188. *The Detection of Reaction Chains by Small Amounts of Nitric Oxide. The Thermal Decomposition of Acetaldehyde and of Propaldehyde.*

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The rate of the homogeneous thermal decomposition of ethyl ether can be reduced to about one-third by the addition of amounts of nitric oxide of the order of a millimetre (Staveley and Hinshelwood, *Proc. Roy. Soc.*, 1936, *A*, **154**, 335; *Nature*, 1936, **137**, 29). This suggests that in the normal decomposition of ether, short chains are involved, which according to current ideas would be radical chains, and that nitric oxide breaks these by removing the free radicals from the system. Since only the average chain length is known, it has not so far been possible to decide whether dissociation of an activated ether molecule always yields radicals, giving chains of about three cycles, or whether only a few molecules give much longer chains. An upper limit to their length is set by the fact that the decomposition of ether has none of the characteristics associated with long chains.

While the inhibiting action of nitric oxide in organic decomposition reactions is not a general one, it is nevertheless not restricted to the single case of ethyl ether. The use of nitric oxide as a means of detecting short chains accordingly opens up two main fields of investigation. One is the detailed examination of the kinetics of typical reactions which are inhibited by nitric oxide, with the object of obtaining further information about their mechanism. The other is the systematic survey of different types of organic reaction in order to find which of these involve a chain mechanism, and to establish any connections between chain-length and molecular structure. Nitric oxide provides a definite quantitative test for the presence of chains, and absence of inhibition may be taken as evidence for their absence. This is shown by two facts : first, that different types of thermal reaction have their rates reduced, but only to definite limits, and, secondly, that nitric oxide reduces the quantum yield in the photocatalytic decomposition of acetaldehyde from several hundred to nearly unity (Mitchell, unpublished observations).

The decomposition of propaldehyde shows inhibition by small amounts of nitric oxide, and as it has points of kinetic interest not found with ethyl ether, it was thought that detailed investigation might be profitable. The decomposition of acetaldehyde, however, is completely exempt from the inhibition. As the results obtained with propaldehyde provide a clue to the reasons for this different behaviour, the two substances will be treated together.

EXPERIMENTAL.

The apparatus and method used in the investigation were essentially the same as those previously employed.

As it has been found that the decomposition of aldehydes is strongly catalysed by small amounts of oxygen, the bulb containing the aldehyde was periodically cooled in a mixture of solid carbon dioxide and acetone and evacuated. Special precautions were taken throughout to avoid access of air.

The Influence of Small Amounts of Nitric Oxide on the Decomposition of Acetaldehyde.—The acetaldehyde used was carefully distilled in an all-glass apparatus (b. p. 20·4—21·0°).

That nitric oxide has no detectable inhibiting influence whatsoever on the decomposition of acetaldehyde is shown by Table I, where $t_{\frac{1}{2}}$ is the time required for 50% of the aldehyde to react.

TABLE I.

Influence of nitric oxide on the decomposition of acetaldehyde.

Temp. 559°. Initial pressure of aldehyde 150 mm.

NO (mm.)	0	0·11	0·53	1·0	5·5
$t_{\frac{1}{2}}$ (sec.)	173	174	172	165	132

The decomposition of acetaldehyde is positively catalysed by large amounts of nitric oxide (Verhoek, *Trans. Faraday Soc.*, **1935**, **31**, 1533). It will be seen from Table I that even 5·5 mm. of nitric oxide noticeably increase the rate of decomposition.

The absence of inhibition shows a non-chain mechanism for the decomposition of acetaldehyde. Rice and Herzfeld (*J. Amer. Chem. Soc.*, **1934**, **56**, 284) have suggested a chain mechanism with the following primary process : $CH_3{\cdot}CHO \longrightarrow CH_3 + CHO$. The observed activation energy of the decomposition is between 55,500 and 47,700 cals., according to the initial pressure, whereas the above primary process would require about 70,000. To account for the observed reaction rate the chains would have to be very long. One would therefore expect to find the wall effects characteristic of long-chain reactions, but in reality at the temperatures in question these are entirely absent (*Proc. Roy. Soc.*, **1935**, *A*, **149**, 355). The fact that the decomposition of acetaldehyde can be accelerated by the addition of azomethane has been taken to support the chain mechanism (Sickman and Allen, *J. Amer. Chem. Soc.*, **1934**, **56**, 1251), methyl radicals being assumed to be formed by the thermal decomposition of the azomethane, and to react with aldehyde molecules. It must be borne in mind, however, that the decomposition of acetaldehyde can also be catalysed by a number of very simple inorganic substances, such as iodine, hydrogen sulphide and nitric oxide. For the high-temperature photochemical reaction, Leermakers (*ibid.*, p. 1537) found a high quantum yield. The photochemical production of free radicals, which might in any case be expected, from what we know of other catalysts (Bairstow and Hinshelwood, *Proc. Roy. Soc.*, **1933**, *A*, **142**, 77; Fromherz, *Z. physikal. Chem.*, **1934**, *B*, **25**, 301; Hinshelwood, J., **1935**, **1111**), to have a catalytic action on the decomposition of acetaldehyde, does not prove their occurrence in the thermal reaction.

