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STUDIES IN CHEMICAL REACTIVITY. I. THE MECHANISM OF THE FORMATION OF VALEROLACTONE

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In spite of the fact that the reaction, hydroxyvaleric acid \longrightarrow valerolactone and water, in presence of various catalyzing acids, has been studied by several authors,¹ the actual mechanism does not seem to have been completely elucidated. The object of the work presented below was, therefore, to study the mechanism of this reaction, in the presence of various concentrations of hydrochloric acid in water, at the temperatures 25° and 35°. This was done first in aqueous solution in presence of the catalyzing acid alone, and afterwards in the presence of sucrose, potassium chloride and lithium chloride, as water-displacing agents. The true order of the reaction was also determined, and the influence of the displacement on the critical increment or energy of activation of the process studied.² The activity of the hydrogen ion in the reaction mixtures containing the above mentioned displacement agents, has been determined by the

¹ (a) Henry, *Z. physik. Chem.*, **10**, 96 (1892). (b) Taylor and Close, *THIS JOURNAL*, **39**, 422 (1917). (c) Kailan and Neumann, *Z. physik. Chem.*, **101**, 63 (1922). It may be stated that previous authors have only examined the reaction at one temperature, namely 25°, in presence of various acids. No data were available for calculating energy terms and no systematic investigation of the effect of added substances on the reaction velocity had been carried out. Such previous data as were comparable were reproduced in the present investigation within 1%. The effect of viscosity on this reaction, as a means of distinguishing between a uni- and a bimolecular reaction, is here studied for the first time.

² Employing the expression, $\frac{d \log k}{dT} = \frac{E}{RT^2}$, E gives the critical increment of the reaction in calories per mole. Compare Lambie and Lewis, *J. Chem. Soc.*, **105**, 2330 (1914).

e.m.f. method in this Laboratory,³ and these values are employed in all the tables given. In the case of the reaction in presence of aqueous hydrochloric acid alone, the velocity of the reaction was found to be proportional to the hydrogen-ion activity, over a range of catalyzing acid from 0.01 *N* to 0.1 *N*. In all cases the hydroxy acid was present in such small amount that its contribution to the hydrogen-ion activity was negligible. In this case the viscosity of the solutions at a given temperature was practically constant, and hence no information could be obtained regarding the possible influence of this factor. In the case where displacing agents were present in the reaction mixtures, the velocity of reaction was found not to be proportional to the hydrogen-ion activity alone, but dependent also on the viscosity of the solution.

Kailan and Neumann found that in aqueous solution the velocity of formation of valerolactone in presence of hydrochloric acid up to concentration 0.2 *N* is proportional to the total concentration of the acid, but conclude that hydrogen ion is the sole independent catalyzing agent for the reaction, no effect being attributable to the undissociated molecule.

Preparation of Valerolactone.—The lactone was prepared from levulinic acid by reduction with 5% sodium amalgam in alkaline solution, substantially as recommended by Taylor and Close.^{1b} The solution of hydroxyvaleric acid for experimental purposes was prepared by the lead hydroxide method given by the same authors. The lactone is shaken under water with a slight excess of lead hydroxide, prepared from the acetate, the lead salt of the hydroxy acid being thus formed. The lead is precipitated by a slow stream of hydrogen sulfide and filtered off, and the excess of hydrogen sulfide then removed by bubbling a stream of air through the solution.

Barium hydroxide solutions were used throughout for estimating the total acid concentration of the reaction mixtures, the strength employed being about 0.05 *N*. The unit of time used is the second.

Table I gives the unimolecular reaction constants obtained at 25° and 35°, denoted by $k_{\text{uni. obs.}}$.⁴ All results given are the mean of concordant duplicate experiments.

³ Compare Moran and Lewis, *J. Chem. Soc.*, **121**, 1613 (1922), and unpublished work.

⁴ This term $k_{\text{uni. obs.}}$ is actually the algebraic sum of the two opposing velocity constants, but the fairly concordant measurements of Henry,^{1a} and of Kailan and Neumann^{1c} and measurements made in this Laboratory show that the equilibrium position in the present case lies far over on the lactone side, corresponding to a 94% formation of lactone. Even in the presence of 30% of sucrose the equilibrium is practically unchanged, being displaced only slightly further towards the lactone side. Hence, the reverse velocity constant is small compared with the direct, and may be neglected. That is, $k_{\text{uni. obs.}}$ is sensibly identical with the velocity constant of the direct process alone.

