Kinetics of heat release during the reaction of *n*-decane with nitrogen dioxide in the liquid phase

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The rates of heat release in the nitrogen dioxide—*n*-decane system at a molar ratio of nitrogen oxides to *n*-decane (β) from $2.4 \cdot 10^{-3}$ to 3.1 and gaseous volumes per mole of *n*-decane (V(g)) equal to 0.05—4.5 were studied in the 55.2—92.8 °C temperature range. The initial rate of the process is determined by the interaction of NO_2 with *n*-decane. The equilibrium constants of dissociation of N_2O_4 in *n*-decane and Henry's constants of NO_2 and N_2O_4 in an *n*-decane solution were determined by complex analysis of the thermodynamic equilibrium in the NO_2—*n*-decane system and dependences of the initial rates on V(g) and β. The experimentally observed self-acceleration of the process in the region of high β and low T values was suggested to be due to the reaction of N_2O_4 with intermediate oxidation products. The rate constants of the reaction of NO_2 with *n*-decane were compared with analogous values determined in its mixtures with HNO_3 solutions.

Key words: nitrogen dioxide, *n*-decane, nitration, oxidation, heat release, kinetics.

It has been previously shown[1] that when *n*-decane interacts with aqueous solutions of HNO_3, in the major part of the kinetic curve the reaction rate is determined by the rate of the interaction of *n*-decane with NO_2 molecules, and only the initial rate of the process is determined by the direct interaction of *n*-decane with HNO_3. These regularities are important for evaluating the safety of technological devices using these mixtures. Therefore, in this work, we studied in more detail the kinetic regularities of the oxidation of *n*-decane by nitrogen dioxide in the liquid phase.

Available data on the kinetics of the reaction of *n*-decane with NO_2 in the liquid phase were obtained in a narrow range of the molar ratio of nitrogen oxides to *n*-decane (β = 0.01—0.05).[2] Previously, kinetic data have been analyzed using inexact values of solubility constants of nitrogen oxides in *n*-decane. The kinetics of the reaction of NO_2 with hydrocarbons in the gas phase at 250—450 °C has been studied at the level of elementary acts.[3] It is established that an increase in the temperature and pressure results in a regular transition from a slow reaction, which proceeds according to the law of a simple type reaction, to a cold-flame reaction and then to a hot-flame reaction with the degenerate-branched mechanism. In the slow reaction, the reaction orders with respect to reagents are close to unity, and the activation energy is ~30 kcal mol^{-1}.[4]

Data on the kinetics of the reaction of NO_2 with hydrocarbons in the liquid phase are necessary for detailed analysis of the kinetics of thermal decomposition of mixtures of nitro compounds with hydrocarbons, because NO_2 is the main primary product of decomposition of almost all nitro compounds.

Experimental

The rates of heat release in the two-phase NO_2 solution in the *n*-decane—gas system were measured on a differential automated calorimeter[5] in glass sealed, completely thermostatted ampules in the 55.2—92.2 °C temperature range. Nitrogen dioxide and *n*-decane were obtained, purified, and stored according to a previously published procedure.[2] The value of the gas volume per mole of the starting *n*-decane (V(g)) was varied within 0.05—4.5 L mol^{-1}. In the majority of experiments, the molar ratio of nitrogen oxides to *n*-decane (β) was varied from $2.4 \cdot 10^{-3}$ to 0.1, and several experiments were carried out in the β range from 2.0 to 3.1.

