

# The Inhibition of the Hydrogen+Oxygen Reaction by Formaldehyde

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The inhibiting action of HCHO on the first and second limits of the  $\text{H}_2 + \text{O}_2$  reaction has been studied in KCl-coated vessels at  $540^\circ\text{C}$ . The efficiency of inhibition is almost inversely proportional to the mole fraction of  $\text{O}_2$ , and is less dependent on the mole fraction of  $\text{H}_2$ . This indicates that the main primary termination process is the reaction  $\text{H} + \text{HCHO}$  (14) which competes with the reaction  $\text{H} + \text{O}_2$  (2); a smaller contribution results from the reaction of  $\text{OH} + \text{HCHO}$  (15) competing with  $\text{OH} + \text{H}_2$  (1), or from  $\text{O} + \text{HCHO} = \text{OH} + \text{HCO}$  (13) competing with  $\text{O} + \text{H}_2 = \text{OH} + \text{H}$  (3). The efficiency of inhibition is independent of diameter showing that the HCO radicals are not destroyed at the surface; this is confirmed by the fact that the fraction of HCO radicals undergoing chain-termination reactions is effectively independent of mixture composition and of pressure over the range 4–100 mm Hg. Evidence against the reactions  $\text{HCO} = \text{H} + \text{CO}$  and  $\text{HCO} + \text{O}_2 = \text{CO}_2 + \text{OH}$  is provided, and it is concluded that chain termination ultimately results either from the reaction  $\text{HCO} + \text{O}_2 = \text{CO} + \text{HO}_2$ , or from the reaction  $\text{HCO} + \text{O}_2 = \text{HCO}_3$ , the  $\text{HCO}_3$  radicals being destroyed at the surface. The results permit the evaluation of the ratios  $k_{14}/k_2$  and  $k_{15}/k_1$  (or  $k_{13}/k_3$ ) and from estimates of  $k_{14}$ , a value of  $k_2$  can be obtained which agrees with earlier estimates.

The inhibiting action of hydrocarbons such as  $\text{C}_2\text{H}_6$ <sup>1-3</sup> and  $\text{C}_3\text{H}_8$ <sup>3, 4</sup> on the  $\text{H}_2 + \text{O}_2$  reaction has been attributed to the occurrence of a direct termination reaction (20a) † between  $\text{O}_2$  and the  $\text{C}_2\text{H}_5$  (or  $\text{C}_3\text{H}_7$ ) radical produced by the attack of H and OH (or O) on the hydrocarbon.



With  $\text{CH}_4$ , the analogous reaction for  $\text{CH}_3$  would produce the  $\text{CH}_2$  radical. There is no evidence that this reaction is important at  $500^\circ\text{C}$ , and in any case the reactivity of the  $\text{CH}_2$  would prevent chain termination. It is not surprising, therefore, that the inhibiting action of  $\text{CH}_4$  is quite different<sup>4-6</sup> from that of  $\text{C}_2\text{H}_6$  and the higher hydrocarbons. Since no direct inhibition by  $\text{CH}_4$  seems feasible, it has been suggested that its action arises from the HCHO formed on oxidation. Although the reaction  $\text{H} + \text{HCHO} = \text{H}_2 + \text{HCO}$  is known to occur readily, the high quantum yields obtained in the photolysis<sup>7, 8</sup> of HCHO at temperatures above  $300^\circ\text{C}$  suggested that the formyl radical might readily decompose into  $\text{H} + \text{CO}$ , thus regenerating the H atom. Preliminary tests showed, however, that HCHO was a powerful inhibitor. Its action was, therefore, examined in detail, first, to provide information on the mechanism of inhibition, secondly, to study the reactions of H and OH (or O) with HCHO, and thirdly, to obtain information on the subsequent reactions of the HCO radicals produced by the primary inhibition process.

## EXPERIMENTAL

The apparatus and procedure were similar to those described earlier.<sup>1</sup> HCHO was prepared as described by Spence and Wild.<sup>9</sup> As with previous studies, a standard mixture

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† The system of numbering used is consistent with that adopted in previous papers.

of high  $N_2$  content was selected, containing 0.28, 0.14 and 0.58 mole fractions of  $H_2(x)$ ,  $O_2(y)$  and  $N_2$  respectively. Independent variation of  $x$  or  $y$  could thus be obtained by interchanging  $N_2$  with either  $H_2$  or  $O_2$  respectively.

## RESULTS

Unless otherwise stated, all measurements were carried out in a 35-mm diam. KCl-coated vessel at 540°C.

### EFFECT OF MIXING TIME AND WITHDRAWAL RATE

Preliminary experiments were carried out in a 51-mm diam. cylindrical vessel using the normal procedure adopted in previous studies of the second limit.<sup>1</sup> One gas, normally  $H_2$ , is admitted separately to the evacuated reaction vessel to a pressure of 140 mm Hg, and the remaining pre-mixed gases added to a total pressure

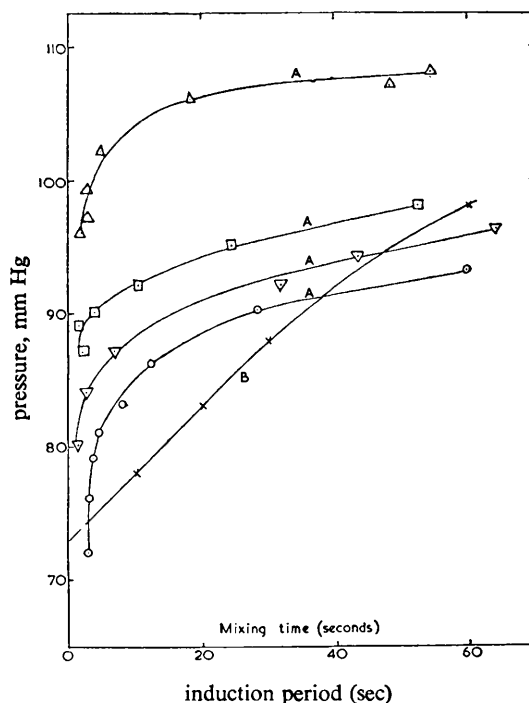


FIG. 1.—A. Induction periods preceding second limit explosions.

