349. *The Kinetics of the Thermal Decomposition of Acraldehyde.*

By H. W. THOMPSON and J. J. FREWING.

THE kinetics of the thermal and photochemical decomposition of aldehydes and ketones have been extensively studied during recent years. The thermal decomposition of propaldehyde (Hinshelwood and Thompson, *Proc. Roy. Soc.*, 1926, **113**, *A*, 221) and of acetone (Hinshelwood and Hutchison, *ibid.*, **111**, *A*, 245) were among the earliest studied examples of a homogeneous quasi-unimolecular reaction, and that of acetaldehyde was proved to be homogeneous but bimolecular (*idem, ibid.*, p. 380). It is an inherent consequence of the mechanism of quasi-unimolecular processes proceeding by a Lindemann collision mechanism that the rate should show a falling off at low pressures. A more detailed re-examination has now shown that such a falling off is not uniform, and the plot of the reciprocal of the time of half-change against the initial pressure has a segmented appearance (Fletcher and Hinshelwood, *Proc. Roy. Soc.*, 1933, **141**, *A*, 41; 1934, **146**, *A*, 327). It appears that the same molecule may decompose in different pressure regions by different mechanisms, each quasi-unimolecular; and it has been supposed that this arises as a result of a localisation of the energy of activation in different parts of the molecule. The energy of activation changes in passing from one pressure region to another.

The photochemical studies involve a correlation of the absorption spectra of the aldehydes and ketones with their fluorescence, and with the products and quantum efficiencies of their photochemical decomposition. Peculiarities arise in that, although there are indications of the operation of predissociation processes, the quantum efficiencies are nevertheless small, and there is considerable simultaneous photopolymerisation.

It seemed desirable to examine the relationships with acraldehyde, in both its thermal and photochemical decomposition, and the results are reported respectively in this and the succeeding paper. If the hypothesis of a localisation of the energy of activation in different parts of the molecule is correct, the rather more complex nature of the acraldehyde molecule might be expected to lead to enhanced effects of the type previously found. On the other hand, the presence of the system of conjugated double bonds might, by analogy with the ideas of electron drift, facilitate internal-energy rearrangements in the molecule.

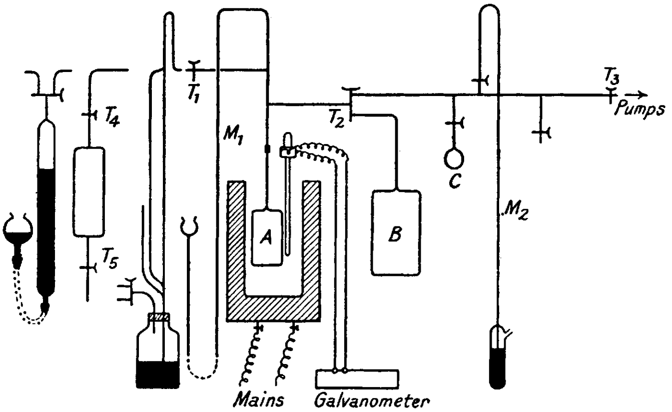
No kinetic measurements on this process are on record.

EXPERIMENTAL.

The acraldehyde used was a commercial product, fractionated in a vacuum. It polymerised slowly, but rapidly after warming, so fresh samples were prepared at frequent intervals. Different samples gave identical results.

The reaction was followed by means of the pressure change at constant volume. The reaction vessel, a cylindrical quartz bulb A (Fig. 1), of *ca.* 200 c.c. capacity, was connected by capillaries to a mercury manometer and to the taps T_1, T_2. " Dead-space " amounted to *ca.* 2%. Inert gases from a reservoir B, or acraldehyde from the bulb C, could be introduced through T_2. The apparatus was evacuated through T_3 by means of a mercury diffusion pump, backed either by a water pump, or by a tube containing charcoal in liquid air, or by a Hyvac oil pump. The tubing between T_2 and T_3 was connected to a mercury manometer and served as a measuring pipette for introducing the smaller pressures of acraldehyde into A by partition. All the apparatus was wound with nichrome wire and heated electrically to *ca.* 70° to prevent condensation of acraldehyde. Apiezon tap grease was used.

FIG. 1.



