$_3$ dissolved in this hydrocarbon or the products of the equilibrium dissociation of the acid.[1] The rate of the heat release per mole of the hydrocarbon in the system, (dQ/dt)/kcal mol^{-1} s^{-1}, is described by the equation

$$\frac{dQ}{dt} = \frac{2\alpha k Q_{HNO_3}\eta(1-\eta)}{B_1}\Bigg/\left(1+\sqrt{1+8\alpha\eta B_2/B_1^2}\right) + k_1(1-\eta),$$

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

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

where α is the stoichiometric coefficient of the accumulation of NO$_2$ per mole of the reacted hydrocarbon; k is the rate constant of the reaction of the hydrocarbon with NO$_2$:

$$k = k'\gamma_{HNO_3}/V\,(s^{-1}); \qquad (2)$$

the values of the true rate constant (k'/L mol^{-1} s^{-1}) of the reaction of NO$_2$ with the hydrocarbon chain have been determined previously;[2] V/L mol^{-1} is the molar volume of the hydrocarbon; γ_{HNO_3} is the stoichiometric coefficient of HNO$_3$ in the oxidation equation; Q_{HNO_3} is the average heat calculated per mole of HNO$_3$; η is the conversion; k_1 is the effective rate of the noncatalytic stage of the reaction of the hydrocarbon with the dissolved HNO$_3$, which is equal to the initial rate of the heat release at $\eta = 0$; K_H^{org}/atm and K_H^{ac}/atm are Henry's constants of the equilibrium distribution of the NO$_2$ and

N_2O_4 molecules between the gas phase and the corresponding liquid phases (organic and acidic); and K_N^{org} is the equilibrium constant of the dissociation of N_2O_4 in the organic phase.

For the analysis of the rate of the heat release by Eq. (1) for *n*-heptane and *n*-octadecane, we used the values of the thermodynamic constants determined for the equilibria in the three-phase gas—*n*-decane—aqueous HNO_3 system. The chemical structures of the hydrocarbons are close, which suggests that their effects on the solubility of NO_2 and N_2O_4 and the dissociation constant of N_2O_4 are almost identical.

Under similar experimental conditions, the rates of the heat release increase as the hydrocarbon chain elongates for all studied solutions of HNO_3 and, as a whole, are proportional to the number of methylene groups in the hydrocarbon molecule ($n - 2$) to the power ~1.3 (n is the number of C atoms in the molecule).

In Eq. (1), the α values and the γ_{HNO_3} and V parameters in the k constant depend on the length of the hydrocarbon chain. The measurement of the content of NO_2 in the system per mole of the reacted hydrocarbon shows that the α value increases as the hydrocarbon chain elongates, and its dependence on n and the molar fraction of HNO_3 in the solution (N) is described by the empirical formula

$$\alpha = 0.87(n - 2)N^{0.81}. \qquad (3)$$

The γ_{HNO_3} value should increase proportionally to the number of the C atoms that have been oxidized, *i.e.*, proportionally to ($n - 2$). The analytical form of the dependence of γ_{HNO_3} on n was established by the comparison of the heat per mole of the hydrocarbon (Q/kcal mol^{-1}) of the reactions of HNO_3 with *n*-heptane (350), *n*-decane (570), and *n*-octadecane (1150) and the value $\gamma_{HNO_3} = 7$ for *n*-decane.[2] The heat of the oxidation calculated per mole of HNO_3 (Q_{HNO_3}) is 80 kcal mol^{-1} for *n*-decane and can hardly change substantially on going from one hydrocarbon to another. Since $Q = \gamma_{HNO_3} \cdot Q_{HNO_3}$, the increase in Q with elongation of the hydrocarbon chain is determined by the correlation

$$\gamma_{HNO_3} = 0.88(n - 2). \qquad (4)$$

The γ_{HNO_3} value is equal to 4.4 and 14.0 for *n*-heptane and *n*-octadecane, respectively. For the determined parameters, $Q = 70(n - 2)$.

According to Eq. (2) for the k constant, the molar volume of the hydrocarbon increases simultaneously with the increase in γ_{HNO_3}:

$$V = 0.053(n - 2)^{0.66}, \qquad (5)$$

and the γ_{HNO_3}/V ratio and, hence, the k value are proportional to $(n - 2)^{0.34}$, and a slight increase in the latter as the chain elongates is related to the corresponding increase in the concentration of the methylene groups in the organic phase.

