nal acetylenes studied.[32] However, the small band shifts indicate that the hydrogen bonds are weak. Furthermore, the spectra show that association is quite incomplete even in the pure liquids. The

(32) The hydrogen bonding in the 1-alkynes must take place between the acetylenic hydrogen on one molecule and the pi electrons of the triple bond on another. In phenylacetylene and the propargyl halides, the pi electrons of the aromatic ring and the unshared electron pairs on the halogens can also serve as basic sites in intermolecular hydrogen bonding.

effect of the intermolecular association upon the gross physical properties of 1-alkynes therefore is slight.

[Contribution from the Institute of Inorganic and Analytical Chemistry, University of Szeged, Szeged, Hungary]

Mechanism of Influencing the Thermal Decomposition of Propionaldehyde by Nitric Oxide

By Z. G. Szabó and F. Márta

The mechanism of influencing the thermal decomposition of propionaldehyde by nitric oxide is established. The correctness of the mechanism as described is partially supported by the fact that the values of the influencing factors found experimentally and calculated on the basis of the mechanism agree excellently in each case. From this mechanism it is evident that the double effect experimentally found can be ascribed to the fact that a portion of the chain carrying radicals is combined with nitric oxide and the ratio of the reactions occurring with stabilized and non-stabilized radicals causes the inhibition or the catalysis, depending on its concentration.

I. Introduction

More than two decades ago Hinshelwood and his co-workers[1] had observed that the rate of the thermal decomposition of organic substances is altered markedly by nitric oxide. The most striking feature was that in certain cases nitric oxide, depending on its concentration, could either increase or decrease the velocity of the *same* process. In order to interpret the inhibiting effect by nitric oxide, it was reasonable to suppose that nitric oxide combines with chain carrying radicals and thus reduces the rate of the process. However, the interpretation of the catalytic effect of nitric oxide has remained essentially unexplained. All the endeavors aiming to establish the mechanism of the reaction affected by nitric oxide, especially in the case of the double effect, have been unsuccessful, owing to the lack of systematic experiments necessary to throw light on this problem.

Some years ago Szabó and his co-workers[2,3] had published their conception by which the influencing by nitric oxide, even also its double effect can be unitarily interpreted. According to the theorem of stabilization of free radicals, nitric oxide forms a more or less stable complex with the chain carriers. These stabilized and non-stabilized radicals then react either with each other or with the molecule of the initial substance. In other words this means that the stabilization of the radicals results in new rupturing and propagating steps, the rate of which may considerably differ from those of the corresponding reactions of the non-stabilized radicals. Thus the same substance may exert two entirely opposite effects depending only on the ratio of concentrations which determine whether the reaction steps of the original non-

stabilized radicals or those of the stabilized radicals are dominating. Because at that time the lack of data in the literature had rendered it possible to prove this theory only roughly, very detailed and systematic investigations have been performed in order to elucidate the mechanism of the effect of nitric oxide. As is well known, nitric oxide exerts a double effect on the thermal decomposition of propionaldehyde. Therefore this reaction seemed to be a proper model for the above purposes.

II. Experimental Method and Results

The apparatus applied in the experiments has already rendered good services at our institute.[4] By applying glass valves instead of greased stopcocks and by carefully keeping impurities off the reaction zone, it was possible to work under extremely clean conditions.

From experimental data it became evident that the thermal decomposition of propionaldehyde is not a monomolecular process of first order—as supposed by Hinshelwood and his co-workers[5,6]—but the reaction runs down according to the Rice–Herzfeld mechanism with rupturing of β,β type.[7] The reaction of this type has the order 3/2 which was proved by our experimental data, $i.e.$, from the dependence of the initial rate on the pressure, from the time of the half-change, and by following the course of the experiments in time. To lend support to the above facts, rate constants calculated according to the first and 3/2 order are compared in Table I. Rate constants calculated according to order 3/2 are summarized in Table II.

From the dependence of rate constants on temperature 52.4 ± 1 kcal. is obtained for the activation energy of the process. Our calculations on the order of reaction and the activation energy are supported by Boyer and Niclause's[8] investigations, too. They found the same order from the dependence of the initial rates on pressure and 50.3 ± 2 kcal. for the activation energy.

(1) L. A. K. Staveley and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A154**, 335 (1936).

(2) Z. G. Szabó, *Nature*, **170**, 246 (1952).