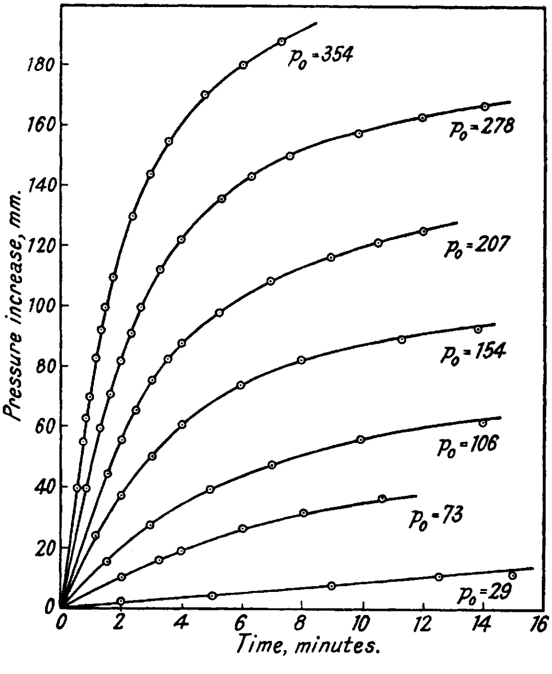
The reaction vessel was held within an electric furnace, and the temperature measured by means of a platinum–platinum-rhodium thermocouple frequently calibrated at the b. p.'s of water and sulphur and the m. p.'s of pure aluminium (658°) and of the eutectic of copper–aluminium (545°). There was a noticeable lag in the attainment of equilibrium between thermocouple and reaction vessel, which may account for some slight irregularities in measurement of rate, but in general the temperature could be kept constant to within 1°.

The progress of the reaction at initial pressures of 15—600 mm. was followed on the mercury manometer M_1. For lower initial pressures, 1—20 mm., a McLeod gauge reading from 1 to 25 mm. was attached at T_1. The capillary of this gauge was heated electrically to a constant temperature of 50° to prevent condensation of acraldehyde upon compression. The procedure was as follows. The sharing ratio between the apparatus from tap T_2 to T_3 and the reaction vessel was first determined for air and for acraldehyde with the reaction vessel successively at 480° and (for air) at 530° : there was no appreciable difference between the two in this respect, so the sharing ratio for acraldehyde at 530° was assumed to be the same as that for air. Similarly, sharing ratios were determined for the system reaction vessel–McLeod gauge, and the latter thereby calibrated. Acraldehyde vapour was then introduced into the apparatus between T_2 and T_3 at such a pressure as to produce after partition the desired pressure in the reaction vessel. After a suitable interval, the contents of the reaction vessel were shared with the McLeod gauge and the pressure measured. This provided one point on the curve showing pressure change as a function of time for a given initial pressure. The experiment was then repeated, the gas being withdrawn from A after a different interval. From the curves so constructed, the period for a given percentage change could be read off. In making the partitions, the taps T_2 and T_1 were always allowed to remain open for the same period; 5 secs. appeared sufficient for the establishment of equilibrium.

The products of reaction at various stages of its course were determined by withdrawing samples of the gas mixture from the reaction vessel into a gas holder over mercury. The latter was attached at T_1 by rubber pressure tubing. Details of the method of analysis are given below.

In order to determine the extent to which the pressure change can be regarded as a correct measure of the decomposition, the rate of disappearance of the acraldehyde was measured as follows. A 500-c.c. pipette, with capillary leads and having a tap at each end, was attached by rubber tubing at T_1, the whole evacuated through the reaction vessel, and the tap at T_1 closed. Acraldehyde at the desired pressure was then introduced into A, and after a suitable interval the contents of A were shared with the pipette by opening T_1. The pressure in the reaction vessel before and after sharing was measured on M_1, whence, " dead-space " being neglected, the fraction of the gas mixture withdrawn was obtained. The tap T_4 was then closed, the pipette disconnected, and tap T_5 opened with the end of the pipette under the surface of 25 c.c. of $N/10$-sodium hydrogen sulphite solution (frequently standardised) so that the latter was sucked into the pipette. The gas was allowed to remain in contact with the liquid for *ca.* 15 mins. with frequent shaking, and the excess unused bisulphite was then titrated against standard iodine solution. The amount of acraldehyde originally present could thus be obtained.

FIG. 2.



Ethylene was prepared by the action of syrupy phosphoric acid on ethyl alcohol. Cylinder argon was freed from oxygen by streaming slowly over heated copper.

Results.