Results and Discussion

The shapes of the curves of the heat release rate depend on the β values and initial temperatures. Some kinetic curves of the heat release rates (dQ/dt) calculated per mole of *n*-decane and normalized to the β value are presented in Fig. 1. For $\beta < 2.9 \cdot 10^{-3}$ at 55 °C, $\beta < 0.013$ at 64.6 °C, and $\beta < 0.02$ at 74.2 °C, the process is described by a kinetic law of the first-order reaction. When β further increases, a self-acceleration is observed at the initial period of the reaction, and the time of achieving the maximum rate increases as β increases. The rate is maximum when the depth of conversion is ~20%. During the reaction, the rate in-

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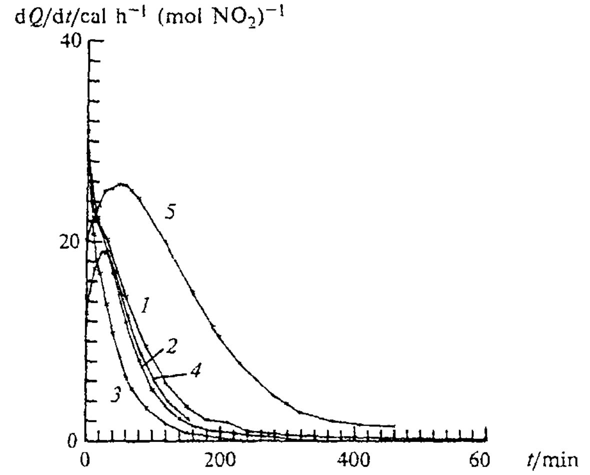

Fig. 1. Time dependence dQ/dt at 74.2 °C for β (mol mol^{-1}): 0.0039 (*1*); 0.0073 (*2*); 0.013 (*3*); 0.020 (*4*); and 0.032 (*5*).

creases by 1.3—1.6 times over the initial value. Before the 30% depth is achieved, these curves are described by a first-order equation of the autocatalytic reaction:

$$d\eta/dt = k(1 - \eta) + k_2(1 - \eta)\eta.$$

When the temperatures are 85.5 °C and higher, the process proceeds according to the first-order kinetic law at all experimental values of β.

When the V(g) value is constant and relatively small (~0.05 L mol^{-1}), the ratio of the initial heat release rate to the overall thermal effect of the reaction

$$(dQ/dt)_{t=0}/\int_0^{\infty}(dQ/dt)\cdot dt = (d\eta/dt)_{t=0}$$

up to a certain β value is independent of β and decreases with further increase in β. When β is constant, the $(d\eta/dt)_{t=0}$ value decreases as V(g) increases. The heats of the processes and rate constants of particular stages under some experimental conditions are presented in Table 1.

The reaction of aliphatic hydrocarbons with an equilibrium mixture of NO_2 and N_2O_4 is a complicated process consisting of consequent-parallel stages of nitration and oxidation. The interaction between hydrocarbon and NO_2 plays the main role for reactions in gas and liquid phases. Under experimental conditions, not more than 3% *n*-decane exists in the gas phase. The

Table 1. Rate constants and thermal effects of the reaction of *n*-decane with NO_2 in the liquid phase