It is seen from the data in Table 1 that at the same temperature, the k' values for different hydrocarbons in the same solution of HNO_3 are close, and their temperature dependence in 64.62% HNO_3 has the form

$$k' = 1 \cdot 10^{17}\exp[-35 \cdot 10^3/(RT)] \text{ (L mol}^{-1}\text{ s}^{-1}\text{)}.$$

The obtained parameters of the Arrhenius equation for k' are close to those determined previously (hereinafter, the dimensionality of the activation energy is kcal mol^{-1}).[8] At the same time, the real temperature dependence of the rate of the heat release is more complex, because in Eq. (1), along with the k constants, the B_1 and B_2 values are temperature-dependent.

The initial oxidation rate constant k_1 was calculated from the integral first-order kinetic equation of autocatalysis at conversions $\eta \le 0.01$ (see Table 1). The determined k_1 values make it possible to calculate the rate of the heat release at different times at the later stages of the reaction. Since these values were calculated for small conversions, whose accuracy of determination is small, the differences between their values are not greater than calculation errors, and we can accept for all hydrocarbons, on the average, that

$$k_1 = 6.6 \cdot 10^8 N^{1.44}\exp[-19.5 \cdot 10^3/(RT)] \text{ (kcal mol}^{-1}\text{ s}^{-1}\text{)}. \qquad (6)$$

It is noteworthy that the value of the activation energy (E_a) for k_1 is considerably lower than that in the expression for k' ($E_a = 35 \cdot 10^3$ kcal mol^{-1}). The initial reaction rate determined by the integral equation from the dependence of η on t coincides with the real rate only in the case when the kinetic law used remains valid during the whole induction period.[9] It is impossible to check the validity of this assumption, because the reaction rate during the induction period is lower than the sensitivity of the microcalorimeter. Therefore, the k_1 values obtained can be considered only for the estimation of real rates.

Data on the nature of the oxidizing agent at the initial stage of the interaction of hydrocarbons with aqueous HNO_3 are scarce. According to the general concepts, the role of the oxidizing agent can be played, along with HNO_3 molecules, by one of the products of the equilibrium reactions in solutions of HNO_3 (N_2O_5, NO_2^+, $H_2NO_3^+$) or the product of the reactions of HNO_3 with admixtures. Unlike the true k' constant, the k_1 parameter is the effective rate constant. The preexponential factor and the activation energy in the expression for k_1 contain the temperature dependence of the concentration of the oxidizing agent at the initial stage of the reaction. The concentration of the oxidant in the hydrocarbon is determined by all of the equilibrium reactions in solutions of HNO_3 and the distribution coefficient of the HNO_3 molecules between the aqueous solution and the hydrocarbon. A possible decrease in this concentration as the temperature increases can lead to the relatively low value of E_a of the initial

Table 1. Experimental conditions and rate constants of the reactions of *n*-heptane and *n*-octadecane with aqueous HNO_3

