301. *Oxidation of Aldehydes in the Gaseous Phase. Part III. The Inhibition of the Oxidation of Acetaldehyde by Nitrogen Peroxide (Dioxide).*

By C. A. McDowell and J. H. Thomas.

The inhibition, by nitrogen peroxide (dioxide), of the low-temperature gas-phase oxidation of acetaldehyde has been studied in detail and it is shown that this compound acts as a strong inhibitor. From a theoretical treatment of this type of inhibition it is shown that the initiation process is a bimolecular reaction between acetaldehyde and oxygen. To account for the experimentally determined activation energy of this reaction it is suggested that the initiation reaction is $CH_3 \cdot CHO + O_2 = CH_3 \cdot CO + HO_2$.

The simple theoretical treatment outlined leads to an expression for the rate of initiation, r_i, which with the experimental results recorded in this paper has a value of $7 \cdot 2 \times 10^{-8}$ mole litre^{-1} sec.$^{-1}$ at 141^6. The chain length of the oxidation is shown to be very short.

IN Part I (*J.*, 1949, 2208) it was shown that the gas-phase oxidation of acetaldehyde is strongly inhibited by small quantities of nitrogen peroxide, and that the inhibition is characterised by a long induction period during which there is practically no change in pressure. At the end of this induction period the pressure falls and the rate of decrease soon becomes approximately the same as that for the uninhibited reaction. The inhibition of a reaction by small quantities of foreign compounds shows that it is characterised by having a chain mechanism; and by a careful study of inhibited reactions it is often possible to derive important information concerning the underlying chain processes (Bäckström, *J. Amer. Chem. Soc.*, 1927, **49**, 1469; *Meddel. K. Veten. Akad. Nobelinst.*, 1927, **6**, Nos. 15, 16; Alyea and Bäckström, *J. Amer. Chem. Soc.*, 1929, **51**, 90; Hinshelwood, " Kinetics of Chemical Change," Oxford, 1940; Semenoff, " Kinetics of Chain Reactions," Oxford, 1935).

The rate of an inhibited chain reaction can be written as

$$R = r_i r_p / (r_t + k_I I) \qquad \qquad (1)$$

where $r_i =$ rate of initiation of chains, $r_p =$ rate of propagation of chains, $r_t =$ rate of termination of chains by normal process, and $k_I I =$ rate of termination of chains by inhibitor of concentration I.

From equation (1) it is seen that a linear relation exists between the reciprocal of the rate of an inhibited reaction and the concentration of the inhibitor. Pease (*J. Amer. Chem. Soc.*, 1933, **55**, 2753) showed that ethyl alcohol inhibited the gas-phase oxidation of acetaldehyde and found that the inhibited reaction obeyed this linear relation.

From equation (1) it is also possible to obtain a simple relation between the induction period and the concentration of inhibitor in the case of a strongly inhibited reaction. The length of the induction period τ will be inversely proportional to the rate of reaction R; then from the above equation we have

$$\tau = K/R = K r_t / r_i r_p + K k_I I / r_i r_p \qquad \qquad (2)$$

where K is a constant for the particular reaction. Thus a plot of τ against I should be linear.

In Fig. 1 we have plotted the induction period τ against the initial concentration of the nitrogen peroxide for several temperatures, and it is seen that the linear relationship is obeyed, thus proving beyond all reasonable doubt that the gas-phase oxidation of acetaldehyde is a chain reaction. At the end of the reaction all the brown colour of the nitrogen peroxide initially present has disappeared, showing that the inhibitor, or some compound derived from it, does in fact react with the radicals produced in the chain reaction.

Since in the uninhibited reaction there is practically no induction period (see Part I) and the pressure decreases from the start of the reaction owing to the formation of peracetic acid, the only reasonable interpretation of the induction period produced by nitrogen peroxide is that it is preventing the formation of peracetic acid and so it, or some compound derived from it, must react with the chain initiator.

