149. *The Slow Combustion of Formaldehyde.*

By Robert Spence.

It has been shown (*J. Amer. Chem. Soc.*, 1930, **52**, 2399, 4837; 1931, **53**, 1689; J., 1932, 686) that formaldehyde is a product of the partial oxidation of simple gaseous hydrocarbons and hydrocarbon radicals; also, it appears at an early stage in the combustion of higher hydrocarbons (cf. Ubbelohde, Drinkwater, and Egerton, *Proc. Roy. Soc.*, 1935, **153**, *A*, 103). The question has been discussed whether it plays a fundamental rôle in the chain of reactions resulting in complete combustion, or whether it is simply a by-product. Spence and Kistiakowsky (*J. Amer. Chem. Soc.*, 1930, **52**, 4837) found that acetylene is oxidised more rapidly than formaldehyde at the same temperature (Fort and Hinshelwood, *Proc. Roy. Soc.*, 1930, **129**, *A*, 284), and that the kinetic and analytical data could be reconciled to some extent by assuming that formaldehyde is essentially a by-product. Nevertheless, there remained the possibility that the supply of active centres generated thermally in the oxidation of formaldehyde may be greatly exceeded in the acetylene reaction, with the result that any formaldehyde produced would be rapidly oxidised. Recently, Steacie and MacDonald (*J. Chem. Physics*, 1936, **4**, 75), investigating the influence of additions of formaldehyde on the combustion of acetylene, found that the rate is considerably diminished thereby. These experiments show that formaldehyde is not a catalyst for the acetylene oxidation, but indicate rather that it deactivates the acetylene chain carriers. As the fate of the formaldehyde is not known, it cannot be decided whether it is itself oxidised as a result of the deactivation. However, the oxidation of formaldehyde alone has been the subject of but few investigations. Measurements by Askey (*J. Amer. Chem. Soc.*, 1930, **52**, 974) and by Fort and Hinshelwood (*loc. cit.*) show that the velocity is dependent upon a power of the formaldehyde concentration, and is practically independent of that of oxygen, the chief products being carbon monoxide and dioxide and water. The course of the reaction is clearly complex, and has now been examined analytically, further kinetic measurements being recorded.

EXPERIMENTAL.

Oxygen, prepared by heating A.R. potassium permanganate in a Pyrex tube, was condensed in a liquid-air trap after passing over solid potassium hydroxide and phosphoric oxide. A large first fraction was removed from the condensate, and the middle fraction collected in a 3-litre Pyrex bulb containing mercury. Formaldehyde was obtained by evaporation of the liquid monomeride (Spence and Wild, J., 1935, 338). The apparatus and quartz spiral manometer were as already described (J., 1934, 1588), but, owing to the higher temperature required for the oxidation, it was necessary to fill the electric oven with brass turnings in order to avoid a sharp temperature gradient in the interior. The gases could be separately introduced into the reaction vessel or previously mixed at 100° in a 500-ml. bulb; and temperatures were measured both by a mercury thermometer and by a thermocouple.

The Heterogeneous Reaction.—The oxidation of formaldehyde to entirely gaseous products may occur in two ways:

$$(1)\ 2CH_2O + O_2 \longrightarrow 2H_2O + 2CO$$
$$(2)\ CH_2O + O_2 \longrightarrow H_2O + CO_2$$

Reaction (1) is accompanied by a 50% increase in pressure, whereas (2) occurs without pressure change. It was found that in the presence of an extensive surface of powdered glass, oxidation according to reaction (2) was complete. A cylindrical reaction vessel packed with powdered Pyrex glass, previously employed (*loc. cit.*), having a volume of 32·4 ml. and a surface-volume ratio > 100, was thoroughly evacuated at 300°. Formaldehyde was admitted alone, and the fall in pressure with time noted. This was rapid at first, a decrease of 20 mm. occurring in 4 minutes, but very soon became constant at about 1 mm. per min. with 200 mm. of formaldehyde present. At this point oxygen was added. The rate of pressure decrease was at once doubled, and then fell off gradually until reaction ceased, as shown in Fig. 1. At the conclusion of an experiment, the gas mixture was drawn through a liquid-air trap by a Töpler pump, and by repeated removal of the liquid air and exhaustion, carbon dioxide could be separated from any formaldehyde, which remained in the trap in a polymerised condition. Gas analyses were performed in a simple Bone and Wheeler apparatus, the Levy tube being used for combustions. Results for two experiments are given below.