The Influence of Small Amounts of Nitric Oxide on the Decomposition of Propaldehyde.—The propaldehyde was fractionated in an all-glass apparatus; b. p. 47·5—48·5°/730 mm.

The chief products of its thermal decomposition are carbon monoxide, ethane, methane, ethylene, and hydrogen. Winkler, Fletcher, and Hinshelwood (*Proc. Roy. Soc.*, **1934**, *A*, **146**, 345) found that the end-point of the reaction increases as the initial pressure decreases. The decomposition of the ethane causes a further very slow pressure increase after the aldehyde has decomposed. Consequently, the true " end-points " were obtained from the pressure–time curves by an extrapolation process. The true end-points of the reaction in the presence of 2 mm. of nitric oxide were found in the same way, and do not differ much from those for the uninhibited reaction. This is shown by Table II.

TABLE II.

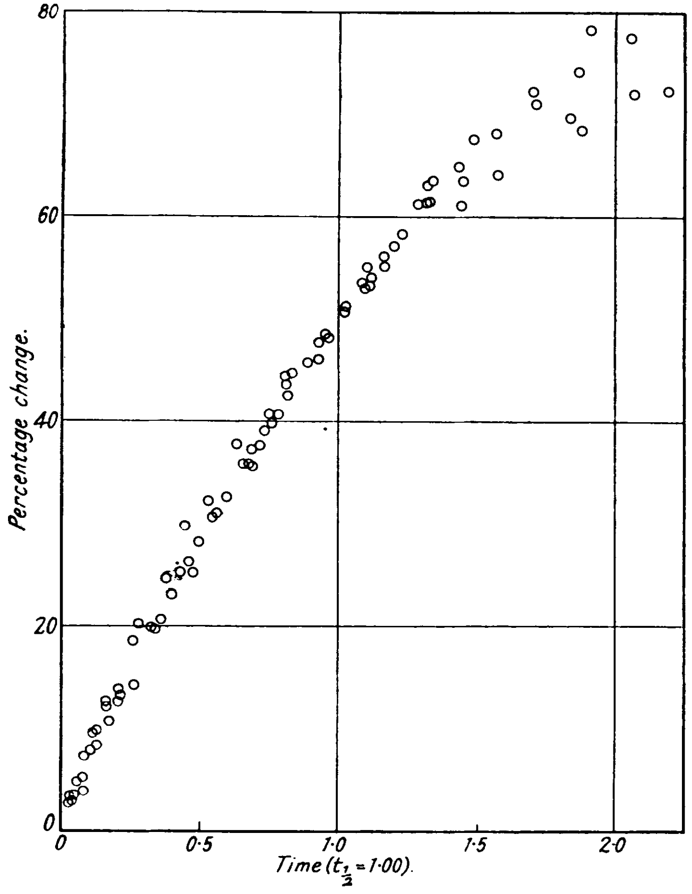
Propaldehyde (549°). *Variation of end-point with initial pressure.*

p_0 = initial pressure, p_e = final pressure at true end-point.

p_0	300	150	40	10
$(p_e - p_0)/p_0$ without NO	1·00	1·04	1·13	1·20
$(p_e - p_0)/p_0$ with 2 mm. NO	1·03	1·05	1·13	1·19

As with ethyl ether, some nitric oxide is removed during the reaction, but the reciprocal of $t_{\frac{1}{2}}$ (the time required for 50% of the aldehyde to decompose) has been used as a measure of the rate in preference to the less accurately measurable initial rates, a procedure justified by the fact that the shape of the pressure–time curve is independent of the temperature and of aldehyde or nitric oxide pressure (as long as the latter is fairly small). This is shown by Fig. 1, in which are plotted the pressure–time curves for 7 runs carried out at various temperatures and pressures, $t_{\frac{1}{2}}$ in each case being made equal to unity.

FIG. 1.