Mixing time:  $\circ$  10 sec;  $\nabla$  20 sec;  $\square$  30 sec;  $\triangle$  60 sec.

B. Second limit as function of mixing time:

35-mm diam., 540°C  $x = 0.28$ ,  $y = 0.14$ ,  $i = 0.030 \times 10^{-2}$

of 500 mm Hg. After allowing a short time for mixing in the reaction vessel, the mixture is rapidly withdrawn to the vicinity of the limit, and the withdrawal is then continued at a controlled rate through a suitable capillary. This procedure was used with the standard mixture containing 0.121 %  $HCHO$ , a fairly rapid withdrawal rate being employed. It was found that the uninhibited limit of 146 mm Hg was reduced to approximately 20 mm Hg with a mixing time of 15 sec, but that this rose to about 130 mm Hg if the mixing time was increased to 120 sec. With a constant mixing time, the limit rose markedly as the withdrawal rate was decreased.

Analysis of a sample taken after a mixing time of 1 min showed that over 70 % of the HCHO had been oxidized. This oxidation of HCHO during the mixing and withdrawal periods prevents the use of the normal withdrawal method adopted for  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$ . The procedure, therefore, was modified so that after a fixed mixing period the gas is suddenly expanded to a pre-determined pressure below the uninhibited limit. If this "expansion pressure"  $P_e$  is less than the inhibited limit  $P$ , the gas explodes after a short induction period (1-2 sec) determined by the time for expansion of the gas through the capillary inlet of the reaction vessel. If  $P_e > P$ , explosion does not occur until sufficient HCHO has been oxidized, the time required increasing as  $(P_e - P)$  increases. Typical results are shown in fig. 1a. The intersection of the two portions of the curve gives the limit with effectively infinite withdrawal rate. This procedure is now repeated with various mixing times. An almost linear plot is obtained (fig. 1b), permitting extrapolation to zero mixing time. The resultant pressure is the inhibited limit corresponding to zero mixing time and infinite withdrawal rate. Because of the tedious nature of this procedure, a restricted range of experimental variables was investigated.

#### EFFECT OF HCHO CONCENTRATION

Fig. 2 shows the relation between the HCHO mole fraction and the extrapolated limit  $P$ , expressed as the ratio  $P/P_2$ , where  $P_2$  is the uninhibited limit. As with  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$ , an almost linear relation is obtained, so that the efficiency of inhibition can conveniently be defined by  $i_4$ , the mole fraction of HCHO required to halve the uninhibited limit.

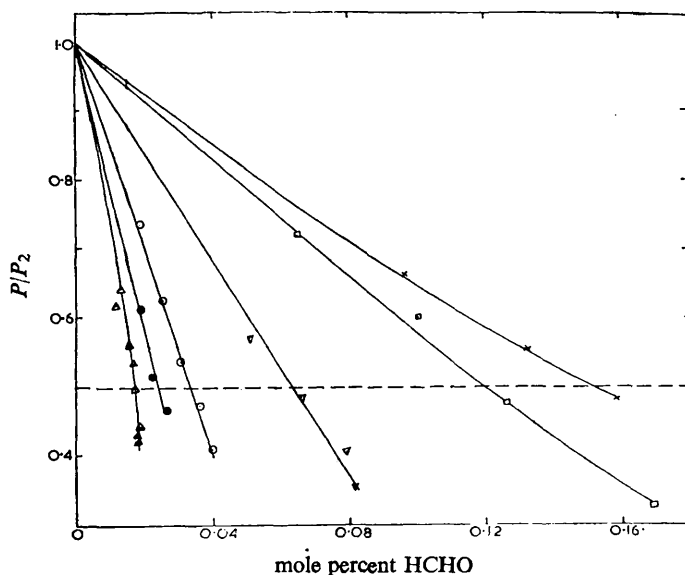


FIG. 2.—Variation of second limit with concentrations of formaldehyde and oxygen, 35-mm diam.,  $540^\circ\text{C}$ ,  $x = 0.28$ ;  $\times y = 0.72$ ;  $\square y = 0.56$ ;  $\nabla y = 0.28$ ;  $\circ y = 0.14$ ;  $\bullet y = 0.10$ ;  $\triangle y = 0.07$ .

#### EFFECT OF MIXTURE COMPOSITION

The almost linear relation between  $i_4$  and  $y$  is shown in fig. 3A, the mole fraction of  $\text{H}_2$  being constant at 0.28. FIG. 3B shows that  $i_4$  varies only slightly with  $x$  at low  $y$  (0.14). This variation becomes more marked at  $y = 0.56$  (fig. 3C).

## EFFECT OF VESSEL DIAMETER

Fig. 4 shows the results of a limited study of the variation of  $i_4$  with vessel diameter over the range 14-35 mm at different mole fractions of  $O_2$ . Calculations,

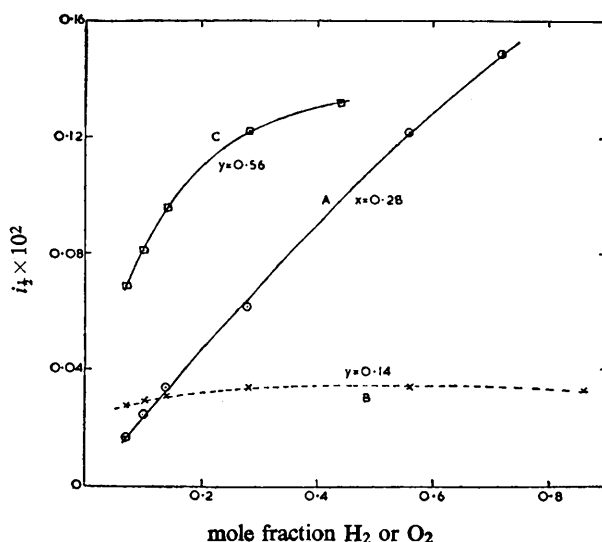


FIG. 3.—Variation of  $i_4$  with mole fractions of hydrogen and oxygen, 35-mm diam., 540°C. A,  $x = 0.28$ ,  $y$  variable; B,  $y = 0.14$ ,  $x$  variable; C,  $y = 0.56$ ,  $x$  variable.

