XXXII.—*Studies in Catalysis. Part VI. The Mutual Influence of two Reactions Proceeding in the Same Medium.*

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THE two reactions considered are the inversion of sucrose and the hydrolysis of methyl acetate. The inversion of sucrose was carried out in presence of varying amounts of methyl acetate, hydrochloric acid being employed as the catalyst. Similarly, the rate of hydrolysis of methyl acetate was measured in the presence of varying amounts of sucrose, trichloroacetic acid being the catalyst. The object of the investigation was to find whether any mutual or reciprocal effects manifested themselves.

The same reactions, proceeding simultaneously, have been examined by V. Henri and J. Larguier des Bancels (*Compt. rend.*, 1901, **53**, 784), who were unable to detect any modification in the rate of either reaction. Crocker (T., 1915, **107**, 1762, and private communication) also observed no reciprocal action when formamide is hydrolysed by hydrochloric acid in presence of sucrose, the sucrose being employed as a convenient means of determining indirectly the rate of hydrolysis. On the other hand, Coppadoro (*Gazzetta*, 1901, **31**, i, 425) found that the presence of methyl acetate depressed the rate of inversion of sucrose, whilst addition of sucrose apparently had no effect on the rate of hydrolysis of the ester. The addition of the reciprocal substance in each case involved the removal of a corresponding quantity of water. In view of the known negative catalytic effect of water (compare Griffith and Lewis, T., 1916, **109**, 67), any decrease in its concentration would be expected to raise the speed of the reaction. It is evident therefore that Coppadoro's results leave the question of the possible mutual effect still open. The present investigation was undertaken partly on this account.

EXPERIMENTAL.

The Effect of Sucrose on the Hydrolysis of Methyl Acetate.

Trichloroacetic acid was employed as the catalyst, its concentration in the reaction mixture being decinormal, and the temperature of measurement 35° . Two c.c. of pure methyl acetate were dissolved in conductivity water, the catalyst added, and the solution made up to 100 c.c. The ordinary unimolecular velocity constant was determined in the usual way, the mean value being 1.572×10^{-3} . A similar solution (100 c.c. in volume) was prepared, and 8 grams of pure sucrose added, the final volume being 105 c.c. Each solution contains the same mass of water, but the volume concentration of each constituent is less in the second case. In the presence of sucrose the mean velocity constant is 1.602×10^{-3} , a value slightly greater than that obtained in the previous case. The velocity constants, however, are not directly comparable. In the first place, the catalysing acid has been diluted in the ratio of 105:100. Further, although the mass of the water is the same, its volume concentration is less in the second case, so that its stoichiometric effect is diminished. The simplest mode of correction is to consider that the concentration of the water in the second case is less than that in the first in the ratio of 100:105. The velocity constant in presence of sucrose, when corrected for the dilution of the catalyst and the dilution of the water, becomes 1.766×10^{-3} . A still more important correction has to be made, namely, that for the anticatalytic effect of the water, which likewise depends on its concentration. This acts in the opposite sense to the two previous corrections. Employing the data of Griffith and Lewis (*loc. cit.*), which were obtained at 25° , it was calculated that the decrease in the concentration of water should raise the velocity constant by 13 per cent., so that the velocity constant in presence of the sucrose should be diminished by that amount, to make it comparable with the first experiment. The final corrected value is 1.53×10^{-3} . This is somewhat less than that obtained in the absence of sucrose. In other words, sucrose is apparently a feeble negative catalyst for the reaction.

These various corrections, however, render the final conclusion somewhat doubtful. The following experiment was therefore carried out. Two c.c. of methyl acetate were dissolved in water, the catalyst added in exactly the same amount as in the case in which sucrose was present, the solution made up to 100 c.c. with water, and further ester added until the final volume reached 105 c.c. Under these conditions not only the mass, but likewise the volume concentration of the water, is the same as that in the experi-

ment quoted, in which sucrose was present. The concentration of the catalysing acid is also the same in the two cases. The resulting velocity constant is 1.77×10^{-3} . This is directly comparable with the velocity constant 1.60×10^{-3} , obtained in presence of the sucrose. The conclusion to be drawn is that sucrose acts as a negative catalyst with respect to the hydrolysis of the ester, the velocity constant of hydrolysis being depressed by 10 per cent., when the concentration of sucrose is 7.6 grams in 100 c.c.

