CXIII.—*The Decomposition of Oxalacetic Acid Phenylhydrazone in Aqueous and Acid Solutions, and a New Method of Determining the Concentration of Hydrogen Ions.**

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THE main problem, towards the solution of which the following investigation is a contribution, was suggested by a series of observations made by Mr. Fenton and one of us (Fenton and Jones, Trans., 1901,

* A preliminary account of some of the experiments to be described has already been published in the *Proceedings of the Cambridge Philosophical Society*, 1902, 11, 337.

79, 91; *Proc.*, 1901, 17, 24; *Proc. Camb. Phil. Soc.*, 1901, 11, 108), which showed that oxalacetic acid phenylhydrazone decomposed in presence of water at 100° into carbon dioxide and pyruvic acid phenylhydrazone. In the presence of strong acids, however, the reaction proceeded differently and pyrazolonecarboxylic acid and water were formed. With weak acids or very dilute strong acids the two reactions occurred simultaneously, and it was shown that the amounts of carbon dioxide given off, using acids of the same normality, were in the inverse order of their "affinity constants."

It was suggested that these reactions might be explained by supposing that the formation of pyruvic acid phenylhydrazone was due to the decomposition of the negative ion according to the following equation :

whereas the production of pyrazolonecarboxylic acid was due to a unimolecular decomposition of the undissociated hydrazone according to the equation :

We set out on the investigation with the idea that this hypothesis was correct, but have found it necessary to abandon it owing to the disagreement of theoretical conclusions with the experimental results. The hypothesis by which we propose to replace the above is that the rate of formation of pyruvic acid phenylhydrazone is a unimolecular decomposition of oxalacetic acid phenylhydrazone, quite independent of the ionisation of the latter as an acid. The rate of formation of pyruvic acid phenylhydrazone is therefore proportional to the concentration of the oxalacetic acid phenylhydrazone present in the solution at a given time. On the other hand, the production of pyrazolonecarboxylic acid is due to a bimolecular reaction, the rate of formation being jointly proportional to the concentration of the hydrogen ions and to that of the oxalacetic acid phenylhydrazone present in the solution. On this theory, the hydrogen ions act as it were catalytically, being themselves unaffected by the reaction; hence we should expect the rate of formation of the pyrazolone compound to be greater in an acid solution.

Intrinsically different as these two hypotheses certainly are, by a curious coincidence they are mathematically almost identical, and up to a certain point yield the same quantitative relations. For brevity, we shall trace the development of the second view (the catalytic

hypothesis) only, pointing out, where necessary, in what respects the formulæ given by the first hypothesis differ from it. It may be mentioned in anticipation that all the mathematical results are confirmed quantitatively by the experiments to be described later. The mathematical solution has been worked out, not as a purely theoretical problem, but in order to settle definitely the nature of the reaction.

In what follows we shall express the quantities of the substances present in terms of the molecular concentration, that is, the number of gram-molecules per litre. Let C_1 be the concentration of the oxalacetic acid phenylhydrazone we start with, and C_2 and C_3 the concentrations of pyruvic acid phenylhydrazone and pyrazolonecarboxylic acid respectively in the solution at any time. Then the amount of unaltered oxalacetic acid phenylhydrazone which is present at the same time is equal to $C_1 - (C_2 + C_3)$. It is convenient to remember that the amount of carbon dioxide which *has been* evolved is proportional to the concentration C_2 of pyruvic acid phenylhydrazone in the solution. Since the rate of formation of pyruvic acid phenylhydrazone (or of evolution of carbon dioxide) is simply proportional to the concentration of the oxalacetic acid phenylhydrazone, we have

$$\frac{dC_2}{dt} = k_1(C_1 - C_2 - C_3),$$

where k_1 is the velocity constant of this reaction and t is the time. The reaction which produces pyrazolonecarboxylic acid being supposed bimolecular and jointly proportional to the concentration of the oxalacetic acid phenylhydrazone and of the hydrogen ions, we have similarly

$$\frac{dC_3}{dt} = k_2X(C_1 - C_2 - C_3),$$

where k is the velocity constant of this reaction and X is the concentration of hydrogen ions. The first hypothesis gives equations identical in form with these, differing only in the fact that the constants k_1 and k_2 are both divided by $\gamma + X$, where γ is the dissociation constant of oxalacetic acid phenylhydrazone.

