608. *The Thermal Decomposition of Acetic Acid.*

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The kinetics of the pyrolysis of acetic acid vapour have been investigated by a flow method in quartz tubes in the temperature range 500—900° c. Acetic acid can decompose either to keten and water, or to carbon dioxide and methane. Both reactions are homogeneous and of first order in carbon-coated tubes. The activation energies are high (67·5 and 62 kcals. respectively) and the frequency factors normal.

On clean quartz surfaces keten is formed by a surface reaction of much lower activation energy. Reversible chemisorption appears to precede reaction on the surface. Small quantities of pure keten can conveniently be prepared in this way.

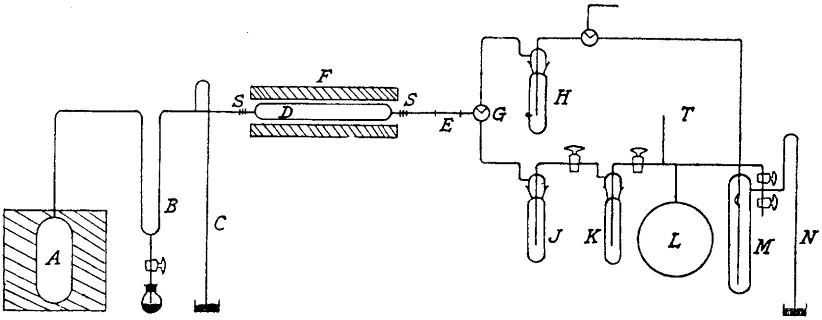
General kinetic expressions have been developed for some reactions in flowing systems.

Although the production of keten by the thermal cracking of acetic acid is now of considerable technical importance (cf. B.P. 435,219), no account of the kinetics of the reaction has been reported. The present paper describes an investigation of the reaction under flow conditions in quartz vessels.

Experimental.

The apparatus is illustrated in Fig. 1. Acetic acid free from dissolved air was contained in the thermostatically heated bulb *A*, which communicated through a mercury cut-off *B* with a manometer *C*, and the silica reaction tube *D* in the furnace *F*. The rate of flow of the vapour was controlled by the capillary *E*. The pressure in *D*, assumed uniform, was varied by changing the temperature of *A*. The connecting tubes between *A* and *D* were heated electrically to prevent condensation of acetic acid vapour. In order to allow stable conditions to be established at the beginning of a run, *E* could be connected directly through the two-way tap *G* and the liquid-air trap *H* with the pumping system. At the beginning of the run proper, the gases were diverted by means of *G* so as to pass through the two traps *J*, *K*, cooled in liquid air. Uncondensed gases were collected in the evacuated bulb *L* of 4 l. capacity. The pressure of the permanent gas in *L* was measured by the glass Bourdon gauge *M*, sensitive to 0·01 mm. Hg. At the end of a run a specimen of the permanent gas was pumped off for analysis through *T* to the Toepler pump; and *J*, *K*, and *L* were evacuated. Any condensate in *K* was then distilled back into *J*. The products were fractionated by warming *J* to −80°, and cooling *K* in liquid air. The total volume of the volatile fraction was then estimated by vaporisation into *L*, the pressure being measured on manometer *N*, and *M* being used as a null instrument. The residue in *J* consisted only of water and unchanged acetic acid, which was determined by titration. The apparatus was constructed of Pyrex glass; graded seals *S*, *S* were used to attach the quartz tube *D*. The pumping system consisted of a three-stage quartz-mercury diffusion pump, backed by an oil pump. The temperature of the furnace was measured by a chromel–alumel thermocouple in contact with the outside of *D*, and standardised at the m. p.s of antimony and silver. The temperature remained constant to ±0·2° during a run.

Fig. 1.



The products were analysed by standard methods except for the −80° fraction, which consisted mainly of keten and carbon dioxide. This mixture is difficult to analyse since the majority of absorbents for keten also dissolve carbon dioxide appreciably. The most satisfactory reagent was found to be anhydrous glycerol to which a few per cent. of concentrated sulphuric acid had been added.* The residual gas,

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* According to I.C.T. these liquids are the only ones in which carbon dioxide is not appreciably soluble. Concentrated sulphuric acid alone reacts violently with keten, giving some gaseous products.

consisting of carbon dioxide with small amounts of ethylene and ethane, was analysed in the usual way.