T /°C	β /mol mol^{-1}	V(g) /L mol^{-1}	Q_{NO_2} /kcal mol^{-1}	k_1	k_2
				s^{-1}	
55.2	0.0025		32	$3.5\cdot10^{-5}$	
55.2	0.0032		33	$3.5\cdot10^{-5}$	
55.2	0.0077	0.056	34	$2.5\cdot10^{-5}$	$1.2\cdot10^{-4}$
55.2	0.0093	0.049	34	$2.1\cdot10^{-5}$	$1.2\cdot10^{-4}$
55.2	0.011	0.033	33	$1.9\cdot10^{-5}$	$4.8\cdot10^{-5}$
55.2	0.055	0.067	47	$9.8\cdot10^{-6}$	$4.8\cdot10^{-5}$
55.2	0.061	0.090	48	$8.7\cdot10^{-6}$	$7.2\cdot10^{-5}$
55.2	0.074	0.061	52	$8.1\cdot10^{-6}$	$8.9\cdot10^{-5}$
55.2	0.11	0.057	49	$6.6\cdot10^{-6}$	$5.2\cdot10^{-5}$
55.2	0.17	0.10	47	$6.9\cdot10^{-6}$	$5.5\cdot10^{-5}$
64.6	0.0025			$9.8\cdot10^{-5}$	
64.6	0.005			$1.0\cdot10^{-4}$	
64.6	0.0085		22	$9.4\cdot10^{-5}$	
64.6	0.01	0.0073	22	$8.9\cdot10^{-5}$	
64.6	0.013	0.069	32	$7.4\cdot10^{-5}$	
64.6	0.024	0.048	30	$5.1\cdot10^{-5}$	$1.5\cdot10^{-4}$
64.6	0.061	0.041	40	$3.4\cdot10^{-5}$	$1.2\cdot10^{-4}$
64.6	0.072	0.084	38	$3.3\cdot10^{-5}$	$1.3\cdot10^{-4}$
64.6	0.10	0.058	40	$2.5\cdot10^{-5}$	$1.4\cdot10^{-4}$
74.2	0.0039	0.051	20	$2.6\cdot10^{-4}$	
74.2	0.0059	0.076	28	$2.7\cdot10^{-4}$	
74.2	0.0073	0.064	28	$2.7\cdot10^{-4}$	
74.2	0.012	0.091	32	$2.6\cdot10^{-4}$	
74.2	0.012	0.053	32	$2.6\cdot10^{-4}$	
74.2	0.013	0.064	39	$2.5\cdot10^{-4}$	$3\cdot10^{-4}$
74.2	0.016	0.070	42	$2.3\cdot10^{-4}$	$3\cdot10^{-4}$
74.2	0.020	0.087	42	$2.0\cdot10^{-4}$	$8\cdot10^{-4}$
74.2	0.023	0.077	43	$1.8\cdot10^{-4}$	$6\cdot10^{-4}$
74.2	0.028	0.0148	52	$1.6\cdot10^{-4}$	$4.4\cdot10^{-4}$
74.2	0.032	0.044	58	$1.5\cdot10^{-4}$	$3.4\cdot10^{-4}$
74.2	0.039	0.119	60	$1.3\cdot10^{-4}$	$3.2\cdot10^{-4}$

ratio of concentrations of NO_2 in the liquid and gas determined from the ideal gas law and Henry's law is about ten. When the reaction rate constants in the liquid and gas are close,[2] the contribution of the gas-phase reaction to the overall rate is not greater than 0.3%. The fact that $(d\eta/dt)_{t=0}$ decreases as $V(g)$ increases testifies that the liquid-phase reaction makes the main contribution to the overall heat release rate, which is limited by the bimolecular interaction of NO_2 with the hydrocarbon. The initial rate of heat release is determined by the expression

$$(dQ/dt)_{t=0} = k'\cdot\gamma_{NO_2}\cdot C_{NO_2}(liq)\cdot Q_{NO_2}/\beta,$$

where $k'/L\ mol^{-1}\ s^{-1}$ is the rate constant of the reaction of *n*-decane with NO_2 in the liquid phase; $C_{NO_2}(liq)$ is the concentration of NO_2 in the liquid phase; γ_{NO_2} is the stoichiometric coefficient of NO_2 in the reaction equation; and Q_{NO_2} is the thermal effect of the interaction per mole of NO_2. After transformation we obtain

$$(dQ/dt)_{t=0} = k\cdot Q_{NO_2}\cdot n_{NO_2}(liq)/\beta. \qquad (1)$$

where $k/s^{-1} = \gamma_{NO_2}\cdot k'\cdot C_d(liq)$ is the effective constant; $C_d(liq)$ is the concentration of *n*-decane in the liquid phase; and $n_{NO_2}(liq)$ is the number of moles of NO_2 in the solution per mole of *n*-decane.