Cross multiplying the above equations, we get,

$$\frac{C_3}{dt} = \frac{K_2X}{k_1} \frac{dC_2}{dt},$$

the integral of which is $C_3 = \frac{k_2X}{k_1}C_2 + A$. Since at the commencement of the reaction no pyruvic acid phenylhydrazone or pyrazolonecarboxylic acid has been formed, we have for $t=0$, $C_3 = C_2 = 0$, whence $A = 0$ and $C_3 = \frac{k_2X}{k_1}C_2$.

Substituting for C_3 , we get,

$$\frac{dC_2}{dt} = k_1 C_1 - (k_1 + k_2 X) C_2.$$

Obviously at the end of the reaction ($t = \infty$ theoretically) the rate of formation of pyruvic acid phenylhydrazone and pyrazolonecarboxylic acid is equal to zero, so that

$$\left[\frac{dC_2}{dt} \right] = 0 = k_1 C_1 - (k_1 + k_2 X) C_2^\infty$$

where C_2^∞ is the concentration of pyruvic acid phenylhydrazone in the solution when the reaction is completed. This yields

$$\frac{C_1}{C_2^\infty} - 1 = \frac{k_2}{k_1} X.$$

This formula has been found to hold both for oxalacetic acid phenylhydrazone and for oxalacetic acid *p*-bromophenylhydrazone, which decomposes similarly.

Returning to the equation,

$$\frac{dC_2}{dt} = k_1 C_1 - (k_1 + k_2 X) C_2,$$

we see that it may be written in the form

$$-\frac{1}{(k_1 + k_2 X)} \frac{d}{dt} (k_1 C_1 - [k_1 + k_2 X] C_2) = k_1 C_1 - [k_1 + k_2 X] C_2,$$

whence $\log(k_1 C_1 - [k_1 + k_2 X] C_2) = -(k_1 + k_2 X)t + B$.

When $t = 0$ $C_2 = 0$, whence $B = \log k_1 C_1$.

Therefore

$$C_2 = \frac{k_1 C_1}{k_1 + k_2 X} (1 - e^{-(k_1 + k_2 X)t}) \\ = a(1 - e^{-bt}) \text{ say.}$$

If we plot a curve with t as abscissæ and corresponding values of C_2 as ordinates, whatever may be the value of the constants a and b , it has the general form of the curve shown in the figure. For convenience of calculation, the curve selected is $y = 10\{1 - e^{-0.000230x}\}$. It is evident that it must pass through the origin for $C_2 = 0$ when $t = 0$, and also that it is asymptotic to the line $C_2 = \frac{k_1 C_1}{k_1 + k_2 X}$, which is parallel to the axis of x and represents the amount of pyruvic acid phenylhydrazone finally formed.

A large number of experiments have been made, as will be described later, in order to determine the rate at which carbon dioxide is evolved

from a solution of oxalacetic acid phenylhydrazone maintained at a constant temperature, and in all cases curves were obtained of the general form indicated by the theory. Perhaps a better way of exhibiting the connection between C_2 and the time is to write the last equation in the form

$$\log \frac{1}{1 - \frac{k_1 + k_2 X}{k_1} \frac{C_2}{C_1}} = (k_1 + k_2 X)t,$$

FIG. 1.—Theoretical curve, $y = \frac{1}{0.1} \{1 - e^{-0.000230x}\}$.

and since the total amount C_2 of pyruvic acid phenylhydrazone produced is $\frac{k_1}{k_1 + k_2 X} C_1$, we may write our equation still more concisely as

$$\log \frac{1}{1 - \frac{C_2}{C_2^\infty}} = (k_1 + k_2 X)t.$$

Hence, if we determine the final quantity of carbon dioxide produced

in any experiment, take the ratio to this of the amount which has been produced up to any given moment, subtract from unity, and plot the logarithm of the inverse of the quantity thus obtained against t , we get a straight line which passes through the origin, and the inclination of which to the axis of t is $\tan^{-1}(k_1 + k_2X)$. The experimental curves have been treated in this manner and yield satisfactory straight lines (compare Figs. 3, 4, and 5).