Heterogeneous oxidation of formaldehyde on Pyrex glass.

$v = 32{\cdot}4$ ml.; $s/v > 100$; $T = 300°$.

	Reactants, mm.			Products, mm.				Calculated values, mm.		
No.	CH_2O.	O_2.	Δp.	O_2.	CO_2.	CO.	H_2.	CH_2O.	O_2.	Δp.
2	205·0	248·0	−92·5	36·3	191·5	11·0	7·3	202·5	227·8	11·0
3	82·0	124·0	−41·2	32·4	80·0	3·1	4·4	83·1	112·4	3·1

The hydrogen was determined by difference, but subsequent blank experiments as well as direct combustion analyses (Table I) justified the conclusion that the small amount of residual gas was hydrogen. The amount produced is about equivalent to the carbon monoxide, which indicates that these gases arise chiefly from the decomposition of formaldehyde. Consequently the carbon monoxide has not been taken into consideration in arriving at the oxygen balance. Reaction (1), therefore, does not occur to any appreciable extent in the presence of an excess of glass surface. A notable discrepancy exists between the initial oxygen figure and that calculated from the analysis. This difference of 20·2 mm. in Expt. 2 must represent condensable oxygenated products such as formic acid, which would remain in the liquid-air trap. The agreement between the initial and the calculated formaldehyde values is probably fortuitous, since considerable quantities of this gas had been adsorbed before admission of the oxygen. If it is assumed that water vapour was produced equivalent in amount to the carbon dioxide, it is clear that a small increase of pressure should have occurred. Actually, there was a considerable decrease, and it must be concluded that 90 mm. out of a total of 191·5 mm. (47%) of water vapour produced in Expt. 2 remained adsorbed on the wall. The corresponding figures for Expt. 3 are 42·8 mm. and 80 mm., or 53·5% adsorbed. Consideration of the pressure–time data indicates that the velocity is substantially the same when the oxygen concentration is doubled, whilst the influence of increasing formaldehyde concentration is likewise small.

FIG. 1.

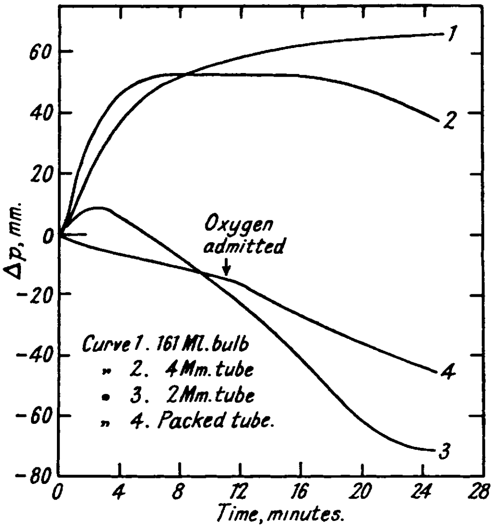
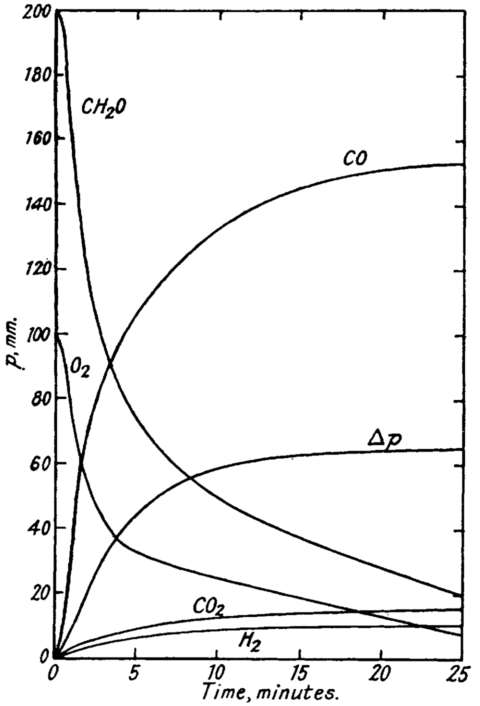


FIG. 2.