The $n_{NO_2}(liq)$ value can be calculated taking into account the equilibrium of dissociation of N_2O_4 in both phases, equilibrium distribution of nitrogen oxides between the phases, and mass balance with respect to the number of moles of nitrogen oxides per mole of *n*-decane:

$$\begin{tikzcd}
N_2O_4(g) \arrow[r, shift left, "K(g)"] \arrow[d, shift left, "K_H(N_2O_4)"'] & 2\,NO_2(g) \arrow[l, shift left] \arrow[d, shift left] \\
N_2O_4(liq) \arrow[r, shift left, "K_N(liq)"] \arrow[u, shift left] & 2\,NO_2(liq) \arrow[l, shift left] \arrow[u, shift left, "K_H(NO_2)"']
\end{tikzcd}$$

(where $K(g)$ (atm) and $K_N(liq)$ are the dissociation constants of N_2O_4 in the gas phase and in a solution of *n*-decane; $K_H(NO_2)$ and $K_H(N_2O_4)$ are Henry's constants for solutions of NO_2 and N_2O_4 in *n*-decane, atm),

$$n_{NO_2}(g) + 2n_{N_2O_4}(g) + n_{NO_2}(liq) + 2n_{N_2O_4}(liq) = \beta, (2)$$

where $n_{NO_2}(g)$, $n_{N_2O_4}(g)$, $n_{NO_2}(liq)$, and $n_{N_2O_4}(liq)$ are the numbers of moles of NO_2 and N_2O_4 in the gas phase and in a solution of *n*-decane calculated per mole of *n*-decane in the system. The numbers of moles of NO_2 and N_2O_4 in solution are referred to one mole of *n*-decane, and the sum of moles in the solution is the following:

$$\Sigma n = 1 + n_{NO_2}(liq) + n_{N_2O_4}(liq).$$

Under the majority of experimental conditions, $n_{NO_2}(liq)$, $n_{N_2O_4}(liq) \ll 1$; therefore, $\Sigma n = 1$ and the molar fractions of NO_2 and N_2O_4 in solution are numerically equal to their number of moles. In this case, the $n_{NO_2}(g)$, $n_{N_2O_4}(g)$, and $n_{N_2O_4}(liq)$ values are expressed through $n_{NO_2}(liq)$ as follows:

$$n_{N_2O_4}(liq) = [K_N(liq)]^{-1}\cdot[n_{NO_2}(liq)]^2,$$

$$n_{NO_2}(g) = K_H(NO_2)\cdot V(g)(RT)^{-1}\cdot n_{NO_2}(liq),$$

$$n_{N_2O_4}(g) = K_H(N_2O_4)\cdot V(g)[RTK_N(liq)]^{-1}\cdot[n_{NO_2}(liq)]^2. \quad (3)$$

The solution of Eqs. (1—3) gives the following expression for the heat release rate:

$$\begin{aligned}(dQ/dt)_{t=0} &= 2kQ_{NO_2}/\{[(K_H(NO_2)\cdot V(g)/RT + 1)^2 + \\ &\quad + 8(K_H(N_2O_4)\cdot V(g)/RTK_N(liq) + 1/K_N(liq))\cdot\beta]^{1/2} + \\ &\quad + K_H(NO_2)\cdot V(g)/RT + 1\} = \\ &= 2kQ_{NO_2}/\{[(n_{NO_2}(g)/n_{NO_2}(liq) + 1)^2 + \\ &\qquad + 8(n_{N_2O_4}(g)/(n_{NO_2}(liq))^2 + \\ &\qquad + n_{N_2O_4}(liq)/(n_{NO_2}(liq))^2)\cdot\beta]^{1/2} + \\ &\qquad + (n_{NO_2}(g)/n_{NO_2}(liq) + 1)^2\}. \qquad (4)\end{aligned}$$

Depending on external experimental conditions ($V(g)$, β, and T values), the expression for the rate (Eq. (4)) is simplified in three limiting cases.

