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THE KINETICS OF THE THERMAL DECOMPOSITION OF ACETIC ANHYDRIDE

By M. SZWARC AND J. MURAWSKI

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The decomposition of acetic anhydride is shown to be a truly unimolecular dissociation process in which

 $(CH_3CO)_2O \rightarrow CH_2 : CO + CH_3 . COOH.$

This decomposition does not involve radicals, the unimolecular rate constant being given as

 $k = 1 \times 10^{12} \exp(-345 \text{co}/RT) \text{ sec.}^{-1}$.

This type of decomposition is favoured by the geometry of acetic anhydride molecule.

The investigator of a dissociation process is frequently faced with the crucial issue of deciding whether the reaction studied is a direct decomposition into two molecules, or a dissociation into two radicals (or atoms) followed by secondary processes. The first mode of decomposition should reveal all the characteristic features of a unimolecular reaction. In this case the transition complex corresponds to a configuration in which two (or more) bonds are partially broken and two (or more) bonds are in a This configuration is attained more readily if the state of formation. necessary deformation of the initial molecule is as small as possible. On the other hand, the split into radicals is a unimolecular process in which only one bond is ruptured. In this case, however, the character of the overall kinetics depends on the subsequent secondary reactions, and it is not uncommon to find that the rate of the overall decomposition is represented by first-order kinetics.

The distinction between these two modes of reaction is not always easy. Frequently the two possible ways of decomposition lead to the same final products of reaction, e.g.

(A) CH_3 . CHO \rightarrow CH₄ + CO a molecular split.

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(B)
$$CH_3 . CHO \rightarrow CH_3^{\bullet} + CHO \\ CH_3 . CHO + CH_3^{\bullet} \rightarrow CH_3^{\bullet} CO^{\bullet} + CH_4 \\ CH_3 . CO^{\bullet} \rightarrow CH_3^{\bullet} + CO \end{pmatrix}$$
 split into radicals followed by a chain process.

In the above example both mechanisms A and B require that methane and carbon monoxide, in molecular ratio of 1/1, should be the final products of the acetaldehyde decomposition.

If the split into radicals initiates a long chain process, the use of inhibitors offers a simple method for discrimination between the molecular and the radical decomposition. For a very short chain process, however, this need not be the case. For example, one might suggest two mechanisms for the decomposition of ethyl bromide

(C)
$$C_2H_5Br \rightarrow C_2H_4 + HBr \dots$$
 a molecular split

(D)

 $\begin{array}{c} C_2H_{\delta}\mathrm{Br} \rightarrow C_2H_{\delta}^{\bullet} + \mathrm{Br} \\ \mathrm{Br} + C_2H_{\delta}\mathrm{Br} \rightarrow C_2H_4\mathrm{Br}^{\bullet} + \mathrm{HBr} \\ C_2H_{\delta}^{\bullet} + C_2H_4\mathrm{Br}^{\bullet} \rightarrow C_2H_{\delta}\mathrm{Br} + C_2H_4 \end{array} \right\} \text{a radical split} \label{eq:constraint}$

Since the radical split (D) does not initiate a chain process, the use of inhibitors might not prove to be decisive for the elucidation of this particular problem.

The use of toluene offers an interesting possibility for studies of this type of problems. It was shown that toluene reacts readily with various radicals according to eqn. (I):¹

$$C_6H_5 \cdot CH_3 + R^{\bullet} \rightarrow C_6H_5 \cdot CH_2^{\bullet} + RH.$$
 (1)

The benzyl radicals produced in reaction (1) dimerize eventually, and thus the formation of dibenzyl is indicative of the generation of radicals (or atoms) in the initial decomposition process. This criterion was used, e.g. in the studies of pyrolysis of some organic bromides, and on this basis it has been concluded that benzyl bromide and allyl bromide decompose into the respective radicals and bromine atoms.² In the present study this technique was applied to the investigation of the pyrolysis of acetyl bromide and acetic anhydride. The results seem to indicate that these compounds decompose directly into molecules, and not into radicals.