(1) *The Nature and Course of the Reaction.*—Typical curves showing the course of several runs at 530° for different initial pressures are shown in Fig. 2. For a unimolecular decomposition giving ethylene and carbon monoxide as the sole products, the pressure increase

would be equal to the original pressure; for a bimolecular interaction of 2 mols. of acraldehyde, leading to butylene and carbon monoxide, the pressure increase would be one-half the original pressure. The actual " end-point " lies between these extremes and varies somewhat with pressure. With 400 mm. initial pressure, $\Delta p/p_0$ is *ca.* 65%, and it rises with decreasing initial pressure, rapidly below 100 mm., so that at 40 mm. it is *ca.* 80%. The " end-points " do not vary appreciably with temperature over the range studied, *viz.*, 490—570°. The process occurring is not, however, a simple superposition of the above two possibilities, for analysis of the products revealed the presence of carbon monoxide, butylene, ethylene, methane, ethane, and hydrogen, which were separated and identified as follows.

The gas mixture withdrawn at the end of a run was first analysed in a modified Haldane apparatus. It was washed successively with water, 33% caustic potash solution, and dilute sulphuric acid, to remove carbon dioxide and unchanged acraldehyde. Only a trace of the former was present. The volume was then measured. " Unsaturated hydrocarbons " were then absorbed by a concentrated solution of mercuric acetate, carbon monoxide by ammoniacal cuprous chloride, and the " residue " analysed separately as below. In the later experiments the " unsaturated hydrocarbons " were differentiated by first absorbing higher olefins (mainly butylene, see below) with concentrated sulphuric acid, and the remaining ethylene by mercuric acetate as before. Absorption with potassium mercuric iodide solution showed that acetylene was not present in appreciable quantity. Between each absorption the gas was washed with dilute sulphuric acid so as to maintain a constant vapour pressure before measurements of volume.

Several preliminary analyses should be mentioned. (i) Unsaturated hydrocarbons and carbon monoxide were first removed from the gas mixture (530°; 90% completed). The remainder was assumed to consist of hydrogen, methane, and ethane, for, apart from other considerations, propane and higher homologues would be unstable at the temperature of the experiments. It was separated into two fractions, one condensed (ethane and methane) and the other not condensed (hydrogen and methane) by liquid air. The volume of each fraction was measured, and its composition determined by combustion, with the following results :

		Non-condensed fraction.			Condensed fraction.			Total, %.		
		Vol., c.c.	H_2.	CH_4.	Vol., c.c.	CH_4.	C_2H_6.	H_2.	CH_4.	C_2H_6.
p_0 = 150 mm.	(1)	1·43	0·80	0·63	1·34	0·78	0·56	29	51	20
	(2)	1·51	0·82	0·69	1·11	0·66	0·45	31	51	18
	(3)	1·26	0·55	0·71	1·21	0·40	0·8	22	45	32
							Mean	27	49	23
p_0 = 300 mm.		3·92	1·30	2·62	2·61	0·25	2·36	20	44	36

(ii) The mixture of reaction products, freed from acraldehyde, was passed into a tube surrounded by melting ethyl ether at — 116°. The uncondensed gas was pumped off. The condensed fraction was examined by combustion. Two experiments gave volume : CO_2 : contraction = 1 : 2·7 : 4 and 1 : 2·8 : 2·3 respectively, which agree qualitatively with the presence of butylene and ethylene. (iii) Although the previous measurements do not exclude the possibility of the presence of propylene rather than butylene, we regard this as unlikely. The following experiment indicates that a butane is present. After removal of residual acraldehyde, the products of a run (530°; p_0 = 150 mm.; 90% completed) were passed into a tube surrounded by liquid oxygen. The uncondensed gases (hydrogen, carbon monoxide, and methane) were discarded. The condensed fraction was allowed to evaporate, and was then cooled at — 126° (eutectic of ether and toluene). The uncondensed fraction was pumped off (A). The condensed fraction was re-evaporated and cooled at — 120° (eutectic of chloroform and ether). The portion not condensed was withdrawn (B), and that condensed then allowed to evaporate and collected (C). Each fraction was examined by combustion. Three experiments gave :

	Vol.	:	CO_2	:	Contractn.		Vol.	:	CO_2	:	Contractn.
(1) A	1	:	1·4	:	1·3	(2) A	1	:	1·91	:	2·1
B	1	:	2·12	:	2·5	B	1	:	2·05	:	2·48
C	1	:	3·8	:	2·6	C	1	:	3·43	:	2·75
(3) A and B	1	:	1·79	:	1·63						
C	1	:	3·45	:	2·61						

Hence, as the temperature of liquefaction rises, the condensed fraction has molecules richer in carbon up to about 4 atoms per molecule. Assuming the fraction C to consist of butylene and ethylene only, its composition can be estimated. The mean results are :

	Butylene, %.	Ethylene, %.
From contraction	75·6	24·4
„ CO_2 formed	71·5	28·5
„ O_2 used	73·0	27·0

showing a very satisfactory agreement. Fraction A appears to be methane and ethane, B ethane and ethylene.