Nitric oxide-inhibited reaction of propaldehyde. Similarity of pressure–time curves for different conditions : seven curves, temperatures from 549° *to* 610°, *aldehyde pressures from* 11 *to* 301 *mm.*, NO *from* 0 *to* 9·4 *mm.*

Table III gives the values of $t_{\frac{1}{2}}$ at 549° with 159 mm. of aldehyde and amounts of nitric oxide varying from 0 to 18 mm. The relation between $1/t_{\frac{1}{2}}$ and nitric oxide pressure is illustrated in Fig. 2, which shows the reaction to be inhibited by nitric oxide, although the curve, unlike that for ethyl ether, has no long flat minimum, the positive catalytic influence of nitric oxide

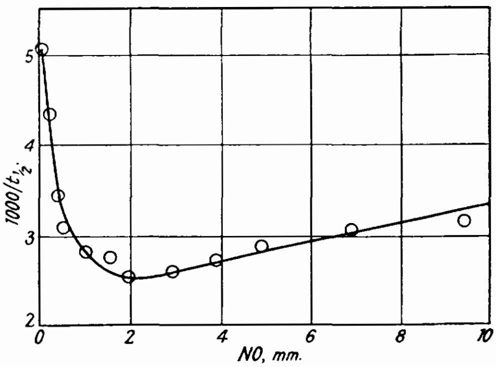
TABLE III.

Propaldehyde (549°). *Variation of* $t_{\frac{1}{2}}$ *with* NO *pressure.*

NO (mm.).	$t_{\frac{1}{2}}$ (sec.).	NO (mm.).	$t_{\frac{1}{2}}$ (sec.).	NO (mm.).	$t_{\frac{1}{2}}$ (sec.).
0	197	1·53	363	6·9	326
0·18	230	1·95	394	9·4	315
0·38	291	2·9	384	10·1	282
0·51	326	3·9	368	12·7	280
1·00	356	4·9	349	14·7	251

being considerably more pronounced. By extrapolating the rising part of the curve until it cuts the pressure axis, it can be seen that, if there were no concurrent catalysis, the minimum rate would be about 44% of that of the uninhibited reaction.

FIG. 2.

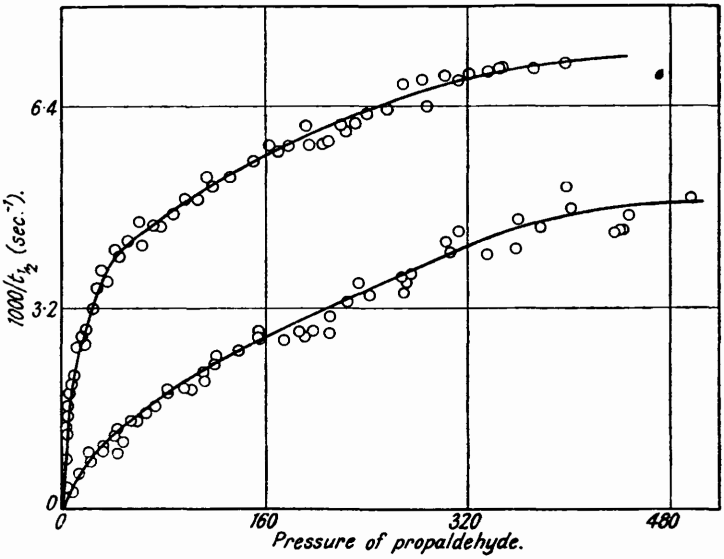


Decomposition of propaldehyde : inhibition by nitric oxide.

$t_{\frac{1}{2}}$ was determined at 549° with 2 mm. of nitric oxide and with initial aldehyde pressures varying from 5 to 500 mm. For pressures less than 40 mm., the reaction was followed with the aid of a cathetometer, which enabled the pressure to be read to 0·1 mm. The results are plotted in Fig. 3, together with those of Winkler, Fletcher, and Hinshelwood for the uninhibited reaction. The most striking thing about the figure is the parallelism between the two curves above about 40 mm., the chain length, as given by the ratio of the velocities of the uninhibited and the inhibited reaction, increasing as the pressure decreases. The interpretation of this is discussed later.

The energy of activation of the normal decomposition of propaldehyde increases as the initial pressure decreases. The temperature coefficient of the reaction inhibited by 2 mm. of nitric oxide was investigated at two different aldehyde pressures, *viz.*, 30 and 350 mm. The observed values of $t_{\frac{1}{2}}$ are corrected for change of concentration with temperature (Table IV). They give satisfactory Arrhenius lines.

FIG. 3.



Influence of nitric oxide on decomposition of propaldehyde at different initial pressures. Upper curve, normal reaction : lower curve, reaction with 2 *mm.* NO.

TABLE IV.

Inhibited decomposition of propaldehyde. Temperature coefficient.