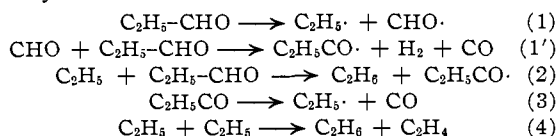(3) Z. G. Szabó, *Acta Chim. Acad. Sci. Hung.*, **3**, 139 (1953).

(4) Z. G. Szabó and D. Gál, *Combustion and Flame*, **1**, 404 (1957).

(5) C. N. Hinshelwood and H. W. Thompson, *Proc. Roy. Soc. (London)*, **A113**, 221 (1926).

(6) C. A. Winkler, C. J. Fletcher and C. N. Hinshelwood, *ibid.*, **A146**, 345 (1934).

(7) P. Goldfinger, M. Letort and M. Niclause, "Contribution á l'Etude de la Structure Moléculaire," Victor Henri Commemorative Volume, Descar, Liége, 1948, p. 283.

(8) A. Boyer and M. Niclause, *J. Chim. Phys.*, **49**, 354 (1952).

TABLE I

COMPARISON OF RATE CONSTANTS CALCULATED ACCORDING TO FIRST AND 3/2 ORDER

149/515°; $P_0 = 250$ mm.

t, min.	ΔP	$\Delta P/\Delta t$	First order $k \times 10^{+2}$	3/2 order $k \times 10^{+3}$
0.25	3.5	8.48	3.44	2.09
0.49	6.5	7.62	3.24	2.09
1.17	10.0	7.51	3.18	2.03
2	15.8	8.00	3.24	2.10
2.35	19.7	6.65	3.17	2.06
3.19	24.3	6.40	3.09	2.04
3.52	28.0	6.60	3.08	2.02
5	35.9	6.95	3.09	2.04
6	41.8	5.95	3.04	2.03
7	48.7	6.87	3.10	2.06
8	54.0	5.29	3.04	2.05
10	65.1	5.56	3.01	2.07
12	74.5	4.71	2.94	2.04
14	83.8	4.66	2.92	2.06
16	92.7	4.31	2.89	2.07
18	100.0	4.16	2.83	2.04
20	107.9	3.95	2.82	2.07
25	123.9	3.20	2.73	2.07
30	136.9	2.60	2.64	2.05
40	160.0	2.30	2.55	2.10
55	181.0	1.40	2.34	2.07
70	196.8	1.05	2.21	2.11
90	209.5	0.63	2.02	2.07
135	226.2	0.37	1.74	2.06
180	234.4	0.18	1.53	2.08

Mean value 2.06

TABLE II

RATE CONSTANTS CALCULATED ACCORDING TO 3/2 ORDER

k in mm.$^{-1/2}$ min.$^{-1}$ $\times 10^{+3}$

T °C.	$P_0 = 100$, mm.	$P_0 = 150$, mm.	$P_0 = 200$, mm.	$P_0 = 250$, mm.	Mean value
515	2.07	2.07	2.07	2.06	2.07
535	5.15	5.10	5.18	5.12	5.137
550	8.73	8.55	8.68	8.38	8.58
565	17.66	17.69	17.52	17.47	17.58

The effect of inert gases and of products formed during the reaction had also been investigated by us, and were found to have no influence on the reaction rate. On the basis of our experimental data the elementary steps which mainly determine the reaction rate are:

$$C_2H_5\text{-CHO} \longrightarrow C_2H_5\cdot + CHO\cdot \qquad (1)$$
$$CHO + C_2H_5\text{-CHO} \longrightarrow C_2H_5CO\cdot + H_2 + CO \qquad (1')$$
$$C_2H_5 + C_2H_5\text{-CHO} \longrightarrow C_2H_6 + C_2H_5CO\cdot \qquad (2)$$
$$C_2H_5CO \longrightarrow C_2H_5\cdot + CO \qquad (3)$$
$$C_2H_5 + C_2H_5 \longrightarrow C_2H_6 + C_2H_4 \qquad (4)$$

From this scheme, by applying the method of the quasi-stationary concentrations of the radicals, by considering the role of the radical CHO from the point of view of the formation of ethyl radical in the sense that it redoubles the primary step in the very rapid 1' and 3 reaction and lastly by taking into account that the consumption of propionaldehyde is negligible in the chain-starting first reaction, Rice-Herzfeld's rate equation containing the 3/2 power of the initial substance can be derived

$$-\frac{d[C_2H_5CHO]}{dt} = k_2 \sqrt{\frac{2k_1}{k_4}} C_2H_5CHO^{3/2} \qquad (a)$$