One can make use of this linear relation between the induction period and the initial concentration of the inhibitor to investigate the nature of the initiation reaction in the oxidation. From equation (1), the fraction of chains terminated by the inhibitor will be $k_I I / (r_t + k_I I)$, so if one molecule of inhibitor is consumed for each chain terminated, the rate of disappearance of the inhibitor will be

$$-dI/dt = r_i k_I I / (r_t + k_I I) \qquad \qquad (3)$$

If the compound under investigation is a strong inhibitor, as is nitrogen peroxide in this system, then $k_I I \gg r_t$, and equation (3) becomes

$$-dI/dt \approx r_i \qquad \qquad \qquad \qquad \text{(4)}$$

i.e., the rate of disappearance, or consumption, of inhibitor equals the rate of the initiation of chains.

Integration of equation (4) gives

$$I_0 - I_t = r_i t \qquad \qquad \qquad \qquad \text{(5)}$$

where I_0 and I_t are, respectively, the concentrations of inhibitor initially and at time t. If at the end of the induction period, *i.e.*, when $t = \tau$, all, or most, of the inhibitor is consumed, $I_0 \gg I_t$, so $I_0 - I_t \approx I_0$ and we can write

$$I_0/\tau \approx r_i \qquad \qquad \qquad \qquad \text{(6)}$$

Other workers have previously derived equation (6) in a similar manner and have shown it to be obeyed approximately in the cases of the inhibition of the liquid-phase oxidation of

FIG. 1.

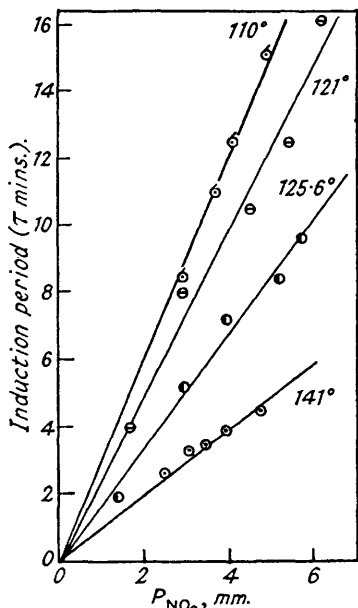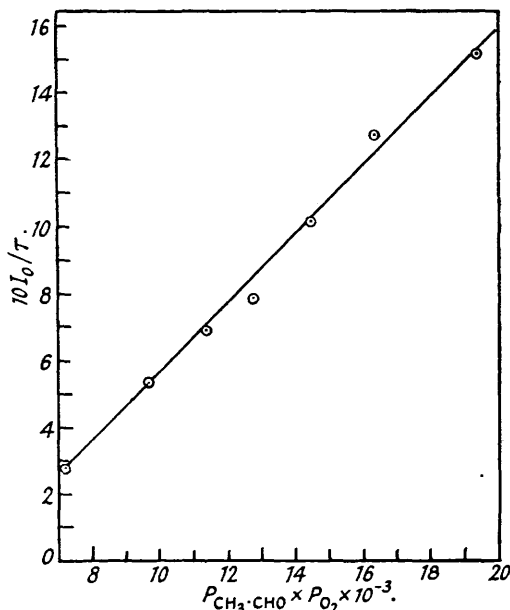*Variation of induction period with concentration of inhibitor.*

FIG. 2.

*Variation of rate of initiation with concentration of reactants.*

tetralin (George, Rideal, and Robertson, *Proc. Roy. Soc.*, 1946, *A*, **185**, 288) and of the polymerisation of styrene and other monomers by quinones (Foord, *J.*, 1940, 48; Goldfinger, Skeist, and Mark, *J. Physical Chem.*, 1943, **47**, 578; Melville and Watson, *Trans. Faraday Soc.*, 1948, **44**, 886).

Bodenstein (*Sitzingsber. Preuss. Akad. Wiss., Phys.-Math. Kl.*, 1931, III, 1) gave the following reactions for the initiation of the oxidation of acetaldehyde :

$$A = A^* \qquad \qquad \qquad \qquad \text{(A)}$$
$$A^* + O_2 = P^* \qquad \qquad \qquad \text{(B)}$$
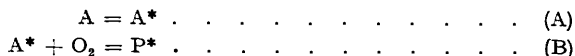
In Part I it was suggested that a more likely initiation process is the simple bimolecular reaction

$$CH_3 \cdot CHO + O_2 = CH_3 \cdot CO + HO_2 \qquad \qquad \text{(C)}$$
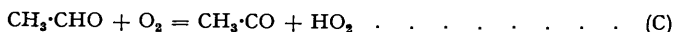
followed by the reaction

$$CH_3 \cdot CO + O_2 = CH_3 \cdot CO_3 \qquad \qquad \qquad \text{(D)}$$

The initiation step (C) was also proposed earlier by Keyer and Neumann (*Acta Physicochim., U.R.S.S.*, 1941, **14**, 451).

