328. *Reaction Chains in the Decomposition of Organic Compounds.*

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The primary act in the decomposition of an organic molecule can be either an internal rearrangement to stable products, or the production of free radicals which may cause further decomposition by a chain process. In some examples both mechanisms operate simultaneously.

Nitric oxide inhibits certain types of gas reaction, an effect attributed to its power of combining with such free radicals as may be formed. This provides a method for determining the relative importance of the two separate reaction mechanisms.

The present paper summarises the evidence which this method has yielded about the conditions determining the production and chain propagating efficiency of free radicals in various organic decompositions.

In many reactions the contribution from the chain processes is negligible. In others it appears that a small proportion only of the primary acts yield radicals, but that these may in some circumstances give rise to long chains.

The recognition of the part played by radicals does not necessitate any fundamental change in our views about the mechanism of activation in unimolecular reactions.

IN reactions such as the decomposition of dimethyl ether two processes are potentially in competition. The first is a rearrangement to give saturated products :

$$CH_3 \cdot O \cdot CH_3 = CH_4 + H \cdot CHO.$$
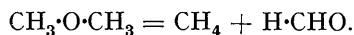
The second is the production of free radicals :

$$CH_3 \cdot O \cdot CH_3 = CH_3 + OCH_3,$$
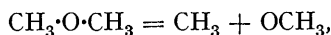
a change which, although occurring much more rarely, has profound consequences, since the radicals may cause the secondary decomposition of many molecules. Whether, in a given example, the subsequent disturbances are enough to compensate for the rarity of the primary process is a matter which only experiment can decide.

Nitric oxide inhibits certain types of gas reaction. The best explanation is that it suppresses reaction chains by combining with free radicals. This effect may be used to investigate the part played by chains in the decomposition of simple organic substances, a problem which has been much discussed in recent years, but in which unambiguous experimental evidence has been largely lacking. This paper summarises the more direct evidence so far obtained by the use of nitric oxide as a chain indicator about the molecular processes involved in these reactions. [Papers from this laboratory will be referred to by the following letters : (a) Staveley and Hinshelwood, *Nature*, 1936, **137**, 29; (b) *idd.*, *Proc. Roy. Soc.*, 1936, *A*, **154**, 335; (c) *idd.*, *J.*, 1936, 812; (d) Hinshelwood and Staveley, *J.*, 1936, 818; (e) Mitchell and Hinshelwood, *Proc. Roy. Soc.*, 1937, *A*, **159**, 32; (f) Staveley and Hinshelwood, *ibid.*, p. 192. These papers contain references to the work of Paneth, Rice and Herzfeld, Patat and Sachsse, Leermakers, and others which need not be repeated here.]

About the nature of the action by which radicals propagate chains two views are possible. The radical may actually remove some portion of the molecule which it attacks, leaving an unstable residue which then breaks down giving a stable product and regenerating a radical similar to the original one. On the other hand, it may simply cause such a disturbance in the molecule which it approaches that the latter is more easily rearranged into stable products, and gives these with a much lower activation energy than it would normally require. According to this view, the chain is simply the series of molecules, the catalytic decomposition of which is brought about by one radical during its lifetime. That free radicals should exert some such action might be expected theoretically (cf. Eucken and Jaacks, *Z. physikal. Chem.*, 1935, *B*, **30**, 85).

Types of Reaction subject to Inhibition by Nitric Oxide.—The accompanying table provides a synopsis of the reactions examined, and includes some hitherto unpublished results.

It will be observed that all the ethers are subject to inhibition, but that the effect diminishes rapidly as the homologous series is ascended (ref. f). With chloral and acetaldehyde, the results are negative, but the effect appears with propaldehyde and in an increased degree with butaldehyde. Considerable inhibition is found with ethane (unpublished results of Staveley), but, rather remarkably, ketones are exempt, as also is methyl alcohol. All these reactions are predominantly homogeneous under the conditions of the experiments. In this connexion the negative result with the purely heterogeneous reaction of methyl formate is interesting in that it helps to dispose of the suggestion that one function of the nitric oxide is to poison the walls of the vessel.