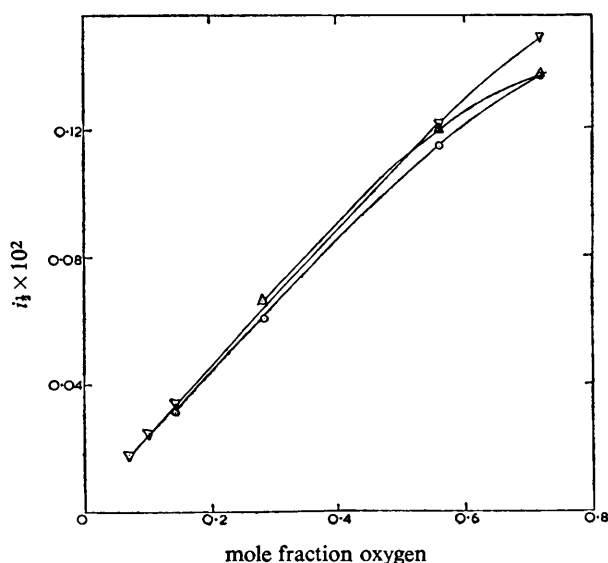


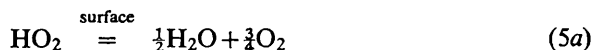
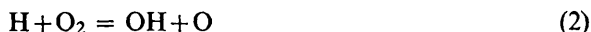
FIG. 4.—Variation of  $i_4$  with vessel diameter, 540°C,  $x = 0.28$ .  $\nabla$  35-mm diam.  $\circ$  24 mm;  $\triangle$  15 mm.

using the treatment detailed elsewhere,<sup>2</sup> show that the small variation observed can be attributed to surface destruction of H atoms. The inhibition process is thus independent of vessel diameter.

## DISCUSSION

## INHIBITION OF THE SECOND LIMIT

The marked dependence of  $i_4$  on  $y$  suggests a competition between  $\text{O}_2$  and  $\text{HCHO}$  for a chain centre, the latter reaction leading to chain termination. If, in KCl-coated vessels, the limit is governed by reactions (1)-(4) and (5a),\* this chain centre can only be the H atom:



Addition of (14) gives the relations,

$$P_2^\circ - P = k_{14}iP_2^\circ Q/2k_2y, \quad (i)$$

$$i_4 = k_2y/k_{14}Q, \quad (ii)$$

where  $P_2^\circ = 2k_2/k_4$  is the uninhibited limit when surface termination is absent.  $Q$  is the fraction of formyl radicals that undergo chain termination reactions. If  $Q$  is either unity, or is independent of mixture composition and pressure, these expressions give the linear  $P$ ,  $i$  and the almost linear  $i_4$ ,  $y$  relations found experimentally.

The less marked effect of  $\text{H}_2$  mole fraction suggests a much smaller contribution from the removal of a chain centre that normally reacts with  $\text{H}_2$ . Since both O and OH react with  $\text{H}_2$ , no unambiguous choice is possible; a slight preference for OH has been indicated elsewhere,<sup>2</sup> and (15)



will be adopted in the remaining discussion.

A mechanism involving reactions (1)-(4), (5a) and (15) gives the relation,

$$P_2^\circ - P = k_{15}iPQ/k_1x, \quad (iii)$$

$$i_4 = k_1x/k_{15}Q. \quad (iv)$$

Eqn. (iii) gives a hyperbolic relation between  $P$  and  $i$ , so that a contribution from (15) can account for the slight curvature of the  $P$ ,  $i$  plot at high values of  $y/x$ , as well as the variation of  $i_4$  with  $x$ .

Introducing both (14) and (15) into the mechanism gives the expression,

$$1/i_4 = (k_{14}Q/k_2y) + [2k_{15}Q/(k_1x + k_{15}i_4Q)]. \quad (v)$$

Assuming that  $Q$  is either unity, or independent of mixture composition and pressure, this expression can be tested by showing that it can predict accurately

\* In discussing the mechanism of the inhibition by  $\text{C}_2\text{H}_6$ ,<sup>2</sup> a more complex mechanism involving reactions (5) and (6) was preferred. Recent work on the slow reaction<sup>10</sup> and second limit<sup>11</sup> in aged boric-acid-coated vessels, and on the gas-phase dissociation of  $\text{H}_2\text{O}_2$ <sup>12,13</sup> has shown that (6) is unimportant.



the variation of  $i_4$  over a wide range of mixture compositions using two suitably selected values for the ratios  $k_{14}Q/k_2$ ,  $k_{15}Q/k_1$ . Preliminary estimates of these ratios can be obtained by simplifying (v) to the form,

$$1/i_4 = k_{14}Q/k_2y + 2k_{15}Q/k_1x. \quad (\text{vi})$$

A plot of  $1/i_4$  against  $1/y$  at constant  $x$ , or of  $1/i_4$  against  $1/x$  at constant  $y$ , gives straight lines, the gradients and intercepts of which enable  $k_{14}Q/k_2$ ,  $k_{15}Q/k_1$  to be estimated.

