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Abstract

Full Text

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INTERACTION OF ALKYL RADICALS WITH NITROGEN DIOXIDE

According to current views, the central elementary process in the vapor-phase nitration of alkanes is the interaction of the alkyl radical R with NO₂. It is assumed that it proceeds along two parallel paths, with the formation of nitro compounds and alkyl nitrites:



The further transformation of alkyl nitrites is usually regarded as the source of the oxidation and destruction products of the paraffin chain that are actually obtained in nitration. It is assumed that the primary act of transformation of the alkyl nitrite is its decomposition according to the equation:



Such decomposition occurs either thermally ⁽¹⁾, or, as Gray ⁽²⁾ suggested, at the moment of formation of the alkyl nitrite according to equation (1b). Gray explains such immediate decomposition by the fact that, upon formation of the R'CH₂—ONO bond, 57 kcal/mole of energy is released, whereas rupture of the neighboring R'CH₂O—NO bond requires only 37 kcal/mole. The alkoxy radical, in its subsequent transformations, gives such oxidation products as aldehydes, CO, CO₂. In addition, by interacting with NO, it can give a nitrite already of secondary origin:



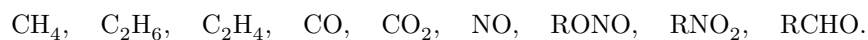
The ideas set forth concerning the mechanism of nitration are hypothetical and have never been tested by a direct experiment. In the present work the direct interaction of R with NO₂ was studied at low temperatures, when thermal transformations of intermediate and final products are excluded. This proved possible because NO₂, having an unpaired electron, is a radical-like molecule, and the interaction $\dot{R} + \text{NO}_2$ proceeds readily at low temperatures. The purpose of the work was to determine whether the two mentioned paths (1a) and (1b) actually take place, to obtain data on the further behavior of RONO, and, from

the dependence of the ratio of the amounts of RNO_2 and RONO formed on temperature, to determine the difference in activation energies (ΔE) and the ratio of the steric factors (f_1 and f_2) of these paths:

$$\frac{\Sigma \text{RNO}_2}{\Sigma \text{RONO}} = \frac{f_1}{f_2} e^{\Delta E/RT}.$$

Alkyl radicals were obtained by the reaction of H atoms with C_2H_4 . A stream of molecular hydrogen containing H atoms was drawn from the discharge tube into the reactor, where C_2H_4 and NO_2 were admixed to it through two inlets. The distance from the point of introduction of C_2H_4 to the point of introduction of NO_2 could be varied, and thus the point at which the radical $\dot{\text{R}}$ met NO_2 along the length of the reactor was changed.

In the products of different series of experiments the following were determined:



The hydrocarbon gases were analyzed chromatographically on charcoal and silica-gel columns; CO , CO_2 , and NO were analyzed by absorption in solutions of cuprous chloride, alkali, and hydrogen peroxide, respectively. Alkyl nitrites were determined by the polarographic method developed by us⁽³⁾. We also developed a method for the polarographic determination of nitroparaffins, alkyl nitrites, and aldehydes in their simultaneous presence.

At first, preliminary study was made of processes which, evidently, may proceed in the reactor along with the main process under investigation, $\dot{\text{R}} + \text{NO}_2$. In the interaction of H atoms with C_2H_4 , only CH_4 and C_2H_6 were found. The heavier hydrocarbons found in this case in a number of works⁽⁴⁻⁶⁾ in various amounts depending on the experimental conditions were not detected under our conditions ($P_{\text{H}_2} = 2.3$ mm, $P_{\text{C}_2\text{H}_4} = 0.05$ mm, $I = 0.07-0.75$ A, $t = 20-90^\circ$). This discrepancy should apparently be attributed to the high concentration of H atoms in our experiments.

It was further shown that, when H atoms interact with NO_2 ($P_{\text{H}_2} = 2.3$ mm, $P_{\text{NO}_2} = 0.08$ mm, $I = 0.75$ A, $t = 20^\circ$), NO is formed. Finally, it was shown that under our conditions of low pressures and low temperatures there is no interaction of C_2H_4 with NO_2 .

The first series of experiments on the study of the interaction of $\dot{\text{R}}$ with NO_2 was carried out with C_2H_4 and NO_2 introduced at one and the same place in the reactor ($P_{\text{H}_2} = 2.3$ mm, $P_{\text{C}_2\text{H}_4} = 0.05$ mm, $P_{\text{NO}_2} = 0.08$ mm, $I = 0.75$ A, $v_{\text{stream}} = 1$ m/sec). In this case the reaction $\dot{\text{R}} + \text{NO}_2$ proceeded in the presence of an excess of H atoms. The results of two typical experiments of this series are given in Table 1.

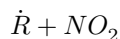
Table 1

Composition of the products of the interaction of \dot{R} with NO_2 in the presence of H atoms, $t = 20^\circ$ (mole percent)

CH_4	C_2H_6	C_2H_4	CO	CO_2	HCHO	RONO	RNO_2
19.1	5.2	59.0	9.0	1.2	5.15	0.94	0.7
22.2	5.65	55.5	6.3	1.24	7.1	1.0	0.85

As is seen from Table 1, both RNO_2 and RONO are detected in the products of the experiments, i.e., two pathways of interaction of \dot{R} with NO_2 are indeed realized. Since thermal decomposition of RNO_2 and RONO at room temperature is excluded, the formation of oxidation products (CO, CO_2 , and HCHO) could be regarded as evidence for the correctness of Gray's ideas on the decomposition of RONO at the moment of formation. In this case it may be assumed that, as a result of the interaction of the radical \dot{RO} formed with H atoms and NO_2 , aldehyde, CO, and CO_2 are obtained, while the presence of RONO in the products would be explained by its secondary formation from the alkoxy radical and NO, produced by the reaction of NO_2 with H atoms. However, special experiments carried out to study the interaction of knowingly introduced C_2H_5ONO with H atoms (but without NO_2) showed that in this case aldehyde and CO are also obtained. In addition, it was found that CH_3NO_2 also interacts with H atoms, the degree of conversion under our conditions reaching 60%.