The analyses were mainly directed to the determination of (*a*) how the reaction products were affected by alteration of the initial pressure, and (*b*) how the composition of the gas mixture changed during the course of a single run. Results on (*a*) are given in the following table, the gas mixture in each case being analysed after proceeding to 90% of completion.

p_0, mm.	C_4H_8, %.	C_2H_4, %.	CO, %.	" Residue," %.	p_0, mm.	C_4H_8, %.	C_2H_4, %.	CO, %.	" Residue," %.
40	10·8	13·9	52·4	22·9	300	11·9	10·0	57·5	20·6
100	13·1	12·4	56·0	18·4	400	11·4	9·1	58·0	21·5
200	13·2	11·7	56·9	18·3					

When carbon monoxide is removed from acraldehyde, the remainder is " C_2H_4." This might appear either as ethylene or as $\frac{1}{2}C_4H_8$, or in other ways such that the carbon monoxide formed is equivalent to the " C_2H_4." Actually, the carbon monoxide is in excess of the required amount; for instance, assuming the residue to be composed of hydrogen, ethane, and methane in approximately equal proportions (see above), the " C_2H_4 " formed along with 52·4% of carbon monoxide at an initial pressure of 40 mm. will be (calculated with respect to carbon)

$$(2 \times 10{\cdot}8) + (1 \times 13{\cdot}9) + (0 \times 7{\cdot}6) + (\tfrac{1}{2} \times 7{\cdot}6) + (1 \times 7{\cdot}6) = 46{\cdot}9\%.$$

A similar result applies for the higher initial pressures. The same is also true if the calculation is made " with respect to hydrogen," although the discrepancy here is smaller. In the decomposition of acraldehyde, therefore, small amounts of condensation products are formed which do not appear in the analyses; in fact, a dark solid is slowly deposited in the reaction vessel.

The percentages of the foregoing table are here recalculated on the basis of a constant volume of carbon monoxide = 100 :

p_0, mm.	C_4H_8.	C_2H_4.	CO.	"Residue."	Total vol.	p_0, mm.	C_4H_8.	C_2H_4.	CO.	"Residue."	Total vol.
40	20·6	26·5	100	43·7	190·8	300	20·7	17·4	100	35·8	173·9
100	23·4	22·1	100	32·9	178·4	400	19·6	15·7	100	37·1	172·4
200	23·2	20·6	100	32·2	176·0						

From the results we should expect the ratios of the " end-points " at 40 mm. and 200 mm. to be 191/176 = 1·09 : the observed ratio is 80/70 = 1·14.

The following table shows typical results of experiments made to determine how the composition of the mixture of products changes during the course of individual runs.

Temperature, 530°.

(1) p_0 = 155 mm.					(2) p_0 = 85 mm.			
% Completion.	C_4H_8.	C_2H_4.	CO.	" Residue."	% Completion.	" Unsaturated."	CO.	" Residue."
15	20·5	11·5	57·0	11·0	20	30·5	57·2	12·3
22	20·9	10·1	57·3	11·7	40	30·0	57·2	12·8
50	19·6	8·4	57·5	14·5	52	30·6	56·3	13·0
75	17·4	9·8	57·3	15·5	81	28·0	56·5	15·5
80	14·9	10·1	58·5	16·5	90	25·5	55·5	19·0
95	13·2	11·0	57·0	18·8				

It is clear from this table that (i) the methane, ethane, and hydrogen are formed as primary products, and not merely as the result of secondary interactions and condensations among the unsaturated hydrocarbons; (ii) during the course of a run the proportion of the residue increases and that of unsaturated hydrocarbons (primarily butylene) decreases.