Before the experimental values of  $i_4$  can be used in this way, they must be corrected for surface destruction of H atoms and OH radicals, the relation being

$$i'_4 = i_4/(1-Z) \quad (\text{vii})$$

where

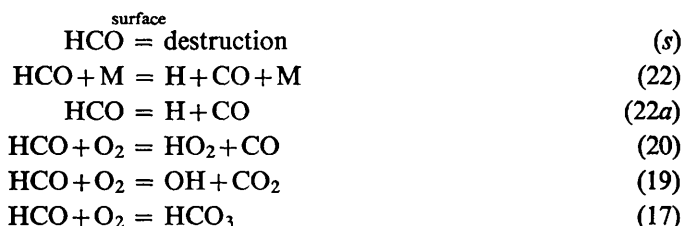
$$Z = \frac{4k''_H - k'_H}{2k_2y} - \frac{k'_{OH}}{(k_1xP_2 + k'_{OH})} + \frac{2k''_{OH}}{(\frac{1}{2}k_1xP_2 + \frac{1}{2}k_{15}i_4P_2Q + k''_{OH})}. \quad (\text{viii})$$

$k'_H$ ,  $k'_{OH}$  and  $k''_H$ ,  $k''_{OH}$  are the surface destruction constants for H, OH at pressures  $P_2$  and  $\frac{1}{2}P_2$  respectively. The basis of this correction and the evaluation of the constants has been discussed elsewhere.<sup>2, 14</sup>

Columns 3, 4 and 5 of table 1 show the experimental values of  $i_4$ , the corrected values,  $i'_4$ , and the calculated values of  $i'_4$  using (v) with values of  $k_{14}Q/k_2 = 320$ ,  $k_{15}Q/k_1 = 42$ . The r.m.s. deviation of observed and calculated values over a very wide range of mixture composition is within 4 %. This agreement, together with the absence of any systematic deviations, supports the proposed mechanism with  $Q$  independent of mixture composition and pressure.

#### FATE OF THE HCO RADICAL

Reactions of the HCO radical suggested in the literature<sup>8, 15-19</sup> include :



The high quantum yields obtained<sup>7, 8</sup> in the photolysis of HCHO at temperatures above 300°C indicate that reaction (22) or (22a) competes successfully with surface destruction of the HCO radical. Early workers<sup>8</sup> considered the dissociation of HCO to be a first-order unimolecular process; more recent views<sup>16, 19</sup> have favoured the second-order process (22), but no decisive experimental evidence is available. The dissociation energy of HCO is still a controversial matter, arguments supporting the "high" value (25-30 kcal) and the "low" value (*ca.* 15 kcal) having been discussed.<sup>19-21</sup> If surface destruction is the sole termination process in the present work, the fraction  $Q$  will be inversely dependent on diameter to the first or second power, according to whether the surface process is inefficient or efficient. The absence of any significant diameter dependence thus eliminates surface termination of HCO radicals.

Further evidence against surface termination is obtained by studying the inhibition of the first limit. The efficiency of inhibition will increase at the first limit if the first-order surface process is competing with the second-order reaction (22)

or if the surface termination is efficient, so that the rate of diffusion to the surface increases as the pressure is reduced. (The accelerating effect of inert gas <sup>16</sup> on the photolysis at 300°C makes it unlikely that the first-order process (22a) is combined with an inefficient pressure-independent surface process, which would make  $Q$  also independent of pressure.) Results described later show that  $Q$  is constant over a wide range of pressure, so that surface destruction can be eliminated.

TABLE 1

$x$	$y$	expt. $i_4 \times 10^2$	corr. $i_4' \times 10^2$	calc. $i_4'' \times 10^2$	$I \times 10^2$	$Q/Q' = I/2i_4'$
0.28	0.72	0.149	0.152	0.145	0.223	0.73
	0.56	0.122	0.125	0.121	0.188	0.78
	0.28	0.062	0.065	0.071	0.117	0.80
	0.14	0.034	0.038	0.039	0.054	0.72
	0.10	0.025	0.028	0.029	0.043	0.77
	0.07	0.017	0.022	0.021	—	—
	0.14	0.033	0.043	0.042	0.066	0.77
0.86		0.034	0.040	0.041	0.058	0.73
0.56		0.031	0.034	0.035	0.052	0.76
0.14		0.029	0.031	0.033	0.048	0.77
0.10		0.028	0.030	0.030	0.047	0.78
0.07		0.132	0.136	0.135	0.212	0.78
0.44	0.56	0.096	0.098	0.096	0.160	0.82
0.14		0.081	0.082	0.083	0.145	0.88
0.10		0.069	0.070	0.070	0.124	0.88

The only alternative termination process involves a reaction of HCO radicals with  $\text{O}_2$ , which could either be (20), or (17), the  $\text{HCO}_3$  radical then being destroyed without continuing the chain. These two possibilities are kinetically equivalent and cannot be distinguished in the present work; for convenience, (20) will be adopted in the remaining discussion. Competition between (20) and (22) would give the relation,

$$Q = k_{20}[\text{O}_2]/(k_{22}[\text{M}] + k_{20}[\text{O}_2]).$$

At very low  $\text{O}_2$  mole fractions,  $Q$  would thus be proportional to the  $\text{O}_2$  mole fraction, and the variation of  $i_4$  with  $y$  apparent in (ii) and (v) would disappear. There is no evidence for this experimentally, so that significant competition between (20) and (22) or (22a) can be eliminated. First-limit studies also provide evidence against (22a) since the importance of this first-order process should increase relative to (20) as the pressure decreases; if the dissociation of HCO is the second-order process (22), however, competition with (20) is independent of total pressure.

Competition between (19) and (20) will make the fraction  $Q$  independent of all variables except temperature. Two arguments eliminate any significant contribution from (19).

(a) Analysis of samples taken during the mixing period indicates that only a few percent of the HCHO oxidized appears as  $\text{CO}_2$ .