1) At relatively high temperatures and great values of $V(g)$, the majority of nitrogen oxides exists in the form of NO_2 in the gas phase. The second term under the square root can be neglected, and for the initial heat release rate we obtain

$$(dQ/dt)_{t=0} = kQ_{NO_2}/[K_H(NO_2)\cdot V(g)/RT + 1],$$

and for the inverse value of the initial rate

$$1/(d\eta/dt)_{t=0} = Q_{NO_2}/(dQ/dt)_{t=0} = 1/k + K_H(NO_2)\cdot V(g)/kRT.$$

The experimental dependences of $Q_{NO_2}/(dQ/dt)_{t=0}$ on $V(g)$ at different temperatures are presented in Fig. 2. The k and $K_H(NO_2)$ values were determined from the

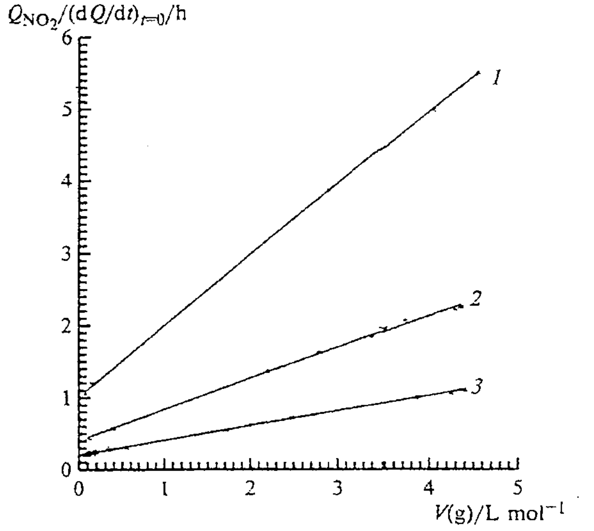

Fig. 2. Dependence of $Q_{NO_2}/(dQ/dt)_{t=0}$ on $V(g)$ at different temperatures (°C): 74.2 (*1*); 85.5 (*2*); and 92.8 (*3*).

tangent slope and a segment cut on the Y axis. The temperature dependence of $K_H(NO_2)$ is determined by the equation

$$K_H(NO_2) = 1.1 \cdot 10^3 \exp(-1300/T) \text{ atm.}$$

2) At relatively low temperatures and small $V(g)$, the fraction of nitrogen oxides in the gas phase is low. In the first term under the square root, the $n_{NO_2}(g)/n_{NO_2}(liq)$ value can be neglected compared to unity, and in the second term, we neglect the $n_{N_2O_4}(g)/((n_{NO_2}(liq))^2$ value compared to $n_{N_2O_4}(liq)/((n_{NO_2}(liq))^2$. In this case, the initial rate is determined by the expression

$$(dQ/dt)_{t=0} = 2kQ_{NO_2}/[1 + \beta/K_N(liq)]^{1/2} + 1.$$

When β are substantially smaller than $K_N(liq)$, the $[\beta/K_N(liq)]^{1/2}$ term can be neglected compared to unity, and finally, the initial rate becomes independent of β:

$$(dQ/dt)_{t=0} = kQ_{NO_2}.$$

3) As β increases, the equilibrium of the NO_2 dimerization is shifted to N_2O_4, and the relative fraction of NO_2 in a solution of *n*-decane decreases. The $[\beta/K_N(liq)]^{1/2}$ term affects the value of the rate, and beginning from certain β values, we can neglect unity compared to $[\beta/K_N(liq)]^{1/2}$:

$$(dQ/dt)_{t=0} = 2kQ_{NO_2}[K_N(liq)/\beta]^{1/2}.$$

The dependence of $\log[(dQ/dt)_{t=0}/Q_{NO_2}]$ on $\log\beta$ at different temperatures and $V(g) \approx 5 \cdot 10^{-2}$ L mol^{-1} is presented in Fig. 3. As β increases, the horizontal regions of the curves are regularly alternated with regions in which the logarithm of the rate decreases and the tangent slope is equal to ≈ −0.5. The abscissa of the intersection point of the horizontal and sloped regions of the curves is determined by the $K_N(liq)$ value and is equal to $4K_N(liq)$. The temperature dependence of $K_N(liq)$ is described by the $8.2 \cdot 10^5 \exp(-6757/T)$ expression and is close to the dependence determined by the direct method.[6]