TABLE I
UNIMOLECULAR CONSTANTS AT 25° AND 35°

Concn. of HCl Moles per liter	$k_{\text{uni. obs.}}$ $\times 10^3$ at 25°	$k_{\text{uni. obs.}}$ $\times 10^3$ at 35°	Apparent critical increment in cal. per mole
0.01	1.151	2.869	16,100
.025	2.871	6.821	15,780
.05	5.575	12.880	15,250
.10	11.300	26.102	15,050

The mere fact that a unimolecular constant can be obtained at any given concentration of hydrochloric acid is not proof that the reaction is actually unimolecular in nature. The process under consideration is catalyzed by the hydrogen ion, and two possibilities are presented: (1) the hydroxy acid molecule and the hydrogen ion react at measurable speed either to give a fugitive complex which then decomposes rapidly, or else to give the resultants direct; this would involve a bimolecular process; (2) rapid formation of a complex of the hydroxy acid molecule and hydrogen ion, followed by a slow, measurable decomposition into the resultants; this reaction would be truly unimolecular, and unaffected by the viscosity of the reaction mixture. In a type of reaction such as that studied it is ordinarily impossible to distinguish between the two suggestions put forward. The only method of determining the correct mechanism is to study the effect of alteration in the viscosity of the medium. If the reaction is truly unimolecular, the alteration in viscosity will have no effect. If it is really bimolecular the viscosity factor must be allowed for. We have found that viscosity plays an essential part in the reaction under consideration. A satisfactory bimolecular constant containing the viscosity term can be obtained, as is shown later, this constant being independent of the environment (the amount of sucrose or neutral salts and of catalyzing acid) and dependent only on temperature.

Mode of Expressing the Velocity Constant

As a result of recent investigations it has been concluded that the correct way in which to express the reactants is in terms of their activities, or thermodynamic concentrations. In the case of ions this function may, in general, be obtained conveniently by e.m.f. measurements. In the case of non-electrolytes, to which the hydroxy acid approximates sufficiently closely, the most direct way of obtaining the same function with sufficient accuracy is from osmotic pressure measurements, the activity being identical with the osmotic pressure divided by RT . Unfortunately, such data are extremely scanty. It has been found in this Laboratory, however, that in the case of sucrose the activity can be calculated with considerable accuracy by expressing the concentration in moles per unit of free or available water present.³ In the case of sucrose, where the hydration is heavy, the free water is much less than the total water present. In the

case of an unsolvated or slightly solvated solute present alone in a solvent, its activity on the same basis would become identical with its concentration as ordinarily expressed. This has been employed in the calculation of $k_{\text{uni. obs.}}$ in Table I. An interesting problem arises, however, as to the mode of expressing the activity of an unsolvated solute dissolved, not in the solvent alone, but in presence of a second heavily hydrated solute, such as sucrose.

The results obtained in this Laboratory indicate that there is no general rule to be followed in such a case. In some cases the primary, unsolvated solute dissolves in the water of hydration of the secondary, heavily hydrated solute. In other cases no such solution occurs.⁵

The present investigation is a further illustration of this behavior. As a rule, however, the actual behavior may be inferred, as in the present case, with some confidence from the fact that while the one assumption leads to constants which are independent of the environment (such as amount of secondary solute) the alternative assumption leads to values which do not exhibit such independence of environment. In the series of measurements recorded in Table I, in which no secondary solute such as sucrose was present, the question regarding the amount of available water does not arise as both the catalyzing acid and the hydroxy acid are present in dilute solution only. In the series where sucrose or neutral salts are present in the reaction mixture, the activity of the hydroxy acid is no longer to be identified with its apparent concentration. We shall proceed first on the assumption that only the free water (that is, the total water less the water of hydration of the sucrose or salts) is available as solvent. If unsatisfactory results are obtained, the alternative assumption will be followed.

