The heat capacity of OH in the ideal gaseous state has been calculated for the temperature range 0.01 to 5000°K. The heat capacity curve shows a sharp maximum at about 0.06°K., which is due to the existence of an unusually large Λ-type doubling in the normal electronic term; a second broad maximum at about 90°K. which results from excitation to the upper level of the inverted $^2\Pi$ electronic state of the normal molecule; and a vibrational component which starts at about 600°K. and attains the equipartition value at about 3500°K. The rotational specific heat enters at about 15°K. and approaches rotational equipartition at about room temperature. At 5000°K. the rotational stretching contributes about 0.18 cal. to the molal heat capacity and the anharmonic character of the oscillations contributes about 0.5 cal.

Accurate values of the entropy and of the "free energy function," suitable for accurate equilibrium computations, have been calculated and tabulated. A table of total energies (in excess of translation) is also included.

A table is included which shows the percentage distribution of OH molecules among the various vibrational levels, as a function of the temperature.

The limits of error of the heat capacity, entropy, free energy and total energy calculation have been determined. At 5000°K. these are: 0.07 cal./mole/degree, 0.02 cal./mole/degree, 0.01 cal./mole/degree and 30 cal./mole, respectively.

The approximate calculation of electronic entropy, for use with the Sackur–Tetrode equation, has been discussed and has been applied to OH at 298.1°K.

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The Thermal Reaction between Acetaldehyde Vapor and Oxygen

BY ROBERT N. PEASE

Some disagreement exists as to the nature of the reaction between acetaldehyde vapor and oxygen. According to Bodenstein,[1] the reaction is homogeneous, and yields mainly per-acetic acid. Hatcher, Steacie, and Howland,[2] on the other hand, find that the rate is increased by a glass packing (indicating wall reaction), and a complex mixture of products is obtained. Both are inclined to regard the reaction as of the chain type but for different reasons. Under these circumstances a re-investigation of the reaction has seemed to be in order. The reaction is of special

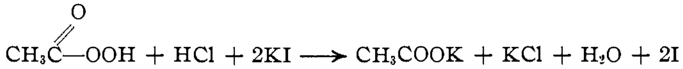
(1) Bodenstein, *Sitzber. preuss Akad. Phys.-Math.*, III, 1 (1931).

(2) Hatcher, Steacie and Howland, *Can. J. Research*, **7**, 149 (1932).

interest in its possible connection with hydrocarbon oxidation, since the latter involves production of aldehydes.

Apparatus and Method

The reaction was followed by means of pressure measurements at constant volume, supplemented by analyses. Measured amounts of acetaldehyde vapor and oxygen were let into a well-evacuated Pyrex glass reaction bulb, the oxygen being admitted last so that the line was filled with this gas as a buffer. Pressure measurements were then made on a mercury manometer. Following these, the system was connected to a trap at −190°. The latter (and the rest of the system) was then evacuated with a Langmuir pump backed by a Töpler pump which permitted collection of the residual gas. The trap was then disconnected, washed out with water, and the water solution was analyzed for per-acid and for total acid. For this, a known amount of standard (0.05 *N*) hydrochloric acid and an excess of potassium iodide were added, and the liberated iodine titrated with 0.05 *N* sodium thiosulfate. Phenolphthalein was then added and the residual acid determined by titration with 0.05 *N* potassium hydroxide. The reaction



$$CH_3C(=O)—OOH + HCl + 2KI \longrightarrow CH_3COOK + KCl + H_2O + 2I$$

requires a mole of hydrochloric acid for each mole of per-acid. The back-titration of residual acid with potassium hydroxide always revealed more than the above equation would lead one to expect. This excess of acid was taken to be acetic acid formed in the reaction bulb.

The residual gas was measured and analyzed for oxygen by absorption in Burrell's "Oxsorbent."

The acetaldehyde used was vacuum-distilled into the apparatus from a sample of Eastman's best product. The oxygen was generated electrolytically and purified.

The reaction tube was heated in an electric oven. The temperature was controlled by hand regulation of the heating current, and was read on a mercury thermometer graduated to 0.2°. The maximum variation of temperature in a single run was ±0.2°. The heat evolved by the reaction made better control impossible.