Experimental

The decompositions of acetyl bromide and acetic anhydride were studied in a flow system using tolucne as a carrier gas. The compound investigated was introduced into the reaction vessel together with a great excess of toluene, the total pressure being of the order of 10-20 mm. Hg, and the time of contact being about 1 sec. The details of the apparatus and of the experimental technique were described in previous communications 14, 19, 29 Pyrolysis of acetyl bromide.—The pyrolysis of acetyl bromide may be

initiated in three ways :

$$CH_3 . CO . Br \rightarrow CH_3 . CO + Br$$
 . . . (2)

$$CH_3 . CO . Br \rightarrow CH_2 : CO + HBr . . . (3)$$

$$CH_3 . CO . Br \rightarrow CH_3Br + CO (4)$$

Reaction (2) represents a radical decomposition, while reactions (3) and (4)illustrate two possible molecular fissions.

Under our experimental conditions, in the presence of an excess of tolucne used as a carrier gas, reaction (2) would be followed by reaction (5):

$$H_{\mathbf{g}} \cdot CH_{\mathbf{3}} + Br \rightarrow C_{\mathbf{g}}H_{\mathbf{g}} \cdot CH_{\mathbf{2}} + HBr \quad . \quad . \quad (5)$$

It would be expected that in the temperature range of our study , i.e. $600^{\circ}-800^{\circ}C$, the acetyl radicals produced would decompose rapidly into methyl radicals and carbon monoxide : 3

¹ (a) Szwarc, J. Chem. Physics, 1949, 17, 431; (b) Proc. Roy. Soc. A, 1949,

198, 267 and 285. ² (u) Szwarc and Ghosh, J. Chem. Physics, 1949, 17, 744; (b) Szwarc, Ghosh and Schon, J. Chem. Physics, 1950, 18, 1142.

³ Steacie, Atomic and Radical Reactions (Reinhold Corp., 1946).

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the methyl radicals being removed by reaction (7) :

$$C_6H_5 \cdot CH_3 + CH_3 \rightarrow C_6H_5 \cdot CH_2 + CH_4.$$

It follows, therefore, that if reaction (2) represented truly the initial step in the decomposition of acetyl bromide the observed products would be HBr, CH₄, CO and dibenzyl.^{*} It was found, however, that although carbon monoxide and small amounts of HBr were produced in the pyrolysis, neither methane nor dibenzyl was ever detected. Consequently it was concluded that this decomposition takes place by a molecular split, most probably according to eqn. (3) and (4). The ratio of CO/HBr (about 1/5) seems to indicate that reaction (4) is much more frequent than reaction (3).

The results of some typical runs are given in Table I. Their reproducibility was not sufficiently good to warrant a detailed investigation of the kinetics of this pyrolysis. The essential point, however, which emerges from this work is the fact that even at these high temperatures (600°-S00° C) the decomposition of acetyl bromide does not produce radicals.

Run	<i>T</i> (°C)	PAcBr	<i>P</i> _t	t (sec.)	%
20	607	o•68	11.3	0.32	0.9
21	607	0.65	11.0	0.36	1.5
24	612	0.63	11.1	0.34	0.9
18	612	0.67	10.5	0.33	1.6
22	612	0.63	10.6	0.33	1.2
τĢ	613	1.18	11.3	0.43	1.8
23	614	1.13	11.0	0.32	<u>1</u> .8
17	628	1.67	16.0	0. 66	5.3
25	651	o•86	12.3	0.32	5.8
7	708	1.63	15.9	0.61	27.5
26	711	0.75	12.3	0.32	10.1
12	711	0.59	15.8	0.23	16.1
2	712	1.52	16.1	0.52	37.0
9	713	1.67	16.0	0.63	35.2
I	714	1.57	15.7	0.20	37.5
3	714	1.53	15.8	0.64	36.5
5	715	1.28	16.0	0.21	37.0
4	716	2.10	15.6	0.64	38.5
270	717	1.02	12.3	0.27	17.7
28p	718	1.38	12.8	0.28	19.8
15	718	0.20	15.2	0.60	13.1
16	719	0.85	15.4	0.60	19.5
11	719	1.88	16.8	o •60	40.0
8	719	1.65	15.9	0 •60	36.8
14	750	0.24	16.0	0.01	35.3
13	769	0.59	15.8	0.57	61·c

TABLE I

% decomposition is calculated as (amount of CO formed in the decomposition over amount of acetyl bromide introduced into the reaction vessel) \times 100.