The Order of the Reaction

Regarding the measurable reaction as the bimolecular one, hydroxy acid molecule + hydrogen ion \longrightarrow a momentary complex, followed by instantaneous decomposition into the resultants, it is to be expected that the viscosity correction on which we base our determination of the order of the reaction will be characteristic of the hydrogen ion as obtained from the electrical conductivity of acids in presence of sucrose. The investigations of Green⁶ and of Kieran⁷ have shown that for hydrogen ion in presence of sucrose the correct value of the index to which the viscosity must be raised is 0.53. In Table II the viscosity term η^x is used, x being taken as 0.53. As will be observed from this table this value leads to a satisfactory bimolecular constant, $k_{\text{bi.}}$, which is independent of the amount of sucrose present in the reaction mixture. The method of calculating $k_{\text{bi.}}$ is as follows.

⁵ Compare Corran and Lewis, *THIS JOURNAL*, **44**, 1673 (1922).

⁶ Green, *J. Chem. Soc.*, **93**, 2023 (1908).

⁷ Kieran, *Trans. Faraday Soc.*, **18**, Oct., 1922.

The observed unimolecular constant is based on the assumption that the rate of reaction at any moment can be expressed thus: rate of reaction = $k_{\text{uni. obs.}} \times C_{\text{hydroxyvaleric acid}}$, where the C term denotes the apparent concentration in moles of solute per liter of solution. From what has been said above, the correct way of expressing the same rate would be:

$$\text{rate of reaction} = \frac{k_{\text{bi.}} \times a_{\text{hydroxy acid}} \times a_{\text{H}^+}}{\eta^x}$$

In this expression a denotes the respective activities. Hence, $k_{\text{bi.}} = \frac{k_{\text{uni. obs.}} \times C_{\text{hydroxy acid}} \times \eta^x}{a_{\text{H}^+} \times a_{\text{hydroxy acid}}}$.

When no water-displacing agents are present the activity of the hydroxyvaleric acid becomes identical with its apparent concentration, within the limits of experimental error, and thus for the case of the data given in Table I we can write,

$$k_{\text{bi.}} = \frac{k_{\text{uni. obs.}} \times \eta^x}{a_{\text{H}^+}} \quad (1)$$

For the case to which Equation 1 applies, the viscosities at any one temperature remain sensibly constant over the range of acid concentrations studied, being approximately that of water itself. Throughout this series of measurements, the viscosities of water at 25° and 35° are taken as unity and 0.803, respectively.

Equation 1 as it stands does not apply to the data obtained when sucrose is present in the reaction mixture. A modification has to be introduced to allow for the fact that less water is present, not only on account of the actual displacement of water by the sucrose, but also on account of the water of hydration of the sucrose, as at this stage it is an open question whether the water of hydration of sucrose is a solvent for the hydroxy acid molecule or not. As pointed out earlier in this paper, the activity of sucrose can be calculated with sufficient accuracy by expressing the concentration as moles of sucrose per amount of free water.³ It is necessary to modify the equation for the alteration in activity of the hydroxy acid on the same basis, that is, by assuming that the activity of the hydroxy acid can be calculated per amount of free water present. If we denote by W the amount of available water expressed as the fraction, $\frac{\text{moles of available water}}{55.55}$

(where 55.55 is the number of moles of water in a liter, expressed as monohydr) and introduce this correction into Equation 1, the form of the equation in the presence of displacing agents becomes

$$k_{\text{bi.}} = \frac{k_{\text{uni. obs.}} \times W \times \eta^x}{a_{\text{H}^+}} \quad (2)$$

Reaction Velocity in the Presence of Sucrose

In the data given in Table I, the quantity denoted by W is sensibly unity, but in the presence of displacing agents it necessarily falls

considerably below unity. Equation 2 is applied in Table II to the velocity of reaction in presence of various amounts of sucrose. The columns are self-explanatory. It need only be pointed out that the available water is here taken to be the actual number of moles of water present, less the water of hydration of the sucrose present as displacing agent.

Moran and Lewis³ have shown that the effective degree of hydration of sucrose over a wide range of concentrations corresponds to $4\text{H}_2\text{O}$. The apparent concentration of hydrochloric acid (moles per liter of solution) remained 0.025 *N* throughout this series. The value of the viscosity index α employed in calculating the values of k_{bi} is 0.53.