Results

Wall Effect and Nature of the Products.—Bodenstein found that the rate was the same in reaction tubes whose volume–surface ratios varied from 1 to 4, and concluded that the reaction was unaffected by wall. Hatcher, Steacie and Howland, on the other hand, found that a broken-glass packing increased the rate by a factor of about 4, and were forced to conclude that the reaction was accelerated by surface.

Data relating to wall effects are presented in Table I. The reaction bulb was of Pyrex glass (5 cm. diameter; 12 cm. long). Each series but the last includes two "check" runs with a 50% mixture, and a run with excess of either gas. The bulb was treated as follows.

Series A.—Boiled out with concentrated nitric acid, washed with distilled water, drained.

Series B.—Filled with broken Pyrex glass (4–10 mesh) which had been boiled with concentrated nitric acid, washed with water and dried.

Series C.—Empty bulb rinsed with 20% aqueous potassium chloride solution drained.

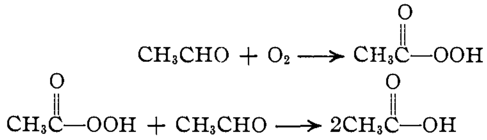
Series D.—Empty bulb boiled out with concentrated nitric acid, washed with water and drained.

TABLE I

WALL EFFECT AND NATURE OF THE PRODUCTS

Run no.	Temp., °C.	Initial pressure, mm. Ald.	Initial pressure, mm. O_2	Formed mm. P-acid	Formed mm. HAc	O_2 equiv. acids	O_2 used, mm.	$-\Delta P$ final, mm.	t_{10-60} min.
			A. Empty Bulb—Washed HNO_3-H_2O						
1	99.9	260	254	...	...	...	156	156	36.2
2	99.8	483	249	179	117	238	243	239	10.2
3	99.6	253	479	111	48	135	150	152	34.2
4	99.8	249	244	86	36	104	109	106	37.0
14	99.6	261	247	119	47	143	152	150	28.6
			B. Packed Bulb						
15	98.9	254	289	90	47	114	128	116	10.9
16	99.0	283	166	...	...	...	126	134	6.3
17	99.0	141	267	49	39	69	78	75	20.4
18	99.0	280	278	...	...	...	136	141	5.4
			C. Empty Bulb—Treated KCl						
19	100.0	258	247	47	124	109	189	138	5.1
20	99.9	258	117	9	136	77	100	120	3.6
21	99.7	130	249	1	74	38	63	68	12.5
22	99.8	262	246	6	135	74	86	125	3.4
			D. Empty Bulb—Washed HNO_3-H_2O						
23	119.9	208	207	131	17	140	153	146	15.0

If the reaction produces nothing but per-acetic acid and acetic acid,



$$CH_3CHO + O_2 \longrightarrow CH_3\overset{\overset{\displaystyle O}{\|}}{C}-OOH$$

$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}-OOH + CH_3CHO \longrightarrow 2CH_3\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

the final decrease in pressure ($-\Delta P$) should equal the oxygen consumed as determined from the difference of oxygen introduced and that recovered. It should also equal the sum of the per-acetic acid and one-half the acetic acid. These three quantities—oxygen equivalent to per-acetic and acetic acid, oxygen used, and final pressure drop—are compared in Table I. It will be seen that the agreement is good for the "clean" empty bulb (washed with nitric acid and water). It is also fair for the packed bulb. However, in the potassium chloride treated empty bulb, there are serious discrepancies. These clearly arise from abnormally low yields of per-acid. This at once suggests that the complex mixture of products obtained by Hatcher, Steacie and Howland was due to contamination of the glass surface of their reaction bulb. The residue of gas from experiments in the potassium chloride coated bulb contained some quantity of gas (10–20%) not absorbed by "Oxsorbent." This unabsorbed gas may have been the carbon dioxide noted by Hatcher, Steacie and Howland.[3]

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(3) Oxsorbent appears to be a chromous chloride solution. This does not absorb carbon dioxide