Influence of Increasing Diameter.—A series of reaction vessels was prepared consisting of lengths of Pyrex tubing folded so as to diminish the bulk whilst retaining as large an internal volume as possible. However, the dead space in the spiral manometer and connecting tubing could not now be neglected, and the proper corrections were applied to the analytical results after determining the volumes and temperatures concerned. In the case of the 1-mm. tubing, the reaction vessel was connected directly to the stop-cock, and the manometer dispensed with, so only the initial pressure could be determined. Moreover, on account of the slow diffusion occurring in the narrow tubes, it was necessary to prepare the gas mixture in a 500-ml. bulb at 100° before admission to the reaction vessel. Analysis showed that approximately only 1·2 mm. of carbon monoxide, 0·18 mm. of carbon dioxide, and 0·12 mm. of hydrogen were formed at this temperature in 85 minutes. Hence any reaction occurring during the preparation of the mixture would be negligible.

TABLE I.

Influence of diameter on the velocity.

200 mm. CH_2O + 100 mm. O_2 at 317° for 25 mins.

				Products, mm.				Calculated values.		
No.	Tube.	v, ml.	Δp.	O_2.	CO_2.	CO.	H_2.	O_2 initial.	O_2 calc.	CO/CO_2.
56	packed	32·4	—	2·4	97·4	18·5	9·7	101·4	104·2	0·19
55	1 mm.	3·4	—	31·4	16·2	98·0	—	96·4	96·6	6·1
54	2 ,,	7·2	−71·5	19·4	14·2	102·3	—	100·4	84·6	7·2
52	4 ,,	39·0	37·3	4·2	23·2	136·5	17·9	102·4	86·7	6·0
45*h*	bulb	161·0	65·8	7·3	15·8	153·5	10·7	98·6	94·5	9·7

In this and the following tables an amount of carbon monoxide equivalent to the hydrogen produced has been subtracted before the oxygen figure (from $O_2+CO_2+\frac{1}{2}CO$) is calculated. Owing to the small volume of gas available for analysis, the whole of the oxygen supplied could not be accounted for in every case, but it is clear that the amount of carbon monoxide produced increases steadily with the diameter, whilst the carbon dioxide drops sharply to 16 mm. in the 1-mm. vessel and then remains constant. These effects are reflected in the amount of oxygen consumed. Extraordinary pressure changes accompany reaction in the narrow vessels, as shown in Fig. 1. In Expt. 54, which is typical, there is a decrease of 71·5 mm. after an initial increase of 8·8 mm. The quantity of water produced in the reaction would account for a contraction of 65 mm. if it were totally adsorbed. Since it is unlikely that adsorption will be greater than the 53% found in the packed tube, about 30 mm. of the contraction must be due to adsorption or polymerisation of formaldehyde.

Kinetic Measurements.—The velocity of organic gaseous oxidation reactions has generally been determined from the rate of change of pressure, although complicating side reactions are always present. The principal products of the oxidation of formaldehyde in an open bulb are carbon monoxide and water. These are accompanied by smaller amounts of carbon dioxide and hydrogen, and a certain amount of polymerisation occurs at the stop-cock. The observed increase in pressure therefore represents only a fraction of the total reaction. In order to determine this relation, the products of the reaction occurring in the 161-ml. bulb have been analysed at definite intervals of time, the results being given in Table II and in Fig. 2.

TABLE II.

The progress of reaction in a single mixture.

Approx. 200 mm. CH_2O + 100 mm. O_2 in a 161-ml. bulb at 317°.