Curiously enough, the hypothesis of decomposition of the negative ion yields formulæ which differ from the preceding only in the value of the constants a and b . On that view, we have a equal to $\frac{k_1\gamma}{\gamma + X}C_1$ instead of to $\frac{k_1C_1}{k_1 + k_2X}$, and b to $\frac{k_1\gamma + k_2X}{\gamma + X}$ instead of to $k_1 + k_2X$, where γ is the dissociation constant of oxalacetic acid phenylhydrazone. In so far as the constant a is concerned, it will be seen that the quantity X enters in the same way into the two formulæ, so that, as is the case with all the preceding results, there is no difference between the consequences of the two hypotheses. But when we turn to the constant b , an important difference arises, in that on the one theory b has the form $a + X$, and in the other $\frac{\beta + X}{\delta + X}$. Now the value of b is readily determined (with sufficient accuracy) from the experimental curves, and is found to increase with X , the concentration of the hydrogen ions in the solution. The increase of b with X is seen to follow at once if b is of the form $a + X$ given by the catalytic theory; but if b is of the form $\frac{\beta + X}{\delta + X}$, then its increase or decrease with X depends on the relative magnitudes of β and δ . If β is $>\delta$, b will decrease as X increases; if β is $<\delta$, b will increase with X .

If, adopting for a moment Fenton and Jones's hypothesis, we write $\frac{k_1\gamma + k_2X}{\gamma + X}$ in the form $k_2\left(\frac{k_1\gamma}{k_2} + X\right)$, we find from our experiments that, on this view, $k_1\gamma/k_2 = 0.02$. We have, moreover, determined the dissociation constant, γ , of oxalacetic acid phenylhydrazone, which we find has the value 0.0011. We have therefore $b = k_2 \left\{ \frac{0.02 + X}{0.0011 + X} \right\}$. Hence, it is evident that, for the case under consideration, β is $>\delta$, so that, on this view, b will always decrease as X increases. Since, for all the experiments we made, the value of b increased as the solutions became more acid, and the constancy of the results showed they were not due to experimental error, we are compelled to reject Fenton and Jones's hypothesis in favour of the theory of catalysis by hydrogen ions developed in the present paper.

This view is further supported by the fact that on heating solid oxalacetic acid phenylhydrazone in the absence of water it yields, not pyrazolonecarboxylic acid, but pyruvic acid phenylhydrazone. Another view which has been suggested to explain these curious reactions is that the formation of pyrazolonecarboxylic acid is due to the dehydrating action of the acid used. This is, however, contradicted by Fenton and Jones's experiments on the effect of the addition of various salts to the acid solutions (Proc., 1901, 17, 24).

Another point in favour of the hypothesis here advocated is the fact that a given amount of the substance yields less carbon dioxide at 100° when dissolved in 100 c.c. of water than when dissolved in 10 c.c. This we should expect owing to the greater dissociation of the acid, whereas on the older view greater dissociation of the acid would give more carbon dioxide. Experiments which have been made in other solvents such as pyridine or toluene, show that, although the reaction is slower, the final quantity of carbon dioxide produced is slightly greater than with water. On the earlier hypothesis we should, however, expect much less carbon dioxide owing to the small ionising power of such solvents compared with that of water. So far as we are aware, there is no single fact which is contrary to the hypothesis of the formation of pyrazolonecarboxylic acid by the catalytic action of the hydrogen ions; whereas there are a large number with which the view of the formation of pyruvic acid phenylhydrazone by the decomposition of the negative ion is not in agreement.

The reaction under consideration is an example of what may be called a *simultaneous linear reaction*. Such a reaction involves the simultaneous production from one substance of at least two others, whilst the rate of formation of each of these is directly proportional to the amount of the original substance present. The theory of every irreversible simultaneous linear reaction involving the formation of only two substances is identical with that given above, except for the values of the constants a and b . An example of a simultaneous reaction which is partly reversible is the decomposition of ethyl hydrogen sulphate into ethylene and ether in presence of alcohol. We have not been able to recall another case like the decomposition of oxalacetic acid phenylhydrazone when both the reactions are quite irreversible.

EXPERIMENTAL.

The experimental portion of the investigation falls naturally into two parts. We shall first consider the experiments on the rate of evolution of carbon dioxide, since they form, from a theoretical point of view, the key to the rest.

The Rate of Evolution of Carbon Dioxide.