The separation of keten from unchanged acetic acid and water appeared to be quantitative under our conditions. For instance on distilling back the keten to the residue in *J*, and repeating the separation, no diminution in the volume of keten was observed.

RESULTS and DISCUSSION.

The products of the reaction were keten, water, methane, carbon dioxide, carbon monoxide, ethylene, carbon (in the reaction vessel) and traces of ethane. The significant reactions occurring under our conditions are probably

$$CH_3{\cdot}CO_2H \longrightarrow CH_2{:}CO + H_2O \quad . . . . \quad (1)$$

$$CH_3{\cdot}CO_2H \longrightarrow CH_4 + CO_2 \quad . . . . \quad (2)$$

$$2CH_2{:}CO \longrightarrow CH_4 + C + 2CO \quad . . . . \quad (3)$$

$$2CH_2{:}CO \longrightarrow C_2H_4 + 2CO \quad . . . . \quad (4)$$

Keten is known to undergo thermal decomposition according to equations (3) and (4) (Ganz and Walters, *J. Amer. Chem. Soc.*, 1941, **63**, 3412).

In early experiments *A* was replaced by a graduated tube so that the amount of acetic acid passed could be directly estimated. It was found that within the limits of experimental error, the whole of the acid decomposed could be accounted for quantitatively by the products on the basis of reactions (1)—(4). This is illustrated by the results in Table I, from which it will be seen that the relative importance of reactions (1) and (2) at a given temperature can vary considerably. Later, it will be shown that the course of reaction is sensitive to the state of the surface of the reaction vessel.

Bumping of the acetic acid in the graduated tube proved troublesome, and the tube was therefore replaced by the wider vessel *A*. The total weight of acid passed in any run was then calculated from the weights of the products.

TABLE I.

		Products, c.c. at 20°/760 mm.					Acetic acid, g.	
Pressure, mm.	*T*, °K.	CO.	CH_4.	$CH_2{:}CO$.	CO_2.	C_2H_4.	Decomposed.	Accounted for in products.
28·5	1089	12·3	63·7	179·4	59·6	2·3	0·658	0·626
30·5	1089	43·7	39·3	947·0	27·4	9·9	2·54	2·55
24·0	1113	22·0	60·6	100·8	48·4	$<0{\cdot}1$	0·430	0·428
37·0	1113	19·75	67·25	84·1	63·1	1·2	0·407	0·393
30·7	1141	59·0	123·5	454·0	104·0	9·7	1·52	1·54

The results were very dependent on the condition of the surface of the reaction vessel, but became reproducible after a number of runs had been done without cleaning the tube. The tube had then become coated with carbon formed by decomposition of keten. Table II shows the analytical results and velocity constants at various pressures, *t* being the duration of the run in minutes, and *S* the surface/volume ratio of the reaction vessel. In this table k_1 and k_2 are first-order velocity constants for reactions (1) and (2), respectively. They were calculated from equation (5) below, which holds for first-order homogeneous reactions $A \longrightarrow yB$ in flowing systems where diffusion can be neglected (cf. Benton, *J. Amer. Chem. Soc.*, 1931, **53**, 2984) :

TABLE II.

Carbon-coated tube : $V = 24{\cdot}3$ c.c., $S = 3{\cdot}2$ cm.$^{-1}$.

			Products, c.c. at 20°/760 mm.							
Press., mm.	*T*, °K.	*t*.	CO.	CH_4.	$CH_2{:}CO$.	CO_2.	C_2H_4.	Conversion, %.	k_1, sec.$^{-1}$.	k_2, sec.$^{-1}$.
12·9	1040	30	0·68	11·6	19·4	11·3	$<0{\cdot}1$	5·49	0·101	0·057
24·7	1040	28	1·03	27·5	25·0	27·0	$<0{\cdot}1$	2·58	0·067	0·069
57·7	1040	10	0·62	27·5	24·1	27·2	$<0{\cdot}1$	2·57	0·081	0·089
166·0	1040	4	0·98	26·2	26·7	25·7	$<0{\cdot}1$	1·86	0·079	0·074
65	1168	8	91·2	355·8	392·8	310·2	1·9	56·0	3·61	2·32

$$k = \frac{g_0}{aVM_0}\left\{y \log\frac{g_0}{g} - \left(\frac{g_0 - g}{g_0}\right)(y - 1)\right\} \quad . . . . \quad (5)$$

where *V* is the volume of the reaction vessel in c.c., M_0 is the molecular weight of the reactant, g_0 and *g* are respectively the rates of flow of *A* into and out of the reactor in g. sec.$^{-1}$, and $a =$

$p/(6{\cdot}24 \times 10^4 T)$, p and T being the total pressure (in mm. Hg) and the absolute temperature in the reaction vessel.