		Reactants, mm.			Products, mm.				Calculated values.	
No.	t, mins.	CH_2O.	O_2.	Δp.	O_2.	CO_2.	CO.	H_2.	O_2.	CO/CO_2.
45*a*	0·5	199·8	98·4	1·5	89·0	—	7·8	—	92·9	—
45*b*	1·0	203·5	98·5	10·0	79·6	2·0	31·1	1·6	96·4	15·6
45*c*	1·5	196·4	98·1	15·4	61·1	3·5	54·7	3·3	90·3	15·6
45*d*	2·0	202·6	97·3	19·4	58·6	4·5	58·6	2·9	91·1	13·0
45*e*	3·0	196·8	96·2	32·4	40·7	6·7	88·5	4·8	89·3	13·2
45*f*	5·0	193·0	95·8	41·7	33·2	8·7	104·9	6·3	90·7	12·1
45*g*	8·0	196·8	98·8	55·4	27·3	12·2	125·0	8·4	97·8	10·2
45*h*	25·0	196·4	98·6	65·8	7·3	15·8	153·5	10·7	94·5	9·7

Approximately 5% of the initial oxygen is unaccounted for, and it seems probable that this may have been lost in the form of condensable products such as formic acid. The relation between ΔCH_2O and Δp is approximately linear in the early stages of the reaction, and if it be assumed that the same relation holds for other mixtures, different rates of reaction can be determined by measurement of the rate of pressure change. Gas analyses of six different mixtures suggest that the assumption is legitimate. The mean value of $\Delta CH_2O/\Delta p$ obtained from Fig. 2, is approximately 3 up to 50% of reaction and then diminishes to about 2·7.

The quantitative value of the kinetic data is unfortunately adversely affected by a slow increase in the activity of the surface, although it is only in fast reactions that serious differences appear, and some approach to an average has been obtained by suitable ordering of the experiments. Wide variations in the concentration of oxygen have little influence on the rate (Table IIIa), whereas an increase in the formaldehyde concentration is accompanied by an

TABLE III.

(a) *Influence of oxygen concentration on the initial rate.*

200 mm. CH_2O; $v = 161$ ml.; $T = 317°$.

No.	11	10	12	13	9	7	17
O_2, mm.	14·1	25·5	29·0	53·5	57·6	102·1	288·5
dp/dt	5·5	6·5	6·5	6·8	5·8	6·0	7·0

(b) *Influence of formaldehyde concentration on the initial rate.*

200 mm. O_2; $v = 161$ ml.; $T = 317°$.

No.	CH_2O, mm.	dp/dt.	dp/dt, calc.*	No.	CH_2O, mm.	dp/dt.	dp/dt, calc.*	No.	CH_2O, mm.	dp/dt.	dp/dt, calc.*
22	39	0·02	0·04	25	116·5	2·5	2·4	28	223	15·0	13·2
26	90	1·0	1·0	20	128·7	2·5	3·2	29	263	29·0	19·6
21	109	2·0	1·9	24	190	8·0	8·9	18	333	31·0	33·4

* For equation upon which calculated values are based, see p. 655.

important increase in the velocity (Table IIIb); dp/dt is given in mm. per min., and for Expt. 22, the value has been calculated from analytical data. Fort and Hinshelwood (*loc. cit.*) have calculated an energy of activation of 20,000 cals. from determinations of the time of half-reaction at different temperatures. It is questionable, however, whether such values form the most satisfactory basis for the calculation, since the velocity of a single reaction does not always decrease according to the initial rate law. For this reason, the initial rates have been measured over a similar range of temperature, and the apparent energy of activation calculated. After correction for the change in formaldehyde concentration in each case, this gives a value of 17,600 cals. According to Askey (*loc. cit.*), increase of temperature results in an increase in the proportion of carbon dioxide in the products. Analysis of the same mixture at 277° and at 337° gave CO/CO_2 ratios of 5·5 and 8·5 respectively, but this result does not appear to be in serious contradiction to Askey's experimental data since the reduction in the final pressure increase upon which his conclusion is based occurs above 346°.

Dependence of initial velocity on temperature.

200 mm. CH_2O + 100 mm. O_2; $v = 161$ ml.