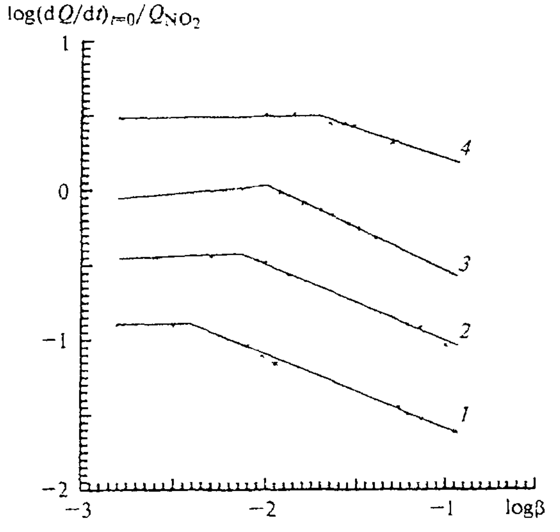

Fig. 3. Dependence of $\log(dQ/dt)_{t=0}/Q_{NO_2}$ on $\log\beta$ at different temperatures (°C): 55.4 (*1*); 64.6 (*2*); 74.2 (*3*); and 85.5 (*4*).

The *k* values determined from different dependences within the experimental scatter of data are expressed by the temperature dependence established for the oxidation of *n*-decane by NO_2 in solutions of HNO_3 ($k = 3.5 \cdot 10^{18} \exp(-17.6 \cdot 10^3/T)$).[1] The values of the $K_N(liq)$ and $K_H(NO_2)$ constants established in this work, in combination with the value of the dissociation rate constant of N_2O_4 in the gas phase, allow one to determine $K_H(N_2O_4) = 4.5 \cdot 10^2 \exp(-2400/T)$ from the thermodynamic cycle. The $K_H(NO_2)$ and $K_H(N_2O_4)$ values for the two-phase system at 90 °C established in the present work are by 7 and 50 times lower than the previously determined values.[6] The error of thermostatting in the determination of partial pressures of NO_2 and N_2O_4 mentioned in Ref. 6 should result in underestimating, in the limiting case, by several times, the $K_H(NO_2)$ and $K_H(N_2O_4)$ values compared to the data of this work. It can be assumed that one reason for overestimating the values of $K_H(NO_2)$ and $K_H(N_2O_4)$ in Ref. 6 is the underestimation of the concentration of nitrogen oxides in the liquid, which is due to the great indeterminacy in determination (from the absorption at the same wavelength) of comparable and small concentrations of N_2O_4 and an admixture in the form of HNO_2. The reaction of *n*-decane with NO_2, which occurs to a certain extent during the thermodynamic experiment, can make a certain contribution to the decrease in the concentration of nitrogen oxides in the liquid. The number of moles of NO_2 and N_2O_4 in the liquid phase decreases during the reaction. For example, at 60 °C the reaction occurs by 10% during ~40 min, which is comparable with the time of the thermodynamic experiment. According to the data in Ref. 6, $K_H(NO_2)V(g) \gg RT$, and under these conditions, a proportional dependence of $Q_{NO_2}/(dQ/dt)_{t=0}$ on $V(g)$ should take place, which was not observed in our experiments.

To determine the γ_{NO_2} values, we compared the published values of the heats of the reaction of *n*-decane with HNO_3 [1] and those of the interaction of *n*-decane with NO_2 obtained in this work. The extent of the oxidation of *n*-decane and the corresponding thermal effect of the reaction increase as β increases.

The observed thermal effect of ~20 kcal mol^{-1} NO_2 can be explained by the fact that the oxidation of *n*-decane to dimethyl-substituted octodecane occurs according to the overall equation

$$2\,C_{10}H_{22} + 2\,NO_2 = C_{20}H_{42} + 2\,HNO_2,$$
$$\Delta H = -20.8 \text{ kcal (mol } NO_2)^{-1}.$$

The heat of formation of *n*-eicosane was used to calculate the heat of this reaction.[7] By analogy to other hydrocarbons, the heat of formation of a branched isomer should be by 1—3 kcal mol^{-1} lower.

