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Fig. 1

Figure 1: Fig. 1

Abstract

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ON THE QUESTION OF THE KINETIC MECHANISM OF THE INTERACTION OF METHANE WITH NITROGEN DIOXIDE

The studies available in the literature on the vapor-phase nitration of alkanes by nitrogen dioxide are chiefly synthetic in character, and the proposed ideas about the kinetic mechanism of this process are based on indirect evidence ([1–9]). It is possible, with high probability, to reject a molecular mechanism for such nitration and to assume that free radicals participate in its occurrence. Whether, however, this process is free-radical or chain in character has so far remained unclear. The present work is devoted to solving this question on the basis of establishing the formal-kinetic regularities of the reaction.

Fig. 1. Form of the kinetic curves Δp—; (t) and P_{NO_2}—; (t) for a mixture of composition $4CH_4 + 1NO_2$ at $T = 450°$. $P_{initial} = 200$ mm Hg. $1 - P_{NO_2}$, $2 - \Delta p$

Earlier ([10]) we showed that, depending on the initial conditions, three types of course of methane nitration by nitrogen dioxide are observed, characterized by kinetic curves of pressure increase–time (Δp—; (t)) differing in form: a) a slow reaction, b) a reaction with a peak on the Δp—t curve, c) a reaction with ignition. In the present communication experimental results are presented that were obtained for the case of the slow reaction at small depths of conversion. The form of the kinetic curves Δp—; (t) and P_{NO_2}—(t) for the slow reaction is shown in Fig. 1.

To determine the reaction orders with respect to the initial substances, the dependence of the initial rates of nitration, at a constant concentration of each of the components, on the concentration of the other was studied. The initial rate of nitration was calculated from the consumption of NO_2. Since, in parallel with the reaction of CH_4 with NO_2, a reaction of dissociation of NO_2 occurs, the initial rates of the process calculated from the consumption of NO_2 are the total rates of nitration and dissociation. Therefore, in order to determine the initial rate of nitration proper (W_{nitr}), the initial rate of NO_2 dissociation (W_{diss}) was subtracted from the total initial rate of the entire process. Since dilution with nitrogen of the mixture $4CH_4 + 1NO_2$ by a factor of 4.6 (from 100 to 460 mm

Hg at $T = 450^\circ$) had no effect on the initial reaction rates, within the indicated dilution there is no need to carry out experiments at constant initial pressure.

The reaction order with respect to CH_4 was determined at $T = 450^\circ$, at a constant initial $P_{NO_2} = 40$ mm Hg, for mixture compositions from $1CH_4 + 1NO_2$ to $12CH_4 + 1NO_2$. The corresponding data are given in Fig. 2. The reaction order with respect to CH_4, determined from the tangent of the angle of inclination of the straight line obtained, is 1 ± 0.1, i.e., practically first order.

To determine the reaction order with respect to NO_2, three series of experiments were carried out at $T = 450^\circ$ with constant initial P_{CH_4}, equal to 100; 153 and

200 mm Hg. In doing so, using the already known order with respect to CH_4, we transformed the results of a series of experiments carried out at initial P_{CH_4} equal to 100 and 153 mm Hg to $P_{CH_4} = 200$ mm Hg. The data are presented in Fig. 3. After their treatment by the method of least squares, the equation of the straight line obtained was:

$$\lg W_{\text{nitr}} = -1.12 + 1.1 \lg P_{NO_2},$$

the tangent of whose angle of inclination gives the order of the reaction with respect to NO_2, equal to 1.1. Thus, the order of the reaction with respect to NO_2, as also with respect to CH_4, is practically equal to unity.

The activation energy of the interaction of CH_4 with NO_2 was determined graphically from the Arrhenius equation for the composition $4CH_4 + 1NO_2$ in the interval

Fig. 2 Fig. 3 Fig. 4

Fig. 2. Determination of the order of the reaction of interaction of CH_4 with NO_2 with respect to CH_4 at $T = 450^\circ$ and $P_{NO_2} = 40$ mm Hg.
1 –root-mean-square error in determining the logarithm of the rate of consumption of NO_2; 2 –root-mean-square error in determining the logarithm of the rate of consumption of NO_2 and the logarithm of the concentration of CH_4.

Fig. 3. Determination of the order of the reaction of interaction of CH_4 with NO_2 with respect to NO_2 at $T = 450^\circ$. Values of P_{CH_4} (in mm Hg): 1 –200, 2 –153, 3 –100. The results of a series of experiments carried out at P_{CH_4} values equal to 153 and 100 mm Hg were transformed to $P_{CH_4} = 200$ mm Hg; 4 – root-mean-square error in determining the logarithm of the rate of consumption of NO_2 and the logarithm of the concentration of NO_2; 5 –coincident result of two measurements.