Many data are to be found in the literature concerning the rate of the 4th and 2nd elementary steps. We take for the activation energy of reaction (2) 7,500 cal., for its pre-exponential factor, on the basis of Volman and Brinton's[9]

(9) H. D. Volman and R. K. Brinton, J. Chem. Phys., 22, 929 (1954).

data, 2.35 × 10⁸ l. mole⁻¹sec.⁻¹. The activation energy of reaction 4 is zero, its A value, according to data of Steacie and his co-workers[10,11] and Shepp and Kutschke,[12] is 1.6 × 10¹⁰ l. mole⁻¹sec.⁻¹. Taking into consideration these data, the value of the rate constant of the primary reaction was calculated; from its dependence on the temperature the activation energy of the starting step was given as 82.8 ± 2 kcal.

Knowing this rate constant it became possible to determine the ethyl radical concentration and kinetic chain-length, too. Carrying out the calculations in the temperature and pressure range applied by us, we obtain 5 × 10⁻¹¹– 6 × 10⁻¹² mole/l. for the concentration of ethyl radicals and 3 × 10⁴ for the kinetic chain length.

The concentration of nitric oxide had never been changed in one direction only but we applied alternately large and small quantities.

It had been established that the effect of nitric oxide is independent of the initial concentration of propionaldehyde. This is shown in Fig. 1. The kinetic curves do not show really any trend as functions of the initial aldehyde concentrations. The values of the influencing factor $F(I)$— see below—are to be obtained from the comparison of kinetic data of reactions taking place with and without nitric oxide.
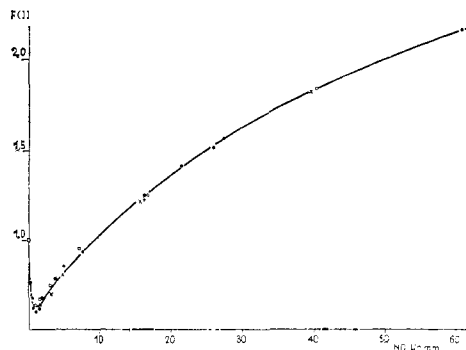

Fig. 1.—Change of $F(I)$ as function of nitric oxide concentration at different initial concentrations of propionaldehyde.

In the presence of nitric oxide the over-all reaction order is also unequivocally 3/2 both in the inhibited and catalyzed intervals. To illustrate this, in the case of catalysis, data are given in Table III.

The results of experiments carried out in presence of nitric oxide at different temperatures are summarized in Fig. 2. From Fig. 2 it is obvious that raising the temperature increases the inhibition and at the same time the extent of catalysis is lowered. Further, the rate minima, belonging to single temperatures, on increasing temperature are shifted toward larger nitric oxide concentration. We shall interpret this phenomenon later.

The experiments in presence of inert gases and of reaction products have proven that even in the presence of nitric oxide heterogeneous processes must not be taken into consideration since the effect of nitric oxide in each case was the same as in their absence. This is to be seen from Table IV, where the $F(I)$ values found in the case of different gases are compared at the same nitric oxide concentrations.

There are different opinions about the fate of nitric oxide after taking part in the reaction. According to several authors[13–15] nitric oxide, during its reaction with different radicals, is destroyed or transferred into a product which in this form cannot exert the original effect. However, there

(10) K. I. Ivin, M. H. Wijnen and E. W. R. Steacie, J. Phys. Chem., 56, 967 (1952).

(11) K. I. Ivin and E. W. R. Steacie, Proc. Roy. Soc. (London), A208, 25 (1951).

(12) A. Shepp and K. O. Kutschke, J. Chem. Phys., 26, 1020 (1957).

(13) L. A. K. Staveley and C. N. Hinshelwood, Proc. Roy. Soc. (London), A159, 192 (1937).

(14) C. R. Freeman, C. J. Danby and C. N. Hinshelwood, ibid., A245, 28 (1958).

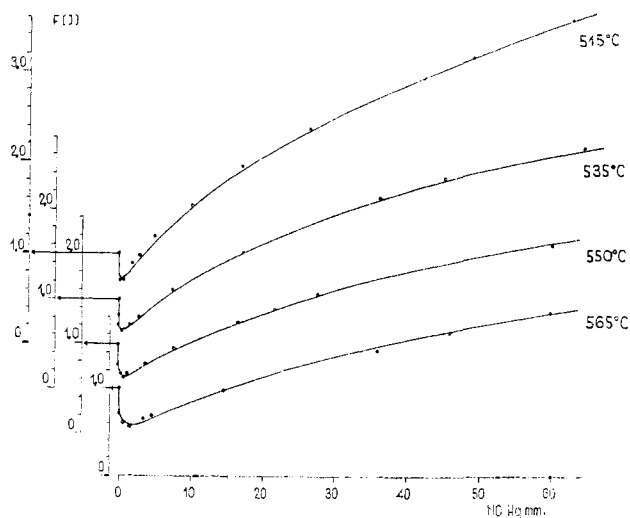(15) C. R. Freeman, C. J. Danby and C. N. Hinshelwood, ibid., A245, 456 (1958).

