Recombination Rates of Substituted Phenylglyoxylate Ions with Hydronium and Deuteronium Ions

In a recent communication[1] the recombination rates of the phenylglyoxylate ion with hydronium ions, water and boric acid were determined in alkaline solution[2]. For this medium the equation for fully rate-controlled currents[3] was applicable.

We wish now to report the comparison[*] of these data with measurements in neutral solution which were interpreted using equations developed for a case in which diffusion limits the current jointly with reaction rate. An approximate expression for joint diffusion and rate control was first derived by WIESNER[4] by introduction of the expression

$$\mu = \sqrt{\frac{1}{2}}\sqrt{\frac{D}{k'}}$$

into the expression of BRDIČKA and WIESNER[5].

$$\frac{i_k}{i_\infty} = \frac{\mu k\,[\mathrm{H^+}]}{\mu k\,[\mathrm{H^+}] + \varkappa\,10^3/nF\bar{q}} \qquad (1)$$

where μ = effective thickness of the interface; D = diffusion coefficient; k' = pseudo-unimolecular rate constant of dissociation reaction; k = rate constant of recombination reaction; $\bar{q}$ = average surface area/drop of mercury; i_k = kinetic current; t = drop time; K = dissociation constant of the reducible acid; $\varkappa$ = Ilkovic constant (for definition see footnote 2); $i_\infty = i_k$ for $k = \infty$.

This resulted in equation

$$\frac{i_k}{i_\infty} = \frac{0{\cdot}57\sqrt{\frac{kt}{K}}\,[\mathrm{H^+}]}{1 + 0{\cdot}57\sqrt{\frac{kt}{K}}\,[\mathrm{H^+}]} \qquad (2)$$

Recently KOUTECKY[6] in a brilliant mathematical paper has solved the system rigorously and has shown that the solution expressed as a table of values is sufficiently approximated by the expression

$$\frac{i_k}{i_\infty} = \frac{0{\cdot}87\sqrt{\frac{kt}{K}}\,[\mathrm{H^+}]}{1 + 0{\cdot}87\sqrt{\frac{kt}{K}}\,[\mathrm{H^+}]} \qquad (3)$$

which is identical with (2) except for the absolute value of the coefficient.

In this paper the asymptotic equation (3) will be used throughout.

The recalculation of our previous results[1] for the pK of phenylglyoxylic acid = 1·39 gives

$$k_{(\mathrm{H_3O^+})} = 3{\cdot}9 \times 10^{11}\ L\ \mathrm{mol^{-1}\,s^{-1}}$$
$$k_{(\mathrm{H_2O})}\ \mathrm{H_2O} = 150\ \mathrm{s^{-1}}$$
$$k_{(\mathrm{H_3BO_3})} = 4{\cdot}41 \times 10^{3}\ L\ \mathrm{mol^{-1}\,s^{-1}}$$

From the present data in neutral solution (Table) under the assumption that hydronium ions are the only important proton donors in neutral solution, $k_{(\mathrm{H_3O^+})}$ has been calculated to be $3{\cdot}58 \times 10^{11}\ L\ \mathrm{mol^{-1}\,s^{-1}}$. The recalculation of data on phenylglyoxylic acid of KOUTECKÝ and BRDIČKA[7] using equation (3), $pK = 1{\cdot}39$ and introducing $f_{(\mathrm{H^+})} = 0{\cdot}80$ gave $k_{(\mathrm{H_3O^+})} = 4{\cdot}77 \times 10^{11}\ L\ \mathrm{mol^{-1}\,s^{-1}}$.

The value determined in the meantime by HANS and HENKE[8] is $4 \times 10^{11}\ L\ \mathrm{mol^{-1}\,s^{-1}}$.

These three different values show not only the measure of accuracy but also show that the $k_{(\mathrm{H_3O^+})}$ as determined in strongly alkaline solution is identical within experimental errors with this constant determined in neutral solution.