(b) If  $k_{19}$  is appreciably greater than  $k_{20}$ , the ratio  $[\text{OH}]/[\text{H}]$  increases considerably above that for the uninhibited reaction. Eqn. (v) is no longer valid under these conditions, an extra factor being introduced into the last term of this equation; the mathematical treatment for  $\text{C}_2\text{H}_6$  has been given elsewhere.<sup>2</sup> Since, as shown in table 1, eqn. (v) expresses the effect of mixture composition over a wide range, it may be assumed that (19) is not important. This argument is only valid if the second primary termination reaction is (15) rather than (13).

## INHIBITION OF THE FIRST LIMIT

The first limit is normally obtained by bracketing between pressures at which explosion does, and does not, occur on admission of the mixture to the evacuated reaction vessel. With HCHO as inhibitor, explosion always occurs provided the pressure  $P'$  is above the uninhibited limit  $P_1^\circ$ . If  $P'$  lies between  $P_1^\circ$  and the inhibited limit  $P_1$ , there is a delay before explosion while the HCHO concentration decreases by oxidation to the value at which explosion can occur; this induction period increases as  $(P_1 - P')$  increases. If  $P' > P_1$ , the induction period is of short duration, determined by the flow of gas from the dosing device into the reaction vessel. Induction period against pressure curves are similar to those given in fig. 1A, and the intersection of the two curves enables the limit to be determined. To obtain a sharper intersection point, a vessel with a 6 mm bore entry tube was used, thus reducing the entry time.

The simplest treatment of the inhibition of the first limit<sup>2</sup> involves the following assumptions: (a) only H atoms are removed by HCHO; (b) only H atoms are destroyed at the surface; (c) this destruction is diffusion controlled (i.e.,  $k_H \propto 1/P$ ); (d) the termolecular termination reaction (4) can be neglected. Putting the net branching factor  $\phi = 0$ , the limit is given by

$$k_H + k_{14}[\text{HCHO}]Q' = 2k_2[\text{O}_2].$$

Writing  $k_H = k'_H/P$ , this can be rearranged to

$$k'_H/P_1^2 + k_{14}iQ' = 2k_2y,$$

where  $Q'$  is the fraction of HCO radicals undergoing termination at the first limit. Assuming  $Q'$  is independent of pressure over the first limit range, a plot of  $1/P_1^2$  against  $i$  will give a straight line of intercept  $(1/P_1^2 = 0)$ ,  $I = 2k_2y/k_{14}Q'$ . Since, if (15) is neglected, the second limit mechanism gives  $i_{\frac{1}{2}} = k_2y/k_{14}Q$ , the ratio  $Q/Q' = I/2i_{\frac{1}{2}}$ . Fig. 5 shows typical results for a wide range of  $\text{O}_2$  mole fractions, the  $\text{H}_2$  mole fraction being constant (0.28). Similar linearity is obtained when  $x$  is varied at constant  $y$  (0.14-0.56). Columns 4 and 6 of table 1 give the values of  $I$  and  $i_{\frac{1}{2}}$ , and column 7 shows that the ratio  $Q/Q'$  is effectively unity.

A more rigorous treatment which allows for the assumptions listed above has been given elsewhere,<sup>2</sup> slight modification being necessary because of the simpler mechanism now adopted for the uninhibited second limit (case C, ref. (2)). Taking a mechanism involving reactions (1)-(4), (5a), (14) and (15), with surface destruction of H and OH, and assuming that the subsequent reactions of the HCO radical do not produce OH radicals (evidence against (19)<sup>1</sup> has already been given), the explosion condition covering both first and second limits<sup>2</sup> is

$$iQ \left[ \frac{k_{14}}{2k_2y} + \frac{k_{15}}{E} \right] = D, \quad (\text{ix})$$

where

$$D = 1 - \frac{P}{P_2} - \frac{k_H}{2k_2yP} - \frac{k_{\text{OH}}}{EP},$$

$$E = k_1x + k_{15}iQ + k_{\text{OH}}/P.$$

The left-hand side of (ix) represents chain-termination processes due to HCHO, while  $D$  contains the termination processes also present in the uninhibited reaction. Since the terms involving  $i$  and  $P$  in  $E$  are relatively small, the term in brackets on the left-hand side of (ix) is almost independent of pressure; a plot of  $D/i$  against



pressure thus indicates the variation of  $Q$  with pressure. For all mixtures, this plot is a straight line,  $D/i$  increasing slightly as  $P$  increases. At least part of this variation can be attributed to the change in  $E$  with  $P$  and  $i$ . This can be allowed for by plotting  $D/i[k_{14}/2k_2y + k_{15}/E]$  against  $P$ . To make this plot, values of  $k_{14}/k_2$ ,  $k_{15}/k_1$  are required; these have been obtained from the values quoted earlier for  $k_{14}Q/k_2$ ,  $k_{15}Q/k_1$ , assuming that  $Q = 1$  at second limit pressures. If the resultant

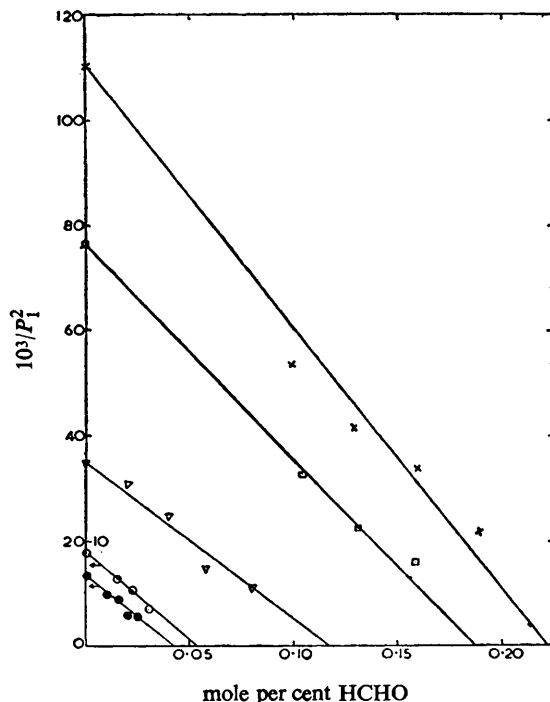


FIG. 5.—Inhibition of first limit by formaldehyde, 35 mm diam. vessel, 540°C.  $x = 0.28$ .