With the exception of the experiments in the potassium chloride-coated bulb, it is reasonable to assume that per-acetic and acetic acids are the chief products, with per-acetic acid predominating. It is true that some acid other than acetic may be present. That the only peroxide present is per-acetic acid is indicated by the fact that the liberation of iodine was instantaneous. This is not true in the case of hydrogen peroxide, acetyl peroxide or of any of the other known organic peroxides.[4] It is even questionable whether the acetic acid is formed in the reaction bulb. It possibly results from interaction of per-acetic acid and acetaldehyde in the aqueous solution. There was no evidence (bubble-formation) of decomposition of per-acetic acid in this solution. In any event no significant changes in the ratios of per-acetic to acetic acid with change in acetaldehyde concentration were noted.

The effect of surface on reaction-rate may be obtained from the times required for the pressure to drop from 10 to 60 mm. below the initial values. These appear in the last column of Table I. Each set of data includes check runs with a 50% mixture and a run each with excess of either gas. Although the check runs show considerable variation, it is quite clear that both packing and coating with potassium chloride cause decided increase in rate. The effect of packing clearly points to a surface reaction as noted by Hatcher, Steacie and Howland. It was rather expected that potassium chloride would decrease the rate by poisoning the surface as in the hydrogen-oxygen reaction.[5] The observed increase in rate means that the potassium chloride coating is a better catalyst for the reaction than clean glass. The fact that Bodenstein found no alteration in rate with the dimensions of the reaction tube is probably due to chance. Since variable rates are obtained with one tube through a series of runs, it is not at all impossible that two different tubes should happen to give nearly equal rates.

Inhibition by Ethyl Alcohol Vapor.—Since increase in wall surface increases the rate, it would be natural to conclude that the reaction is simply a wall reaction; and this conclusion would be strengthened by the fact that the nature of the products depends upon the nature of the walls. Nevertheless, both Bodenstein and Hatcher, Steacie and Howland believe the reaction to be of the chain type. Bodenstein stresses particularly the fact that the somewhat analogous reaction between liquid benzaldehyde and oxygen has been shown by Bäckström to be a chain reaction,[6] and that diphenylamine, which inhibits benzaldehyde oxidation, also inhibits acetaldehyde oxidation. Hatcher, Steacie and Howland are rather more impressed with the fact that the kinetics, which will be discussed later, resemble those of other reactions believed to be of the

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[4] For references see Rieche, "Alkyl Peroxide und Ozonide," T. Steinkopf, Dresden, 1931.

[5] Pease, THIS JOURNAL, **52**, 5106 (1930).

[6] Bäckström, *ibid.*, **49**, 1460 (1927).

chain type. It might have been added that the photochemical oxidation of acetaldehyde vapor has a high quantum yield, indicating chains.[7] This is rather inconclusive since the product of the photochemical reaction is acetyl peroxide instead of per-acetic acid, but it is suggestive.

As Hinshelwood[8] has pointed out, it is particularly difficult in a case of this kind to demonstrate the existence of reaction chains. An inhibitor may be simply a catalyst poison and not a chain-breaker at all. In particular, so non-volatile a substance as diphenylamine (b. p. 310°) may well be suspected in this connection.

It appeared that a somewhat more stringent test could be applied. It was first demonstrated that small amounts of water vapor did not alter the rate (Table II). The effect of ethyl alcohol vapor was then determined since Bowen and Teitz found that this substance inhibits the photochemical reaction in solution. Since water vapor has a rather better chance of adsorption on glass than has ethyl alcohol, both on grounds of volatility and of specific interaction, an inhibitory influence of alcohol could not well be ascribed to catalyst poisoning. Yet it was found that ethyl alcohol vapor does inhibit the reaction.