The velocity of the reaction was examined by measuring the rate at which carbon dioxide was evolved from a dilute solution of the hydrazone maintained at a constant temperature. As solvent, either water or dilute sulphuric acid was employed. The apparatus used is depicted in the accompanying diagram (Fig. 2). One hundred c.c. of the solvent were placed in the wide-necked flask, *A*, and the hydrazone, dissolved in the minimum quantity of alcohol, was introduced through the tube *B*. The mixture was stirred by means of the stirrer, *C*, which was capable of vertical and rotatory motion, owing to the interposition of the thin rubber tube, *D*. The T-piece *E* led off into the manometer

FIG. 2.

FGH, filled except in the first few experiments with turpentine, which, after several liquids had been tried, was found to be the most suitable. The large bulb, *F*, was inserted in order to furnish an approximately constant zero pressure level. The whole of the system from *A* to *G* was immersed in a small tin plate tank the sides of which were covered with asbestos. The tank was filled with water which was stirred by a pair of horizontal fans rotating about the same axis, this passed through the centre of the tank, and was driven by a small motor. The burners used to heat the tank were regulated by a thermostat, so that the water could be kept at any desired temperature. In order to regulate the temperature more efficiently, the body of the thermostat was made of a roll of composition tubing which fitted close to the inside of the tank. The temperature could be kept constant to one-twentieth of a degree.

In making an experiment, the apparatus was first tested to see if the temperature was steady. This was done by inserting the cork in *B* and observing the liquid in the manometer. If the temperature was adjusted, there was only a slight rise of the liquid, which stopped after a few seconds. On introducing alcohol without any hydrazone into *B*, it was found that there was a sudden rise in the manometer, which, if the liquid was well stirred, became steady after about 20 seconds. In making a real experiment with the hydrazone dissolved in about 1 c.c. of alcohol, it was therefore found necessary to neglect the initial motion of the manometer. This involved no uncertainty as there was

FIG. 3.—Curves for water.

always a definite interval before carbon dioxide began to be evolved. As soon as the evolution commenced, readings of the height of the manometer and the time were taken every few seconds. These became somewhat irregular towards the end of the experiment, when the rate of evolution of gas was very small, owing to minute oscillations in the temperature of the bath. A correction was afterwards applied to the readings for the volume of liquid in the tube.

With this apparatus, a great number of observations were made, using varying amounts of the hydrazone, with water, *N*/10 sulphuric acid, and *N*/20 sulphuric acid respectively as solvents. In all cases,

100 c.c. of the solvent were placed in the flask and the hydrazone, dissolved in the minimum quantity of alcohol, added as soon as the temperature became steady. With water, very good readings were obtained when 0.1 gram of the hydrazone was used, but owing to the smaller quantity of carbon dioxide evolved in acid solutions some

FIG. 4.—Curves for $N/20$ H_2SO_4 .

irregularity in the readings was more noticeable when dilute sulphuric acid was used. With these solvents, therefore, larger quantities (up to 0.45 gram) were taken, and the irregularities then became inappreciable. The amount of carbon dioxide given off in each case was found to be, at any rate approximately, proportional to the amount of substance used.

The curves (Figs. 3, 4, and 5) have been plotted from three of these series of observations and show the rate of evolution of carbon dioxide from solutions in water, $N/20$ sulphuric acid, and $N/10$ sulphuric acid respectively. The ordinates are readings of the manometer, reduced to an artificial zero, and are proportional to the volume of carbon dioxide which has been given off. The abscissæ are seconds multiplied by 100. The curve for water is for 0.1 gram, that for $N/20$ sulphuric acid is for 0.2 gram, whilst that for $N/10$ sulphuric acid is for 0.3 gram

FIG. 5.—Curves for $N/10$ H_2SO_4 .

of the hydrazone. It will be noticed that all these curves have the same form as the theoretical curve on p. 1144.

With each curve is plotted the corresponding series of values of $\log \frac{1}{1 - \frac{C_2}{C_2}}$ with the time. In each case, these were found to be straight

lines as required by the theory. The values of the ordinates for this function are given on the right hand side, those for the amount of

carbon dioxide evolved on the left hand side, of each diagram. Since $\log 1/\left[1 - \frac{C_2}{C_2^\infty}\right]$ is proportional to t , it is evident that $-\frac{1}{t}\log\left(1 - \frac{C_2}{C_2^\infty}\right)$ should be constant for all values of t . The degree in which this was attained will be seen from the last column of the following table (the figures are for 0.1 gram of oxalacetic acid phenylhydrazone dissolved in 100 c.c. of water). The value of C_2^∞ was taken (from the curve) to be 320.