Several experiments were also carried out at 35° to show that on displacement of the water by the sucrose, or even by the ester itself, the velocity constant thereby increased. The results are given in the following table, k being the ordinary unimolecular constant, calculated to the base e .

Hydrolysis of Methyl Acetate at 35° by N/10-Hydrochloric Acid.

Total volume of solution = 50 c.c.

Expt. No.	Ester in c.c.	Water in grams.	Sucrose in grams.	k .
1	1	48.93	0	0.001680
2	2	47.97	0	0.001712
3	1	45.90	5	0.001869
4	1	42.82	10	0.002119
5	2	44.90	5	0.001926

With addition of sucrose, and consequent displacement of water, the velocity constant steadily increases. That is, the negative catalytic effect of the sucrose is negligible compared with the negative effect of the water. Had both effects been of the same order of magnitude, addition of sucrose in the above manner would have been expected to give rise to a minimum value of the velocity constant at a certain concentration of sucrose and water. This effect has been discovered in the converse case, namely, the inversion of sucrose in presence of methyl acetate, as described in the next section.

The Effect of Methyl Acetate on the Rate of Inversion of Sucrose.

The velocity constant of inversion at 35° was determined by the polarimeter method, using in the first series of experiments $N/10$ -hydrochloric acid, and in the second, $N/2$ -acid, in presence of 1, 2, 5, and 10 c.c. of methyl acetate in 50 c.c. of solution. The velocity constant, k , is to the base e . The symbol W stands for the number of gram-mols. of water present per litre of solution. k/W is the velocity constant referred to constant concentration of water. The value of the initial reading of the polarimeter, when $t=0$, is obtained by the method employed in Part II. (T., 1915,

107, 237). The presence of the ester introduced no special difficulty into the readings themselves. In the case in which the concentration of ester is small, the same end-point is obtained as in the case of sucrose in water alone. When, however, the concentration of ester becomes considerable, for example, when 5—10 c.c. of ester are present in 50 c.c. of solution, the solvent itself changes during the course of the experiment owing to the hydrolysis of the ester, and this affects the angle of rotation.

In the table quoted below, as illustrating the order of accuracy of the measurements, the necessary correction is made in the column headed "*a* (corr.)." The mode of correction is as follows. In a particular case, in which 10 c.c. of ester were present, the final rotation, *a*, for the given invert-sugar content should have been -9.00° , but in presence of the partly hydrolysed ester the final reading was -8.07° . The reading at zero time contains no error due to hydrolysis. The final reading is in error by the amount 0.93° . It was assumed that the error could be expressed with sufficient accuracy as a linear function of the time. A graph was therefore constructed, from which the necessary correction at any time could be read off.*

Ten per cent. Sucrose Solution containing 10 c.c. of Methyl Acetate in 50 c.c. Temp., 35°. Catalyst, 0.1N-Hydrochloric Acid.

Time in minutes.	<i>a</i> .	<i>a</i> corr.	<i>k</i> .
0	—	18.93	—
30	15.84	15.62	0.004200
45	14.53	14.27	0.004053
60	13.02	12.71	0.004195
75	11.82	11.48	0.004136
90	10.73	10.36	0.004074
100	10.04	9.65	0.004055
123	8.25	7.81	0.004127
141	7.08	6.61	0.004126
160	5.76	5.25	0.004207
180	4.92	4.39	0.004084
190	4.11	3.55	0.004210
200	3.54	2.97	0.004237
inf.	-8.07	-9.00	—