TABLE II

EFFECTS OF FOREIGN GASES AND VAPORS

Run no.	Temp., °C.	Initial press., mm.		Formed, mm.			O_2 used, mm.	$-\Delta P$ final, mm.	t_{10-60}, min.	Added gas, mm.
		Ald.	O_2	P-acid	HAc	O_2 equiv. acids				
Comparison C_2H_5OH and H_2O										
29	120.1	205	206	136	23	148	165	146	11.7	0
31	120.1	206	207	130	20	140	139	145	11.8	20.0 H_2O
37	119.8	204	206	111	22	122	110	125	16.3	10.0 EtOH
35	120.2	202	201	84	22	95	122	101	23.9	20.0 EtOH
36	119.8	204	204	...	..	...	...	68	38.8	40.0 EtOH
38	119.9	204	408	57	22	69	...	71	36.4	40.0 EtOH
40	119.8	205	205	133	19	143	137	146	11.1	0
Addition of N_2, H_2, C_2H_6										
23	120.0	208	207	131	17	140	153	146	12.1	0
24	120.0	206	206	120	9	129	139	136	13.8	208 C_2H_6
25	120.2	208	206	132	21	143	150	152	11.2	208 N_2
26	150.3	110	109	74	6	77	89	77	13.5	110 C_2H_6
27	150.0	110	112	75	6	78	88	83	12.8	111 N_2
28	150.0	106	107	73	8	77	81	77	14.6	106 H_2
29	120.1	205	206	136	23	148	165	146	11.7	0

Bäckström[9] expresses the action of an inhibitor by the equation

$$\text{Rate} = \frac{k_1}{k_2c + k_3}$$

where k_1 is a constant characteristic of the chain-continuing process; k_3 is

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(7) Bowen and Teitz, *J. Chem. Soc.*, 234–243 (1930).

(8) Hinshelwood, *Trans. Faraday Soc.*, **28**, III, March (1932).

(9) Bäckström, THIS JOURNAL, **49**, 1469 (1927).

a constant characteristic of the chain-breaking process, in absence of added inhibitor; c is concentration of inhibitor; k_2c is a quantity expressing chain-breaking by the added inhibitor. Since t_{10-60} is inversely as the rate, we may write

$$t_{10-60} = \frac{k_2c + k_2}{k_1} = \frac{k_2}{k_1}c + \frac{k_3}{k_1}$$

where c is now the partial pressure of inhibitor. It is evident that a plot of t_{10-60} against c should give a straight line. This is the case for ethyl alcohol (see Fig. 1). Thus, the relation between rate and inhibitor concentration is analogous to that in cases where the inhibitor is known to break chains.

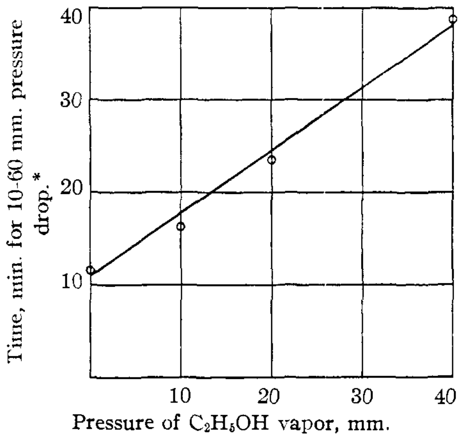

Fig. 1.—Inhibition by ethyl alcohol vapor.

* This is the time in minutes for the pressure to drop from the tenth to the sixtieth millimeter below the initial value.

Unfortunately, however, a case of catalyst poisoning can yield the same relation. The Langmuir adsorption theory gives for the fraction, x, of surface covered by an adsorbed substance,

$$x = ap/(b + ap)$$

where a is a constant for condensation; b is a constant for evaporation; p is the pressure of adsorbed substance. Suppose the alcohol is adsorbed on the fraction, x, of the surface. The fraction of surface available for reaction is $1 - x$. Thus

$$\begin{aligned}\text{Rate} &= k(1 - x)\\ &= kb/(b + ap)\end{aligned}$$

This is of exactly the same form as Bäckström's equation for the action of inhibitor in breaking chains. The agreement with this equation therefore might equally well be due to catalyst poisoning. However, there remains the fact that water vapor does not inhibit. The balance of evidence is thus in favor of the assumption that alcohol inhibits by breaking chains, and hence that chains exist.