The first-order constant for the overall rate of decomposition is $k_1 + k_2$, which is thus obtained from (5). The ratio k_1/k_2 is equal to the ratio of keten to carbon dioxide formed. In our experiments the contact times were of the order of 0·1 sec., and so diffusion can reasonably be neglected. The volume changes due to (3) and (4) may be neglected, since only a small fraction of the keten was decomposed. It is clear from Table II that k_1 and k_2 are both reasonably constant, and both reactions are therefore presumably of the first order.

A further series of runs was carried out in packed reaction vessels. Results are given in Table III. Comparison of the last run in this table with the runs at the same temperature in Table II shows that packing the tube has no appreciable effect on the velocity constants. The coefficient k_2 appears to fall off at pressures less than about 60 mm. in the packed tube; it may also do so in the unpacked tube. This behaviour is characteristic of homogeneous first-order gas reactions.

Arrhenius plots for the two reactions are given in Fig. 2. The points for k_1 for packed and unpacked tubes lie satisfactorily on a straight line corresponding to $E_1 = 67{\cdot}5$ kcals., with a frequency factor $A_1 = 9 \times 10^{12}$ sec.$^{-1}$. The plot for k_2 is not so satisfactory; where available, values of k_2 for pressures above 60 mm. have been used. The low points correspond to pressures of about 25 mm. and would not be expected to lie on the same line. The value for E_2 from Fig. 2 is 62 kcals., and the frequency factor $A_2 = 8 \times 10^{11}$ sec.$^{-1}$. Both frequency factors lie within the range considered normal for first-order gas reactions.

FIG. 2.

Arrhenius plot for carbon-coated tubes.

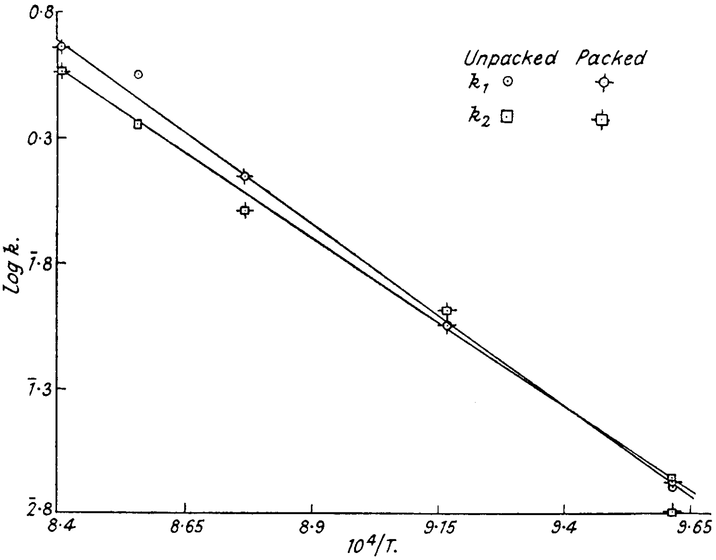


TABLE III.

Carbon-coated packed tube.