TABLE II

REACTION VELOCITY IN THE PRESENCE OF VARIOUS AMOUNTS OF SUCROSE

Concn. of sucrose %	$K_{\text{uni. obs.}} \times 10^6$ at 25°	$K_{\text{uni. obs.}} \times 10^6$ at 35°	a_{H^+} (Moran)	Viscosity at 25°	Viscosity at 35°	W	$K_{\text{bi.}} \times 10^3$ at 25°	$K_{\text{bi.}} \times 10^3$ at 35°
0	2.871	6.821	0.0223	1.000	0.803	1.000	1.289	2.592
5	3.214	7.628	.0238	1.128	0.894	0.957	1.298	2.754
10	3.584	8.351	.0266	1.313	1.031	0.914	1.412	2.880
20	4.055	9.429	.0320	1.794	1.405	0.830	1.432	2.790
30	4.421	10.205	.0388	2.618	1.985	0.747	1.411	2.861
50	4.813	11.040	.0558	6.825	4.780	0.580	1.386	2.728
60	4.944	11.304	.0670	12.710	8.607	0.496	1.304	2.691

Av. $k_{\text{bi.}}$ at 25° = 1.352×10^{-3}

Av. $k_{\text{bi.}}$ at 35° = 2.756×10^{-3}

Critical increment from $k_{\text{bi.}}$ values = 13,000 cal. per mole.

It will be observed that the values of $k_{\text{bi.}}$ as calculated above are reasonably constant at a given temperature,⁸ that is, they are independent of the sucrose concentration. Further, the degree of constancy of the $k_{\text{bi.}}$ values is evidence for the correctness of the assumption underlying the W values, namely, that *the water of hydration of sucrose is not a solvent for the reaction in question*. This in turn completely supports the conclusion of Moran and Lewis³ that such water is not a solvent for hydrogen ion.

Reaction Velocity in the Absence of Sucrose

On the evidence afforded by Table II for the correctness of the assumption that the reaction actually measured is bimolecular, as the values of $k_{\text{bi.}}$ contain a viscosity term, the results given in Table I are recalculated on the basis of Equation 1, the viscosities at the two temperatures being taken as unity and 0.803, respectively. The W ratio in this case is unity, and the power to which the viscosity is raised is also in this case unity. The values of $k_{\text{bi.}}$ obtained are given in Table III.

⁸ In the values obtained for $k_{\text{bi.}}$ at 25° it will be observed that the first and fourth differ considerably. The conclusion that the quantity denoted by $k_{\text{bi.}}$ is really a constant is based on the general behavior of the system when substances other than sucrose are present (See Tables III, VI, VIII) and when temperatures other than 25° are taken into consideration.

TABLE III
REACTION VELOCITY IN THE ABSENCE OF SUCROSE

a_{H^+}	k_{bi} , $\times 10^3$ at 25°	k_{bi} , $\times 10^3$ at 35°	Critical increment in cals. per mole
0.00976	1.223	2.656	13,780
.02225	1.289	2.592	13,400
.04620	1.217	2.545	13,350
.08010	1.305	2.756	13,480

$$\text{Av. } k_{bi} \text{ at } 25^\circ = 1.261 \times 10^{-3}$$

$$\text{Av. } k_{bi} \text{ at } 35^\circ = 2.637 \times 10^{-3}$$

$$\text{Av. critical increment} = 13,480 \text{ cal. per mole.}$$

Again, sufficient constancy in the values of k_{bi} , is found, values independent of the concentration of the catalyzing acid. Further, the absolute values obtained agree closely with the corresponding values obtained in the presence of sucrose. The absolute values of the critical increment of the reaction obtained in the two cases are in good agreement, and about 2,000 cal. per mole less than the apparent value obtained in Table I, from the values of $k_{uni. obs.}$

Reaction Velocity in the Presence of Potassium Chloride

It is well known that the activity of the hydrogen ion in solutions of hydrochloric acid is considerably enhanced by the addition of certain neutral salts. Taylor and Close^{1b} and Kailan and Neumann^{1c} have found that the presence of potassium chloride increases the catalytic effect of hydrochloric acid on this particular reaction. Their results, however, refer to one temperature only. In this series experiments were carried out at 25° and 35° with various amounts of potassium chloride present in the reaction mixture. The apparent concentration of hydrochloric acid was 0.1 *N*, the corresponding activity of the hydrogen ion in solutions containing various amounts of potassium chloride having been measured in this Laboratory by Dr. Moran, by the e.m.f. method. The values of $k_{uni. obs.}$ obtained are given in Table IV.