Pyrolysis of acetic anhydride.—The decomposition of acetic anhydride was investigated in the temperature range of $280^{\circ}-650^{\circ}$ C. The only products of decomposition seems to be ketene and acetic acid in a molar ratio of 1/1; formation of dibenzyl was not observed in any experiment. Ketene was estimated by a gasometric method using a technique described in previous communications (e.g. see the method of determination of ammonia¹⁰). For irs

* The fate of acetyl radicals in the above system was determined by investigating the pyrolysis of diacetyl and benzyl methyl kelone.⁴ We found that these compounds decompose according to the following equations:

$$CH_3 . CO . CO . CH_3 \rightarrow 2CH_3 . CO$$

 C_6H_5 . CH_2 . CO. $CH_3 \rightarrow C_6H_5$. $CH_2 + CH_3CO$

followed by reactions (6) and (7). The observed products of decomposition were indeed CH_4 , CO and dibenzyl.

⁴ Murawski and Szwarc (unpublished results).

(7)

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identification we used the reaction with diluted sodium hydroxide which yields eventually acetic acid. Neither hydrogen nor methane was observed amongst the products of decomposition.

Determination of acetic acid was based on the titration of the residue condensed in a trap cooled to -80° C. This residue contained toluene used as a carrier gas the undecomposed acetic anhydride and the acetic acid formed in the reaction. Since the amount of acetic anhydride introduced into the reaction was determined by direct weighing, the amount of NaOH used for the titration yielded the amount of acetic acid as given by the equation :

(moles of acetic acid) = 2 (moles of acetic anhydride) - (moles of NaOH used in the titration).

Table II summarizes the experimental results giving the amounts of ketene observed which should be equal to the amounts of acetic acid formed according to eqn. (8):

$$(CH_3, CO)_2 : O \rightarrow CH_2 : CO + CH_3 : COOH.$$
 (8)

The amounts of acetic acid determined by titration are tabulated in the next column. The agreement between both sets of data is very satisfactory.

Run No.	Amount of ketene = amount of acid calc. (mmole)	Amount of acid estimated by titration (mmole)	
9, 10, 11	8.81	9:00	
12, 13, 14	6.45	6:65	
15, 16	20.75	21:60	
17, 18	9.03	8:80	
19, 20	7.55	7:53	
24p, $25p$	14.62	14:64	
26p, $27p$, $28p$	12.02	12:30	

TABLE II

These results, however, by no means prove that the stoichiometry of the decomposition of acetic anhydride is represented correctly by eqn. (8). The same agreement would be obtained if this decomposition would proceed according to eqn. (9):

 $(CH_3, CO)_2 \cdot O \rightarrow 2CH_2 : CO + H_2O. \qquad (9)$

The discrimination between both modes of pyrolysis was possible by examining the results of complete decomposition. Eqn. (8) requires that the maximum amount of ketene formed would be equivalent to the amount of moles of acetic anhydride introduced into the reaction vessel. On the other hand, twice as large an amount of ketene would be expected on the basis of eqn. (9). Table III

TABLE III

Run No.	Temp. °C	PAc20 mm.	P _t mm.	Time of contact sec.	Moles of ketene Moles of acetic anhydride
9 8 3 4 2 1 5 6 7	443 570 629 630 631 632 632 632 656 656	0.25 0.25 1.31 0.62 0.28 0.23 0.11 0.25 0.52	13.0 13.0 13.6 13.0 13.1 13.3 12.8 13.2 12.9	1·30 1·00 0·74 0·70 0·70 0·70 0·70 0·71 0·71 0·69	0.97 1.00 1.03 0.97 0.99 0.97 0.98 1.02 1.03

 P_t denotes the total pressure in the reaction vessel.

presents the required results and demonstrates that in the temperature range $440^{\circ.650}$ C the molar ratio of ketene produced to acetic anhydride introduced is always 1.0. This indicates that in this temperature region the reaction

approached 100 % decomposition which is represented by eqn. (8). The validity of eqn. (8) was confirmed further by identification of acetic acid in the products of pyrolysis. This result was achieved in the following way. The tolucne recovered from an experiment carried out at 600° C, i.e. under the conditions where complete decomposition of acetic anhydride is expected, was divided into two equal portions. To the first portion 200 ml. of distilled water was added. The mixture was left for 4 hr. with shaking, then it was titrated against N/10 NaOH, using phenolphthalein as an indicator. The second portion was mixed with 100 ml. of freshly distilled aniline, left the dire for the used there to the the the total with the left of distilled water. standing for $\frac{1}{4}$ hr. and then treated with 200 ml. of distilled water. The mixture was shaken and the water layer was subsequently separated. The organic layer was washed repeatedly with distilled water, then the combined water layers were titrated as previously.