p, mm.	T, °K.	t, mins.	V, c.c.	S, cm.$^{-1}$.	Products, c.c. at 20°, 760 mm. CO.	CH$_4$.	CH$_2$:CO.	CO$_2$.	C$_2$H$_4$.	Conversion, %.	k_1, sec.$^{-1}$.	k_2, sec.$^{-1}$.
9	1090	56	16·7	12·7	4·5	45·5	50·3	43·2	0·3	14·6	0·32	0·25
10·8	1090	60	16·7	12·7	4·5	50·5	59·8	48·2	0·2	13·3	0·32	0·24
24	1090	20	16·7	12·7	2·3	46·7	55·5	45·5	0·4	8·1	0·37	0·29
33·9	1090	15	16·7	12·7	3·1	57·9	49·6	56·4	0·4	6·5	0·35	0·34
64·8	1090	10	16·7	12·7	4·8	92·2	72·0	89·8	0·6	6·1	0·36	0·41
158	1090	3·5	16·7	12·7	4·8	81·8	63·1	79·4	0·5	6·05	0·36	0·42
24·2	1140	20	16·7	12·7	19·8	138·2	150·2	128·3	1·0	28·5	1·41	1·07
24·8	1189	20	16·7	12·7	86·4	273·6	212·6	240·4	2·1	28·8	4·65	3·74
23·8	1040	30	19·5	22·6	1·31	20·0	24·5	19·4	0·1	2·8	0·085	0·064

The fact that the constants are not altered significantly by considerable changes in the surface/volume ratio (*i.e.*, S) of the reaction vessel shows that reactions (1) and (2) are not surface reactions in carbon-coated silica tubes. They must be either homogeneous gas reactions, or chain processes starting and ending on the walls. It will be seen later that the former explanation is the more probable.

Different but fairly reproducible results were obtained when the coating of carbon was burned off the tube immediately before a run, provided that the runs were not too long. Typical series of results are presented in Tables IV and V. The most striking feature is that the relative yield of keten is very much larger than with the carbon-coated tube. The overall conversion is also very much higher, especially in the packed tube. The yield of ethylene is also appreciably higher in the clean tube; the ratio C_2H_4/CO increases somewhat with increasing pressure, reaching a value of 0·377 at 163·5 mm. However, reaction (3) still occurs to an appreciable extent even at this pressure.

Tables IV and V show that the first-order velocity constants, especially k_1, fall off with increasing pressure in clean tubes. Reaction (1) shows a variable order between 0 and 1, which suggests that a surface process is involved. Moreover, since the order is less than 1, the reaction is probably a pure surface reaction and not a surface-catalysed chain reaction. The conversions are also higher in the packed tube.

TABLE IV.

Clean unpacked tube: $T = 1039°$ K.; $V = 24·3$ c.c.; $S = 3·2$ cm.$^{-1}$.

		Products, c.c. at 20°, 760 mm.							
Press., mm.	t, mins.	CO.	CH_4.	CH_2:CO.	CO_2.	C_2H_4.	Conversion, %.	k_1, sec.$^{-1}$. From eqn. (5).	k_2. sec.$^{-1}$, From eqn. (5).
14	25	4·5	12·5	155·5	11·2	0·9	42·1	1·36	0·094
24	10	1·6	10·5	96·5	10·0	0·5	17·3	0·41	0·092
75	6	2·2	15·6	58·5	14·8	0·5	7·4	0·35	0·086
132	3	1·9	18·1	42·3	17·5	0·4	3·44	0·22	0·082

TABLE V.

Clean packed tube: $T = 1028°$ K.; $V = 17·3$ c.c.; $S = 47$ cm.$^{-1}$.

		Products, c.c. at 20°, 760 mm.									
Press., mm.	t, mins.	CO.	CH_4.	CH_2:CO.	CO_2.	C_2H_4.	C_2H_6.	Conversion, %.	k_1, sec.$^{-1}$, calc. from eqn. (5).	k_2, sec.$^{-1}$, calc. from eqn. (5).	k_2, sec.$^{-1}$, calc. from eqn. (14).
26	25	17·9	14·1	280	2·6	4·3	0·4	95·3	6·4	0·055	0·065
27	10	6·4	14·2	123	1·3	2·5	<0·1	96·3	7·8	0·060	0·067
44	15	11·3	9·7	428	4·5	2·8	0·2	82·6	5·6	0·056	0·066
67	10	9·5	9·9	623	5·2	2·6	0·5	71·2	6·0	0·050	0·046
68	15	17·9	14·8	998	5·9	4·8	0·3	74·3	6·8	0·033	0·032
68	15	18·9	16·3	928	16·1	5·2	0·8	75·6	6·6	0·081	0·095
93	5	8·0	8·9	464	8·0	2·4	1·0	58·5	5·2	0·078	0·080
94	5	8·0	8·7	418	4·7	2·5	0·6	52·2	4·3	0·047	0·051
153	5	9·8	15·6	673	10·7	3·5	0·5	32·9	3·3	0·051	0·051
155	2	4·3	6·8	275	4·7	1·3	1·1	34·2	3·4	0·056	0·054
163	5	12·4	16·5	649	19·2	4·7	0·4	30·8	2·9	0·067	0·088