TABLE IV
REACTION VELOCITY IN THE PRESENCE OF POTASSIUM CHLORIDE

Concn. of KCl Moles per liter of solution	$k_{uni. obs.} \times 10^5$ at 25°	$k_{uni. obs.} \times 10^5$ at 35°
0.000	11.30	26.10
0.6705	12.61	28.80
1.3410	15.32	34.74
2.0115	18.20	41.45
2.6820	22.07	50.26

These values were recalculated on the basis of Equation 2, the degree of hydration of potassium chloride being taken as corresponding⁹ to 9H₂O. The power α of the viscosity term has been shown to approach unity as the

⁹ Unpublished work by Dr. T. Moran.

size of the ion increases and the molecular size of the displacing agent decreases,⁷ and on account of this, and also on account of the very small variation from the value for pure water of potassium chloride solutions, the power of the viscosity employed in this case is unity. The W term has the same significance in Table V as in Table II. The values so obtained are given in Table V.

TABLE V
RECALCULATION ON THE BASIS OF EQUATION 2

Concn. of KCl Moles per liter of solution	σ_{H^+} Moran	Viscosity 25°	Viscosity 35°	W	$k_{bi} \times 10^3$ 25°	$k_{bi} \times 10^3$ 35°
0.000	0.080	1.000	0.803	1.000	1.404	2.900
0.6705	.089	0.990	.834	0.871	1.222	2.350
1.3410	.104	0.987	.832	0.743	1.083	2.065
2.0115	.125	1.008	.838	0.614	0.878	1.700
2.6820	.154	1.013	.847	0.485	0.688	1.340

It is evident from the values obtained in Table V that the assumption that the water of hydration of potassium chloride is unavailable as solvent for the hydroxy acid molecule is not in accordance with the actual behavior in this case.¹⁰

Values of k_{bi} were then calculated from the same values of $k_{uni,obs}$ on the basis of the alternative assumption, namely, that the *water of hydration of potassium chloride is free to act as solvent for the hydroxy acid molecule*, the only difference in the expression employed being in the water term, which we now denote by W_1 , and which is defined by the fraction, $W_1 =$ (total water present in the reaction mixture)/55.55.

The values obtained for k_{bi} on this basis are given in Table VI.

TABLE VI

Concn. of KCl Moles per liter of solution	W_1	$k_{bi} \times 10^3$ 25°	$k_{bi} \times 10^3$ 35°
0.000	1.000	1.404	2.900
0.6705	0.980	1.380	2.716
1.3410	0.960	1.400	2.708
2.0115	0.940	1.372	2.720
2.6820	0.919	1.352	2.640

Av. k_{bi} at 25° = 1.380×10^{-3}

Av. k_{bi} at 35° = 2.738×10^{-3}

Critical increment from k_{bi} values = 12,450 cal. per mole.

It will be observed that, on this alternative assumption, fairly constant values for k_{bi} are obtained, the absolute values of the constants and of the critical increment being in agreement with the corresponding values obtained in Tables II and III.

¹⁰ It will be observed that the activity of the hydrogen ion employed throughout this work is obtained from direct e.m.f. measurements, and any solvent action, or the reverse, on the part of the hydrated displacing agent, *in so far as the hydrogen ion itself is concerned*, is automatically taken into account.

An unexpected contrast in the behavior of sucrose and of potassium chloride with respect to the hydroxy acid molecule appears, in that the water of hydration of sucrose is *not* available as solvent, whereas the water of hydration of potassium chloride *is* available. Before attempting to explain this contrast in behavior, a further series of experiments was carried out with lithium chloride present in the reaction mixture as water-displacing agent. This salt is highly hydrated in solution, though no exact value is known for the extent of hydration. The activity of hydrogen ion in aqueous solutions of hydrochloric acid in presence of various amounts of lithium chloride has been measured in this Laboratory by Dr. Moran.

Reaction Velocity in the Presence of Lithium Chloride

Table VII gives the values obtained for $k_{\text{uni. obs.}}$ in the presence of various amounts of lithium chloride. The apparent concentration of hydrochloric acid is 0.1 *N* throughout the experiments.