C_2 .	C_2/C_2^∞ .	$-\log(1 - C_2/C_2^\infty)$.	t .	$-\frac{1}{t}\log\left(1 - \frac{C_2}{C_2^\infty}\right)$.
0	0	0	0	
50	0.1563	0.074	70	1.06×10^{-3}
80	0.25	0.125	130	0.96×10^{-3}
100	0.313	0.163	172	0.95×10^{-3}
125	0.390	0.215	236	0.91×10^{-3}
150	0.469	0.275	312	0.88×10^{-3}
175	0.547	0.344	392	0.88×10^{-3}
200	0.626	0.427	480	0.89×10^{-3}
225	0.703	0.527	585	0.90×10^{-3}
250	0.781	0.660	720	0.92×10^{-3}
275	0.850	0.854	940	0.91×10^{-3}

The values for both small and large values of t are affected much more than proportionately by experimental error, so that the true value of the constant b from the above table would be 0.88—0.90.

It will be noticed that the slope of these lines increases as the solution becomes more acid, and this was found to be so in every case examined. This is a point of considerable importance, since the hypothesis of the decomposition of the negative ion requires that the slope of the lines should decrease with the concentration of the acid in the solution used. The following numbers indicate the differences and agreement in the numbers which have been observed:

Strength of sulphuric acid.	Values of $-\frac{1}{t}\log\left(1 - \frac{C_2}{C_2^\infty}\right)$.	Mean values of $-\frac{1}{t}\log\left(1 - \frac{C_2}{C_2^\infty}\right)$.
$N/10$	$\left\{ \begin{array}{l} 10^{-3} \times 1.17 \\ 10^{-3} \times 1.33 \end{array} \right\}$	1.25×10^{-3}
$N/20$	$\left\{ \begin{array}{l} 10^{-3} \times 1.04 \\ 10^{-3} \times 0.92 \end{array} \right\}$	0.98×10^{-3}
0	$\left\{ \begin{array}{l} 10^{-3} \times 0.886 \\ 10^{-3} \times 0.82 \\ 10^{-3} \times 0.80 \end{array} \right\}$	0.83×10^{-3}

As there is some uncertainty about the position in which the lines should be drawn to fit the observations best, the above agreement is quite satisfactory. We shall postpone the further discussion of these results until after the experiments on the total amount of carbon dioxide evolved have been considered.

The Total Amount of Carbon Dioxide Evolved.

To determine the total amount of carbon dioxide evolved, several methods were tried, of which the following was selected as giving the most concordant results. The apparatus used is represented in Fig. 6. The substance (0.1 gram) together with 100 c.c. of the solvent (water or dilute sulphuric acid) was placed in the flask, *A*, which was heated to 100° in a water-bath. A gentle stream of air, which had been freed from carbon dioxide by bubbling through potash solution, was passed through the liquid in *A* at such a rate that the bubbles moved slowly up the tube, *D*. The tube *C*, which was ground so as to fit

FIG. 6.

closely into *D*, had a narrow orifice so that the bubbles which escaped from it were very small. By suitably inclining the tube *D*, which contained standard baryta solution, the time the bubbles took to pass up the tube could be altered by any desired amount. In this way, the length of time during which the mixture of carbon dioxide and air was in contact with the absorbing solution could be regulated at will. It was found that, when the time exceeded a certain limit, constant results were obtained, showing that all the carbon dioxide had been absorbed.

The bulb, *B*, was inserted to prevent any of the acid solution in *A* splashing over into the absorption tube, *D*. A blank experiment showed that the amount of acid which splashed over, if any, could not be detected.