Fig. 2.—Comparison of calculated and experimentally found $F(I)$ values: •, measured; —, calculated data. $515°, \beta = 1.3$, $\delta_1 = 4.1, \delta_2 = 0.003$; $535°, \beta = 0.85, \delta_1 = 3.1, \delta_2 = 0.0017$; $550°, \beta = 0.65$; $\delta_1 = 2.75, \delta_2 = 0.0011$; $565°, \beta = 0.50, \delta_1 = 2.30, \delta_2 = 0.0007$.
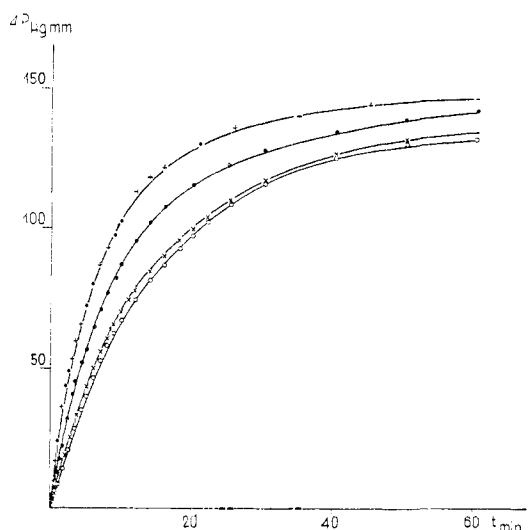

Fig. 3.—Decomposition of propionaldehyde without nitric oxide and at different nitric oxide concentrations: •, no nitric oxide; O, 1.2 mm. nitric oxide; ×, 0.8 mm. nitric oxide; +, 21.5 mm. nitric oxide.

are references in literature[14,16,17] that nitric oxide is not consumed during the reaction. We ascertained that the rate of the inhibited reaction during the total process does not approach the rate of the reaction without nitric oxide. Fig. 3 illustrates this. These experimental facts indicated that nitric oxide is not consumed during this reaction, as it is reacting irreversibly, e.g., in the decomposition of dimethylether.[18] A more convincing fact is rendered from the experiments in which, after the reaction performed with a given nitric oxide concentration, the same amount of aldehyde as previously applied was introduced into the reaction vessel and the decomposition took place totally. During this second reaction—without introducing new nitric oxide—the effect of the influencing substance was of exactly the same extent as in the first case.

(16) L. S. Echols and R. N. Pease, THIS JOURNAL, 61, 1024 (1939).

(17) H. A. Taylor and V. V. Vesselovsky, J. Phys. Chem., 39, 1095 (1935).

(18) L. A. K. Staveley and C. N. Hinshelwood, Proc. Roy. Soc. (London), A159, 192 (1937).

TABLE III
RATE CONSTANTS CALCULATED ACCORDING TO 3/2 ORDER IN PRESENCE OF NO
137/515°; $P_{aldehyde} = 150$ mm., $P_{NO} = 48.5$ mm.

t, min.	ΔP, mm.	$k \times 10^{+2}$
0.22	4.4	6.81
0.49	8.6	6.52
1.15	14.0	6.67
1.41	18.5	6.70
2.18	24.1	6.51
2.44	28.0	6.53
3.8	31.5	6.56
3.48	37.3	6.65
4.18	41.0	6.58
5	46.4	6.64
6	52.3	6.52
7	58.7	6.59
8	64.5	6.61
9	69.1	6.54
10	74.0	6.61
12	82.0	6.57
14	90.0	6.77
16	95.6	6.68
18	100.2	6.62
20	104.0	6.54
25	112.6	6.52
27	116.0	6.63
33	123.0	6.70
205	148.2	6.59

Mean value 6.61

TABLE IV
EFFECT OF NEUTRAL GASES ON THE VALUE OF $F(I)$
$550°$ $P_{aldehyde} = 150$ mm.