As the initial pressure increases, there is a greater proportion of butylene and a smaller one of " residue " among the primary products. The following table gives results at several initial pressures. The temperature was 530° and in each case the reaction was 20% completed.

p_0.	C_4H_8.	C_2H_4.	CO.	" Residue."	p_0.	C_4H_8.	C_2H_4.	CO.	" Residue."
40	17·7	11·3	57·3	13·6	155	20·4	10·6	57·2	11·8
85	20·0	10·5	57·2	12·3	300	21·2	12·1	58·5	8·2

It is possible to understand the results of the last four tables if it is assumed that at very low pressures the primary process involves predominantly the formation of ethylene and residue, whilst at higher pressures butylene is also a primary product. At still higher pressures, the proportion of " residue " increases by virtue of condensations leading at the same time to a decrease in the proportion of butylene.

(2) *Pressure Change as a Measure of the Reaction.*—In view of the rather complicated nature of the decomposition, it was desirable to determine how far the pressure change could be employed as a measure of the disappearance of acraldehyde. This rate was accordingly followed by titration as already described. Curves were constructed at a given temperature and for each of a series of initial pressures, 40—500 mm., showing pressure change as a function of acraldehyde decomposed. Allowance was made for the " dead-space "; this could be calculated roughly, and was in addition found to be about 3% by allowing a run to proceed to completion before titration.

Typical results at 530° and two different initial pressures are given in the following table.

(1) $p_0 = 500$ mm.

Δp, mm.	Titre.	Titre corrected for dead space (v).	Titre diff. (Δv).	$100\Delta v/v_0$.
0	57·2	55·0	0	0
25	49·6	47·4	7·6	13·8
50	43·4	41·2	13·8	25·1
75	37·5	35·3	19·7	35·8
100	32·2	30·0	25·0	45·5
145	24·1	21·9	33·1	60·2
202	14·0	11·8	43·2	78·5
268	6·8	4·6	50·4	91·5
289	4·8	2·6	52·4	95·2
310 (end)	2·2	0·0	55·0	100·0

(2) $p_0 = 100$ mm.

Δp, mm.	Titre.	Titre corrected for dead space (v).	Titre diff. (Δv).	$100\Delta v/v_0$.
0	17·9	17·3	0	0
5	16·4	15·8	1·5	8·7
10	15·3	14·7	2·6	15·0
15	13·5	12·9	4·4	25·4
20	12·7	12·1	5·2	30·0
25	11·1	10·5	6·8	39·3
35	8·7	8·1	9·2	53·1
50	5·4	4·8	12·5	72·3
60	3·4	2·8	14·5	83·8
75 (end)	0·6	0·0	17·3	100·0

Measurements were made at 491° and at 530°. The pressure increase corresponding to the disappearance of half the acraldehyde for a given initial pressure was not appreciably affected over this range of temperature.

From the data obtained with ten different initial pressures over the range 40—500 mm., curves were constructed from which, for a given initial pressure of acraldehyde, the pressure increase corresponding to one-third, one-half, and three-quarters of the aldehyde decomposed could be read off. From the following table, in which pressures are expressed as a % of p_0, it can be seen that half the pressure change does not correspond to the true " half-life " at any pressure, and the necessity for this procedure becomes apparent.

p_0, mm.	$\Delta p_{1/3}$.	$\Delta p_{1/2}$.	$\Delta p_{3/4}$.	Δp_{final}.
50	18·8	31·6	50·4	79
100	18·5	30·6	47·0	75
200	17·5	27·2	43·5	70
300	16·3	25·7	41·8	66
500	14·0	22·9	38·8	64

(3) *The Homogeneity of the Reaction.*—The great reproducibility of the process (if oxygen is carefully excluded from the reaction vessel) is almost adequate proof of its homogeneity. It was, however, examined in several different vessels of different surface/volume ratio. In different unpacked silica vessels there was no alteration in rate. In a cylindrical vessel packed with silica tubes, having a surface/volume ratio some 3 times as great as that of the unpacked vessels, the " end-points " were uniformly rather lower (2—3%) than in the unpacked vessel. If corrections are made for this minor variation in end-point, the reaction is still somewhat slower in the packed vessel, but the effect is slight. At 530°, for values of p_0 varying between 40 and 354 mm., the ratio of $t_{\frac{1}{2}}$ in the packed and unpacked vessels varied between 0·82 and 0·97 (mean 0·91). The retardation is not as large as might be expected if appreciably long reaction chains were involved. Essentially the reaction is homogeneous.