Since the reactions are no longer of first order, equation (5) will not hold in this case. If it is assumed that the rate of the surface reaction follows a Langmuir-type expression, the overall rate in a static system is given by

$$-\frac{d[A]}{dt} = (k_1 + k_2)[A] + \frac{k_s S[A]}{1 + \alpha[A]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where k_s is the velocity constant for the surface reaction, and α is constant at constant temperature. In the flowing system with the reactions (7), (8), and (9), equations (10), (11), and (12) may be shown to hold:

$$A \longrightarrow yB_1,\ \text{rate } k_1[A] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$A \longrightarrow yB_2,\ \text{rate } k_2[A] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$A \longrightarrow yB_1,\ \text{rate } k_s S[A]/(1 + \alpha[A]) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$M_0 V = \frac{yg_0}{\theta}\left\{\frac{1}{a}\log\frac{g_0}{g} - \frac{\alpha^2 a(k_1 + k_2)k_s S}{[\theta(y-1) - \alpha a(k_1 + k_2)]^2} \times \log\frac{\theta y g_0 - g[\theta(y-1) - \alpha a(k_1 + k_2)]}{\theta y g_0 - g_0[\theta(y-1) - \alpha a(k_1 + k_2)]}\right\} - \frac{(y-1)(y-1-\alpha a)(g_0 - g)}{a[\theta(y-1) - \alpha a(k_1 + k_2)]} \quad . \quad . \quad (10)$$

$$\frac{\{B_2\}M_0}{k_2} = \frac{(y-1-aa)(g_0-g)}{\theta(y-1)-aa(k_1+k_2)} + \frac{yaak_sSg_0}{[\theta(y-1)-aa(k_1+k_2)]^2} \times \log\frac{\theta yg_0 - g[\theta(y-1)-aa(k_1+k_2)]}{\theta yg_0 - g_0[\theta(y-1)-aa(k_1+k_2)]} \quad . \quad . \quad (11)$$

$$\frac{\{B_1\}M_0}{k_1+k_sS} = \frac{(y-1)(g_0-g)}{\theta(y-1)-aa(k_1+k_2)} - \frac{yaag_0(k_1+k_2)}{[\theta(y-1)-aa(k_1+k_2)]^2} \times \log\frac{\theta yg_0 - g[\theta(y-1)-aa(k_1+k_2)]}{\theta yg_0 - g_0[\theta(y-1)-aa(k_1+k_2)]} \quad . \quad . \quad (12)$$

where $\theta = k_1 + k_2 + k_sS$, and $\{B_1\}$, $\{B_2\}$ are the amounts of A in moles converted into B_1, B_2, respectively, in unit time. In the present case $y = 2$, B_1 and B_2 refer to keten (K) and carbon dioxide respectively. Combination of (10) and (12) then gives

$$M_0a\{k\} = -\frac{g_0}{a}\left\{2\log\frac{g_0}{g} - \frac{g_0-g}{g_0}\right\} + M_0V(k_1+k_sS) \quad . \quad . \quad . \quad . \quad . \quad (13)$$

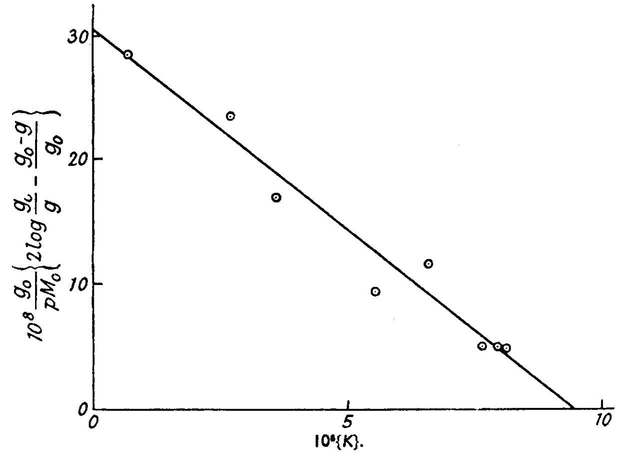
Further, if, as is the case with the present reaction, $k_sS \gg k_1 + k_2$,

$$M_0\{CO_2\} = \frac{g_0k_2}{k_sS}\left\{\frac{g_0-g}{g_0}(1-aa) + 2aa\log\frac{2g_0-g}{g_0}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Equation (13) may be used to determine $k_1 + k_2 + k_sS$ and, from results of a series of runs at different pressures, equation (14) then allows absolute values of $k_2 + k_sS$ to be estimated.