	54 mm. N_2	53 mm. H_2	50 mm. C_2H_6
	19.5 mm. NO	16 mm. NO	7.5 mm. NO
$F(I)$	1.31	1.21	0.92
	19.5 mm. NO	16 mm. NO	7.5 mm. NO
$F(I)$	1.31	1.21	0.92

III. Discussion

In the case of the decomposition of propionaldehyde, not influenced by nitric oxide, as we have seen, the rate controlling reaction steps to be considered are

$$A \longrightarrow 2R \qquad\qquad 1$$
$$R + A \longrightarrow R + E \qquad 2^I$$
$$R + R \longrightarrow E \qquad\qquad 4^I$$
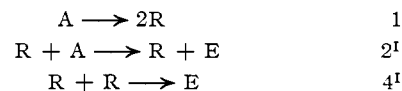
where A, R and E denote the concentration of the propionaldehyde, the ethyl radical and of the end product, respectively.
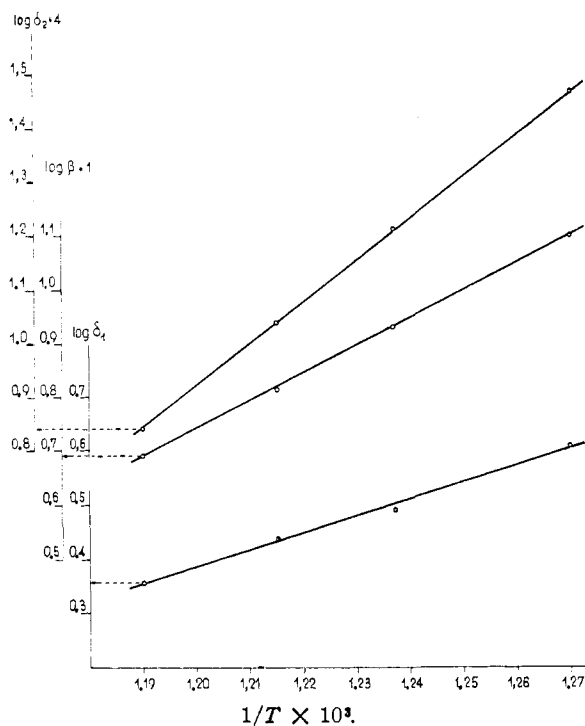
As has been pointed out in eq. (2), from this mechanism the rate equation can be deduced.

$$-\frac{dA}{dt} = k_2^I \sqrt{\frac{2k_1}{k_4}}{}^i A^{3/2} \qquad (b)$$

When some I influencing substance is added to the reaction mixture (in this case nitric oxide), it reacts with radicals formed during the process according to the reaction
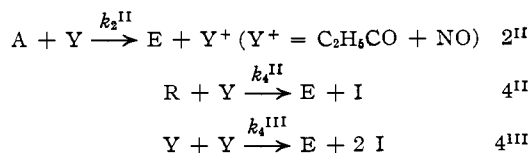
$$R + NO(I) \underset{K^-}{\overset{K^+}{\rightleftarrows}} RNO = Y$$
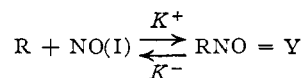
and forms with them a complex of certain stability

Fig. 4.—Temperature dependence of β, δ_1 and δ_2.

defined by the equilibrium always established

$$K = \frac{K^-}{K^+} = \frac{[R][NO]}{[RNO]}$$

However, in this case the following elementary acts must be added to the elementary steps of the non-influenced reaction

$$A + Y \xrightarrow{k_2{}^{II}} E + Y^+ \ (Y^+ = C_2H_5CO + NO) \quad 2^{II}$$

$$R + Y \xrightarrow{k_4{}^{II}} E + I \qquad\qquad 4^{II}$$

$$Y + Y \xrightarrow{k_4{}^{III}} E + 2\ I \qquad\qquad 4^{III}$$

where 2^{II}, 4^{II} and 4^{III} are the new chain carrying and chain breaking steps arising from stabilized radicals RNO. In an earlier paper[19] we had already pointed out that from this enlarged mechanism rate equation (3) can be deduced

$$-\frac{dA}{dt} = k_2{}^I \sqrt{\frac{2k_1}{k_4}}{}^t F(I) A^{3/2} \qquad (3)$$

where

$$F(I) = \frac{1 + \beta I}{\sqrt{1 + 2\delta_1 I + \delta_2 I^2}} \qquad (4)$$

is the above mentioned influencing factor, reflecting the extent of variations of the reaction rate. The constants in expression $F(I)$ give the ratios

$$\beta = \frac{k_2{}^{11}}{k_2{}^I}\frac{1}{K} \ ; \ \delta_1 = \frac{k_4{}^{II}}{k_4{}^I}\frac{1}{K}; \ \delta_2 = \frac{k_4{}^{III}}{k_4{}^I}\frac{1}{K^2}$$

of the chain carrying and chain rupturing steps of the influenced and non-influenced reactions, respectively.