(4) *The " Order " of the Reaction.*—For a first-order process $t_{\frac{1}{2}}/t_{\frac{1}{3}} = 1{\cdot}71$ and $t_{\frac{3}{4}}/t_{\frac{1}{2}} = 2$; for one of the second order, these ratios are respectively 2 and 3. The values found in the present case lie between these limits (Table I). Mean values at other temperatures were: 510°, 1·78 and 2·43; 550°, 1·81 and 2·1; 540°, 1·77 and 2·12.

For a bimolecular process the velocity constant k should be given by $1/t_{\frac{1}{2}}c_0$ or $k_1 = 1/t_{\frac{1}{2}}p_0$.

TABLE I.

Temperature 508°.

p_0.	$(dp/dt)_0 \times 10$, mm./sec.	$t_{1/2}$, secs.	$t_{1/2}/t_{1/3}$.	$t_{3/4}/t_{1/2}$.	$10^4/t_{1/2}p_0$.	$(10^5/p_0^2)\ (dp/dt)_0$	$10^3/t_{1/2}$.
15·5	0·023	2016	1·63	—	0·32	0·96	0·5
19·0	0·040	1560	1·71	—	0·34	1·11	0·64
22·2	0·052	1540	1·85	—	0·30	1·05	0·65
29·0	0·102	1055	1·85	—	0·33	1·21	0·95
36·0	0·143	820	1·74	—	0·34	1·10	1·22
50·0	0·28	625	1·78	—	0·32	1·12	1·60
61·5	0·45	558	1·74	—	0·29	1·19	1·79
75	0·55	474	1·82	1·94	0·28	0·98	2·11
80	0·72	500	1·88	1·97	0·25	1·12	2·00
103	0·87	420	1·84	2·10	0·23	0·82	2·38
104	0·82	423	1·76	2·15	0·23	0·76	2·36
123	1·22	356	1·74	2·18	0·23	0·81	2·81
162	2·03	294	1·89	2·35	0·21	0·77	3·40
209	2·88	231	1·68	2·21	0·21	0·66	4·33
260	4·07	186	1·68	2·31	0·21	0·60	5·38
276	4·81	183	1·70	2·28	0·20	0·63	5·46
305	5·37	162	1·66	2·38	0·20	0·58	6·17
359	6·5	145	1·81	2·28	0·19	0·51	6·90
404	9·41	132	1·69	2·54	0·19	0·58	7·58
484	10·41	114	1·68	2·52	0·18	0·44	8·77
514	12·50	108	1·77	2·41	0·18	0·47	9·26
600	14·67	95	1·73	2·79	0·17	0·41	10·53
651	20·0	85	1·81	2·59	0·18	0·47	11·76

As Tables I and II show, this quantity, although reasonably constant over the entire pressure range, decreases uniformly as the initial pressure increases, and reaches a steady value above 200 mm.

In the same way, the expression $k_2 = (dp/dt)_0/p_0^2$ shows a drift in passing from lower to higher pressures. It varies three-fold over the pressure range 5—500 mm. The first-order expression $(dp/dt)_0/p_0$ varies 20-fold over the same pressure range. The facts suggest that at higher pressures the predominant reaction is bimolecular, but that at lower pressures there is a superposed first-order process.

The constants k_2 differ from k_1 by a factor of about 3. A similar result has been noticed by Fletcher in the decomposition of formaldehyde (*Proc. Roy. Soc.*, 1934, **146**, *A*, 357). The discrepancy is so uniform over the entire pressure range that we are inclined to regard it as due, not so much to inaccuracies in the initial rates, as to the fact that the order varies during the course of the run; k_1 is, moreover, determined from $t_{\frac{1}{2}}$, whereas k_2 is obtained from $(dp/dt)_0$.

TABLE II.

Temperature 540°.

p_0.	$(dp/dt)_0$, mm./sec.	$10^4/p_0t_{1/2}$.	$(10^5/p_0^2)\ (dp/dt)_0$.	$10^3/t_{1/2}$.
21	0·137	0·92	3·21	1·94
30	0·31	0·93	3·44	2·78
37	0·475	0·86	3·46	3·20
45	0·57	0·83	2·82	3·74
59	0·92	0·74	2·64	4·39
70	1·18	0·68	2·41	4·81
90	1·78	0·65	2·20	5·85
109	2·63	0·65	2·24	7·09
123	3·0	0·63	1·99	7·81
134	3·54	0·61	1·97	8·13
146	4·08	0·61	1·91	8·85
179	5·75	0·56	1·79	10·10
204	6·91	0·58	1·66	11·76
223	8·33	0·52	1·67	12·5
262	10·07	0·51	1·40	13·51
300	13·67	0·48	1·52	14·49
315	14·33	0·50	1·44	15·87
355	15·67	0·46	1·25	16·39