FIG. 3.

Runs in clean packed tube at 878° K.



The results at any one temperature can be interpreted satisfactorily by means of equation (13). A typical series is shown in Fig. 3, from which it may be seen that {K} plotted against $\frac{g_0}{pM_0}\left(2\log\frac{g_0}{g} - \frac{g_0-g}{g_0}\right)$ gives a straight line, as required by (13). Values for α and k_s are given for four temperatures in Table VI. These values do not give linear Arrhenius plots. We have not been able to establish whether or not this effect is genuine, since the experiments are not sufficiently reproducible. This is not surprising because the nature of the surface must change progressively throughout a run, and it has been shown that the reaction is very sensitive to the state of the surface. Qualitatively the values are acceptable, since α decreases with increasing temperature, and the temperature coefficients of α and k_s correspond to reasonable activation energies of the order −10 kcals. and 30 kcals., respectively. In Table V values are given for k_2

TABLE VI.

Values of α *and* k_s *in clean packed tubes* : S = 47 *cm.*$^{-1}$; V = 17·3 *c.c.*

T°, K.	1028	971	924	878
$10^{-6}\alpha$, l. mole^{-1}	0·89	0·67	1·18	1·75
$10k_s$, cm.sec.$^{-1}$	1·77	0·50	0·31	0·20

calculated from equation (14). The scatter in these is quite large, probably because of the difficulty of determining carbon dioxide accurately in the presence of a large excess of keten. The mean value, 0·063 sec.$^{-1}$, does, however, agree closely with that estimated from Fig. 2 (0·054 sec.$^{-1}$) for runs in carbon-coated tubes at 1028° K. The decarboxylation reaction therefore seems to show no surface catalysis in quartz vessels.

A series of runs was carried out in the same tube at 1028° K. with coarser packing, corresponding to $S = 22·6$ cm.$^{-1}$. These gave $k_sS = 5·13$ sec.$^{-1}$, or $k_s = 0·227$ cm. sec.$^{-1}$. Comparison with Table VI shows that k_sS is approximately proportional to S. This seems to establish that the reaction is not a chain process, but a pure surface reaction, since a chain would require an order greater than unity unless the chains started and finished on the walls, and in this case the overall rate would be more or less independent of S.

In the runs at low temperatures, decomposition of keten and decarboxylation become progressively less important. Detailed analyses are not given, since the amounts of minor products were too small for accurate determination. Incidentally, small quantities of pure keten could probably be best prepared by low-temperature pyrolysis of acetic acid in clean packed quartz tubes. Keten prepared in this way at 878° K., after separation from water and unchanged acetic acid by distillation at −80° as described, contains less than 1% of volatile impurities. The purity of the keten increases with decreasing temperature; it is feasible to work at 760° K. (487° C.), at which temperature the conversion was 2% per pass at 25 mm. pressure under our conditions.

One further effect may be noted. If the data of Table IV for the clean unpacked tube are plotted according to equation (13), a straight line is also obtained corresponding to $\alpha = 5·1 \times 10^6$. This value of α is much larger than those given in Table VI. In deriving (13) it was assumed that the surface was uniformly distributed throughout the volume of the reaction vessel, *i.e.*, that mixing occurs rapidly over its cross-section. Although this assumption is reasonable for the packed tube it is not so for the unpacked, in which stream-line flow should occur under our conditions. The non-uniformity of composition across the cross-section would be expected to become less as the pressure is reduced. A correspondingly larger fraction of the acetic acid will then come into contact with the surface, and the apparent velocity constant should increase with decreasing pressure. This effect provides additional evidence that the formation of keten is surface-catalysed in clean quartz tubes. The relative constancy of k_2 (Table IV) therefore suggests strongly that the decarboxylation is a homogeneous unimolecular gas reaction.

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