Nos.	T.	dp/dt.	No.	T.	dp/dt.
35, 37	277°	5·0	32	327°	13·0
33, 34	297	8·0	36	337	18·5

DISCUSSION.

It is important, first, to decide whether the reaction is simple or of the chain type. The influence of diameter is always a useful criterion in this connexion, and it can be seen from Table I that an increase in diameter is accompanied by an increase in the rate of formation of carbon monoxide. The existence of an induction period and the complex reaction kinetics observed are also in accord with the idea of a chain mechanism. It is, nevertheless, surprising that the production of carbon monoxide, which presumably occurs homogeneously, should still be quite rapid in vessels of 1 mm. diameter, and it might be alleged that the apparent diminution in velocity is entirely due to the removal of formaldehyde by polymerisation or adsorption. However, the amount of oxygen reacting in the 4-mm. tube is approximately equal to that in the open bulb, and it seems probable that the inhibition of reaction (1) is real. In the packed tube, the amount of carbon monoxide arising from oxidation is very small, although pressure–time measurements indicate that the homogeneous reaction in an open bulb at this temperature is the faster. Inhibition of the homogeneous reaction appears to occur, therefore, at some diameter less than 1 mm., and it may be confidently assumed that the oxidation of formaldehyde in open vessels is a chain reaction. Considered from the point of view of Semenoff's theories ("Chain Reactions and Chemical Kinetics," 1935, pp. 344—376), the form of the Δp–time curve and the general kinetic properties place the reaction in the acetylene–aldehyde class of oxidations. Indeed, Semenoff's predictions with regard to this type of reaction have to a certain extent been fulfilled, *viz.*, that the velocity in a single experiment may remain approximately constant for a considerable fraction of the reaction or decrease more slowly than would be expected from the initial rate law, and that the velocity–time curve should be initially concave. In certain of the most rapid reactions studied, the velocity was constant or nearly so until some 60% of the formaldehyde had disappeared. In most of the cases shown in Table IV, however, the rate adheres more closely to the theoretical. The rate–time curve deduced from the analytical data for the production of carbon monoxide is slightly but definitely concave, and it seems improbable that this concavity can be due to the slow heating of the gas mixture, which is prepared at 100° and passes into the vessel *via* capillary tubing at 317°. If anything, the carbon monoxide figure for $\frac{1}{2}$ minute is too large, since the gas cannot be wholly removed upon opening the stop-cock but is reduced first of all to a pressure of a few cm. and then slowly pumped out by the Töpler pump. Semenoff has shown that the velocity of oxidation of a saturated hydrocarbon increases with time according to the equation $\log \Delta p = \text{const.} + \psi_0 t$. If we consider Expt. 47, in which the increase of velocity with time can be noticed, and plot $\log \Delta p$ against t as in Fig. 3, only the first few points lie on a straight line. In the oxidation of formaldehyde, therefore, the maximum rate is attained at a comparatively early stage, and not when only half of the organic reactant remains, as in the case of saturated hydrocarbons. From the linear portion of the curve we have $\psi_{0\,\text{min.}} = 0{\cdot}34$, and since $\phi_0 = 2{\cdot}3\psi_0$ (Semenoff, *ibid.*), $\phi_{0\,\text{sec.}} = 0{\cdot}013$. This compares with the value 0·04 obtained for acetylene at 320°, which was unfortunately given as 0·4 in the previous paper (Spence, *loc. cit.*). According to Semenoff's view, reactions of this type are characterised by an interaction between the chains. The larger the supply of initial centres, the greater the chance of interaction, with the result that the induction period would become shorter, and the velocity would tend to maintain its initial value for a longer period. Bäckström (*Z. physikal. Chem.* 1934, *B*, **25**, 99) has proposed a chain mechanism for the oxidation of aldehydes which accounts very well for the liquid-phase oxidation, and it seems probable that a similar mechanism involving interacting, branched chains might prove satisfactory in this case. Direct adaptation of Bäckström's scheme would lead to a highly complicated series of

Fig. 3.