Thus, both for testing Gray's hypothesis and for finding the true ratio between the RNO_2 and RONO formed, it was necessary to carry out the reaction under study,



in the absence of an excess of H atoms. This was achieved by moving the point of introduction of nitrogen dioxide 90 mm away from the point of meeting of ethylene and atomic hydrogen, increasing the amount of ethylene fed to $P_{C_2H_4} = 0.16$ mm, and decreasing the current in the discharge tube to 0.07 A. All this led to a decrease in the concentration of atomic hydrogen at the point where \dot{R} met NO_2 . As it turned out, in carrying out such an experiment, CO, CO_2 , and aldehydes are absent from the products of the experiment; this means that interaction of RONO with atomic hydrogen does not occur.

Table 2

Behavior of CH_3NO_2 under experimental conditions without an excess of H atoms

Current in discharge tube, A	Found CH_3NO_2 , mm, without introduction of CH_3NO_2	Found CH_3NO_2 , mm, with introduction of CH_3NO_2
0.00	0.0	0.0216
0.07	0.00966	0.0309

To prove that under these conditions there is also no interaction of atomic hydrogen with RNO_2 , we introduced a known amount of CH_3NO_2 into the reaction, feeding it together with NO_2 . As is seen from Table 2, the amount of CH_3NO_2 found in such experiments is equal to the sum of the amount formed in the ordinary experiment under the same conditions (i.e., without addition of CH_3NO_2) and the amount artificially added.

Table 3

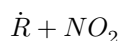
Composition of the products of interaction of \dot{R} with NO_2 without an excess of H atoms

$t, ^\circ C$	Found, mol. %, $RONO$	Found, mol. %, RNO_2	$\frac{RNO_2}{RONO}$	$t, ^\circ C$	Found, mol. %, $RONO$	Found, mol. %, RNO_2	$\frac{RNO_2}{RONO}$
96	31.8	68.2	2.14	-15	21.6	78.4	3.62
50	29.8	70.2	2.35	96	30.0	70.0	2.33
18	29.0	71.0	2.45	50	26.5	73.5	2.76
18	26.3	73.7	2.8	18	22.0	78.0	3.55
				-15	17.6	82.4	4.67

Thus, under the conditions found, there is no interaction of atomic hydrogen either with nitroparaffin or with alkyl nitrite.

The results of two series of experiments, carried out at four different temperatures, are presented in Table 3.

CO, CO_2 , and HCHO were absent from the products of the experiments at all temperatures (at 96° traces of aldehyde were found by the qualitative reaction with dimedone, which apparently indicates the beginning of thermal decomposition of $RONO$ at this temperature). Thus, in this case the products of the interaction



are only RNO_2 and $RONO$.

Fig. 1. Determination of the difference in activation energy of the two paths of interaction of R with NO_2 .

a —first series of experiments; b —second series of experiments.

Following Gray' s ideas about the decomposition of $RONO$ at the moment of its formation by the reaction $\dot{R} + NO_2$, it is impossible to explain its presence in the products of the experiments described above. The “secondary” nitrite, according to Gray, is formed by equation (3). However, under the conditions of our experiments in the reaction zone there may be present only

only insignificant amounts of NO could exist in a large excess of NO_2 . Consequently, as a result of the secondary reaction of RO with NO_2 , only alkyl nitrate $RONO_2$ could be formed. Polarographic analysis does not make it possible to distinguish $RONO$ from $RONO_2$, since both are reduced at the same half-wave potential. Therefore we carried out a spectrophotometric analysis of the products of the experiments, which confirmed the presence of alkyl nitrite in them. In this case the amount of alkyl nitrite determined spectrophotometrically is equal to the total amount of nitrite and nitrate determined polarographically, i.e., in fact only alkyl nitrite is found in the products. This result makes it possible to speak of the incorrectness of Gray' s ideas about the decomposition of nitrite at the moment of its formation from \dot{R} and NO_2 . Apparently, distribution of the excess energy among bonds (without their rupture) and its dissipation in subsequent deactivating collisions are possible.

Table 4

Difference in activation energies and ratio of steric factors for two pathways of the interaction of \dot{R} with NO_2

ΔE , kcal/mol	f_1/f_2
0.84	0.66
1.21	0.50

Using the temperature dependence of the ratio $\frac{RNO_2}{RONO}$, the difference in activation energies of the two pathways of the interaction of \dot{R} with NO_2 can be determined; it is approximately equal to 1 kcal/mol (Fig. 1 and Table 4). From the same dependence we find the ratio of the steric factors $f_1/f_2 \approx 0.6$.

Table 5

Effect of the surface on the interaction of \dot{R} with NO_2

Found, mol. %	Found, mol. %	$\frac{RNO_2}{RONO}$
RNO_2	$RONO$	

	Found, mol. %	Found, mol. %	$\frac{RNO_2}{RONO}$
Without coating	78	22	3.5
Coated with KCl	76.5	23.5	3.3
Coated with $K_2B_4O_7$	77.5	22.5	3.4

Thus, the formation of alkyl nitrite requires a somewhat greater activation energy and has a larger steric factor than the formation of nitroparaffin.

To check the role of the surface in the reaction $\dot{R}+NO_2$, experiments were carried out in a reactor whose surface was coated with KCl and $K_2B_4O_7$. No change in the composition or amounts of the products was found, which indicates the homogeneous character of the reaction of alkyl radicals with nitrogen dioxide (Table 5).

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