The connection between the influencing factor and the time of half-change[20] can be derived,

(19) Z. G. Szabo, P. Huhn and A. Bergh, "Advances in Catalysis and Related Subjects," 9, 333 (1957).

(20) P. Huhn and F. Marta, Acta Phys. Chim. Szeged, IV, 38 (1958).
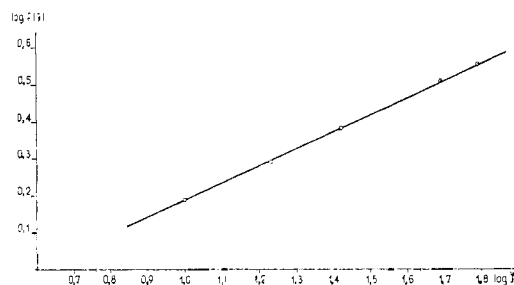
Fig. 5.—The plotting of logarithms of $F(I)$ against logarithms of nitric oxide concentration.

as previously, after explicit integration of the rate equations of influenced and non-influenced reactions; then having compared them, we have the expression

$$F(I) = \frac{t_{1/2}{}^{(0)}}{t_{1/2}{}^{(I)}}$$

which renders it possible to check easily the influencing factor with the experimental results. In the way of this comparison the values of constants β, δ_1 and δ_2 can be determined. Some simple relations serve as basis for this determination, existing between the characteristic data of the influencing factor and its constants (cf. ref. 19). Using the constant obtained, the value of $F(I)$ at different nitric oxide concentrations can be calculated. The agreement between the values of $F(I)$ calculated from equation 4 and experimentally found, is shown in Fig. 2 in which data of our experiments, carried out at different temperatures, are plotted. As may be seen from the figures, the calculated and experimentally found values agree very well. This agreement proves simultaneously that for the interpretation of the nitric oxide effect a correct mechanism was assumed since the influencing factor is derived on the basis of this scheme. Constants β, δ_1 and δ_2 being partly products and partly quotient expressions, plotting their logarithms as an Arrhenius function, shows excellent linearity (Fig. 4). On comparing this fact with the peculiar way of determination of the values β, δ_1 and δ_2 and further with the fact that the effect of the influencing substance—as it is proved by experimental results—can be selected in a factor depending only on the concentration of the influencing substance, the correctness of the assumed mechanism seems to be confirmed.

In the discussion of experimental data we had already mentioned that the effect of nitric oxide is independent of the concentration of propionaldehyde. Equation 4 of the influencing factor really contains only the dependence on the nitric oxide. This statement may seem curious at first, since one often comes across the opinion that the inhibition depends on the concentration of the initial substance only when the inhibitor removes the radical reacting directly with the initial molecule. In our case the inhibitor stabilizes the radical reacting directly with the aldehyde molecule; therefore it may be expected that the influencing factor also depends on the initial concentration of aldehyde. But it is not so. However, this circumstance cannot be regarded as a contradiction, i.e., the inter-

dependence of the influencing factor and of the concentration of the initial substance exists only in the case of certain concrete mechanisms and is not a general characteristic of the mechanism of inhibited reactions. This is shown in the general reaction scheme suggested by Szabó and his co-workers,[19] namely, the influencing depends firstly on the molecularity of the rupturing reactions, secondly on the order of the influenced and non-influenced reaction. From the above mentioned reaction scheme, it can be stated that the influencing factor depends on the concentration of the influencing substance *alone* only when the reaction order is 3/2 both in the case of influenced and non-influenced reactions, further when the constants of the rupturing reactions, k_4^I and k_4^{III}, are bimolecular. This condition is fulfilled in the decomposition of propionaldehyde influenced by nitric oxide.