Equation (6) can be used in the following way to decide between the unimolecular process

given by Bodenstein and a bimolecular initiation process such as that suggested by us. If we determine I_0/τ for a series of mixtures with different aldehyde/oxygen ratios, for the former case we should have a linear relation between I_0/τ and the concentration of the aldehyde, whereas if the bimolecular process is correct, we should only obtain a linear relation between I_0/τ and the product of the concentrations of acetaldehyde and oxygen.

Table I shows the effect on the induction period of varying the aldehyde/oxygen ratio whilst keeping the amount of inhibitor approximately constant. Col. 3 gives the product [Aldehyde][Oxygen], and col. 6 the corresponding value of I_0/τ.

TABLE I.

Effect on the induction period of varying the aldehyde/oxygen ratio in mixtures of acetaldehyde, oxygen, and nitrogen peroxide.

Temperature 125·7°.

[CH₃·CHO], mm.	[O₂], mm.	[CH₃·CHO][O₂] × 10⁻³.	[NO₂], mm.	τ, mins.	I_0/τ.
104·1	186·8	19·4	4·9	2·25	1·52
150·1	109·1	16·4	5·4	4·2	1·28
103·2	141·1	14·5	4·9	4·8	1·02
113·5	112·9	12·8	5·2	6·6	0·79
103·4	110·5	11·4	5·2	8·25	0·695
87·0	111·7	8·7	5·4	10·0	0·54
104·1	69·0	7·2	4·9	17·6	0·282

These results show clearly that I_0/τ does not vary linearly with the aldehyde concentration. A plot (Fig. 2) of I_0/τ against the product [Aldehyde][Oxygen], yields a straight line, showing that the initiation process in the oxidation of acetaldehyde is a bimolecular reaction between oxygen and acetaldehyde and also confirming the above theory.

It was stated earlier that at the end of the induction period the pressure dropped and continued to decrease at a rate approximately the same as that for the uninhibited reaction. Closer examination of the rate of decrease of pressure after the induction period as a function of the amount of nitrogen peroxide originally present in the mixture brings to light certain interesting features. In Table II are given the induction periods and the rates of the subsequent decrease in pressure, represented as $1/t_{10-50}$ (*i.e.*, the reciprocal of the time for the pressure to fall from 10 mm. to 50 mm. below the original value), for a particular mixture of acetaldehyde and oxygen with different amounts of nitrogen peroxide added.

TABLE II.

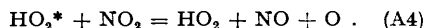*Effect of nitrogen peroxide concentration on main reaction.*

Throughout these experiments pressure of acetaldehyde = 103 mm., pressure of oxygen = 107 mm.

	Temperature 110°.			Temperature 121°.			Temperature 141°.	
NO₂, mm.	Induction period, mins.	$1/t_{10-50}$, min.⁻¹.	NO₂, mm.	Induction period, mins.	$1/t_{10-50}$, min.⁻¹.	NO₂, mm.	Induction period, mins.	$1/t_{10-50}$, min.⁻¹.
0	0	0·0202	0	0	0·0383	0	0	0·0720
2·9	8·5	0·0325	1·7	4·0	0·0422	2·5	2·6	0·0770
3·7	11·0	0·0328	2·9	8·0	0·0465	3·3	3·1	0·0861
4·1	12·5	0·0322	4·5	10·5	0·0467	3·5	3·5	0·0861
5·0	15·1	0·0288	5·4	12·5	0·0455	4·0	3·9	0·0747
7·3	21·8	0·0218	6·2	16·1	0·0327	4·8	4·5	—
						5·9	—	0·0593