Mean 0.004140

The mean value of a duplicate experiment was..... 0.004149

Hence the mean of both is..... 0.004145

* The justification for the above procedure rests on the following experiments. A solution containing 10 per cent. of sucrose (without catalyst) showed a rotation of 23.55° . A second solution, also containing 10 per cent. of sucrose and 10 c.c. of methyl acetate in 50 c.c. and without catalyst, showed a rotation of 23.51° , indicating that the unhydrolysed ester has a negligible influence on the rotation. In the velocity measurements themselves, the final reading is necessarily made in presence of an equilibrium mixture of ester, alcohol, and acid. In water alone, the final reading for 10

The solutions employed were prepared in the following way. In the first case, in which no ester was present, a certain amount of hydrochloric acid solution was mixed with a given quantity of 20 per cent. solution of sucrose, and the whole made up to 50 c.c. The same stock solution was employed throughout the series. The final composition of the solution which did not contain ester was: sucrose, 10 per cent. + 0.1*N*-hydrochloric acid. The mass of water was 46.81 grams or 52.01 mols. per litre. When methyl acetate was also present, less water was required to make the mixture up to 50 c.c., the volume of water being measured from a burette. In all cases the masses of the varying constituents, ester and water, were known.

The following table gives a summary of the mean velocity constants obtained:

Summarising Table.

Ten per cent. Solutions of Sucrose. 0.1*N*-Hydrochloric Acid.

No. of c.c. of solution.	Concentration of methyl acetate. Mols. per litre.	<i>W</i> = gram-mols. water per litre. (Molecular weight of water taken as 18.)	<i>k</i> .	<i>k</i> / <i>W</i> × 10 ⁵ .	$\sqrt{(\text{H}_2\text{O})_2}$ per litre.	<i>k</i> corr. × 10 ⁴ .
0	0.0	52.01	0.00355	6.82	5.099	6.96
1	0.258	50.90	0.00354	6.95	5.046	7.01
2	0.516	49.84	0.00343	6.88	4.992	6.87
5	1.29	46.98	0.00372	7.92	4.848	7.68
10	2.58	41.81	0.00414	9.91	4.573	9.06

Ten per cent. Solutions of Sucrose. 0.5*N*-Hydrochloric Acid.

No. of c.c. of solution.	Concentration of methyl acetate. Mols. per litre.	<i>W</i> = gram-mols. of water per litre.	<i>k</i> .	<i>k</i> / <i>W</i> × 10 ⁴ .	$\sqrt{(\text{H}_2\text{O})_2}$ per litre.	<i>k</i> corr. × 10 ⁵ .
0	0.0	51.44	0.02127	4.13	5.071	4.19
1	0.258	50.55	0.02093	4.14	5.028	4.16
2	0.516	49.50	0.02127	4.30	4.975	4.28
5	1.29	46.28	0.02307	4.99	4.810	4.80
10	2.58	41.00	0.02564	6.25	4.528	5.66

The inversion of sucrose being a bimolecular reaction, the observed velocity constants, *k*, are not directly comparable. In order to introduce the necessary stoicheiometric correction for the water content, two modes of calculation have been adopted. In the first, the water has been treated as though it consisted entirely of simple molecules, thereby giving the quantity *k*/*W*. In the second, the water has been considered as existing practically entirely in the per cent. sucrose is -9.0° . Fifty c.c. of this solution were concentrated to about 40 c.c. and rediluted. The same rotation was observed. A second solution (50 c.c.) was concentrated to 40 c.c., and then diluted with an equilibrium mixture of ester, alcohol, and acid. The reading was -8.06° , which agrees well with the final value, -8.07° , obtained in the experiment quoted in the table. This indicates that the change in the end-point from -9.00° to -8.07° is due to the presence of the hydrolysed ester.

double molecular form. The concentration of single molecules, which are assumed to take part in the reaction, is thus proportional to the square root of the concentration of the polymeride. These quantities are given in the column headed $\sqrt{(\text{H}_2\text{O})_2}$. By dividing the observed velocity constant k by this expression, we obtain the quantity denoted by k corr. Neither mode of correction can be exact, but they exhibit the limits of what the true correction would be. It will be observed that, using the values of k/W , the minimum persists with the more dilute acid, but has just vanished with the more concentrated. Using the k corr. values, the minimum persists with both concentrations of acid. We may conclude, therefore, that the minimum has a real existence, as was anticipated on the basis of the considerations discussed earlier in the paper.