Temp.		606°	589°	569°	549°	529°	509°	489°
$\log_{10}t_{½}$	30 mm.	1·922	2·279	2·588	2·976	3·354	—	—
	350 mm.	—	—	1·982	2·356	2·697	3·064	3·398

The values for the activation energies (uncorrected for variation of the collision rate with temperature) are 58,500 cals. at 30 mm. and 51,000 cals. at 350 mm., so that, as for the uninhibited reaction, the activation energy increases as the initial pressure decreases. The corresponding values for the normal decomposition are 63,500 and 56,000 cals. respectively, *i.e.*, about 5,000 cals. greater than those for the inhibited decomposition. Thus the chains must get slightly longer as the temperature rises, whereas in the case of ethyl ether they get shorter.

DISCUSSION.

It is well known that if the rate of an organic decomposition reaction, as given by the reciprocal of the time of half-change, is plotted against the initial pressure, the curve rises from the origin, bends over, and ultimately becomes more or less parallel to the pressure axis. If in any given reaction there is only one type of activated molecule, then, theoretically, this curve should show a gradual change of slope and tend to become exactly parallel to the pressure axis at high pressures. The initial slope of the curve is proportional to the rate of production of activated molecules, and its limiting height to the probability of their decomposition. Closer examination of the rate–pressure curve, however, has revealed that it sometimes has a segmented appearance, as though it were composed of several elementary curves, each characterised by a specific set of constants. Acetone, acetaldehyde, and propaldehyde, and also nitrous oxide, are examples of substances which yield this type of curve. It has been concluded that in these cases there are several varieties of activated molecule, differing in the location of the energy and having different decomposition probabilities (Hinshelwood, Fletcher, Verhoek, and Winkler, *Proc. Roy. Soc.*, 1934, *A*, **146**, 327).

The various activated states of the acetaldehyde molecule all lead to the same products, but with propaldehyde the nature of the decomposition products varies somewhat with pressure. In these two reactions the activation energy increases as the pressure falls, and to account for the observed rates more degrees of freedom must be invoked at low than at high pressures The rate–pressure curves for those modes of activation manifested in the lowest segments rise steeply but soon bend over. For these states the rate of activation is high, owing to the relatively large number of degrees of freedom which can contribute to the activation energy, while the decomposition probability is small on account of the correspondingly scattered distribution.

The most obvious interpretation of Fig. 3 is that nitric oxide considerably reduces the limiting height of that component which produces the first and steepest segment, leaving the other components unaffected.*

The first and steepest segment in the curve for propaldehyde is much longer than with acetaldehyde, as is evident from Fig. 4. In other words, the mode of activation manifested in this segment plays a considerably more important part in the decomposition of propaldehyde than in that of acetaldehyde.

The different types of activated acetaldehyde molecule all react as though the aldehydic hydrogen atom migrates to the alkyl carbon atom, with simultaneous rupture of the carbon–carbon link, giving carbon monoxide and methane. Similarly, the types of activated propaldehyde molecules responsible for the upper segments of the curve lead to carbon monoxide and ethane, but that type to which the first and steepest segment is due

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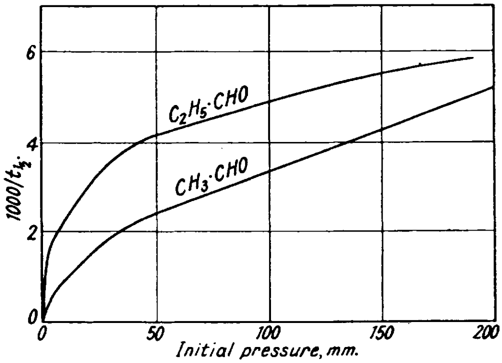
* The simplest way of analysing the curves is as follows. Rate, y, is plotted against pressure, x, and tangents are drawn at many points; dy/dx is plotted against x, and a smooth curve drawn. Tangents are again drawn at many points, and d^2y/dx^2 plotted against x. More than one maximum on this curve indicates that the original curve could not have been described in terms of a single function, because one type of decomposition probability would have to show a steady increase or decrease. When this test is applied, multiple maxima cannot be avoided without obvious disregard of the experimental points.

undergoes an alternative decomposition, giving methane, ethylene, and hydrogen as primary products. This mode of activation, which is not possible for acetaldehyde, corresponds precisely to that segment of the rate–pressure curve, which with propaldehyde is suppressed by the nitric oxide.