Mean Chain Lengths.—We have called the ratio of the rates of the uninhibited and fully inhibited reactions the mean chain length. According to this convention a molecule which decomposes by a pure rearrangement process, giving no radicals to bring about further decomposition, is regarded as giving a chain of unit length. Thus a mean chain length of 4·4 with diethyl ether might mean that every primarily decomposing molecule gives radicals which cause the decomposition of about three or four more, or that only one in 100, say, of the primary processes gives radicals, but that these cause the decomposition of about 350 molecules. The average length of the chains derived from those molecules which do in fact yield the radicals we may call the *absolute* chain length.

Two arguments lead us to believe that this absolute chain length is high. First, the energies required to break the carbon–carbon and carbon–oxygen bonds, although not known exactly, are undoubtedly considerably greater than the activation energies of the chain-free reactions, as may be seen from the table. Therefore the number of primary processes giving free radicals must be a small fraction only of those in which rearrangement occurs, so that for an appreciable mean chain length the absolute length must be· con-

siderable. Quantitative calculations on this basis are useless until bond energies are known more accurately. Secondly, nitric oxide is consumed in the course of the reactions which it inhibits. If we can assume, on the basis of photochemical experiments made at lower temperatures (ref. *e*), that one molecule is used up for each chain broken, then the absolute length can be estimated. For dimethyl ether (ref. *f*) it comes out to be 400. This, however, is really a lower limit, since, at the high temperatures employed, nitric oxide is almost certainly removed in oxidation reactions distinct from the chain-breaking processes. An upper limit, on the other hand, is set to the absolute chain length by the absence of any

Substance.	Effect of small amounts of NO on the decompn.	Mean chain length.	Activation energy of the chain-free reaction.	Activation energy of the chain-propagating reaction.	Bond strength.	Number of square terms needed to account for rate of chain-free reaction.
Hydrocarbons.						
Ethane	Inhibition	21 (600°) 50 mm. 6 (600°) 500 mm.	74,500	10,000	~80,000	—
Ethers.						
Dimethyl	Inhibition	17 (540°)	62,000	12,000	~82,000	10
Methyl ethyl	,,	8·4 (540°)	62,000	12,000	—	10
Diethyl	,,	4·4 (540°)	67,000	10,000	—	18
Ethyl propyl	,,	3·2 (540°)	—	—	—	—
Dipropyl	,,	2·7 (540°)	60,500	—	—	17
Di*iso*propyl	,,	1·4 (540°)	65,500	—	—	>24
Aldehydes.						
Acetaldehyde	No inhbtn.	1·0	46,000	10,000	~84,000	2
Propaldehyde	Inhibition	2·3 (549°) 159 mm. 3·9 (549°) 30 mm.	56,000 350 mm. 63,500 30 mm.	8,000	~80,000	6 350 mm.
Butaldehyde	Inhibition	3·5 (500°) 100 mm. 6·0 (500°) 30 mm.	55,500 100 mm.	—	~80,000	—
Chloral	No inhbtn.	1·0	49,000	—	—	—
Ketones.						
Acetone	No inhbtn.	1·0	68,000	—	~84,000	—
Methyl ethyl ketone	,,	1·0	—	—	—	—
Esters.						
Methyl formate	,,	Heterogeneous	—	—	—	—
Alcohols.						
Methyl alcohol	,,	1·0	68,000	—	~84,000	12

The iodine-catalysed decompositions of aldehydes and ethers are *not* inhibited by nitric oxide (Mitchell, unpublished experiments).

marked retardation of the reaction by the packing of the vessel. The effects found are not more than of the order 10—20%, and are never in any way comparable with those observed in reactions such as the combination of hydrogen and oxygen. In view of the sensitiveness of the rates to small temperature errors, the effects are almost too small to be regarded as significant at all in the absence of independent evidence.

Factors determining the Occurrence of Chains.—The contrast between acetaldehyde, which at 500—600° undergoes the change $CH_3 \cdot CHO = CH_4 + CO$ without the appearance of free radicals, and that of ethane, which at somewhat higher temperatures suffers the decomposition $C_2H_6 = C_2H_4 + H_2$ with the intervention of enough radicals or atoms to give a mean chain length as great as 20, is striking enough to merit discussion.