We have made measurements with phenylglyoxylic acid in heavy water (99·1% D_2O) under the same conditions as in ordinary water and found $k_{(\mathrm{D_3O^+})} = 7{\cdot}65 \times 10^{10}\ L\ \mathrm{mol^{-1}\,s^{-1}}$. The ratio of the rates in H_2O and D_2O was

$$\frac{k_{(\mathrm{H_3O^+})}}{k_{(\mathrm{D_3O^+})}} = 4{\cdot}7 .$$

A series of substituted phenylglyoxylic acids was prepared and the recombination velocity constant of each was determined (see Table).

From the data it is possible to calculate HAMMETT's σ and ϱ constants for the *para*-methoxy and *para*-methyl substituted acids.

The substituent constant $\sigma = \log K_i - \log K_i^\circ$ [9].

Where k_i = ionisation constant of substituted acid; k_i° = ionisation constant of unsubstituted acid = $pK^\circ - pK$.

Then, $\sigma\ p\text{-OCH}_3 = -\,0{\cdot}26$ and $\sigma\ p\text{-CH}_3 = -\,0{\cdot}13$.

The average values quoted by HAMMETT[9] are

$$\sigma_{p\text{-OCH}_3} = -0{\cdot}27 \text{ and } \sigma_{p\text{-CH}_3} = -0{\cdot}17.$$

The reaction constant ϱ can be calculated also using the HAMMETT equation[9].

$$\log k - \log k^\circ = \sigma\varrho .$$

Where k = reaction constant for substituted acid; k° = reaction constant for unsubstituted acid.

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[*] By an error in our paper [K. WIESNER, M. WHEATLEY, and J. M. LOS, J. Amer. chem. Soc. *76*, 4858 (1954)] the computed pK of phenylglyoxylic acid was reported as 2·3 instead of 1·3. While this does not change any of the conclusions of this publication, it changes the absolute values of kH_3O^+, $k\mathrm{H_2O}$ and $k\mathrm{H_3BO_3}$. A new determination of the pK has now given the value 1·39. This is the value for which the results of our measurements in alkaline solution were recalculated and are given in the text for comparison with the present results.

[1] K. WIESNER, M. WHEATLEY, and J. M. LOS, J. Amer. chem. Soc. *76*, 4858 (1954).

[2] For a general reference on theoretical polarography see: I. M. KOLTHOFF, *Polarography* Vol. 1. 2nd ed. (Interscience Publishers Inc., 2505th Ave., New York 1, N. Y.).

For information on the theory of determination of extremely rapid reaction rates from polarographic kinetic waves see: R. BRDIČKA, *Die Kinetik der Elektrodenvorgänge in der Polarographie. – Proceedings of the 1st International polarographic congress in Prague.* Part. III (Přirodevědecké Vydavatelství 1951), p. 332. – K. WIESNER, *Concept of Polarographic Currents Limited by Rate of a Chemical Reaction and Some of Its Applications*), Analyt. Chem. *27*, 1712 (1955). – P. DELAHAY, *New Instrumental Methods in electrochemistry* (Interscience Publishers, New York, 1954).

[3] K. WIESNER, Chem. Listy *41*, 6 (1947). – J. KOUTECKÝ and R. BRDIČKA, Coll. Czech. chem. Communic. *12*, 337 (1947).

[4] K. WIESNER, Chem. Listy *41*, 6 (1947).

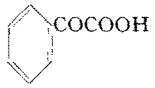
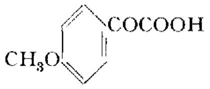
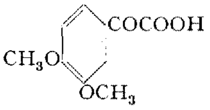
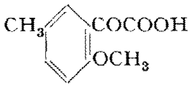
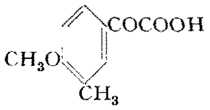
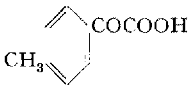
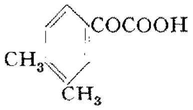
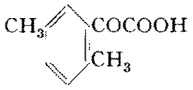
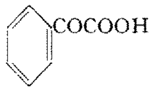
[5] R. BRDIČKA and K. WIESNER, Chem. Listy *40*, 66 (1946).