(5) *Variation of the Period of Half Change with Initial Pressure.*—Fig. 3 shows the plot of $1/t_{\frac{1}{2}}$ against p_0 at 530°; and the inset is an enlarged portion for low initial pressures at 508°. There is no doubt that the curve is segmented. At 530° the changes of slope occur at *ca.* 200 mm. and 15 mm.; and there may be a feebler one at 40 mm. The effects are not so pronounced as with propaldehyde, but more like those found with acetaldehyde. From our results at different temperatures, it appears that the pressure regions at which changes of slope occur vary at different temperatures. For example, at 550° and 530° the changes are at 140 and 280 mm. respectively, instead of 200 mm.

(6) *The Temperature Coefficient of the Reaction.*—The following table gives values of $t_{\frac{1}{2}}$ (in secs.) for various pressures at different temperatures. For each pressure the plot of $\log t_{\frac{1}{2}}$ against $1/T$ is almost a straight line. The energies of activation, uncorrected for the variation of collision rate with temperature, are given below.

T, Abs.	Initial pressure, mm.					
	30.	60.	100.	200.	300.	400.
500°	—	—	571	308	222	177
508	1031	588	408	235	167	133
510	—	—	385	213	154	123
520	690	417	286	160	120	97

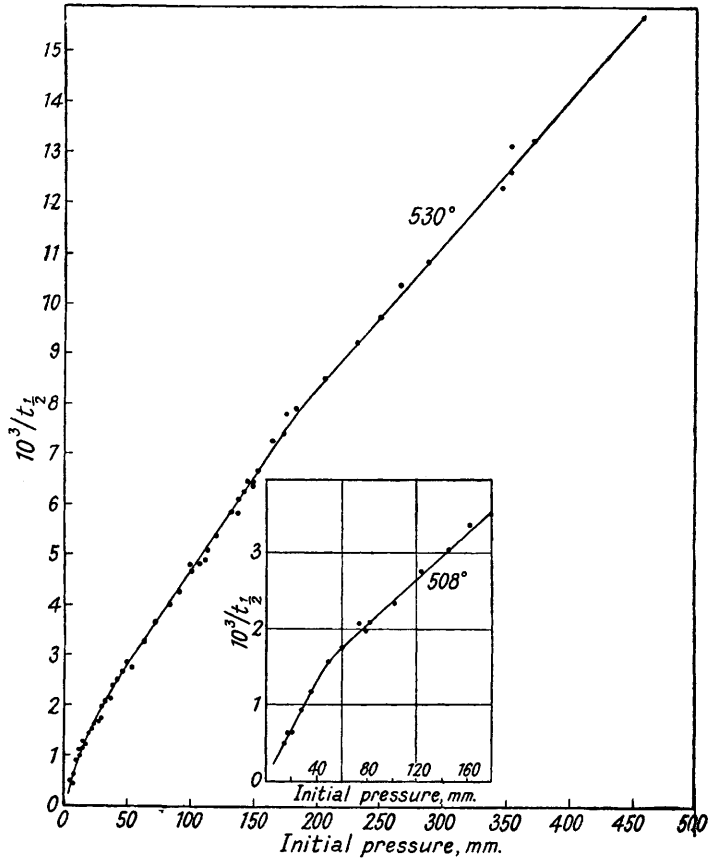
T, Abs.	Initial pressure, mm.					
	30.	60.	100.	200.	300.	400.
530°	532	323	215	120	88	72
540	364	230	156	88	68	—
550	290	174	118	—	—	—
570	145	96	71	—	—	—

Energy of activation.

Initial pressure, mm.	30	60	100	200	300	400
$10^{-3} \times E$, cals.	42·2	40·8	40·7	37·8	36·5	35·4

The energy of activation was also determined for a concentration corresponding to 300 mm. at 530°. The value obtained was 38,400 cals., which, corrected for the variation of collision rate with temperature, becomes 37,600 cals. The corresponding value for a concentration corresponding to 100 mm. at 530° is 41,800 cals.

Fig. 3.