$\times y = 0.72$ ;  $\square y = 0.56$ ;  $\nabla y = 0.28$ ;  $\circ y = 0.14$ ;  $\bullet y = 0.10$ .

plot of  $D/i[k_{14}/2k_2y + k_{15}/E]$  indicates a variation of  $Q$  with pressure, successive approximation methods would be necessary. Fig. 6-8 show, however, that  $Q$  is effectively constant over a wide range of pressure (20:1 for many mixtures). The absolute value of the ordinate scale has no significance, the fact that it is close to unity merely reflecting the initial assumption that  $Q = 1$ . The first limit points are determined by the difference of two experimental limits, and are thus sensitive to experimental error, particularly when the difference is small.

### CONCLUSIONS

The inhibition of both the first and second limits of the  $\text{H}_2 + \text{O}_2$  reaction in KCl-coated vessels can be expressed by a mechanism involving reactions (1)-(4), (5a), (14) and (15), with surface destruction of H and OH (or O). A variety of evidence indicates that the HCO radicals formed in reactions (14) and (15) are not destroyed at the surface, do not decompose into  $\text{H} + \text{CO}$  by reactions (22) or (22a), and do not react with  $\text{O}_2$  to give  $\text{CO}_2 + \text{OH}$ . It thus appears that effectively all the HCO radicals fail to regenerate fresh centres, and are destroyed either by reaction (20), or by reaction (17), the  $\text{HCO}_3$  radical then being destroyed at the surface. Since  $Q = 1$ ,

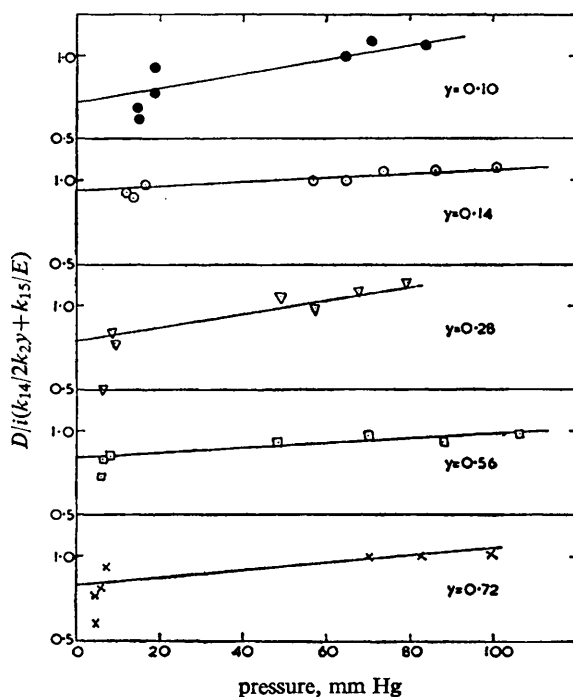


FIG. 6.—Variation of inhibition efficiency with pressure, 35 mm diam. vessel, 540°C;  $x = 0.28$ .

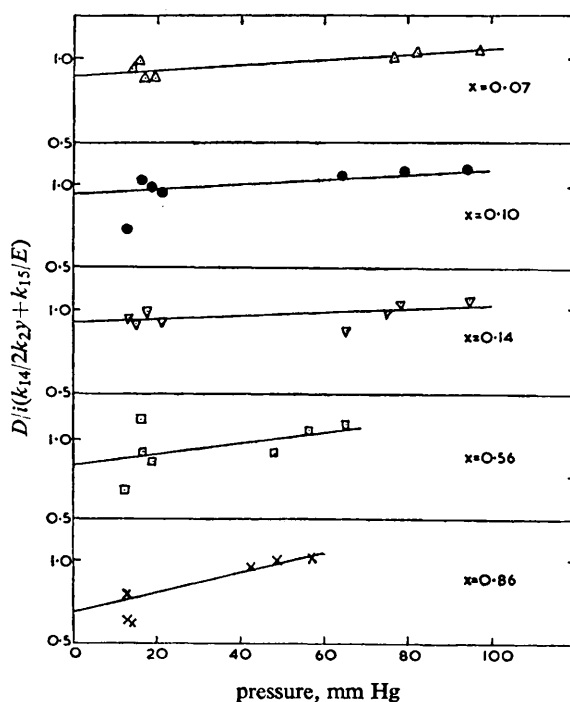


FIG. 7.—Variation of inhibition efficiency with pressure, 35 mm diam. vessel, 540°C;  $y = 0.14$ .

the values of  $k_{14}Q/k_2 = 320$ ,  $k_{15}Q/k_1 = 42$  previously quoted also give the values of  $k_{14}/k_2$ ,  $k_{15}/k_1$ .

The value of  $k_{14}/k_2$  at 520°C can be used to obtain  $k_2$  at 540°C by estimating  $k_{14}$  at 540°C from recent studies which enable  $k_{14}$  to be estimated in the range 300–400°C. Alternatively, if a value for  $k_2$  at 540°C is assumed, a value for  $k_{14}$  at 540°C can be obtained and combined with the values at lower temperatures to yield an activation energy for (14). Since  $E_{14}$  is small,  $k_{14}$  will have a small temperature

