l we have also found it necessary to assume five frequency shifts not otherwise employed. When a potassium chromate filter was used, line 15 was greatly strengthened compared with, for example, lines 12 and 14; this leaves little doubt that line 15 arises from Hg 4358 modified by shift a. There remains, possibly, some ambiguity in the origin of lines e, f, i and l. We have attempted to remove this ambiguity by using the potassium chromate filter; but because of the extreme weakness of these lines we have not been entirely successful.

In the fourth column of table 2 are given calculated infra-red wavelengths corresponding to the frequency shifts. In the fifth and sixth columns are the wave-lengths and intensities of the maxima of infra-red absorption observed by Coblentz.² If a latitude of 0.3μ be allowed, all of the observed Raman shifts can be brought into agreement with infrared absorption maxima in so far as the investigated regions overlap. In view of the considerable number of frequencies involved in both spectra, the necessity of allowing so much latitude leaves some of the coincidences unconvincing. In any case, the intensities in scattering and in absorption bear no evident relation. This question has been discussed elsewhere.³

¹ J. W. Williams and A. Hollaender, Proc. Nat. Acad. Sci., 15, 421 (1929).

² Coblentz, "Investigation of Infra-red Spectra," Carnegie Inst. Publications, 1 (1905).

⁸ Dickinson, Dillon and Rasetti, Phys. Rev., 34 (1929).

THE THERMAL DECOMPOSITION OF ACETONE IN THE GASEOUS STATE

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Communicated August 2, 1929

In the field of reaction kinetics, the study of unimolecular homogeneous gas reactions is, from a theoretical standpoint, most interesting. At the present time but few really homogeneous, unimolecular reactions are known and this work was undertaken with the object of extending the number of organic decompositions of this type. In all the investigations of such decompositions made so far, the method used to follow the reaction has been to measure the rate of increase of pressure and from this to obtain the velocity constant. This method has two obvious disadvantages: (1) we must know what the products of decomposition are, and (2) these must not decompose or react with each other appreciably at the temperature of the experiment. Unfortunately in the case of organic compounds, these conditions seriously limit experimental work so that the decomposition of an organic series cannot be followed using this method. Consequently we have developed a method in which we follow the concentration of the decomposing compound analytically and in this way avoid all the troublesome uncertainties connected with the products of decompositions; provided that these do not react with the decomposing substance, and that we are dealing with a single homogeneous unimolecular change, our measurement of the rate should be free from error. The limitation of this method is that we must devise a quantitative method for estimating the organic compound; fortunately this can be done in a great many classes of compounds so that this method enables us greatly to extend the range of these investigations.

1. Previous Work.—Hinshelwood and Hutchinson¹ have recently measured by a manometric method, the rate of decomposition of acetone vapor in a quartz bulb maintained at temperatures of 500-600 °C. They deduced from their results that the decomposition is unimolecular and in accordance with the following scheme:

$$CH_3COCH_3 \longrightarrow CO + CH_3 + CH_3$$
.

The two methyl groups then react to give methane, ethylene and hydrogen.

It is well known², however, that when acetone is passed through a heated glass tube, methane separates from the molecule and ketene results, according to the following equation,

$$CH_3COCH_3 \longrightarrow CH_2:CO + CH_4$$

and Taylor³ has suggested the possibility that Hinshelwood and Hutchinson really measured the rate of thermal decomposition of ketene. Apart from any uncertainty in the previous work it seemed desirable to develop a method which would be applicable not only to acetone but to its homologs, since a knowledge of their rates of decomposition and energies of activation would be of great interest.

2. Experimental Method.—A flow system was employed in which pure dry nitrogen saturated with the vapor of the acetone or higher ketone was passed at a known rate through a quartz tube heated in an electric furnace. The gases were then passed into a series of small wash bottles containing water in which the acetone could be estimated by hydroxylamine hydrochloride,⁴ or by Messinger's method.⁵ This method had been already worked out in this Laboratory;⁶ in order to prove that the products of the decomposition did not react with the acetone it seemed desirable to show that one molecule of CO was present for every molecule of acetone decomposed. Dr. Slagle⁶ had shown that the quantity of CO produced was much less than that expected. Consequently we tested for the presence of ketene in the gases leaving the tube and found very considerable quantities. We therefore made measurements of the amounts of ketene formed when acetone is heated in a quartz tube.