Entry	C_{HNO_3} (wt.%)	T /°C	V^g /L mol^{-1}	n^{ac} /mol mol^{-1}	k_1 /kcal mol^{-1} s^{-1}	k /s^{-1}	k' /L mol^{-1} s^{-1}
				n-Heptane			
1	64.62	57.8	0.90	81.4	$2.2 \cdot 10^{-5}$	$2.3 \cdot 10^{-5}$	$7.3 \cdot 10^{-7}$
2	64.62	90.6	1.30	83.2	$9.02 \cdot 10^{-5}$	$2.0 \cdot 10^{-3}$	$6.2 \cdot 10^{-5}$
3	25.07	92.8	2.86	259.4	$3.46 \cdot 10^{-5}$	$4.6 \cdot 10^{-4}$	$9.3 \cdot 10^{-6}$
4	34.09	92.8	3.12	241.0	$5.3 \cdot 10^{-5}$	$5.4 \cdot 10^{-3}$	$1.7 \cdot 10^{-4}$
5	44.06	92.8	3.73	227.0	$1.1 \cdot 10^{-4}$	$1.2 \cdot 10^{-3}$	$3.7 \cdot 10^{-5}$
6	53.92	92.8	2.96	219.0	$9.5 \cdot 10^{-5}$	$1.6 \cdot 10^{-3}$	$5.0 \cdot 10^{-5}$
7	64.62	92.8	2.65	115.0	$1.63 \cdot 10^{-4}$	$2.4 \cdot 10^{-3}$	$7.4 \cdot 10^{-5}$
8	64.62	92.8	29.70	2778.0	$1.5 \cdot 10^{-4}$	$2.4 \cdot 10^{-3}$	$7.5 \cdot 10^{-5}$
9	75.33	92.8	2.87	159.0	$4.18 \cdot 10^{-4}$	$2.7 \cdot 10^{-3}$	$8.5 \cdot 10^{-5}$
10	64.62	100.3	1.50	88.0	$7.2 \cdot 10^{-4}$	$4.7 \cdot 10^{-3}$	$1.5 \cdot 10^{-4}$
11	64.62	100.3	34.20	1910.0	$7.0 \cdot 10^{-4}$	$2.9 \cdot 10^{-3}$	$9.2 \cdot 10^{-5}$
12	64.62	115.8	1.56	84.5	$2.1 \cdot 10^{-3}$	$3.2 \cdot 10^{-2}$	$9.9 \cdot 10^{-4}$
13	64.62	115.8	9.10	575.0	$2.0 \cdot 10^{-3}$	$2.8 \cdot 10^{-2}$	$8.7 \cdot 10^{-4}$
14	64.62	115.8	11.33	2224.0	$1.9 \cdot 10^{-3}$	$3.2 \cdot 10^{-2}$	$9.9 \cdot 10^{-4}$
15	64.62	115.8	14.20	984.0	$1.8 \cdot 10^{-3}$	$2.7 \cdot 10^{-2}$	$8.4 \cdot 10^{-4}$
				n-Octadecane			
16	64.62	72.0	3.70	184.0	$2.2 \cdot 10^{-5}$	$1.6 \cdot 10^{-4}$	$3.5 \cdot 10^{-6}$
17	64.62	80.0	3.40	206.0	$5.2 \cdot 10^{-5}$	$4.8 \cdot 10^{-4}$	$1.0 \cdot 10^{-5}$
18	25.07	92.8	8.20	653.0	$6.2 \cdot 10^{-5}$	$6.8 \cdot 10^{-4}$	$1.4 \cdot 10^{-5}$
19	34.09	92.8	6.22	624.0	$8.2 \cdot 10^{-5}$	$8 \cdot 10^{-4}$	$1.7 \cdot 10^{-5}$
20	44.06	92.8	7.30	585.0	$9.9 \cdot 10^{-5}$	$1.8 \cdot 10^{-3}$	$3.7 \cdot 10^{-5}$
21	53.92	92.8	7.92	538.0	$1.26 \cdot 10^{-4}$	$2.4 \cdot 10^{-3}$	$5.2 \cdot 10^{-5}$
22	64.62	92.8	4.30	213.0	$1.9 \cdot 10^{-4}$	$3.6 \cdot 10^{-3}$	$7.7 \cdot 10^{-5}$
23	64.62	92.8	8.80	445.0	$1.86 \cdot 10^{-4}$	$3.5 \cdot 10^{-3}$	$7.6 \cdot 10^{-5}$
24	64.62	92.8	19.70	913.0	$2.38 \cdot 10^{-4}$	$3.5 \cdot 10^{-3}$	$7.6 \cdot 10^{-5}$
25	64.62	92.8	2.33	191.1	$2 \cdot 10^{-4}$	$3.6 \cdot 10^{-3}$	$7.7 \cdot 10^{-5}$
26	64.62	92.8	23.40	1616.0	$1.94 \cdot 10^{-4}$	$3.7 \cdot 10^{-3}$	$7.8 \cdot 10^{-5}$
27	75.53	92.8	8.98	413.0	$6.4 \cdot 10^{-4}$	$4.0 \cdot 10^{-3}$	$8.6 \cdot 10^{-5}$
28	64.62	100.3	3.70	216.0	$4.1 \cdot 10^{-4}$	$4.3 \cdot 10^{-3}$	$9.1 \cdot 10^{-5}$
29	64.62	101.0	3.10	183.0	$4.0 \cdot 10^{-4}$	$4.4 \cdot 10^{-3}$	$9.3 \cdot 10^{-5}$
30	64.62	115.8	3.64	201.0	$1.9 \cdot 10^{-3}$	$4.8 \cdot 10^{-2}$	$1.0 \cdot 10^{-3}$
31	64.62	115.8	20.00	1291.0	$2.1 \cdot 10^{-3}$	$4.7 \cdot 10^{-2}$	$1.0 \cdot 10^{-3}$
32	64.62	115.8	74.20	4172.0	$2.08 \cdot 10^{-3}$	$4.8 \cdot 10^{-2}$	$1.0 \cdot 10^{-3}$

stage of the reaction. When the temperature decreases, the contribution of the initial rate to the overall process increases, and the relative contribution of the autocatalytic reaction decreases.