Before the effect of nitric oxide was discovered, it had been suggested that in the reactions giving rise in each case to the lowest segment, the activation energy is located in the region of the molecule remote from the aldehyde groups, *i.e.*, in the C–H bonds of the alkyl groups, and that the greater prominence of this segment with propaldehyde is due to the larger alkyl group. In the case of acetaldehyde, the energy in the methyl group seems to be able to migrate ultimately into the vital part and cause dissociation into carbon monoxide and methane. But when the activation energy is distributed in the ethyl group in propaldehyde, production of a free radical becomes more likely. Thus it is conceivable that these activated propaldehyde molecules dissociate in some such manner as this: $CH_3{\cdot}CH_2{\cdot}CHO \longrightarrow CH_3 + CH_2{\cdot}CHO$, the methyl radicals then bringing about further decomposition, though it does not seem possible to advance any one mechanism for this chain process with certainty from the mere fact that it somehow leads to the ultimate formation of hydrogen, ethylene, methane, and carbon monoxide.

FIG. 4.



Comparison of acetaldehyde and propaldehyde : rate–pressure curves.

The question whether all active molecules or only some of them give chains has now been partially answered, since we have concluded that only those molecules in which the activation energy is large, and located in the region of the molecule most remote from the aldehyde group dissociate into radicals and so initiate chains or cause catalytic decomposition. But it is still uncertain whether all active molecules of this particular type yield chains, or only a fraction of them.

The activation energy of the uninhibited reaction increases as the pressure decreases, and our conclusion that it is the type of activated molecules with the largest activation energy which yields free radicals agrees with the observation of Patat and Sachsse (*Z. physikal. Chem.*, 1935, *B*, **31**, 105) that the concentration of free radicals set up during reactions is greater the nearer the observed activation energy is to the energy required to break the carbon–carbon link. It is significant in this connexion that the observed activation energy of the decomposition of acetaldehyde is about 9,000 cals. less than that for propaldehyde at the same initial pressure.

To account for the observed rate of the inhibited decomposition of propaldehyde at a pressure of 350 mm., the activation energy (51,000 cals.) must be assumed to be distributed in about 6 square terms, and at 30 mm. (when it is 58,500 cals.) in about 10.

Bearing of the Results on Current Theories of Unimolecular Reactions.—The two principal problems of unimolecular reactions are (*a*) to account for the high activation rate and (*b*) to account for the form of the curve connecting rate and pressure. Problem (*a*) is solved either by assuming the activation energy to be distributed in many degrees of freedom or by assuming long chains. In all examples to which the nitric oxide method has been applied, the average length of the chains is far too small for the second alternative. Moreover, even when all the chains are suppressed, many square terms are needed to account for the rate of the residual reaction. The activation energies require correction for variation of the chain length with temperature, and this alters the exact number of square terms required. In communications from this laboratory nothing has ever been concluded about the number of degrees of freedom involved, except that it is in general considerable though never unreasonably great, nor have correlations been suggested between this number and the structure of the molecules. This position is unchanged by the increase in the number required for the ethers and the decrease for propaldehyde. It remains to be seen whether there are any correlations between structure and number of square terms for a series of chain-free reactions.

With regard to (*b*), in a chain-free reaction the form of the curve depends upon what function the transformation probability of activated molecules is of the magnitude and location of their activation energy. One view is that the probability varies continuously with the energy (Rice, Ramsperger, Kassel) and this is almost certainly correct in principle. But we believe the matter to be often more complex than this, in that the decomposition probabilities fall into groups, and give rise to what we have called the segmented curve. By this, we mean a curve requiring more than one function for its representation, and do not imply that it exhibits any discontinuity. Variable chain length might distort the curve and necessitate modification of either of these views. With ethyl ether, the form of the curve is unchanged by the suppression of the chains, which must therefore be of constant length, so that any conclusions about the transformation probabilities would be unaffected.

Apart from the fact that segmented curves are found with acetone, nitrous oxide, and acetaldehyde, where there are no chains, their existence is rendered more probable by the results with propaldehyde, which are best explained by supposing that nitric oxide affects one component only of a composite curve, the curve for the chain-free reaction still appearing to be composite.

SUMMARY.

The use of nitric oxide in small amounts as a chain detector has shown that the thermal decomposition of propaldehyde involves chains with an average length of about two units, but that that of acetaldehyde is free from chains. Both reactions are kinetically composite, and in the case of propaldehyde the nitric oxide suppresses a component not present with acetaldehyde. Chains appear to result only from a certain type of activated propaldehyde molecule, possibly one activated in the ethyl group, which has no counterpart in the reaction of acetaldehyde.

Correction of the activation energy for variation of chain length with temperature changes the number of square terms in which the activation energy must be assumed to be distributed, but makes no difference to existing views about the mechanism of activation.

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