Discussion of Results.

Sucrose and methyl acetate have been shown to exert a mutual effect on one another in the sense that each functions as a weak negative catalyst with respect to the other. The most obvious explanation of this effect is to attribute it to a distribution of the catalyst, hydrions, between the two substances. It is generally assumed that in catalytic reactions of this type complex ions are produced, which in their simplest form would be represented by $(\text{H}_2\text{O}, \text{ester}, \text{H}^+)$ and $(\text{H}_2\text{O}, \text{sucrose}, \text{H}^+)$. Unpublished results, obtained in this laboratory, support the conclusion regarding the formation of a complex sucrose-hydrogen ion. On addition of sucrose to the methyl acetate system, there would be a tendency for a certain amount of the complex ester ion to diminish in order to allow of the formation of the complex sucrose ion, and consequently the rate of hydrolysis would be diminished. Although this view is attractive, it is doubtful whether it is adequate. Its adequacy depends essentially on the existence of a sensible amount of complex ion in any single case, as otherwise the equilibrium conditions, say, of the reaction $(\text{ester}, \text{H}_2\text{O}) + \text{H}^+ \rightleftharpoons \text{complex ion}$ would not be influenced by addition of sucrose. The equilibrium conditions would be represented by:

$$K \times E(H - e) = e,$$

where E and H represent the concentrations of the simple additive compound and hydrogen ion respectively, had no complex ion been formed, and e is the concentration of the complex ion. E is supposed, for the sake of simplicity, to be large compared with e . The rate of hydrolysis is then given by:

$$dx/dt = ke = kK(E - x)(H - e),$$

and therefore,

$$k = kK(H - e).$$

The quantity e is, however, not independent of time. As the reaction proceeds, e diminishes, and therefore $(H - e)$ increases. The observed velocity constant should therefore increase with time. This is in disagreement with experiment. The constancy of k_{obs} necessitates similar constancy in the term $(H - e)$. We conclude, therefore, that e is negligibly small compared with the total concentration of the hydrions. The fact that the velocity constant is also independent of the concentration of the ester points to the small value of the complex ion. If, however, the hydrion concentration remains sensibly constant under these conditions, it cannot be appreciably affected by addition of sucrose, for the same reasons. One may conclude, therefore, that the possible distribution of the catalyst between the catalysable substances is not the cause of the mutual effect observed. Several possibilities present themselves, but it is not possible at the present time to draw a definite conclusion.

The existence of the minimum velocity constant, which Coppadoro failed to detect, is due to the opposing effect introduced by the decrease in the concentration of the water. It has already been shown that water exercises a marked negative catalytic effect, probably due to its high dissociating power. As the water is displaced from the system, its concentration falls, and with its concentration its dissociating influence on the ester-water complex, which takes part in the reaction. This complex therefore exists at a higher concentration when some of the water is removed, and consequently the velocity constant is increased.

It is evident from the results obtained in the case of these two reactions that the mutual effect is small and is easily masked by the much greater effect introduced as a result of the elimination of water. The latter is a factor which has been too generally overlooked.

Summary.

The inversion of sucrose has been observed in presence of methyl acetate, which was being hydrolysed at the same time. The presence of the ester diminishes slightly the rate of inversion of the sucrose. The velocity constants pass through a minimum value, due to the decrease in the negative catalytic effect of the water which is displaced as the ester is added.

It was also found that the presence of sucrose diminished the velocity of hydrolysis of the ester. No minimum was observed in this case owing to its presence being masked by the greater effect produced by the removal of the water.

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