[6] J. KOUTECKÝ, Coll. Czech. chem. Communic. *18*, 597 (1953).

[7] J. KOUTECKÝ and R. BRDIČKA, Coll. Czech. chem. Communic. *12*, 337 (1947).

[8] W. HANS and K. H. HENKE, Z. Elektrochem. *57*, 595 (1953).

[9] L. P. HAMMETT, *Physical Organic Chemistry* (McGraw Hill, London and New York 1940), p. 186.

Acid	Dissociation Constant K	pK	Polarographic pK	Recombination k mol^{-1} s^{-1}	Droptime t s	Dissociation k' l' mol^{-1} s^{-1}
	$4{\cdot}07 \times 10^{-2}$	1·39	6·81	$3{\cdot}58 \times 10^{11}$	4·1	$1{\cdot}46 \times 10^{10}$
	$2{\cdot}25 \times 10^{-2}$	1·65	6·78	$1{\cdot}24 \times 10^{11}$	3·5	$2{\cdot}77 \times 10^{9}$
	$1{\cdot}63 \times 10^{-2}$	1·79	7·52	$4{\cdot}13 \times 10^{12}$	3·64	$6{\cdot}70 \times 10^{10}$
	$2{\cdot}4 \times 10^{-2}$	1·62	6·92	$4{\cdot}42 \times 10^{11}$	3·64	$1{\cdot}06 \times 10^{10}$
	$1{\cdot}66 \times 10^{-2}$	1·78	7·05	$4{\cdot}85 \times 10^{11}$	3·64	$8{\cdot}06 \times 10^{9}$
	$3{\cdot}0 \times 10^{-2}$	1·52	6·80	$2{\cdot}79 \times 10^{11}$	3·64	$8{\cdot}44 \times 10^{9}$
	$4{\cdot}4 \times 10^{-2}$	1·36	6·96	$8{\cdot}44 \times 10^{11}$	3·64	$3{\cdot}68 \times 10^{10}$
	$3{\cdot}55 \times 10^{-2}$	1·45	7·26	$2{\cdot}73 \times 10^{12}$	3·64	$9{\cdot}68 \times 10^{10}$
 in D$_2$O	$1{\cdot}59 \times 10^{-2}$	1·79	6·69	$7{\cdot}65 \times 10^{10}$	4·40	$1{\cdot}24 \times 10^{9}$

Plotting log k against σ for the para-substituted acids and for the unsubstituted acid we obtain a straight line the gradient of which gives $\varrho = 1{\cdot}43$.

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Zusammenfassung

Die Rekombinationsgeschwindigkeit von Phenylglyoxylationen und Hydroniumionen wird aufs neue in neutraler Lösung bestimmt, und es wird gezeigt, dass sie dem Wert, der von uns früher in alkalischer Lösung gefunden wurde, entspricht. Beide Werte stimmen auch mit den Literaturangaben überein.

Die Rekombinationsgeschwindigkeiten einer Serie von substituierten Phenylglyoxylsäuren und die Rekombinationsgeschwindigkeit von Phenylglyoxylat- und Deuteroniumionen werden angegeben.

In Vitro Calcification of Collagen

We have found that under suitable conditions it is possible to obtain calcium phosphate inside collagen fibres in the form of hydroxyapatite. This was observed in the course of a series of studies undertaken in continuation of the observations on the oriented crystallization of soluble inorganic salts in collagen[1]. Several insoluble compounds like silver oxide, white lead, calcium fluoride and calcium carbonate could be crystallized inside collagen fibres by keeping them in solutions containing suitable concentrations of the required ions. Attempts were then made to precipitate calcium phosphate from Ringer solution, mixtures of mono- and disodium phosphate solutions with calcium chloride solution and small variations of these, but they were not successful. Sometimes calcium carbonate or calcium orthophosphate dihydrate crystallized in the collagen but only slightly. However, if collagen fibres are kept in a water suspension of precipitated calcium phosphate (B.D.H.) then an excellent precipitation of hydroxyapa-

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[1] G. N. RAMACHANDRAN and G. K. AMBADY, Exper. *11*, 343 (1955).