As we have seen the reaction rate in the presence of nitric oxide can be written by the equation

$$-\frac{dA}{dt} = k_2^I \sqrt{\frac{2k_1}{k_4^I}} A^{3/2} F(I)$$

This equation sums up the dependence of nitric oxide in the influencing factor, and on this basis we cannot speak about any reaction order in the effect of nitric oxide. However, in the examination of inhibition and catalytic phenomena—especially to interpret the zone following after the minimum of catalysis or inhibition—certain authors very frequently take up some reaction order of the influencing substance. It deserves attention to examine whether expression 4 of the influencing factor $F(I)$ is compatible with any reaction order. In the present case, the change of values of the influencing factor proves that this is possible, in the present range of 15–200 mm. of NO when in $F(I)\beta I \gg 1$ and $2\delta_1 I \gg 1 + \delta_2 I^2$ in first approximation is given. In this phase the influencing

$$F(I) = \frac{\beta I}{\sqrt{2\delta_1 I}} = \frac{\beta}{\sqrt{2\delta_1}} \sqrt{I}$$

factor behaves nearly as an expression proportional to $\sqrt{I}$. This may be more convincingly shown when plotting $\log F(I)$ against $\log I$, *i.e.*, if

$$F(I) = CI^\nu$$

from what we can write

$$\log F(I) = \log C + \nu \log I$$

On this basis, from the *local* linearity, we can draw conclusions as to the supposed order of reaction. This plotting is to be seen in Fig. 5. In the range of 15–200 mm. pressure the linearity is satisfactory and from the slope of the curve 0.45 follows for the value of the exponent ν.

This mechanism attributed to the reaction is in accordance also with the experimental fact that nitric oxide, introduced into the reacting system, exerts its effect not by consuming itself; in our mechanism nitric oxide is really regenerated at the same time as the reaction products are formed.

The explanation of the effect of nitric oxide on the decomposition mechanism of propionaldehyde may be sought in the relation of the new steps introduced by nitric oxide and of the original ele-

mentary steps. These relations depend on the concentration of the influencing substance.
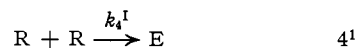
The inhibition at low nitric oxide concentration, therefore, is attributed to the fact that the frequency of the reaction
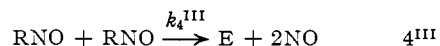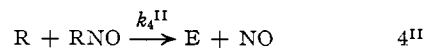
$$R + A \xrightarrow{k_2^I} R + E \qquad 2^I$$
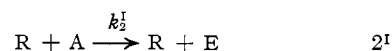
owing to the decrease of the concentration of radicals R, becomes smaller which cannot be compensated even by including the reaction step

$$RNO + A \xrightarrow{k_2^{II}} E + R' \qquad 2^{II}$$
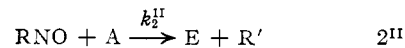
since, besides the original breaking reaction

$$R + R \xrightarrow{k_4^I} E \qquad 4^I$$

rupturing steps

$$R + RNO \xrightarrow{k_4^{II}} E + NO \qquad 4^{II}$$

$$RNO + RNO \xrightarrow{k_4^{III}} E + 2NO \qquad 4^{III}$$

also occur, *i.e.*, a more considerable increase of the breaking rate, especially in the reaction 4^{II}, results in a fall in the velocity of the process, since this fall is not compensated by the relative increase caused by reaction 2^{II}. At a certain nitric oxide concentration the fall in the rate ceases. Then the breaking reaction 4^{II} which depends on the square-root of I, does not compensate any further the acceleration caused by reaction 2^{II}. Therefore the rate begins to rise, it may even become greater than the rate of the pure reaction. However, it does not increase infinitely, because the rupture 4^{III} becoming more and more dominating with the increasing nitric oxide concentration, compensates the increase of the numerator toward the infinite with the increase of the denominator toward the infinite in the same order. Of course, in the zone where the catalytic effect dominates, the reaction, causing inhibition, also exists, but in this case the reaction steps, increasing the rate of the process dominate, while in the inhibited phase those resulting in its decrease are overwhelming.

The effect of temperature on the influenced reaction presented in Fig. 2, which mean that a rising temperature the extent of inhibition increases and attains minimum at larger nitric oxide concentration, while the extent of catalysis, when compared with that of the lower temperature, diminished, also may be interpreted easily. It is sufficient only to take into consideration the temperature dependence of the relations of β, *i.e.*, that of 2^I and 2^{II} chain carrying steps and δ_1 and δ_2, those of the breaking reactions, respectively. From this it is obvious that the value of β more markedly decreases with rising temperature than that of the breaking steps, especially on comparing with δ_1, the decisive role of which, from the point of view of the rate of the process, we have seen already. This is the cause of the phenomena experimentally found, *i.e.*, that at lower temperatures the curve is steeper in its initial course, it changes earlier and the catalysis is of greater extent, while at higher temperatures the slope is smaller, the transition comes later and the catalysis is of smaller extent. The temperature dependence of

δ_1 and δ_2 gives two activation energies. From Fig. 4 it is further to be seen that the slope of δ_2 is nearly twice that of δ_1. Assuming the activation energies for the breaking reactions zero or at least nearly the same amount, it follows that the temperature dependence of δ_1 and δ_2, respectively, is governed through the reaction heat of the stabilization, i.e., through the K.