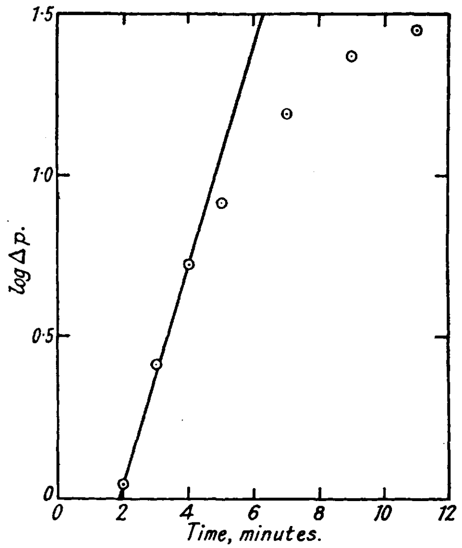
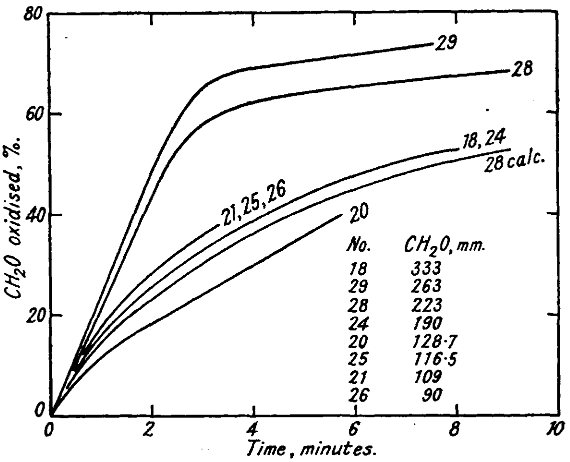


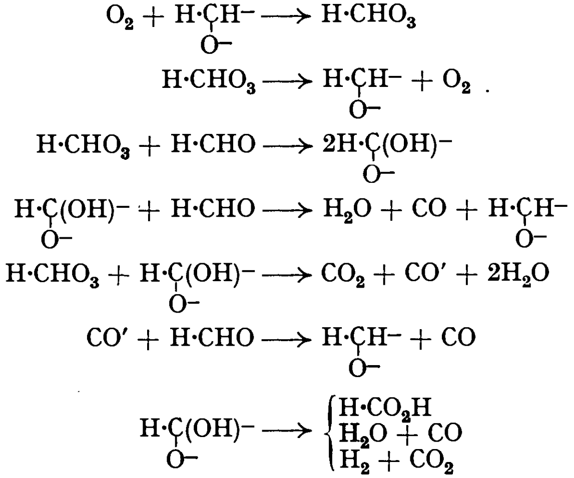
Fig. 4.



Expt. 47; 200 mm. CH_2O + 100 mm. O_2; T = 277°.

t, mins.	2	3	4	5	7	9	11
Δp	1·1	2·6	5·3	8·2	15·6	23·4	28·2
$\log \Delta p$	0·0414	0·4150	0·7234	0·9139	1·1931	1·3692	1·4502

reactions, but it has been possible to devise the following mechanism by supposing that at 320° the activated aldehyde will react rapidly with oxygen, giving an unstable complex.



(1) $$\mathrm{O_2 + H\cdot\underset{O-}{C}H- \longrightarrow H\cdot CHO_3}$$

(2) $$\mathrm{H\cdot CHO_3 \longrightarrow H\cdot\underset{O-}{C}H- + O_2}\ .$$

(3) $$\mathrm{H\cdot CHO_3 + H\cdot CHO \longrightarrow 2H\cdot\underset{O-}{C}(OH)-}$$

(4) $$\mathrm{H\cdot\underset{O-}{C}(OH)- + H\cdot CHO \longrightarrow H_2O + CO + H\cdot\underset{O-}{C}H-}$$

(5) $$\mathrm{H\cdot CHO_3 + H\cdot\underset{O-}{C}(OH)- \longrightarrow CO_2 + CO' + 2H_2O}$$