TABLE VII

REACTION VELOCITY IN THE PRESENCE OF LITHIUM CHLORIDE

Concn. of LiCl Moles per liter of solution	$k_{\text{uni. obs.}} \times 10^6$ 25°	$k_{\text{uni. obs.}} \times 10^6$ 35°	Concn. of LiCl Moles per liter of solution	$k_{\text{uni. obs.}} \times 10^6$ 25°	$k_{\text{uni. obs.}} \times 10^6$ 35°
0.000	11.30	26.10	1.1715	18.63	42.03
0.3905	12.35	28.22	1.5620	21.52	50.30
0.7810	14.80	34.10	1.9525	27.46	63.50

As the extent of hydration of lithium chloride in solution is not accurately known, the second assumption, namely, that the water of hydration, whatever its amount, is available as solvent in this case, was employed first (Table VIII). If this assumption does not apply, then the determination of the necessary value to make the alternative assumption apply

TABLE VIII

Concn. LiCl Moles per liter of solution	a_{H^+} Moran	Viscosity 25°	Viscosity 35°	W_1	$k_{\text{bi.}}$ $\times 10^{-3}$ 25°	$k_{\text{bi.}}$ $\times 10^{-3}$ 35°
0.000	0.080	1.000	0.803	1.000	1.404	2.900
0.3905	.091	1.052	0.848	0.991	1.403	2.627
0.7810	.110	1.110	0.896	0.984	1.445	2.751
1.1715	.141	1.169	0.942	0.977	1.497	2.753
1.5620	.175	1.229	0.992	0.969	1.445	2.770
1.9525	.221	1.286	1.038	0.961	1.520	2.870

Av. $k_{\text{bi.}}$ at 25° = 1.452×10^{-3}

Av. $k_{\text{bi.}}$ at 35° = 2.783×10^{-3}

Av. critical increment = 12,000 cal. per mole.

would give an approximate measure of the extent of hydration of lithium chloride in solution. In Table VIII, the term W_1 has the same significance as in Table VI. The viscosity index is again taken to be unity, though this will not be so good an approximation as in the case of displacement by potassium chloride.

These values are reasonably constant, though a little higher than the corresponding values given in the earlier tables. It must be pointed out that the use of the index unity in the viscosity term will in this case be less exact than in the former cases (compare Tables III and V) where the viscosity change was much smaller. The value of 0.9 for the index would be more exact, since the power of the viscosity correction as affecting hydrogen ion will not be as high as unity.⁷ If this power were applied, the values of k_{bi} , at 25° would be a little lower, and at 35° a little higher, and in closer agreement with preceding values. The lower values for the critical increment obtained in the presence of potassium and lithium chlorides are also due to the inexact value of the viscosity index.

The agreement between this table and Table VI is, however, sufficient to emphasize the distinction between the water of hydration of sucrose and that of neutral salts in respect to their solvent action on the hydroxy acid molecule.

In the summary of results given in Table IX, the approximate constancy of the values of k_{bi} , under widely differing environmental conditions will be observed. It will be well to point out again that in the series, sucrose plus hydrochloric acid, the term W is employed, allowance being made for the water of hydration of the displacing agent. In the two series where neutral salts act as water-displacing agents, the term W_1 is used, no such allowance being included.

TABLE IX
SUMMARY OF RESULTS

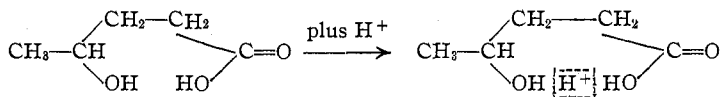
Series	k_{bi} , $\times 10^3$ 25°	k_{bi} , $\times 10^3$ 35°	Critical increment in cals. per mole
HCl alone	1.26	2.64	13,400
HCl + sucrose	1.35	2.76	13,000
HCl + KCl	1.38	2.74	12,500
HCl + LiCl	1.45	2.78	12,000

The Mechanism of the Reaction

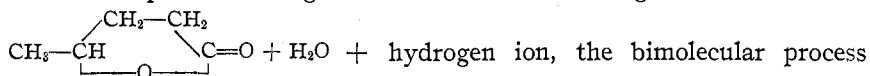
The degree of constancy of the values of k_{bi} , calculated on the basis of Equations 1 and 2 at the two temperatures, is fairly conclusive evidence that the reaction actually measured is bimolecular, namely, hydroxyvaleric acid + hydrogen ion \longrightarrow $\left\{ \begin{array}{l} \text{a momentary complex,} \\ \text{or resultants direct.} \end{array} \right.$ The suggestion is made that a complex of fugitive existence is actually formed between the hydroxy acid molecule and the hydrogen ion, the complex breaking down very rapidly into the resultants, with liberation of the hydrogen ion. The most likely mechanism appears to be as follows.