Fig. 4. Determination of the activation energy of the interaction of CH_4 with NO_2. Mixture $4CH_4 + 1NO_2$. The results of a series of experiments carried out at $P_{\text{init}} = 50$ mm Hg (1) were transformed to $P_{\text{init}} = 100$ mm Hg. (2), (3) – root-mean-square error in determining the logarithm of the rate of consumption of NO_2; 4 –coincident result of two measurements.

temperatures from 400 to 500° for $P_{\text{init}} = 50$ and 100 mm Hg. The results of a series of experiments carried out at $P_{\text{init}} = 50$ mm Hg were transformed to $P_{\text{init}} = 100$ mm Hg, which proved possible to do since the reaction orders were already known. The initial rates of nitration were determined, as indicated above, from the difference between the initial total rate of consumption of NO_2 and the initial rate of dissociation of NO_2. The data for determining E_{nitr} are given in Fig. 4. The straight line was drawn in accordance with the equation obtained by the method of least squares:

$$\lg W_{\text{nitr}} = 9.2 - 6.5\frac{1}{T} \cdot 10^3.$$

The tangent of the angle of inclination of the straight line corresponds to the value $E_{\text{nitr}} = 30.5$ kcal/mole.

In our case, by studying a process that represents a combination of two parallel reactions—the nitration of the hydrocarbon and the dissociation of NO_2—it was possible to determine the value of E_{nitr} by yet another independent route, namely: by comparing the rates of these two reactions.

Let us write the rate equations for these reactions at the same temperature and concentrations of NO_2:

$$W_{\text{nitr}} = f_{\text{nitr}} Z e^{-E_{\text{nitr}}/RT} [CH_4][NO_2], \tag{I}$$

$$W_{\text{diss}} = f_{\text{diss}} Z e^{-E_{\text{diss}}/RT} [NO_2]^2, \tag{II}$$

where Z is the number of collisions and f is the steric factor. Dividing equation (I) by equation (II) and taking the logarithm of the quotient, we obtain

$$E_{\text{nitr}} = \left(\lg \frac{f_{\text{nitr}}}{f_{\text{diss}}} + \lg \frac{[CH_4]}{[NO_2]} - \lg \frac{W_{\text{nitr}}}{W_{\text{diss}}} \right) \frac{RT}{0.43} + E_{\text{diss}}. \tag{III}$$

According to the data of ([11]), $E_{\text{diss}} = 26.9$ kcal/mol, $f_{\text{diss}} = 0.06$; according to the data of ([12]), $E_{\text{diss}} = 27.1$ kcal/mol, and according to our data $E_{\text{diss}} = 27$ kcal/mol. The steric factor for nitration, f_{nitr}, is unknown. In general, for a bimolecular reaction it has values lying in the interval from 10^{-4} to 1.

Taking the limiting values for f_{nitr}, we obtain: for $f_{\text{nitr}} = 10^{-4}$, $E_{\text{nitr}} = 18.4$ kcal/mol, and for $f_{\text{nitr}} = 1$, $E_{\text{nitr}} = 31.9$ kcal/mol (initial conditions, see Table 1, experiment No. 325). There is, however, a possibility of narrowing the range of values of E_{nitr}. As the temperature increases, $W_{\text{nitr}}/W_{\text{diss}}$ increases. Thus, for the composition $4CH_4+1NO_2$, at $P_{\text{initial}} = 50$ mm Hg and 400°, $W_{\text{nitr}}/W_{\text{diss}} = 3$, while at 500°, $W_{\text{nitr}}/W_{\text{diss}} = 12.5$. Consequently, the value of E_{nitr} must be greater than E_{diss}, i.e., E_{nitr} lies in the interval 27–32 kcal/mol. Table 1 gives

data on the determination of E_{nitr} by comparing the rates of nitration of CH_4 and dissociation of NO_2 for various compositions and temperatures.

Comparing the value of E_{nitr} determined from the Arrhenius equation and by the method of comparing the rates of two parallel reactions, we have chosen the value $E_{\text{nitr}} = 30$ kcal/mol.

After adopting the value of E_{nitr}, one can estimate f_{nitr} by substituting the experimentally determined rate values into equation (I). The steric factor for nitration of methane by NO_2 proved to be equal to 0.5.