The effect of the change in the concentration of HNO_3 in the solution on the initial rate of its reaction with hydrocarbons (k_1) is fairly low and almost equal for all hydrocarbons studied. When the concentration of HNO_3 increases from 25.07 to 75.53 wt.%, the k_1 value increases by 10—12 times.

The decrease in α with the decrease in the concentration of HNO_3 is one of the reasons for weakening of the autocatalysis effect. The real decrease in the degree of autoacceleration for all hydrocarbons is greater than the α value, which can be explained by a decrease in the equilibrium concentration of NO_2 due to the ionization of N_2O_3, N_2O_4, and HNO_2:

$$NO + NO_2 + H_2O \rightleftharpoons 2\,HNO_2 \rightleftharpoons H_3O^+ + NO_2^-,$$

$$NO + NO_2 \rightleftharpoons N_2O_3 \rightleftharpoons NO^+ + NO_2^-,$$

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-,$$

whose depth increases as the dielectric constant of the medium increases. For calculations of the oxidation rate in practice, this decrease can be formally assigned to a decrease in k' when the concentration of HNO_3 decreases

$$k' = 2.8 \cdot 10^{17} N \exp[-35 \cdot 10^3/(RT)]. \qquad (7)$$

Thus, when the α, γ_{HNO_3}, V_0, k_1, and k' values from Eqs. (2)—(7) are inserted into expression (1), we obtain the expression for calculating the rate of oxidation of any hydrocarbon of the kerosene fraction at different temperatures and concentrations of HNO_3 in the solution.

Since the interaction of the hydrocarbon with NO_2 is the main reaction that contributes to the heat release, we carried out the experiments on the oxidation of *n*-heptane by nitrogen dioxide at 115.2 °C and V^g = 22.8—36.7 L mol^{-1}, when all *n*-heptane is transferred to the gas phase. *n*-Heptane is probably the heaviest hydrocarbon, whose interaction with NO_2 can be studied in the gas phase in the temperature range studied; when *n* further increases, the equilibrium vapor pressure becomes too low.

The rate of the reaction of *n*-heptane with NO_2 in the gas phase is described by the expression

$$(\mathrm{d}Q/\mathrm{d}t)^g = \gamma_{NO_2} \cdot Q_{NO_2} \cdot k^g \cdot C^g \cdot C^g_{NO_2} \cdot V^g =$$
$$= k^g_{eff} \cdot p \cdot V^g \cdot n^{org}_{NO_2} \cdot K^{org}_H (NO_2)/(RT)^2,$$

where $k^g_{eff} = \gamma_{NO_2} \cdot Q_{NO_2} \cdot k^g$, k^g and k^g_{eff} are the true and effective rate constants of the reaction in the gas phase, respectively; p is the pressure of the hydrocarbon vapor; C^g and $C^g_{NO_2}$ are the concentrations of the hydrocarbon and NO_2 in the gas phase, respectively; γ_{NO_2} is the stoichiometric coefficient of the reaction of NO_2 with *n*-heptane; and $n_{NO_2}^{org}$ is the number of moles of NO_2 in the organic phase per mole of the hydrocarbon; the calculation of $n_{NO_2}^{org}$ has been given previously.[2] The evaporation decreases the content of the hydrocarbon in the liquid phase and the rate of its oxidation. In this case, the rate of the heat release is determined by the correlation

$$\mathrm{d}Q/\mathrm{d}t = (\mathrm{d}Q/\mathrm{d}t)_0[1 - pV^g/(RT)],$$

where $(\mathrm{d}Q/\mathrm{d}t)_0$ is the rate of the heat release in the absence of evaporation (see Eq. (1)).

The gas-phase oxidation of *n*-heptane proceeds with a very weak acceleration, which is evidently related to a small contribution of the surface reaction. The rate of the reaction of *n*-heptane with NO_2 in the gas phase was estimated from the initial rates of the process. The average value of k^g from four experiments in the interval C_{NO_2} = 0.096—0.170 mol L^{-1} is $2.2 \cdot 10^{-4}$ L mol^{-1} s^{-1}, which is by ~4.5 times lower than the rate constant of the liquid-phase reaction. The real change in the heat release is determined by the difference between the k' and k^g values and the concentrations of the hydrocarbon and NO_2 in both phases.