The hydrogen ion, on collision with an undissociated hydroxy acid molecule, takes up a temporary position between the two hydroxyl groups, which are structurally adjacent. No definite chemical union is stipulated.

This entry into the repulsive field between the two similar groups will lessen the repulsion, and cause elimination of a water molecule practically instantaneously, the hydrogen ion being liberated simultaneously, thus:



This complex on losing a water molecule would give



between the hydroxy acid and the hydrogen ion being the actual process measured. It will be observed that in the above mechanism the hydroxy acid molecule is taken to be unhydrated in solution. The available evidence, such as it is, indicates that this is justifiable. Thus H. C. Jones¹¹ has concluded on the basis of freezing-point and conductivity measurements that the two hydroxy acids, tartaric and citric are neither polymerized nor hydrated in aqueous solution.

The Capacity of Water of Hydration to Act as Solvent

The contrast in behavior of the water of hydration of sucrose and that of neutral salts is unexpected. In seeking a cause for this contrast we have to take into account the following experimental conclusions: (1) the water of hydration of sucrose is *not* free to act as solvent for the hydroxy acid molecule; (2) the water of hydration of potassium and lithium chlorides *is* available as solvent for the hydroxy acid molecule; (3) hydrogen ion is *insoluble* in the water of hydration of sucrose³ and also *insoluble* in the water of hydration of potassium and lithium chlorides (unpublished work by Dr. Moran); (4) potassium and chloride ions, both of which are hydrated, are soluble in the water of hydration of sucrose;⁵ (5) sucrose tetrahydrate is soluble in the water of hydration of acetic acid; this follows from the fact that, as experimentally determined in this Laboratory, sucrose dissolved in *M* acetic acid possesses a normal molecular weight when the water of hydration of acetic acid is regarded as part of the available solvent, and not otherwise.¹²

In view of these facts, it does not appear possible to relate the solubility effect simply to the electric charge in the case of ions, as distinct from the absence of charge in the case of molecules.

The solvent power exhibited by the water of hydration appears to be an effect specific to both colliding individuals. In so far as data are available, it may be said that when both colliding individuals are hydrated, mutual

¹¹ Jones, *Carnegie Inst. Pub.*, 60 (1907).

¹² For the hydration of acetic acid compare Lewis, Merriman and Moran, *This Journal*, 45, 702 (1923)

solubility or penetration occurs. If only one individual is hydrated no generalization can as yet be made.

Summary

1. The conversion of hydroxyvaleric acid into valerolactone under the catalytic influence of hydrogen ion is shown to be a bimolecular process, the reaction actually measured being the rate of effective collision between the suitably activated hydroxyvaleric acid and the hydrogen ion.

2. A characteristic bimolecular constant is obtained at a given temperature, which is not altered by change in concentration of the catalyst, or by the presence of sucrose, potassium chloride, or lithium chloride in the reaction mixture. This constant involves the activities of the reactants, and also the viscosity of the solution raised to a power characteristic of the hydrogen ion. This power is not a constant, but varies with the relative size of the individuals in the solution, as determined independently from electrical-conductivity measurements.

3. There is a sharp contrast in behavior between the water of hydration of sucrose, on the one hand, and that of potassium and lithium chlorides on the other, in respect of the effect upon the hydroxyvaleric acid molecule. The water of hydration of sucrose is not available as solvent, whereas that of the neutral salts is available. In none of these cases, however, is hydrogen ion soluble in water of hydration. The point is considered, but no definite conclusion is arrived at.

4. The true critical increment of the reaction is found to be 12,750 calories per mole of hydroxyvaleric acid transformed. This value is considerably less than the corresponding value obtained on the assumption that the reaction is unimolecular, the difference being 3,000 calories per mole. The unimolecular critical increment has, however, no real significance for the process actually measured, which is shown to be truly bimolecular.

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STUDIES ON CERTAIN PHYSICAL PROPERTIES OF ARSENIC TRIOXIDE IN WATER SOLUTION

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Notwithstanding the enormous amount of investigational work on arsenic trioxide, some important physical properties of this substance are not accurately known. For this reason it seemed desirable to make determinations of the density, refractive index, solubility and hydrogen-ion concentration of aqueous solutions of this substance as well as of the amount of arsenious acid formed in such a solution.