In Fig. 3 we have plotted $1/t_{10-50}$ against the pressure of nitrogen peroxide added. The curves show that nitrogen peroxide, or a product derived from it, has a catalytic effect on the reaction following the induction period up to about 3 mm. or 1·3% of nitrogen peroxide added, after which the rate begins to decrease. This influence of nitrogen peroxide on the main acetaldehyde–oxygen reaction between 110° and 140° is very similar to that observed by Kane (*Proc. Roy. Soc.*, 1939, *A*, **171**, 251) on the acetaldehyde cool flame. He found that the addition of small quantities of nitrogen peroxide had a promoting effect on the ignition of acetaldehyde–oxygen mixtures at 260°, *i.e.*, the minimum ignition pressure was considerably lowered. Larger amounts of nitrogen peroxide (greater than 3%) caused the ignition pressure to increase again. The time lag before ignition continued to increase with the amount of inhibition added. This is exactly parallel to our observations in the 110—141° temperature range.

The catalytic effect of nitrogen peroxide on the main oxidation reaction is presumably due to small amounts of this compound which are left at the end of the induction period. This influence of the residual nitrogen peroxide on the oxidation is probably very similar to its sensitization of the hydrogen–oxygen reaction (Dixon, *Trans. Inst. Min. Eng.*, 1930—1931, **80**, 21; Gibson and Hinshelwood, *Trans. Faraday Soc.*, 1928, **27**, 559; Thompson and Hinshelwood, *Proc. Roy. Soc.*, 1929, *A*, **124**, 219; Norrish and Griffith, *ibid.*, 1933, *A*, **139**, 147; Foord and Norrish, *ibid.*, 1935, *A*, **152**, 196; 1936, *A*, **157**, 503; Dainton and Norrish, *ibid.*, 1941, *A*, **177**, 393, 411, 421), the methane–oxygen reaction (Norrish and Griffith, *loc. cit.*), and the carbon monoxide–oxygen reaction (Sagulin and Semenoff, *Chem. Reviews*, 1929, **6**, 350). It is exactly parallel to Chamberlain and Walsh's observations (Third Symposium on Combustion, Flame and Explosion Phenomena, Maidson, U.S.A., 1948, p. 368) that small quantities of nitrogen peroxide raised the minimum pressure required for the appearance of cool flames in ethyl ether–oxygen mixtures, whereas it reduced the pressure required for the appearance of the hot flame.

Hinshelwood and Williamson ("The Reaction between Hydrogen and Oxygen," Oxford, 1934) attributed the sensitization of the hydrogen–oxygen reaction by nitrogen peroxide to this compound's causing chain branching. This suggestion was developed by Foord and Norrish (*loc. cit.*), and more recently Dainton and Norrish (*loc. cit.*) have shown that chain branching does occur by the reaction between excited $HO_2{}^*$ radicals and nitrogen peroxide thus :

$$HO_2{}^* + NO_2 = HO_2 + NO + O \ . \quad (A4)$$

The oxygen atom produced can, of course, start further chains. Chamberlain and Walsh (*Rev. Inst. franç. Petr. et Ann. Comb. liquides*, 1948, **4**, 313) have attributed the catalytic effect of nitrogen peroxide on the oxidation of ether and hydrocarbons to the same process. They assume that excited $HO_2{}^*$ radicals are formed during such oxidation processes. Though we have suggested (Part I) that HO_2 radicals are formed during the low-temperature oxidation of acetaldehyde, we do not regard them as being endowed with any excess

FIG. 3.

Effect of NO_2 on rate of main reaction.

energy because in our suggested mechanism these radicals are always produced by a normal metathetical process. An important step, however, in our mechanism is the reaction

$$CH_3{\cdot}CO + O_2 = CH_3{\cdot}CO_3 \ . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (A2)$$

and this will, of course, give rise to peracetyl radicals endowed with their heat of formation and these are equivalent to the hot $HO_2{}^*$ radicals shown by Dainton and Norrish to cause chain branching in the hydrogen–oxygen reaction. We attribute the catalytic effect of nitrogen peroxide on the low-temperature oxidation of acetaldehyde to the process

$$CH_3{\cdot}CO_3{}^* + NO_2 = CH_3{\cdot}CO_3 + NO + O \ . \quad . \quad . \quad . \quad . \quad (A5)$$