(7) *Influence of Added Gases Upon the Rate of Reaction.*—The influence of the products of reaction, of argon, of hydrogen, and of ethylene upon the rate of reaction was examined. The last two gases, if present in excess, do not appreciably affect the initial rate, but considerably alter the "end-point," so it is difficult to determine the extent of their catalytic action. Similarly, the products of the reaction in small amount do not noticeably affect the reaction rate, but if present in excess they disturb the end-point. Argon has little influence upon the reaction.

Discussion, and Molecular Statistics.

The above results suggest that in many respects the decomposition of acraldehyde involves a mechanism similar to that proposed for the decomposition of other aldehydes.

The segmented curve relating $1/t_{\frac{1}{2}}$ and initial pressure can best be interpreted by supposing that several independent quasi-unimolecular and one bimolecular decomposition are superposed. Up to pressures of 600 mm., the curve shows no tendency to become horizontal, and thus differs from that of propaldehyde. On the other hand, the relationships here cannot be the same as with acetaldehyde, for, by virtue of the formation of butylene, a genuine bimolecular process must be superposed upon the quasi-unimolecular processes. No ethane is formed in the decomposition of acetaldehyde, and there is no evidence for the existence of other than quasi-unimolecular mechanisms. The order of reaction as indicated by $t_{\frac{1}{2}}/t_{\frac{1}{4}}$ and $t_{\frac{3}{4}}/t_{\frac{1}{2}}$ is between 1 and 2, but as determined by this method in such a complicated system, it may be of little significance.

At lower pressures the energy of activation rises, in agreement with previous work; and, as would be expected if the unimolecular decomposition were most prominent at lower pressures, there is a greater proportion of methane, hydrogen, and ethane at these pressures than at the higher ones.

In view of the superposition of the various processes, it is difficult to make strict calculations on the molecular statistics of the reaction. At 530° and 100 mm. initial pressure, the value of the bimolecular constant $k_2 = (dp/dt)_0/p_0^2 = 1{\cdot}7 \times 10^{-5}$, whereas $k_1 = 1/t_{\frac{1}{2}}p_0 = 4{\cdot}3 \times 10^{-5}$. The mean is $3{\cdot}0 \times 10^{-5}$. This will not be the accurate bimolecular constant, but it will not be far from it (the limiting value of k_1 at the highest pressures is $3{\cdot}4 \times 10^{-5}$). Then $k_{\text{bimol.}} = 1{\cdot}50$ g.-mol./l./sec. At 760 mm. and 803° Abs., the number of molecules reacting per c.c. per sec. will be $2{\cdot}1 \times 10^{17}$. The number of activated collisions calculated from the formula $2{\cdot}5\sqrt{2}\pi\sigma^2\bar{u}n^2 . e^{-42,000/RT}$ is $5{\cdot}5 \times 10^{17}$, which is in agreement within the limits of the calculation. At lower pressures the increased energy of activation will make it necessary to assume that the energy is distributed among more than two squared terms. At higher pressures, on the other hand, the rate of activation by collision will be greater than the rate of reaction. At 300 mm. the discrepancy is about 20 times. An explanation of this is withheld. The anomaly is also apparent in the low value of E at higher pressures. The reaction proceeds for equal rates (equal $t_{\frac{1}{2}}$) at about 40° lower than the decomposition of acetaldehyde, the energy of activation for which is *ca.* 50,000 cals. in the region of higher pressures. If the rate-determining factor were solely E/RT, we should expect an energy of activation of at least 45,000 cals. The discrepancy of *ca.* 6000 cals. is outside the limits of experimental error. It is worth noting that the only quasi-unimolecular decomposition showing an anomaly of this kind is the isomerisation of methyl maleate (Nelles and Kistiakowsky, *J. Amer. Chem. Soc.*, 1932, **54**, 2208), which, like acraldehyde, contains a system of conjugated double bonds. Whether this is of real significance or not can only be determined by a study of other examples.

SUMMARY.

The kinetics of the thermal decomposition of acraldehyde have been investigated. The products in the region of 530° are butylene, ethylene, carbon monoxide, methane, ethane, and hydrogen. The reaction appears to be composite, and several independent quasi-unimolecular processes are superposed upon a bimolecular one. The plot of the reciprocal of the period of half change against the initial pressure has a segmented appearance. There is a relatively greater proportion of methane, ethane, and hydrogen among the products at lower pressures. The energy of activation of the reaction increases as the initial pressure falls. The molecular statistics of the process are discussed.

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THE OLD CHEMISTRY DEPARTMENT, UNIVERSITY MUSEUM,
OXFORD.

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