3. Experimental Results.—A preliminary experiment confirmed the presence of ketene in the gases coming from the quartz tube at 630 °C.; these were passed through a solution of aniline in ether and the excess aniline and ether was evaporated off. The residue was shown to be acetanilide by the melting point and by mixing the residue with acetanilide and taking a second melting point. In this preliminary experiment about 20% of the acetone introduced into the quartz tube was converted into ketene. The amount of ketene was also determined by absorbing it in N/10 sodium hydroxide and measuring the amount of base neutralized. Using this method, a number of runs were made to determine the influence of rate of flow on the yield of ketene and the results are summarized in table 1. An additional series of experiments was then performed to find

		TABLE	1					
TEMPERATURE OF FURNACE = 635 °C.								
Min. in furnace	1.56	1.56	2.36	2.36	4.00	4.00	4.00	
Mols ketene formed per								
mol. acetone introduced	0.256	0.260	0.255	0.254	0.249	0.254	0.249	

what proportion of the decomposed acetone could be recovered as ketene and the results are given in table 2. The average half-life for acetone at

TABLE 2 TEMPERATURE OF FURNACE = 588 °C.

0.4213	0.3357	0.4008
0.3624	0.2711	0.3499
0.0589	0.0646	0.0509
0.582	0.552	0.622
2.45	2.47	2.42
	0.4213 0.3624 0.0589 0.582 2.45	0.4213 0.3357 0.3624 0.2711 0.0589 0.0646 0.582 0.552 2.45 2.47

this temperature is 2.5 min. as compared with 3.1 min. obtained by Hinshelwood and Hutchinson.¹

4. Discussion.—The results obtained so far show that for every 100 molecules of acetone decomposed approximately 60 molecules of ketene can be recovered, which is about the same as the yields reported by Hurd and Tallyn⁷ who heated the acetone in a pyrex tube. It seems likely, therefore, that the primary process in the homogeneous unimolecular decomposition of acetone is the separation of a molecule of methane and formation of ketene. Presumably at the high temperature in the furnace the ketene undergoes a bimolecular decomposition as follows:

$$2CH_2:CO = C_2H_4 + 2CO.$$

According to this scheme 100 molecules of decomposed acetone should give 100 molecules of methane, 30 molecules of ethylene and 60 molecules

of carbon monoxide, which corresponds very closely with the results of the gas analysis made by Hinshelwood and Hutchinson.¹

5. Conclusion.—The decomposition of acetone has been followed by an analytical method and it has been found that about 60% of the acetone decomposed can be recovered as ketene. Methods in which rate of change of pressure are used for following the course of the reaction are therefore unreliable.

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¹ Hinshelwood and Hutchinson, Proc. Roy. Soc., 111A, 245 (1926).

² See Hurd, The Pyrolysis of Carbon Compounds, p. 247. Chemical Catalog Co., 1929.

³ Taylor, J. Phys. Chem., 30, 1433 (1926); book review.

⁴ Meyer, Lehrbuch der Organisch-Chemischen Methodik, p. 846. Springer, 1922.

⁵ Goodwin, J. Am. Chem. Soc., 42, 39 (1920).

⁶ Slagle, Dissertation, "Decomposition of Aliphatic Ketones in the Gas Phase," Johns Hopkins University, 1929.

⁷ Hurd and Tallyn, J. Am. Chem. Soc., 47, 1427 (1925).

THE EQUILIBRIUM CONSTANTS OF REACTIONS INVOLVING HYDROXYL

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Communicated July 26, 1929

A recent interpolation of band spectra data has indicated that the heat of dissociation of OH should be 138 k. cal.¹ An accurate value for the heat required in this dissociation would enable one to calculate the equilibrium constants of reactions involving this molecule.² Thus Bonhoeffer³ and Reichardt have calculated the equilibrium constant of the following reaction, using their value for the heat of dissociation of water into H and OH:

$$2H_2O = H_2 + 2OH$$
 $K_{OH} = \frac{[H_2] \ [OH]^2}{[H_2O]^2}$

As my value for the heat of dissociation of OH is some 14 k. cal. larger than that corresponding to Bonhoeffer and Reichardt's data, I have recalculated their constants and contributed some additional ones.

In order to calculate the free energies of these reactions, use was made of the familiar equations:

$$F = H - TS$$
$$\Delta F = \Delta H - T\Delta S = -RT \ln K$$