The regularities obtained make it possible to calculate the rates of the heat release in the reactions of mixtures of aliphatic hydrocarbons of the kerosene fraction with aqueous HNO_3. In the analysis of the reaction rates of mixtures of hydrocarbons and kerosene, it is more convenient to refer this rate to 1 kg of the mixture. The $\mathrm{d}Q/\mathrm{d}t$ value referred to 1 kg of the hydrocarbon should be multiplied by $10^3 M^{-1}$, where M is the molecular weight of the hydrocarbon, which in the n = 7—18 interval can be approximated by the formula $M = 29.1(n-2)^{0.78}$. Then the rate of the heat release of 1 kg of the hydrocarbon, $(\mathrm{d}Q/\mathrm{d}t)^*$/kcal kg^{-1} s^{-1}, can be determined by the expression

$$(\mathrm{d}Q/\mathrm{d}t)^* = 2.3 \cdot 10^7 (n-2)^{-0.78} N^{1.44} \times$$
$$\times \exp[-19.5 \cdot 10^3/(RT)](1-\eta) +$$
$$+ 2.2 \cdot 10^{22} (n-2)^{0.56} N^{1.81} \exp[-35 \cdot 10^3/(RT)] \times$$
$$\times (1-\eta)\eta/B_1\left(1 + \sqrt{1 + 8\alpha\eta B_2/B_1^2}\right). \qquad (8)$$

The rate of the heat release in the interaction of 1 kg of a mixture of hydrocarbons with a solution of HNO_3 can be calculated from Eq. (8), replacing the number of methylene groups in an individual hydrocarbon (n − 2) by the average number of methylene groups in 1 kg of the mixture of hydrocarbons ($\Sigma m_i(n_i - 2)$, where m_i is the molar fraction of the hydrocarbon with the number of C atoms in the molecule equal to n_i in 1 kg of the mixture). For a mixture of linear hydrocarbons with a symmetrical distribution of fractions over the chain length with a maximum in the medium part of the interval of the hydrocarbon chain lengths, the rate of the reaction with aqueous HNO_3 is approximately equal to the rate of the oxidation of an individual hydrocarbon, whose content in the mixture is maximum, by nitric acid. According to the dependence of $(\mathrm{d}Q/\mathrm{d}t)^*$ on n, the higher the fraction of the hydrocarbon with the average molecular weight in the distribution, the less the difference between the true and estimated values. For the calculation by Eq. (8) in two limiting cases: (1) only hydrocarbon with n = 12; (2) equal content of all hydrocarbons in the n = 7—18 range, the difference is not more than 2%. The average fractions in kerosene, mainly containing paraffins, is represented by dodecane;

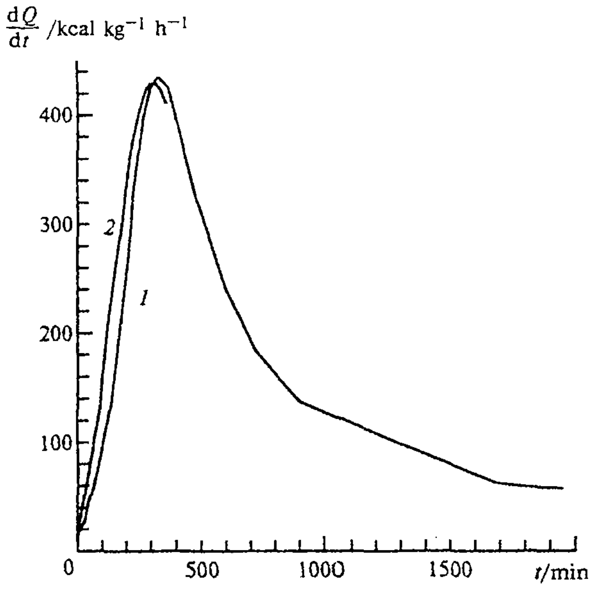

Fig. 3. Dependences of the rate of the heat release on the duration of the reaction of 64.62% HNO_3 with kerosene (*1*) and *n*-decane (*2*) at 92.8 °C; V^g = 7.2 (*1*), 5.9 L mol^{-1} (*2*); n^{ac} = 451 (*1*), 768 (*2*).