When no further precipitation of barium carbonate in *D* could be observed (generally after running for about 20–30 minutes), the current of air was stopped and the liquid carefully washed out of *C* and *D* with recently boiled distilled water. This liquid was then

titrated with standard hydrochloric acid, using phenolphthalein as indicator. The amount of carbon dioxide was thus given by the change in the neutralising power of the solution. The hydrochloric acid used was $N/20$, and the 25 c.c. of baryta, which were always used, required 33.1 c.c. of this acid for neutralisation. The amount of hydrochloric acid, which corresponded to the carbon dioxide given off, varied between 4.2 c.c. and 15 c.c. We could thus only expect to determine the latter with an accuracy of 2 per cent.

With this apparatus, several series of experiments were made with oxalacetic acid phenylhydrazone, using solutions of sulphuric acid, the strengths of which varied from 0 to $N/10$. The results which were obtained are shown in the following table. Each of the numbers given in column II is the mean of a number (from three to ten) of experiments. Since the concentration C_2^∞ of the pyruvic acid phenylhydrazone at the end of the reaction is proportional to the amount of carbon dioxide which has been evolved, and the amount of carbon dioxide evolved, if the whole were to become pyruvic acid phenylhydrazone, would be 10 c.c., the values in column III are simply

$$\frac{10}{\text{Value in column II}} - 1.$$

I.	II.	III.	IV.	V.
Strength of sulphuric acid.	Volume of CO_2 from 0.1 gram.	$\frac{C_1}{C_2^\infty} - 1$.	X .	$\frac{k_2}{k_1}$.
$N/10$	2.42 c.c.	3.13	0.06	52
$N/15$	3.17 "	2.15	0.043	50
$N/20$	3.79 "	1.63	0.0335	48.6
$N/30$	4.7 "	1.13	0.023	49
$N/60$	5.95 "	0.68	0.013	52
$N/120$	6.85 "	0.46	0.007	65
N/∞ (water)	8.5 "	0.18	0.0	∞

The corresponding concentration of the hydrogen ions is given in column IV. According to the theory (compare p. 1143), the value of $\frac{1}{X} \left[\frac{C_1}{C_2^\infty} - 1 \right]$ should be a constant $\frac{k_2}{k_1}$. The values obtained by dividing the numbers in column III by those in column IV are given in column V. The values in column IV were calculated from Kohlrausch's measurements (*Ann. Phys. Chem.*, 1885, [iii], 26, 161) at 18° , whereas the values of $\frac{C_1}{C_2^\infty} - 1$ are proportional to the concentration at 100° .

This may explain the slight variation in the values of the constant k_2/k_1 near the top of column V, the gradual increase towards the bottom

FIG. 7.—Oxalacetic acid hydrazone.

being due to the increasing effect of the acidity of the hydrazone itself in the more dilute solutions.

These relations are more strikingly shown by the accompanying diagram (Fig. 7, p. 1154).

Experiments with Oxalacetic Acid p-Bromophenylhydrazone.

With this apparatus, we have also made experiments on the *p*-bromo-derivative. Owing to difficulty in obtaining the substance, only a few observations have been made. They show, however, that the decomposition of this substance follows the same laws, as is evident from the accompanying table and diagram :

Variation of Quantity of Carbon Dioxide evolved from Oxalacetic Acid p-Bromophenylhydrazone with Acidity of Solution.

Strength of sulphuric acid.	Volume of CO ₂ from 0.1 gram.	$\frac{C}{C_2} - 1.$	$x.$	$k_2/k_1.$
<i>N</i> /10	2.33 c.c.	3.3	0.06	47
<i>N</i> /20	3.62 „	1.76	0.0335	38
<i>N</i> /30	4.02 „	1.49	0.023	43
<i>N</i> / ∞ (water)	6.2 „	0.615	0.0	—

The *p*-bromo-derivative, as shown by the greater distance from the origin at which the straight line in Fig. 8 (p. 1156) cuts the axis of *y*, seems to be a considerably stronger acid than oxalacetic acid phenylhydrazone. In calculating the values of k_2/k_1 given above, we have therefore subtracted 0.5, the effect due to the substance itself, from the values of $C_1/C_2^2 - 1$ given in the table. We see then that the introduction of a bromine atom into the phenyl group has very little effect on the ratio k_2/k_1 of the two reactions, only making it a few per cent. smaller.

Measurement of the Concentration of Hydrogen Ions in Solution.