The oxidation to $C_{20}H_{42}$ can occur at low values of β, when the *iso*-decyl radical formed in the primary act of the oxidation

$$C_{10}H_{22} + NO_2 \rightarrow C_8H_{17}C^{\cdot}HCH_3 + HNO_2,$$

has comparable probabilities of recombining with a similar radical and entering the secondary reaction of the oxidation by nitrogen dioxide.

Heat effects lower than 38.5 kcal (mol NO_2)$^{-1}$ can be explained by the nitration reactions with the reduction of NO_2 to NO

$$C_{10}H_{22} + 1.5\ NO_2 = C_{10}H_{21}NO_2 + 0.5\ NO + 0.5\ H_2O,$$
$$\Delta H = -30.8\ \text{kcal (mol NO}_2)^{-1}$$

and oxidation to alcohol, aldehyde, acid, and finally, to CO_2; NO_2 is reduced to NO

$$3\ C_{10}H_{22} + 0.3\ NO_2 = 30\ CO_2 + 0.3\ NO + 33\ H_2O,$$
$$\Delta H = -38.5\ \text{kcal (mol NO}_2)^{-1}.$$

When NO_2 is reduced to NO, the heats of the nitration and oxidation to different products differ by only 8 kcal mol^{-1}.

The heat effects of >38.5 kcal (mol NO_2)$^{-1}$ can be explained only by the reduction of NO_2 to N_2 during the nitration

$$8\ C_{10}H_{22} + 10\ NO_2 = N_2 + 8\ C_{10}H_{21}NO_2 + 4\ H_2O,$$
$$\Delta H = -44\ \text{kcal (mol NO}_2)^{-1},$$

or during the oxidation of *n*-decane to alcohol, aldehyde, acid, and up to CO_2:

$$4\ C_{10}H_{22} + 2\ NO_2 = 4\ C_{10}H_{21}OH + N_2,$$
$$\Delta H = -93.4\ \text{kcal (mol NO}_2)^{-1};$$

$$4\ C_{10}H_{22} + 6\ NO_2 = 4\ C_9H_{19}COOH + 3\ N_2 + 4\ H_2O,$$
$$\Delta H = -114.4\ \text{kcal (mol NO}_2)^{-1};$$

$$12\ C_{10}H_{22} + 186\ NO_2 = 120\ CO_2 + 93\ N_2 + 131\ H_2O,$$
$$\Delta H = -112.2\ \text{kcal (mol NO}_2)^{-1}.$$

It has been previously shown[2] that no deep oxidation with evolution of CO or CO_2 occurs during the reaction of NO_2 with *n*-decane at small β. Nitro derivatives, alcohol, NO, H_2O, and partially N_2 were the main products of the reaction.

The experimentally observed thermal effects of the reaction of *n*-decane with NO_2 (at great β) and with solutions of HNO_3 calculated per both mole of *n*-decane and mole of NO_2 can be explained only by the fact that the oxidation to CO_2 and reduction of NO_2 to N_2 occur to a certain extent. For the oxidation reactions without decomposition of the carbon chain, the heat per mole of *n*-decane is lower than the experimental heat.

The total heats of oxidation of *n*-decane by solutions of HNO_3 and NO_2 calculated per mole of *n*-decane [$Q_t(HNO_3)$ and $Q_t(NO_2)$, kcal mol^{-1} of *n*-decane] are related to the heats of oxidation of *n*-decane calculated per mole of HNO_3 and NO_2 (Q_{HNO_3}, kcal (mol HNO_3)$^{-1}$ and Q_{NO_2}, kcal (mol NO_2)$^{-1}$) by the correlations $Q_t(HNO_3) = \gamma_{HNO_3} \cdot Q_{HNO_3}$ and $Q_t(NO_2) = \gamma_{NO_2} \cdot Q_{NO_2}$. The difference in the heats $Q_t(HNO_3) - Q_t(NO_2)$ in the case of the same reaction products in the oxidation by solutions of HNO_3 and NO_2 is equal to $\gamma_{HNO_3} \cdot \Delta H_1$, where ΔH_1 is the heat of the process:

$$2\ HNO_3 + NO = 3\ NO_2 + H_2O,$$
$$\Delta H_1 = 8.2\ \text{kcal (mol HNO}_3)^{-1} \quad (5)$$

or $\gamma_{HNO_3} \cdot \Delta H_2$, where ΔH_2 is the heat of the process:

$$8\ HNO_3 + N_2 = 10\ NO_2 + 4\ H_2O,$$
$$\Delta H_2 = 17\ \text{kcal (mol HNO}_3)^{-1}. \quad (6)$$

According to Eqs. (5, 6), the stoichiometric coefficients of HNO_3 and NO_2 are related by the correlations $\gamma_{HNO_3} = 0.66\ \gamma_{NO_2}$ or $\gamma_{HNO_3} = 0.8\ \gamma_{NO_2}$, respectively. The thermal effect of the oxidation of *n*-decane per mole of NO_2 at β values equal to 2 and higher, which are close to the number of moles of NO_2 formed in the oxidation of *n*-decane by solutions of HNO_3,[1] is equal to ~70 kcal (mol NO_2)$^{-1}$. This thermal effect can be the result of the oxidation and nitration reactions with the partial reduction of NO_2 to N_2. According to known data,[2] N_2 and NO in the oxidation products are correlated as 1 : 2, hence:

$$0.8\gamma_{NO_2} \cdot 17 \cdot 0.34 + 0.66\gamma_{NO_2} \cdot 8.2 \cdot 0.66 - \gamma_{NO_2} \cdot 70 = -575.$$[1]

The value of 9.3 was obtained for γ_{NO_2}, while $\gamma_{HNO_3} = 6.6$. The temperature dependence of the rate constant of the reaction of NO_2 with *n*-decane in the two-phase system can be presented in the form $k' = 8.0 \cdot 10^{16} \exp(-17.6 \cdot 10^3/T)$, L mol^{-1} s^{-1}. The pre-exponential of the rate constant in the three-phase system is 1.4-fold higher, which can be explained by the change in the dielectric and solvating properties of the medium with partial dissolution of HNO_3 in *n*-decane.

Since the conditions under which the acceleration appears correspond to the conditions of the maximum formation of N_2O_4 in solution (high content of $NO_2 + N_2O_4$, low temperatures), it can be assumed that the interaction of N_2O_4 with the products of the *n*-decane oxidation containing C—O—H or C=O is the reason for the acceleration during the process. In this case, the rate of the catalytic stage is determined by the expression

$$k_2 \cdot C_{dec}{}^{org} = k_2{}' \cdot C_{N_2O_4}{}^{org} \cdot C_{ROH,\infty}{}^{org},$$

where $k_2{}'$ is the rate constant of the reaction of N_2O_4 with alcohol; $C_{ROH,\infty}{}^{org}$ is the concentration of the alcohol formed in the oxidation of *n*-decane; and $C_{N_2O_4}{}^{org}$ is the concentration of N_2O_4 in *n*-decane. The effective rate constant of the catalytic stage slightly changes as the concentration of N_2O_4 in the system increases, which can be explained by a single decrease in the concentration of the alcohol due to a deeper oxidation with the increase in the total content of nitrogen oxides per mole of *n*-decane. Using the values of k_2 and $C_{\mathrm{ROH},\infty}{}^{\mathrm{org}}$ for β ~ 0.012—0.016 and $C_{\mathrm{dec}}{}^{\mathrm{org}}$ and $C_{\mathrm{N_2O_4}}{}^{\mathrm{org}}$ calculated from the dissociation constant $K_{\mathrm{N}}{}^{\mathrm{org}}$ for $\beta = 0.012$, we obtained the value of 120 L mol^{-1} s^{-1} (with the same order of magnitude as that directly measured previously[8]) for k_2' at 74.4 °C. This confirms the assumption that the acceleration is related to the reactions of N_2O_4.

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