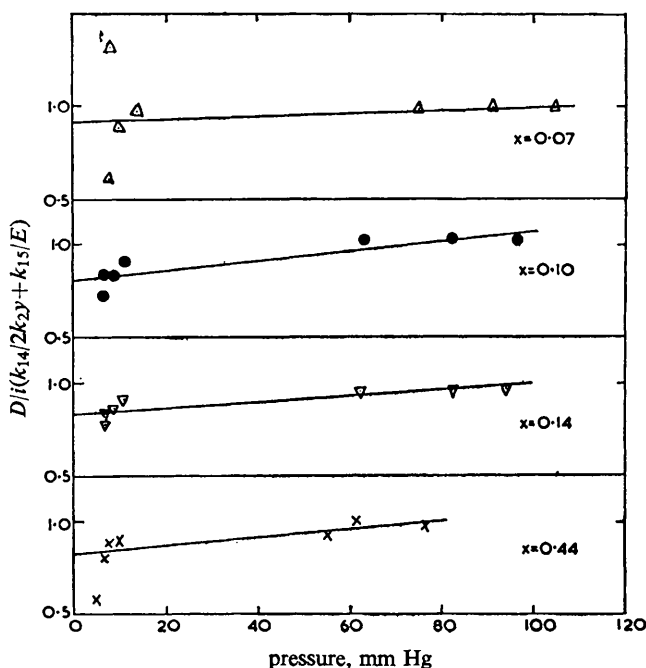


FIG. 8.—Variation of inhibition efficiency with pressure, 35 mm diam. vessel, 540°C;  $y = 0.56$ .

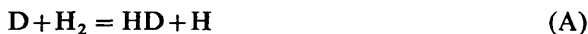
coefficient, and this latter procedure is only profitable if accurate values are available both for  $k_2$  at 540°C and for  $k_{14}$  at the lower temperatures. Since neither condition is satisfied,  $k_2$  at 540°C will be estimated from  $k_{14}/k_2$ . Two studies of the photolysis of  $\text{HCHO}$  enable  $k_{14}$  to be estimated.

(a) Klein, McNesby, Scheer and Schoen<sup>22</sup> studied the  $\text{HD}/\text{D}_2$  yields when  $\text{D}_2\text{CO}$  is photolyzed in the presence of  $\text{H}_2$  in the temperature range 308–400°C. Their results fitted the relations,

$$k_A/k_{14A} = 1.46 \exp(-2400/RT); \quad (\text{x})$$

$$A_A/A_{14A} = 1.46 \pm 0.3; \quad E_A - E_{14A} = 2400 \pm 200 \text{ cal},$$

for



and



Klein *et al.*<sup>22</sup> obtain values for  $A_{14A}$ ,  $E_{14A}$  by using the data of Boata *et al.*<sup>23</sup> for reaction (A); these values, and later values obtained by McNesby, Scheer and Klein,<sup>24</sup> are slightly in error, since the figure given by Boata *et al.* for the “classical activation energy” of transition state theory<sup>25</sup> has been used, rather than that appropriate

to a collisional treatment; moreover, all the values for activation energies given by Boata *et al.* should be increased by approximately 1.0 kcal, since their published values are based on measurements at constant pressure, rather than at constant concentration.

If  $R_F$  is the ratio  $k_{14}/k_{14A}$ , then

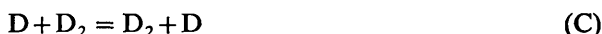
$$k_{14} = \frac{R_F k_A}{1.46 \exp(-2400/RT)}. \quad (\text{xi})$$

To evaluate  $k_{14}$ ,  $k_A$  and  $R_F$  are required. The most accurate velocity constants for hydrogen-exchange reactions are probably those given by Shavitt<sup>26</sup> whose calculations are consistent with the accurate measurements of Boata *et al.*<sup>23</sup> The transition state treatment of reaction (A) gives an expression which cannot be fitted to the collision expression  $k = AT^{\frac{1}{2}} \exp(-E/RT)$ , since  $E$  varies with temperature, but over the limited temperature range 600–800°K, Shavitt's data fit the relation \*

$$k_A = 0.708 \times 10^{12} T^{\frac{1}{2}} \exp(-6065/RT). \quad (\text{xii})$$

Three alternative evaluations of  $k_{14}/k_{14A}$  are possible.

(i) It may be assumed that  $k_{14}/k_{14A} = k_B/k_C$ ; this effectively assumes that the difference in zero-point energy of reactants and activated complex in (14) and (14A) has the same effect as in reactions (B) and (C):



Over the range 600–1000°K, Shavitt's values can be accurately represented by the equation:

$$k_B/k_C = 1.287 \exp(965/RT). \quad (\text{xiii})$$

Combining (xi), (xii) and (xiii) gives the relation

$$k_{14} = 0.62 \times 10^{12} T^{\frac{1}{2}} \exp(-2700/RT). \quad (\text{xiv})$$

(ii) It may be assumed that there is no effect of zero-point energy, so that  $k_{14}/k_{14A}$  is the ratio (1.40) of collision frequencies, giving

$$k_{14} = 0.68 \times 10^{12} T^{\frac{1}{2}} \exp(-3665/RT). \quad (\text{xv})$$

(iii) By studying the  $[\text{H}_2]/[\text{HD}]$  yield in the photolysis of  $\text{H}_2\text{CO} + \text{D}_2\text{CO}$  mixtures over the range 250–400°C, McNesby, Scheer and Klein<sup>24</sup> find  $(E_{14B} - E_{14}) = 1010 \pm 80$  cal,  $A_{14}/A_{14B} = 1.13 \pm 0.09$ . They show that these figures are consistent with the values  $(E_{14B} - E_{14} = 1000$  cal,  $A_{14}/A_{14B} = 0.8)$  obtained using the theoretical treatment given by Bigeleisen<sup>27, 28</sup> for isotopically substituted molecules, on the assumption of a loosely-bound activated complex. This leads to the relations  $E_{14A} = E_{14B}$ ,  $A_{14A} = A_{14B}$ , so that

$$k_{14} = 0.48 \times 10^{12} T^{\frac{1}{2}} \exp(-2665/RT). \quad (\text{xvi})$$



The values of  $k_{14}$  at 540°C calculated from (xiv), (xv) and (xvi) are  $3.35 \times 10^{12}$ ,  $2.0 \times 10^{12}$  and  $2.6 \times 10^{12}$  respectively. The corresponding values of  $k_2$  at 540°C, from the ratio  $k_{14}/k_2 = 320$ , are 1.05, 0.62 and  $0.81 \times 10^{10}$  respectively.