Addition of Foreign Gases.—Foreign gases accelerate the slow hydrogen–oxygen reaction. This is ascribed to a "blanketing" action of the foreign gas, which impedes the breaking of chains at the surface of the reaction vessel. In the acetaldehyde oxidation there is no evidence that chains are broken at the surface (packing does not inhibit reaction) and no such effect would be expected. None is found. Neither nitrogen nor hydrogen nor ethane has any appreciable influence on the rate (Table II).

It was rather expected that ethane would act as an inhibitor. Bone and Hill[10] found that addition of 1% of acetaldehyde vapor to a 50% ethane–oxygen mixture led to a violent explosion at 316°. This suggested that the oxidation of acetaldehyde initiated chains in the ethane–oxygen mixture. It might thus be expected that at a somewhat lower temperature ethane would at least break chains in acetaldehyde–oxygen mixtures. This certainly does not occur appreciably even at 150°.

Kinetics of the Reaction.—Further evidence that the acetaldehyde oxidation is a chain reaction arises from the fact that the reaction kinetics are similar to those of other oxidations believed to be of the chain type. In the reaction of oxygen with hydrogen, methane, ethane, formaldehyde and methanol,[11] the rate depends much more on the concentration of substance being oxidized than on that of the oxygen, and reaction is auto-accelerated. This is also true of the acetaldehyde oxidation. With constant acetaldehyde concentration, the rate is independent of the oxygen concentration; whereas with constant oxygen concentration, the rate is approximately proportional to the square of the acetaldehyde concentration (Table III). The curves of Fig. 2 illustrate the auto-accelerative feature of the reaction.

Bodenstein has suggested that the reaction rate could be represented by either of two equations, the second involving chains

$$\frac{d[P]}{dt} = k'[A]([P] + \text{const.}) \qquad \text{(I)}$$

$$\frac{d[P]}{dt} = k\frac{[A]^2}{[O_2] + \text{const.}} \qquad \text{(II)}$$

[P] is per-acid concentration; [A] is acetaldehyde concentration. Either equation gives a fair representation of the results of any one run, but neither expresses the fact that initial rate is proportional to the square of the initial aldehyde concentration and independent of the oxygen concentration. On the other hand, the equation

$$\frac{d[P]}{dt} = k[A]^2$$

which is suggested by the data of Table III obviously will not account for the rate through a single run.

Two additional facts concerning the reaction may be given. Comparison of runs No. 36 and No. 38 (Table II) shows that the inhibitory power of alcohol is independent of the oxygen concentration. This suggests that the rate is truly independent of the oxygen concentration. It might have entered both in the numerator and denominator of the rate equation. Second, the auto-catalytic feature is more drawn-out at the lower temperatures. This may be seen by comparing times from 0

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(10) Bone and Hill, *Proc. Roy. Soc.* (London), **A129**, 434 (1930).

(11) H_2—Gibson and Hinshelwood, *ibid.*, **A119**, 591 (1928). CH_4, HCHO, CH_3OH—, Fort and Hinshelwood, *ibid.*, **A129**, 284 (1930). C_2H_6—Bone and Hill, *ibid.*, **A129**, 434 (1930).

TABLE III

EFFECT OF VARYING CONCENTRATION

Run no.	Temp., °C.	Initial press., mm. Ald.	O_2	Formed, mm. P-acid	HAc	O_2 equiv. acids	O_2 used, mm.	$-\Delta P$ final, mm.	t_{10-60}, min.
Oxygen Varied, Aldehyde Constant									
44	119.7	204	307	125	18	143	168	151	11.5
40	119.8	205	205	133	19	143	137	146	10.9
45	119.9	208	104	88	15	96	88	97	10.9
Aldehyde Varied, Oxygen Constant									
42	119.8	310	208	178	34	195	186	192	4.8
40	119.8	205	205	133	19	143	137	146	10.9
43	119.9	103	204	48	8	52	58	61	65.2