Table 2. Rate constants of the oxidation of mixtures of *n*-octadecane with different additives of 64.62% HNO_3

Additive	Concentration of additive (wt.%)	V^g /L mol^{-1}	n^{ac} /mol mol^{-1}	k_1 /kcal kg^{-1} s^{-1}	$k \cdot 10^3$ /s^{-1}
	0	8.8	445	$7.3 \cdot 10^{-4}$	3.5
Cyclohexane	10.1	6.5	384	$1.3 \cdot 10^{-3}$	3.5
Benzene	12.2	6.5	416	$1.2 \cdot 10^{-3}$	2.7
Toluene	16.3	6.1	359	$4.6 \cdot 10^{-2}$	2.8
1-*n*-Decene	13.4	5.7	396	$2.6 \cdot 10^{-2}$	3.6

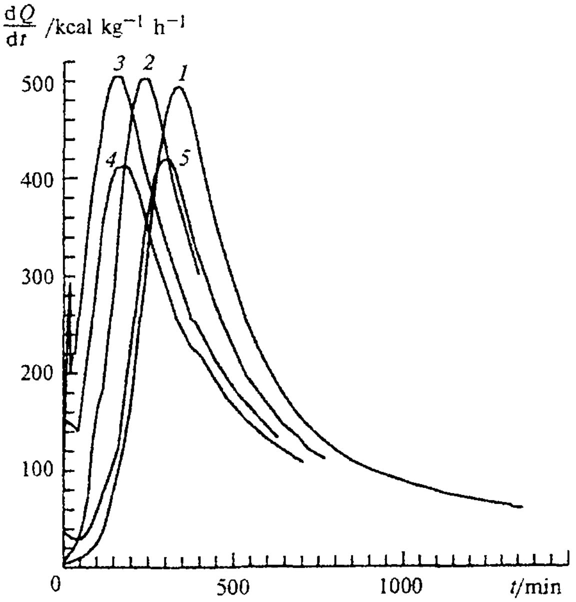

Fig. 4. Dependences of the rate of the heat release on the duration of the reactions of 64.62% HNO_3 with *n*-octadecane at 92.8 °C in the absence of additives (*1*) and in the presence of cyclohexane (*2*), 1-decene (*3*), toluene (*4*), and benzene (*5*).

the rate of the heat release per 1 kg of these kerosenes is determined by the insertion of $n = 12$ into Eq. (8).

A comparison of the curves of the heat release for kerosene and *n*-decane under close conditions is demonstrated in Fig. 3. The kinetic regularities of the oxidation of kerosene are very close to the corresponding regularities for individual hydrocarbons.

The majority of technical lots of kerosene have a complex and indefinite composition; they contain aliphatic, naphthenic, aromatic, and even unsaturated hydrocarbons. Therefore, we studied the effect of these compounds on the kinetics of the heat release during the oxidation of *n*-octadecane by 64.62% HNO_3 at 92.8 °C (Table 2, Fig. 4). The addition of aromatic and unsaturated hydrocarbons increases dramatically the initial rate of the heat release and shortens the time of achieving the maximum rate, but affects slightly the rates of the subsequent stages of the process. Additives of naphthenic hydrocarbons almost do not change the kinetic parameters of the reaction. The direct experimental determination of the rates of the heat release is required for the reliable estimation of the safety of the process when technical lots of kerosene with an indefinite composition is used; the measurement of the initial rate and the *k* values obtained in this work are sufficient for rough estimation.

The kinetic data presented above make it possible to calculate critical conditions, under which the process becomes uncontrolled, and the corresponding induction periods under almost all conditions. The possibility of a sharp increase in the rate of the heat release in the system considered should be specially analyzed; this can be caused, along with the temperature increase, by a sharp decrease in the V^g value resulting in an increase in the content of NO_2 in the liquid phase. Possible admixtures in kerosene mainly increase the initial rate of the process and affect slightly the rates of the subsequent stages. Therefore, according to the quasi-statistical theory of thermal explosion, in terms of which the critical condition is determined by the maximum value of the rate of the heat release,[10] these admixtures should virtually not change the critical conditions. However, the increase in the initial rate results in shortening of the time passed before the moment when the reaction becomes uncontrolled (induction period), which decreases sharply the safety of the process for the work beyond the critical conditions.

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