(b) Schoen<sup>17</sup> photolyzed  $\text{H}_2\text{CO}$  in the presence of  $\text{D}_2$  and determined the  $\text{H}_2/\text{HD}$  ratio as a function of  $[\text{HCHO}]/[\text{D}_2]$ , using the value of  $k_D$  given by Farkas and Farkas<sup>29</sup> to calculate  $k_{14}$ . The values he quotes (table 2, ref. (17)) appear to



\* All velocity constants are given in mole  $\text{cm}^3$  sec units.

be in error, since they cannot be obtained from the data of Farkas and Farkas. Moreover, Boata *et al.*<sup>23</sup> consider that the values given by Farkas and Farkas are too high by a factor of approximately two. Modifying the straight line (fig. 1, ref. (16)) to pass through the origin as required by theory,  $k_{14}/k_D = 13.5$  at  $300^\circ\text{C}$ . Using  $k_D = 1.96 \times 10^{10}$  at  $300^\circ\text{C}$  (Shavitt),  $k_{14} = 0.265 \times 10^{12}$ . It would be unwise to use Schoen's data to obtain the temperature coefficient of  $k_{14}$ , but the above value may be compared with  $1.40 \times 10^{12}$ ,  $0.65 \times 10^{12}$  and  $1.10 \times 10^{12}$  obtained from (xiv), (xv) and (xvi) respectively. This implies that Schoen's value for  $k_{14}$  corresponds to  $k_2 = 0.3 \times 10^{10}$  at  $540^\circ\text{C}$ .

These estimates of  $k_2$  may be compared with those obtained by Semenov<sup>30</sup> from measurement of the branching factor within the explosion peninsula, by Baldwin<sup>14</sup> from first-limit studies, and by Baldwin and Simmons<sup>2</sup> from studies of the inhibition of the  $\text{H}_2 + \text{O}_2$  reaction by ethane; this last figure is the least reliable and may be in error by a factor of up to ten, since it involves considerable extrapolation of the data<sup>31</sup> for  $\text{H} + \text{C}_2\text{H}_6$ . The results are summarized below; the last three values obtained at  $520^\circ\text{C}$  have been increased approximately 30 % at  $540^\circ\text{C}$  corresponding to  $E_2 = 17$  kcal.

	ref.	$k_2$ ( $520^\circ\text{C}$ )	$k_2$ ( $540^\circ\text{C}$ )
Klein <i>et al.</i> (i)	22		$1.05 \times 10^{10}$
(ii)			$0.62 \times 10^{10}$
(iii)			$0.81 \times 10^{10}$
Schoen	17		$0.3 \times 10^{10}$
Semenov	30	$0.66 \times 10^{10}$	$0.86 \times 10^{10}$
Baldwin	14	$0.27 \times 10^{10}$	$0.35 \times 10^{10}$
Baldwin and Simmons	2	$0.07 \times 10^{10}$	$0.09 \times 10^{10}$

The new estimates are thus strikingly consistent with the earlier values and a figure of  $k_2 = 0.6 \times 10^{10}$  at  $540^\circ\text{C}$  can be considered accurate to within 50 %.

Combining this estimate with those of Fenimore<sup>32</sup> in the temperature range  $1285\text{--}1500^\circ\text{K}$ , gives  $k_2 = 3.3 \times 10^{14} \exp(-17,600/RT)$ ; assuming a possible 50 % error in both low- and high-temperature estimates, the extreme values are  $1.4 \times 10^{15} \exp(-20,700/RT)$  and  $7.5 \times 10^{13} \exp(-14,600/RT)$ . If the  $T^{\frac{1}{2}}$  dependence of collisional-activation theory is introduced, the corresponding expression is  $6.0 \times 10^{12} T^{\frac{1}{2}} \exp(-16,000/RT)$  with the extreme values  $2.6 \times 10^{13} T^{\frac{1}{2}} \exp(-19,600/RT)$  and  $1.4 \times 10^{12} T^{\frac{1}{2}} \exp(-13,500/RT)$ . The lower limits are, of course, ruled out by the endothermicity of (2).

The only figures published for  $k_1$  and  $k_{15}$  are those of Avramenko and Lorentso<sup>33, 34</sup> whose procedure has been criticized by Steacie.<sup>35</sup> Their figures give the ratio  $k_{15}/k_1 = 0.5$  at  $540^\circ\text{C}$ , which, if correct, would eliminate reaction (15) as an important termination process since a ratio of 42 is required to account for the inhibition effects. However, their figures<sup>36</sup> for  $\text{OH} + \text{C}_2\text{H}_6$  (15a) give the ratio  $k_{15a}/k_1$  as 23, which, in view of the extrapolation involved compares reasonably with the value of 13 obtained from inhibition studies<sup>2</sup> on the assumption that  $\text{OH} + \text{C}_2\text{H}_6$  is the termination process. It would be rather surprising if the termination process involved O for  $\text{HCHO}$ , and OH for  $\text{C}_2\text{H}_6$ . For this reason, Avramenko's figures are considered inconclusive until further evidence is available. Moreover, Hoare<sup>37</sup> has recently obtained a value for  $k_{15}/k_{1a}$



of 60 at  $540^\circ\text{C}$ . Combining this with an estimate<sup>38</sup> at  $500^\circ$  for  $k_{1a}/k_1$  of 0.33 gives  $k_{15}/k_1 = 20$  with a possible error of about 100 %, resulting from an uncertainty

of perhaps 50 % in  $k_{15}/k_{1a}$  together with the effect of 40°C on the ratio  $k_{1a}/k_1$ . This result is sufficiently close to the value of 42 from inhibition studies to indicate that removal of OH must be important, even if removal of O is occurring.

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