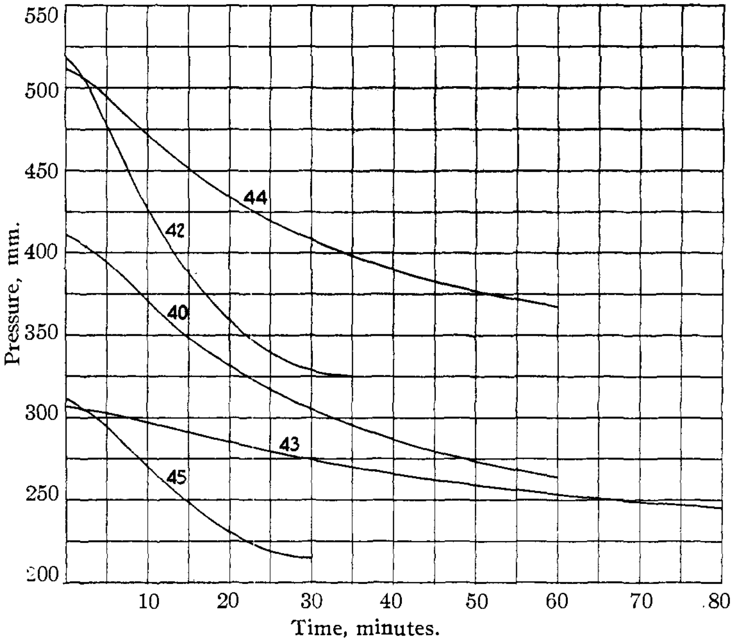

Fig. 2.—Rate curves at 120°.

Initial Pressures

Oxygen Varied, Aldehyde Constant

No. 44 204 mm. aldehyde; 307 mm. oxygen
No. 40 205 mm. aldehyde; 205 mm. oxygen
No. 45 208 mm. aldehyde; 104 mm. oxygen

Aldehyde Varied, Oxygen Constant

No. 42 208 mm. oxygen; 310 mm. aldehyde
No. 40 205 mm. oxygen; 205 mm. aldehyde
No. 43 204 mm. oxygen; 103 mm. aldehyde

to 50 mm. with times from 50 to 100 mm. pressure drop (Table IV). Acceleration continues beyond 50 mm. pressure drop at 90 and 100° but not at 110 or 120°. This points to the occurrence of at least two reactions with different temperature coefficients. The same conclusion might be drawn from a comparison of rates with and without packing (Table I). If the packing increases the amount of surface ten to twenty times, a corresponding increase in rate might have been noted. The actual increase is only three to five. The existence of a heterogeneous and a homogeneous reaction might be inferred.

TABLE IV

COMPARISON t_{0-50} AND t_{50-100}

Run no.	Temp., °C.	Initial press., mm.		t_{0-50}, min.	t_{50-100}, min.	$\frac{t_{50-100}}{t_{0-50}}$
		Ald.	O_2			
7	89.6	276	276	60.0	46.5	0.78
4	99.9	249	244	39.8	35.2	.88
5	109.5	264	253	18.8	19.8	1.05
6	119.0	272	265	10.0	10.5	1.05

The writer is not prepared to suggest a complete mechanism for the acetaldehyde oxidation. Granting that the reaction is of the chain type, the acceleration by packing indicates that chains start from the surface. Since the preponderant effect of the surface is acceleration and not repression of reaction, the breaking of chains at the surface is of less importance. This is substantiated by the fact that inert gases do not accelerate the reaction as they do the hydrogen–oxygen combination. Chains are then probably ended in the gas phase.

Summary

1. The reaction between acetaldehyde vapor and oxygen has been re-investigated.

2. Per-acetic acid is the preponderant product except when the reaction vessel is coated with potassium chloride.

3. The reaction is accelerated by a broken glass packing, and also by coating the reaction vessel with potassium chloride.

4. The reaction is inhibited by ethyl alcohol vapor but not by water vapor. Nitrogen, hydrogen and ethane are without effect on the rate.

5. The initial rate is proportional to the square of the acetaldehyde concentration and independent of the oxygen concentration. The reaction is auto-accelerated.

6. The reaction is believed to be of the chain type, with chains starting on the walls and ending in the gas phase, but this is not decisively proved.

PRINCETON, NEW JERSEY

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