Table 1

Determination of the activation energy of the reaction of methane with nitrogen dioxide by comparing the rates of methane nitration and nitrogen dioxide dissociation
$E_{\text{diss}} = 26.9$ kcal/mol, $f_{\text{diss}} = 0.06$; $f_{\text{nitr}} = 1.0$

Experiment No.	T,° C	$CH_4 : NO_2$	P_{initial}, mm Hg	P_{CH_4}, mm Hg	P_{NO_2}, mm Hg	W_{nitr}, mm Hg/sec	W_{diss}, mm Hg/sec	E, kcal/mol
325	450	1 : 1	78.5	39.25	39.25	0.67	1.14	29.5 ± 2.5
450	450	6 : 1	239	200	39	3.42	1.14	29.5 ± 2.5
17	500	2 : 1	52.5	35	17.5	4.0	0.8	28.4 ± 1.4
193	500	4 : 1	103.5	82.8	20.7	3.44	1.1	29.4 ± 2.4
508	440	4 : 1	100	80	20	0.68	0.22	29.2 ± 2.2
315	450	4 : 1	121.4	97.8	23.6	1.08	0.42	29.6 ± 2.6

Experiments were carried out in order to determine whether the nitration of methane is a homogeneous or heterogeneous reaction. Replacement of the quartz reactor by a molybdenum one, aging of the reactor, changing the S/V ratio (from 0.97 to 20.0), and coating the reactor walls with KCl had no noticeable effect on the rate of the reaction. This allows one to conclude that the reaction is homogeneous in character.

The kinetic study described for the vapor-phase nitration of CH_4 by nitrogen dioxide led to the following expression for the rate of this reaction:

$$W_{\text{nitr}} = 0.5 \cdot 10^{-10} e^{-\frac{30000}{RT}} \cdot (CH_4)(NO_2)\ \text{l}^{-1} \cdot \text{sec}^{-1}.$$

The question arises whether the reaction rate found is determined by a single, most difficult bimolecular stage of the free-radical process, or whether it is the rate of a complex chain process imitating a bimolecular reaction. A number of authors ([3], [4]) propose the following primary stage of nitration:

$$\mathrm{RH} + \mathrm{NO_2} \rightarrow \dot{\mathrm{R}} + \mathrm{HNO_2}. \tag{1}$$

At present, data have appeared in the literature both confirming the existence of HNO_2 in the gas phase ([13]) and giving values for the heat of formation of gaseous HNO_2 ([14], [15]). The latter makes it possible, for reaction (1) (in the case of methane), first, to carry out a thermochemical calculation of its heat effect and, second, to make an approximate estimate of its activation energy, assuming the applicability to it of the empirical Semenov-Polanyi formula ([16]) for endothermic radical reactions. At $\Delta H_{\mathrm{HNO_2}} = -13.7$ kcal/mole ([14]), $E_{\mathrm{nitr}} = 32.7$ kcal/mole, while at $\Delta H_{\mathrm{HNO_2}} = -20$ kcal/mole ([15]), $E_{\mathrm{nitr}} = 27.9$ kcal/mole.

Thus, the activation energies calculated by us for reaction (1) are close to those determined in the present work from experimental data.

It is also noteworthy that, for the nitration reaction, first orders with respect to CH_4 and NO_2 were obtained, i.e., the same dependence on the concentration of the initial substances as for reaction (1).

All this compels the conclusion that the kinetic regularities of the methane nitration reaction found by us are due to reaction (1), which therefore is the rate-determining stage of the entire process as a whole.

Additional confirmation of this conclusion is provided by results obtained in our laboratory by I. V. Patsevich, who showed that the difference in the activation energies of the two paths of interaction of alkyl radicals with NO_2:

$$\mathrm{RNO_2} \overset{6}{\leftarrow} \dot{\mathrm{R}} + \mathrm{NO_2} \overset{6}{\rightarrow} \mathrm{RONO}$$

is equal to ~ 1 kcal/mole, while the ratio of the steric factors is 0.6. Hence, at 450°, the ratio of the rates is

$$W_a/W_b = 0.6\, e^{1000/2\cdot 723} = 1.2.$$

Since each act of formation of RNO_2 is a chain termination, the maximum chain length in the nitration process cannot be greater than two links. With such a ratio of the rates of reactions (a) and (b), nitration cannot be regarded as a complex chain process imitating a bimolecular reaction.

As a result, the mechanism of methane nitration at those stages where secondary reactions of the intermediate products may be neglected reduces to the following. The difficult act of initiation of alkyl radicals by reaction (1) ($E_{\mathrm{nitr}} = 30$

kcal/mole, $f_{\text{nitr}} = 0.5$) is followed by the interaction of these radicals with NO_2, apparently proceeding with a small activation energy, by reactions (a) and (b), since NO_2 is a radical-like molecule. Therefore it may be considered that the activation energy found, 30 kcal/mole, is the activation energy of the initiation reaction.

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Note: Figure translations are in progress. See original paper for figures.