Two factors are important. One is the relative ease of two competing processes : the rearrangement in one act into stable products, and, on the other hand, the splitting into radicals. The other factor is the efficiency with which the latter cause further decomposition. If the activation energy for the rearrangement is smaller than the bond energy by a great enough margin, no free radicals will be produced except at temperatures where

the reaction velocity is too great to be measured. This seems to explain the contrast between acetaldehyde and ethane, since the observed activation energies are 46,000 and 74,500 cals. respectively. The energy required to break the C–C bond being of the order 80,000 cals., with acetaldehyde the competing rearrangement process has an advantage of about 30,000 cals., while with ethane the advantage cannot be more than a few thousand cals. This explanation is confirmed by the fact that artificially introduced radicals cause a decomposition of acetaldehyde with an activation energy of only about 10,000 cals., which is comparable with the value for ethane (Leermakers, and ref. *e* : also Staveley, un-published results).

The activation energies for the reactions between the radicals and the original substance, which measure the ease of propagation of the chain, are obtained in two ways, which give concordant results : (1) from photochemical measurements (ref. *e*), and (2) from measure-ments of the amount of nitric oxide required to reduce the rate of the thermal reaction in a given ratio. The values, which are approximate only, vary from 8,000 to 12,000 cals.

Propaldehyde shows an interesting transition between ethane and acetaldehyde. The curve relating reaction rate and pressure has the segmented appearance due to the super-position of processes involving different species of activated molecules. One of the segments with propaldehyde is attributed to a mode of reaction where the activation energy is localised in the ethyl group. By the nitric oxide method it is found that the activated molecules belonging to this species alone produce a detectable proportion of radicals. When the chains due to these are suppressed, the rate–pressure curve becomes exactly like that for acetaldehyde, a fact which in itself is a confirmation of our interpretation of the nature of these curves. The mean activation energy for the chain-yielding mode is several thousand calories more than that for the others. The fact that the proportion of radicals rises from zero to a finite value as the activation energy increases is another example of the general principle already illustrated by the contrast of acetaldehyde and ethane. With butaldehyde where the alkyl group is larger than with propaldehyde, the mean chain length is still greater.

With the ethers, the activation energies for the rearrangement processes are from 60,000 to 68,000 cals., being thus 10,000—20,000 cals. lower than the bond energies. If it is assumed as a rough approximation that the probability of the two competing modes of decomposition is determined only by the activation energies, not more than one in some hundreds of the primarily decomposing molecules gives radicals. The mean chain length being a few units, the absolute length must be 2—3 powers of 10. By assuming a value of this order, the concentration of free radicals can be estimated. The energy of activation of the propagation process is such that the radical causes the decomposition of only one ether molecule in several hundred : thus the radical must meet 10^5—10^6 ether molecules in the course of its life. If its final removal occurs in a binary collision with another radical present at comparable concentration with itself, then this concentration must be 10^{-5}—10^{-6} of the ether concentration. At 829° Abs., in the inhibited decomposition of diethyl ether, 4×10^{15} molecules react per c.c. per second when the initial pressure is 200 mm. If about 10^{-3} of this number give radicals, the rate of production is of the order 4×10^{12} per c.c. per sec. These must be removed by recombination. At the estimated concentration the number of binary collisions exceeds 10^{15}, which is great enough to allow us to assume an even greater absolute chain length without improbability

The activation energy for acetone is even higher than that of the ethers, yet there are no chains. It would seem, therefore, that their absence is due to the insensitiveness of the acetone molecule to the action of radicals. This is, in fact, confirmed by experiments on the artificial introduction of radicals (Rice, Rodowskas, and Lewis, *J. Amer. Chem. Soc.,* 1934, **56**, 2497). The acetone molecule is also insensitive to the action of iodine, which causes the decomposition of ethers, aldehydes, and esters.

Variation of Chain Length with Temperature.—The essential steps in the chain process must be : primary radical formation ; propagation ; chain breaking, which may be simply represented as follows :