The oxygen atom can cause chain branching by reacting with acetaldehyde thus :

$$CH_3{\cdot}CHO + O = CH_3{\cdot}CO + OH \ . \quad . \quad . \quad . \quad . \quad . \quad . \quad (A6)$$
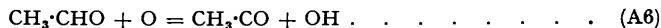
The decrease in the catalytic effect with increasing concentration of nitrogen peroxide (see Fig. 3) may be due to this substance tending to combine with the chain carrier, the acetyl radical; or, more probably, to the excess of nitric oxide produced by reaction (A5) tending to inhibit the chain-branching process by reacting with the active centres. In this connection, it is noteworthy that nitric oxide inhibits the formation of carbon monoxide during the photolysis of acetone, and Anderson and Rollefson (*J. Amer. Chem. Soc.*, 1941, **63**, 816) have attributed this to the following reactions :

$$CH_3{\cdot}CO{\cdot}CH_3 + h\nu = CH_3{\cdot}CO + CH_3$$
$$CH_3{\cdot}CO + NO = CH_3{\cdot}CO{\cdot}NO$$
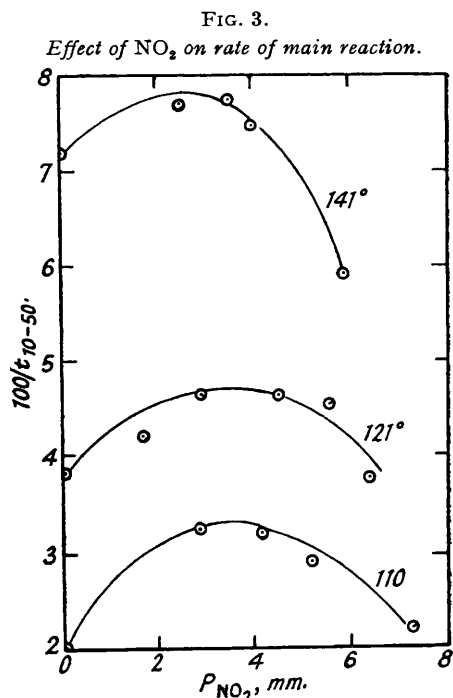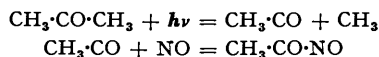
Rate of Initiation, and Chain Length.—Equation (6) shows that I_0/τ is the rate of initiation. For a particular experiment at 141°, I_0, the initial concentration of nitrogen peroxide, was $1\cdot405 \times 10^{-5}$ mole litre^{-1}, and the induction period 195 seconds; hence the rate of initiation is $7\cdot2 \times 10^{-8}$ mole litre^{-1} sec.$^{-1}$. Hence, from equation (6a) we can calculate the absolute velocity constant for the initiation reaction. In the above experiment [CH$_3$·CHO] was $42\cdot2 \times 10^{-5}$ mole litre^{-1}, and [O$_2$] was $41\cdot95 \times 10^{-5}$ mole litre^{-1}; hence $k_1 = 0\cdot4$ mole litre^{-1} sec.$^{-1}$. With this value of k_1 and the value of $13\cdot8$ kcals. for the activation energy of the initiation reaction, we calculate an approximate value of $10^{6\cdot95}$ for the frequency factor, A, in the Arrhenius equation $k = A\mathrm{e}^{-E/RT}$.

If we regard the low-temperature oxidation of acetaldehyde as being a simple chain reaction to which we may apply the stationary-state hypothesis, it is possible to estimate, approximately, the chain length. In the stationary state, the rate of initiation r_i equals the rate of chain termination r_t. The overall rate of reaction $R = r_i r_p/r_t = -\mathrm{d}P/\mathrm{d}t$; hence, since $r_i = r_t$, we have $-\mathrm{d}P/\mathrm{d}t \approx r_p$. The chain length, r_p/r_i, is therefore $-(\mathrm{d}P/\mathrm{d}t)/r_i = -(\tau/I_0)(\mathrm{d}P/\mathrm{d}t)$. In the following table are given values of r_i and $-\mathrm{d}P/\mathrm{d}t$ for various temperatures and the values for the chain length.

Approximate chain length for the low-temperature oxidation of acetaldehyde.