(6) $$\mathrm{CO' + H\cdot CHO \longrightarrow H\cdot\underset{O-}{C}H- + CO}$$

(7) $$\mathrm{H\cdot\underset{O-}{C}(OH)- \longrightarrow \left\{\begin{array}{l} H\cdot CO_2H \\ H_2O + CO \\ H_2 + CO_2 \end{array}\right.}$$

Branching occurs by the formation of two activated formic acid molecules by reaction (3), whilst the chain interaction (5) counteracts the chain-breaking process (7) so that the reaction, once started, will continue until the cycle breaks down. It is assumed that activated formic acid is concerned in the chain, otherwise this substance might be expected to become an important end-product. Formaldehyde is activated according to reaction (6) by collision with an excited carbon monoxide molecule, but excited carbon dioxide or water could equally well be represented as the activating agent. After collection of constants, the following parabolic equation is obtained :

$$-\,d[\mathrm{CH_2O}]/dt = k'[\mathrm{CH_2O}]^2 - k''[\mathrm{CH_2O}] + k'''$$

where $k' = 3k_3k_4/k_5$, $k'' = 4k_3k_7/k_5$, and $k''' = k_3k_7^2/k_4k_5$. When empirical values calculated from the initial-rate measurements given in Table IIIb are substituted, we have

$$-\,d[\mathrm{CH_2O}]/dt = 1{\cdot}17 \times 10^{-4}[\mathrm{CH_2O}]^2 - 9{\cdot}21 \times 10^{-2}[\mathrm{CH_2O}] + 1{\cdot}9395$$

and the initial rates obtained from this equation are compared with those obtained experimentally in Table IIIb. The value of the constant term is slightly greater than that expected from the theoretical relations between k', k'', and k''', and it is conceivable that another term should be included representing the initial supply of active centres. The ratio k_4/k_7, calculated from the empirical values of k' and k'', is about 1/50, *i.e.*, the activated formic acid is relatively easily decomposed or deactivated. It would appear also that k_5 is large, so that chain interaction occurs readily. In the above equation, $-\,d[\mathrm{CH_2O}]/dt$ is a minimum at $[\mathrm{CH_2O}] = 39{\cdot}4$ mm., but owing to the lack of experimental data in this region, no attempt has been made to remedy this. Moreover, it is doubtful whether the Bodenstein method of derivation of a velocity expression is strictly applicable in this case, since stationary concentrations of intermediates are probably not attained. However, we can attempt to calculate the course of a single experiment from the integrated form of the velocity equation :

$$t = 81{\cdot}55 \tan^{-1}x/[9{\cdot}545 \times 10^{-2}a(a - x) - 3{\cdot}755(2a - x) + 158{\cdot}1]$$

where a is the initial pressure of formaldehyde, and x the decrease in formaldehyde pressure after t minutes. Curves have been plotted for each initial pressure and the percentage reaction after given intervals of time obtained. These values are compared with the experimental data in Table IV. Where more than 50% of reaction has occurred, the factor $\Delta[\mathrm{CH_2O}]/\Delta p$ for the particular pressure increase concerned has been deduced from Fig. 2.

TABLE IV.

The experimental and the calculated course of reaction in different mixtures.

O_2 = 100 mm.; v = 161 ml.; T = 317°.

CH_2O, 333 mm.			CH_2O, 263 mm.			CH_2O, 223 mm.			CH_2O, 190 mm.		
t.	%, obs.	%, calc.	*t*.	%, obs.	%, calc.	*t*.	%, obs.	%, calc.	*t*.	%, obs.	%, calc.
0·5	14·4	13·2	0·2	6·8	4·6	0·2	4·0	3·6	2	22·2	20·4
1	25·2	22·5	1	33·0	17·7	1	20·7	14·6	4	35·1	32·8
2	38·7	36·0	2	63·3	29·1	2	44·4	23·2	6	42·6	39·0
3	47·0	44·8	4	70·8	42·4	5	64·0	41·2	10	52·1	49·6
4	52·9	50·5	6	73·5	49·1	11	69·0	55·8			
CH_2O, 128·7 mm.			CH_2O, 116·5 mm.			CH_2O, 109 mm.			CH_2O, 90 mm.		
1	5·8	6·8	1	6·4	5·7	2	10·5	9·2	2	6·7	6·1
4	16·3	20·5	2	12·9	10·3	4	19·0	16·1	4	13·7	11·1
8	25·6	32·4	4	21·9	17·8	8	31·1	25·7	8	23·7	19·1
16	39·9	44·8	8	35·8	28·3	12	37·7	32·2	12	30·0	24·7