The following results were obtained .

Amount of acetic anhydride introduced

into the reaction vessel

Titration of the first portion Titration of the second portion = 4.3 millimoles. = 2.20 millimoles of NaOH.

=: 2·15 millimoles of NaOH.

To standardize the method we prepared a solution of 6.9 millimoles of acetic anhydride in 100 ml. of toluene, and analyzed it in the described way :

Amount of acetic anhydride = 6.9 millimoles

Titration of the first portion = 6.8 millimoles of NaOH Titration of the second portion = 3.7 millimoles of NaOH.

These results seem to be unequivocal, and we consider that the formation of acetic acid in the pyrolysis of acetic anhydride has been proved beyond doubt. We can, therefore, measure the rate of decomposition of acetic anhydride by the rate of formation of ketene. Table IV gives the experimental data; we

Run No.	Temp. ℃	P _{Ac2} O mm.	P _t mm.	Time of contact sec.	% decomp.	$k \times 10^2$ sec1	
15 16 28¢ 29¢ 11 17 25¢ 23 26¢ 20 10 18 14 13 12 27¢ 24¢	284 291 299 305 322 331 335 340 340 343 344 346 351 353 356 356 356 371	1.43 0.55 0.54 0.54 0.33 1.25 0.45 0.25 0.38 1.68 0.38 0.70 0.02 1.42 0.27 0.42 0.24	13.3 13.0 11.3 11.1 13.5 13.3 11.1 12.3 11.0 6.3 6.3 13.2 12.8 13.3 13.0 10.7 10.8	1.08 1.12 0.43 0.42 1.00 0.38 0.40 0.37 1.05 1.03 1.03 1.03 1.03 0.95 1.02 0.34 0.34	3.5 5.2 3.8 5.2 20.5 30.0 17.4 19.2 19.5 53.1 53.7 65.5 64.0 69.0 46.0 53.0	3·3 4·7 8·9 12·4 21·6 35·5 50·2 53·2 53·2 58·6 70·4 65·7 74·3 103·0 106·0 114·0 186·0 217·0	
10 28p	372 373	0.40	12·9 10·8	0·93 0·34	89•0 55•0	235·0 238·0	
	,		1		•		

TABLE IV

Runs denoted by p were carried out in a packed reaction vessel.

conclude that the decomposition of acetic anhydride is a homogeneous firstorder gas reaction (note runs to and 28p, and runs 23 and 26p for confirmation of the homogeneity of the reaction : runs 13 and 14 demonstrate that the unimolecular rate constant is not changed by a variation of the partial pressure of acetic anhydride over a factor of 70, i.e. from 0.02 mm. Hg to 1.4 mm. Hg, and finally the last two tabulated runs show the independence of the unimolecular rate constant of the time of contact.





FIG. 2.

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Fig. 1 gives the plot of log unimolecular rate constant against 1/T. This leads to an activation energy of 34.5 kcal./mole and to a frequency factor of 1×10^{12} sec.⁻¹. The last result, in conjunction with the observed first-order character of the decomposition, seems to indicate that we deal here with a truly unimolecular decomposition, in which the molecule of acetic anhydride decomposes into two molecules, ketene and acetic acid. The possibility of a radical split is excluded by the absence of dibenzyl. An examination of Fig. 2 which represents the model of the molecule of acetic anhydride shows that such a molecular split does not require any twisting of the initial molecule; the transition state seems to be attained quite easily. The hydrogen atom denoted on Fig. 2 by H touches the oxygen atom denoted by O, and the O—H bond is formed, and the molecule splits in the places denoted by arrows.



FIG. 1.—Results obtained in the packed reaction vessel are represented by black circles.

Since the decomposition of acetic anhydride seems to be a clear-cut example of a truly unimolecular dissociation of a molecule into two smaller molecules, we intend to examine this decomposition under a greater variety of conditions. Thus we hope to throw light on the problems of energy transfer which govern the gradual change of unimolecular kinetics from first- into second-order kinetics.

Chemistry Department, University of Manchester, Manchester 13.