Temp.	r_i, mm./min.	$-\mathrm{d}P/\mathrm{d}t$, mm./min.	Chain length.	Temp.	r_i, mm./min.	$-\mathrm{d}P/\mathrm{d}t$, mm./min.	Chain length.
110°	0·32	0·808	2·5	125·6°	0·62	1·91	3·08
121	0·41	1·54	3·6	141	1·02	2·88	2·82

The chain length of approximately 3 thus derived is very short and is to be compared with the short chains in the liquid-phase oxidation of alcohols by the bisulphite radical ion (Alyea and Bäckström, *loc. cit*), and the low-temperature gas-phase oxidation of acetylene. The similarity between the oxidation of acetaldehyde and acetylene has been discussed previously (Bodenstein, *loc. cit.*; Semenoff, *loc. cit.*). Using Kistiakowsky and Lenher's experimental data (*J. Amer. Chem. Soc.*, 1930, **52**, 3785), Bodenstein derived a chain length of approximately 3 for this reaction also.

Discussion of the Initiation Reaction.—It is obvious from the experiments described above that the reaction between acetaldehyde and oxygen is a radical-chain reaction and that the induction period is due to inhibition by the interaction of nitrogen peroxide, or some compound derived from it, with the active species or chain carrier. The fact that the equation

$$I_0/\tau \approx k_1[\text{Aldehyde}][\text{Oxygen}] \quad \ldots \ldots \ldots \quad (6a)$$

is obeyed, as shown by Fig. 2, proves beyond all reasonable doubt that the chain is initiated by a bimolecular reaction between acetaldehyde and oxygen.

Equation (6a) means that I_0/τ is a measure of the rate of initiation of the oxidation, and the variation of this quantity with temperature will yield a value for the activation energy of the initiation reaction. A plot of the slopes of the straight lines in Fig. 1, *i.e.*, $\mathrm{d}P_{\text{NO}_2}/\mathrm{d}t$ against the reciprocal of the absolute temperature, yields a value of $13\cdot8$ kcals./mole for the activation energy of the initiation reaction. In Part I it was shown that the overall activation energy for the oxidation of acetaldehyde was $14\cdot2$ kcals./mole, a value which has been confirmed by the recent work of Letort and Letort (*Compt. rend.*, 1948, **226**, 77). Hence, most of the activation energy for the overall reaction is due to the initiation reaction as suggested in Part I, and as was shown to be the case for the oxidation of formaldehyde (Axford and Norrish, *Proc. Roy. Soc.*, 1948, *A*, **192**, 518).

As indicated above, we assume the oxidation to be initiated by the reaction (C), and in Part I (*loc. cit.*) we have given evidence to show that such a process would necessarily have an activation energy of between 10 and 20 kcals.

The activation energy for this reaction will, of course, be approximately equal to the difference between the heat of formation of the perhydroxyl radical (HO$_2$) and the dissociation energy of the aldehydic C–H bond in acetaldehyde. When the previous papers were written neither of these quantities was known with much accuracy, the former being taken as $\sim$60 kcals. (Walsh, *J.*, 1948, 331). Since then more reliable data on the dissociation energy of the functional C–H bond in acetaldehyde have become available. We previously outlined evidence which showed that this was much weaker than any of the other C–H bonds in that molecule, and on this account we indicated that this would be the most likely point of oxygen attack. Further, we were able to show from the then available information that this bond must have a dissociation energy of approximately 70—80 kcals. That the aldehydic C–H bond

is in fact the weakest C–H bond in acetaldehyde has been proved by a mass-spectrometric study of mixtures of normal and deuterated acetaldehydes by Brinton and Blacet (*J. Chem. Physics*, 1949, **17**, 797). That work, however, does not yield a value for the dissociation energy. From an independent study of the dissociation of acetaldehyde, and other acetyl compounds, by electron impact in a mass-spectrometer (McDowell and Warren, to be published soon) it has been possible to assign a value of between 3 and 3·5 electron volts, *i.e.*, 70—80 kcals. to the dissociation energy of this bond. Some confirmation of these estimates is provided by the value of 80 kcals. obtained by Carson and Skinner (*J.*, 1949, 936) from a thermochemical study of the hydrolysis of acetyl halides. Thus the previous estimate of the activation energy for the suggested initiation reaction is seen to have been fairly correct and the agreement with the experimental value derived from the results given in the present paper strengthens the arguments in favour of regarding it as the true initiation process for the low-temperature oxidation of acetaldehyde.