It will readily be seen that the decomposition of oxalacetic acid phenylhydrazone forms an easy method of measuring the concentration of hydrogen ions in solution, and therefore of determining the dissociation constants of acids. The apparatus is simple (Fig 6), and the experiments only require a short time. In making a determination, 0.1 gram of oxalacetic acid phenylhydrazone is heated with 100 c.c. of the solution to 100°, and the amount of carbon dioxide evolved is estimated. Let this be *b* c.c. at 0° and 760 mm. Then the concentration of the hydrogen ions in the solution is given by

$$X = \frac{k_1}{k_2} \left(\frac{C_1}{b} - 1 \right) = \frac{1}{50} (10/b - 1).$$

To test the method, experiments were made with an $N/20$ hydrochloric acid solution. Four experiments gave 2.95, 2.75, 2.95, and 2.95 c.c. of carbon dioxide respectively. Taking the mean, we get for the concentration of the hydrogen ions $X=0.049$. The value obtained from Krannhals's measurements of the conductivity at 100° is $X=0.0475$. The two methods therefore give concordant results.

The sensitiveness of this reaction is much greater for small concentrations of hydrogen ions than for large ones. If the effect of the

FIG. 8.—Oxalacetic acid p-bromophenylhydrazone.

acidity of the substance itself were carefully worked out so that it could be corrected for accurately, this might be made a very valuable practical method of determining the concentration of hydrogen ions in moderately dilute solutions.

The Velocities of the Reactions.

We are now in a position to deduce the absolute values k_1 and k_2 of the velocity constants of the reactions which take place. From the

total amount of carbon dioxide given off in acid solutions of various strengths we found $k_1/k_2 = 0.02$. We have also seen (p. 1144) that the constant b , obtained from the rate at which carbon dioxide is evolved, is $k_1 + k_2X$. We may therefore put

$$b = k_2\{k_1/k_2 + X\} = k_2(0.02 + X).$$

For $N/20$ H_2SO_4 we had $X = 0.0335$ and $b = 98 \times 10^{-3}$.

whence

$$k_2 = 1.83 \times 10^{-2} \text{ sec}^{-1},$$

and

$$k_1 = 3.66 \times 10^{-4} \text{ sec}^{-1},$$

that is, the rate of formation of pyruvic acid phenylhydrazone from oxalacetic acid phenylhydrazone at 80° is 0.000366 per second, whilst that of pyrazolonecarboxylic acid is 0.0183 per second. Using these numbers, we can calculate the value of the constant b for the other dilutions at which experiments were made. The results of this calculation are given in the following table :

Strength of sulphuric acid.	Value of b found from curves (Table, page 1151).	Value of b calculated.
$N/10$	1.25×10^{-3}	1.46×10^{-3}
$N/20$	0.98×10^{-3}	0.98×10^{-3}
0 (water)	0.83×10^{-3}	0.58×10^{-3}

In the case of water, 0.002 has been allowed for the concentration of the hydrogen ions due to the hydrazone itself. It will be noticed that the differences from the middle value (that for $N/20$ sulphuric acid) are greater for the values of b which are calculated than for those found from the experiments. The differences are, however, not much greater than the uncertainty of the experimental results. The important thing is that the value of b actually increases with the acidity of the solution; according to the hypothesis of the decomposition of the negative ion, b should decrease as the solution became more strongly acid.

Conclusion.

The fact that to a great extent the phenomena described in the present paper can be quantitatively deduced from two so widely different hypotheses as those which have been examined seems very striking. This is due to the identity of the theory of all linear simultaneous irreversible reactions, and to the fact that both hypotheses describe the decomposition of oxalacetic acid phenylhydrazone as such a reaction.

Since the rate of formation of pyrazolonecarboxylic acid is jointly

proportional to the concentrations of oxalacetic acid phenylhydrazone and of hydrogen ions, it is evident that a molecule of pyrazolonecarboxylic acid is formed every time a hydrogen ion possesses a certain orientation with regard to a molecule of oxalacetic acid phenylhydrazone. The explanation of this effect of the hydrogen ion is probably to be sought in the basic character of the pyrazolone ring.

It is hoped that interesting results will be obtained when the variation with the temperature of the velocity constants, k_1 and k_2 , of the two reactions under consideration has been investigated.

Finally, we wish to thank Mr. Fenton for his kindness in handing over this problem to us, and Professors Liveing and Dewar for placing the resources of their laboratories at our disposal.

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