Thus it can be seen that the reaction mechanism taken up by us from a unitary viewpoint gives an illustrative interpretation of the course of the re- action in good agreement with experimental data. For the interpretation of the maximum inhibition it is not necessary to suppose the existence of a molecular reaction, which is inevitable when sup- posing that the effect of nitric oxide appears only in the breaking of the chains, and it is also un- necessary to interpret the catalysis through a direct reaction of nitric oxide with the initial substance, which would not be correct even because the rate does not increase proportionally to the concentra- tion of nitric oxide.

Electron Impact Spectroscopy of Ethylene Oxide and Propylene Oxide[1]

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RECEIVED AUGUST 8, 1960

Appearance potentials and relative abundances are reported for the principal positive ions in the mass spectra of ethylene oxide and propylene oxide, obtained using a Bendix 12-100 time-of-flight mass spectrometer. Probable ionization and dis- sociation processes are given consistent with computed energetics and the heats of formation of the various ions derived from the energetics are tabulated. Molecular ionization potentials are calculated using the equivalent orbital method of Hall and are compared to the observed ionization potentials of 10.65 ± 0.1 e.v. for ethylene oxide and 9.80 ± 0.1 e.v. for propylene oxide.

Introduction

Electron impact spectroscopy has been reported for a number of oxygen-containing molecules, in- cluding among others, ethers, alcohols, acids, ketones, esters and some inorganic oxygen-contain- ing compounds.[2] However, very little has been done with the cyclic ethers, although the API tables of mass spectra[3] and Beynon[4] list the mass spectral cracking patterns for a number of the cyclic ethers. The present study was initiated to obtain fundamental information concerning the ionization potentials, bond dissociation energies, heats of formation of the various ionic products of the ionization and dissociation processes and the manner in which the mass spectra are produced for these compounds. The measured ionization poten- tial for ethylene oxide is compared with others reported in the literature while that for propylene oxide is newly reported. These results have been used in a theoretical calculation of ionization potentials for other epoxides.

Experimental

The mass spectra and appearance potentials herein re- ported were obtained using a Bendix time-of-flight (TOF) model 12-100 mass spectrometer with an analog output system consisting of a monitor and a scanner. Wiley[5] and others[6-10] have described the TOF mass spectrometer, and recently Harrington[11] has described in detail the Bendix TOF instrument.

The ions formed were pulsed at a repetition rate of 10 kc. into an electric field of 3000 v., providing ion accelera- tion. The drift tube has a flight path of one meter. Only analyses for positive ions were made. Ion currents were measured using an electrometer amplifier following the ectron multiplier and the results recorded on a Sanborn model 152 recording system.

Mass spectra were obtained for nominal electron energies of 70 v. The ionizing voltage scale was calibrated by com- paring the observed ionization potentials of krypton, xenon and mercury (background from the diffusion pump) with the known spectroscopic values.[12] Appearance potentials were evaluated by the method of extrapolated difference described by Warren.[13] This method has been found to give results in good agreement with reliable kinetic data.[14] The linear portion of the ionization efficiency (i.e.) curves were forced to be parallel in plotting and then the voltage difference, ΔE, between the two i.e. curves at any given current, i, was plotted as a function of i. The resultant curve, upon extrapolation to $i = 0$, gave a value of ΔE which was algebraically added to the ionization potential of the standard to obtain the appearance potential for the ion in question.

Figure 1 shows the calibration of the electron energy scale for this work. The slope of this calibration curve is 1.034. Ionization potentials were also determined using the tech- nique of Lossing, Tickner and Bryce.[15] A typical plot of the i.e. curves for ethylene oxide and propylene oxide is shown in Fig. 2 and is compared to that for the krypton standard.

The samples (white label) of ethylene oxide and propylene oxide were obtained from Eastman Organic Chemicals.

(1) This work was supported in part by the U. S. Atomic Energy Commission, under Contract No. AT(11-1)-751 with Kansas State University. Portion of a dissertation to be presented by E. J. Gallegos to the Graduate School of Kansas State University in partial fulfill- ment for the degree of Doctor of Philosophy in Chemistry.

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