$$(1)\ XY = X + Y; \quad (2)\ X + XY = \text{Products} + X; \quad (3)\ 2X = X_2.$$
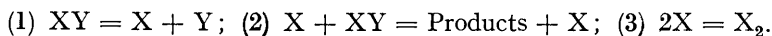
Let k_1, k_2, and k_3 be the velocity constants of these reactions. Writing down the equation for a stationary concentration of X, we find that for a given concentration of XY the rate is proportional to $k_2(k_1/k_3)^{\frac{1}{2}}$, whence $E_{obs.} = E_2 + \frac{1}{2}E_1 - \frac{1}{2}E_3$, where E_3 is probably quite small, and will be neglected, though our final conclusions are not affected by doing so. Whether or not the apparent chain length of a reaction in which both radical chains and direct rearrangements occur increases or decreases with rise in temperature depends upon whether $E_2 + \frac{1}{2}E_1$ is greater or less than E_0, the value for the rearrangement. Since $E_1 > E_0 > E_2$, the sign of $E_2 + \frac{1}{2}E_1 - E_0$ is evidently a matter of numerical accident. There is thus no great theoretical significance in the fact that with the ethers the apparent chain length increases slightly as the temperature falls, whereas with propaldehyde it decreases. Elaboration of the reaction scheme will leave the general lines of the above argument unchanged.

Variation of Chain Length with Pressure.—With diethyl ether the mean chain length varies little in the range 50—500 mm. With propaldehyde it falls as the pressure increases, but for a special reason, already discussed, connected with the nature of the rate–pressure curve itself. For ethane the apparent chain length falls from 21 at 50 mm. to 6 at 500 mm.

Theory predicts a great variety of possible behaviours. Each of the two primary processes, the rearrangement reaction and the radical formation, is unimolecular with its own pressure dependence. There are two important kinds of chain-breaking reaction : recombination of radicals in binary collisions, and recombination with the intervention of a third molecule. To account for the decrease of chain length with increasing pressure in the case of ethane, detailed calculation shows that we must make one of two assumptions. One is that the rate of the radical-yielding process varies less rapidly with pressure than that of the competing process. In this case the assumption of either binary or of ternary collisions would be possible for the recombination process. On the other hand, we can assume that the two primary processes have the same pressure-dependence, in which case the assumption of ternary collisions for the recombination process cannot be avoided. A definite decision between the two possibilities cannot be reached on the evidence of pressure-dependence alone. It would be interesting to analyse the problem further, since, in the photochemical decomposition of acetaldehyde it appears clearly from the kinetics that the recombination of the methyl radicals is a bimolecular process, and if the chains in the ethane reaction are ended by a termolecular process, then it would suggest that, not methyl radicals, but hydrogen atoms are concerned.

Function of the Nitric Oxide.—Nitric oxide contains an odd number of electrons and is therefore virtually a free radical itself. It might therefore be expected to combine with other free radicals, and is in fact known to combine with hydrogen atoms. The primary product would presumably be a nitroso-compound which would very rapidly undergo further reactions. It is known that nitric oxide oxidises organic compounds and is itself reduced to nitrogen or ammonia. Thompson and Meissner have, in fact, observed spectroscopically the formation of ammonia during the decomposition of dimethyl ether in presence of nitric oxide. There must be a complicated series of reactions leading to these end-products. If nitroso-compounds are formed, they might isomerise to oximes which would lose water giving cyanides. Cyanides do not, however, appear in detectable amounts. Although the subsequent changes are complicated and largely unknown, on general grounds there can hardly be any doubt that the actual chain-breaking process is the combination of the radical with the nitric oxide.

The Theory of Unimolecular Reactions.—The question arises how far the existence of unsuspected chain processes vitiated earlier conclusions about the mechanism of activation in unimolecular reactions. It may be said that our views on this matter require no substantial modification. In the first place, reactions such as the decomposition of acetone appear to involve no chains. Secondly, experiments on the suppression of chains with nitric oxide have shown that the characteristics of the residual processes are still those normally accepted as distinguishing unimolecular reactions.

The evidence may be summarised as follows :

(1) The variation of rate with pressure for the inhibited decompositions of ethers is the same as that for reactions free from chains (*b, c, f*).

(2) To account for the observed rates of the inhibited reactions the activation energy must still be assumed to be distributed in many square terms (*f*). For a series of ethers the number of square terms bears a more natural relation to the structure of the molecule than it appeared to do before the interference by chain processes was allowed for.

(3) In the study of propaldehyde it was inferred that the radicals arose only from certain types of activated molecule : this is itself evidence in support of the earlier conclusion that different modes of activation contribute to the reaction (*c, d*).

(4) The characteristic influence of hydrogen is found with the inhibited decompositions of diethyl ether and of propaldehyde (*d*).

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