The theoretical curve for Expt. 28 (CH_2O, 223 mm.) has been plotted in Fig. 4, and the experimental curves constructed on this as a base line. Six experimental curves representing formaldehyde pressures ranging from 90 to 333 mm. lie quite close to the theoretical, whilst in two cases the initial velocity remains unchanged until about 50% of the formaldehyde has reacted. This effect can scarcely be due to overheating of the gas, since it does not occur in every instance, even at high initial rates; nor can it be due to some abnormal reaction, for the usual products appear in the usual ratios. In, *e.g.*, Expt. 29, 263 mm. CH_2O + 100 mm. O_2 gave 22·5 mm. CO_2, 162·0 mm. CO, and 16·8 mm. H_2 in 10 minutes, whilst only 2·8 mm. of O_2 remained. The pressure should have increased by 89·4 mm. whereas an increase of 73 mm. was recorded, the difference presumably being due to polymerisation. There was no further pressure increase after 6 minutes, and the percentage reaction calculated from Δp in the manner described previously was 73·5, in good agreement with the analytical results, which correspond to 70% of reaction. Although the tendency towards a lower order of reaction appears to depend to some extent on the initial velocity, this is clearly not the only factor. The effect is most pronounced in experiments occurring later in the series, when the surface is most active, and it seems reasonable to conclude that the state of the surface is of great importance in this connexion. Perhaps the chains branch on a surface which is in a suitable state of activity, but it will be necessary to obtain further results before any definite conclusions can be drawn.

It is important, if the combustion mechanism is to be complete, to take account of the carbon dioxide and the hydrogen which are produced. Consideration of Table II shows that the carbon dioxide formed in an open bulb at 317° cannot wholly originate from the purely heterogeneous reaction, since there is no direct proportionality between the extent of surface and the concentration of carbon dioxide. It is supposed, in the mechanism, that hydrogen and carbon dioxide are produced by one of three possible deactivations or decompositions of the activated formic acid. Hydrogen may also arise from the decomposition of formaldehyde itself. Thus, concentrations of carbon monoxide and of hydrogen of the order of 0·5 mm. are produced from 200 mm. of formaldehyde at 317° in 10 minutes. It is possible that this decomposition is accelerated by oxygen, but in view of the close parallelism between the amounts of hydrogen and of carbon dioxide produced in the oxidation (cf. Table II), decomposition of the activated formic acid seems to be the more likely source of the hydrogen. The fact that the ratio CO/CO_2 decreases during the course of a single experiment points to the same conclusion, since reaction (4) should occur less frequently as the formaldehyde is consumed, whilst (5) and particularly (7) should become relatively more important. As regards the heterogeneous reaction, little further can be said. Davies (*Phil. Mag.*, 1936, **21**, 513; and unpublished results) has found that under suitable conditions of concentration and temperature, the combustion of methane on a platinum wire is complete, but when carbon monoxide is adsorbed on the wire, the reaction is inhibited. Now, if the production of normal carbon monoxide were an important stage in the oxidation, rapid self-poisoning should take place. The fact that this does not occur indicates that carbon dioxide must be produced directly or through the nascent or active carbon monoxide of the type postulated in the foregoing mechanism. Some experiments recently carried out in collaboration with Dr. Davies, and shortly to be published, indicate that similar considerations apply in the case of formaldehyde.

SUMMARY.

Formaldehyde reacts rapidly with oxygen in Pyrex glass vessels at 317°. In unpacked vessels, of diameters ranging from 1 mm. upwards, the chief products are carbon monoxide and water, whilst in a vessel packed with powdered glass, combustion to carbon dioxide and water is complete.

The kinetics of the reaction have been studied, and a chain mechanism has been proposed which partly accounts for the results.

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