

793. *The Kinetics of Hydrogen Isotope Exchange Reactions. Part VIII.* Hydrogen Exchange between Aromatic Compounds and Aqueous Solutions of Weak Acids. Hammett's Acidity Function in Such Solutions.*

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Existing measurements of Hammett's acidity function, H_0 , for aqueous solutions of dichloroacetic acid, trifluoroacetic acid, and potassium hydrogen sulphate have been supplemented. Previous data for potassium hydrogen sulphate have been found in error; the acidity scale for it is reproducible and consistent with expectations based on the scales exhibited by other weak inorganic acids. The scale for dichloroacetic acid lacks generality, and no increase in indicator ionisation is observed when small quantities of water are added to the effectively anhydrous acid. This behaviour is discussed in the light of Bruckenstein and Kolthoff's results for acetic acid.

Previous kinetic work in aqueous solutions of weak acids is discussed in connection with the new H_0 data. In particular, Bell and Brown's conclusions, from their study of the decomposition of paraldehyde in aqueous potassium hydrogen sulphate solutions, are revised.

Measurements of the rate of the tritium isotope exchange between nuclear-labelled 1 : 2 : 3-trimethoxybenzene and the aforementioned acidic systems are reported. The pattern of the results is similar to that observed for the decomposition of paraldehyde.

FOR aqueous solutions of moderately weak acids, relatively few measurements of Hammett's acidity function¹ have been reported.² Those which are derived from studies^{3,4} with trifluoro- and trichloro-acetic acids, dichloroacetic acid, and potassium hydrogen sulphate are of special interest arising from the fact that, unlike the H_0 values² exhibited by other *mineral* acids, both of comparable and greater strengths, they exhibit extensive regions where H_0 appears to change little, if at all, with acid concentration. Few indicators were used in these studies and a tentative, yet attractive, explanation of the behaviour of the *organic* acid solutions, in terms of large specific salting-in effects, has been advanced,² but this cannot cover the simple mineral acid potassium hydrogen sulphate, whose reported behaviour therefore appears particularly strange.

Of the many⁵ acid-catalysed reactions whose rates are normally governed by H_0 , only two, the hydrolysis of sucrose⁶ and the decomposition of paraldehyde,⁴ have been studied with the weak acids mentioned above. The former reaction in solutions of trichloroacetic acid, and the latter in tri- and di-chloroacetic acid solutions and in solutions of potassium hydrogen sulphate, appear to depart from their usual dependence on H_0 : their rates continue to increase when H_0 approaches constancy. Large specific salt effects can again be invoked⁵ in explanation for the organic acids but hardly for potassium hydrogen sulphate. The operation of an additional reaction mechanism is an alternative explanation.⁴

To throw more light on these matters, and on the general status of Hammett's function for weak acids, (a) the acidity-function measurements for dichloroacetic acid-water mixtures have been extended to cover the entire composition range, (b) the more dilute solutions of this acid, and also those of trifluoroacetic acid and potassium hydrogen sulphate, have been studied with additional indicators, and (c) an acid-catalysed reaction, namely

* Part VII, *J.*, 1958, 1927.

¹ Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co. Inc., New York, 1940.

² Paul and Long, *Chem. Rev.*, 1957, **57**, 1.

³ Randles and Tedder, *J.*, 1955, 1218.

⁴ Bell and Brown, *J.*, 1954, 774.

⁵ Long and Paul, *Chem. Rev.*, 1957, **57**, 935.

⁶ Hantzsch and Weissberger, *Z. phys. Chem.*, 1927, **125**, 251.

aromatic hydrogen isotope exchange, whose rate is normally controlled by H_0 , but which is of a different type from both the sucrose hydrolysis and the paraldehyde decomposition, has been studied in these weakly acidic solutions.

EXPERIMENTAL

Acidity-function Measurements.—These were made, by standard methods,^{2, 7} with a Beckman spectrophotometer at $23^\circ \pm 2^\circ$. For all solutions, including the nearly anhydrous region of dichloroacetic acid–water mixtures, ϵ_B , the maximum extinction coefficient of the basic form of an indicator, was taken to be equal to its value determined in water. In justification of this procedure, weakly basic indicators such as 6-bromo-2:4-dinitroaniline in anhydrous dichloroacetic acid, and 4-chloro-2-nitroaniline, *o*-nitroaniline, and *p*-nitrodiphenylamine in acetic acid, showed ϵ_B in every case to be within *ca.* 4% of the value obtained in water. H_0 was calculated from the best pK_a values given by Paul and Long.²

Hydrogen-exchange Experiments.—The level of acidity in solutions of weak acids is necessarily low, so a more reactive aromatic compound than had been studied^{8, 9} was needed if the exchange rate was to be conveniently measurable at ordinary temperatures. The partial rate factors for anisole,⁹ and the known dependence⁸ of the aromatic hydrogen exchange rate on H_0 , suggested that 1:2:3-trimethoxybenzene would be suitable, as was found to be so, although it was less reactive than expected.¹⁰ The equivalent positions *ortho* to the 1- and the 3-methoxyl group must be *ca.* 10^6 times more reactive than the remaining 5-position. As before, the exchange was studied as the loss of heavy isotope from the aromatic compound to an excess of light solvent. In other work we have used deuterium, and followed the exchange by infrared analysis. This technique requires a monodeuterated material, and $[^2H_1]1:2:3$ -trimethoxybenzene is not readily accessible. Tritium was therefore used as the label. Tritiated material was prepared (as below) and the rate of loss of tritium to an excess of the acid mixture in question, measured under homogeneous conditions. In these circumstances, the rate constants are of the first order.

The exchange was followed by the same general method for all the acid mixtures. Tritiated compound was dissolved in acid contained in flasks fitted with ground-glass stoppers, and immersed in a thermostat bath at 25° . After known periods samples were withdrawn, diluted with water, and (for trifluoro- and dichloro-acetic acids) neutralised with concentrated cooled sodium hydroxide. (Enough acid mixture to contain *ca.* 0.08 g. of trimethoxybenzene was taken. This weight and the substrate solubility determined the volumes employed. In no case was the substrate concentration allowed to exceed 0.04M.) The neutralised solution was extracted with ether, and the ether extract kept over calcium chloride and a little anhydrous sodium carbonate. Evaporation of the ether left crystalline material of good m. p.

The tritium content of a sample was found by scintillation counting. A weighed amount was dissolved in a scintillation solution containing xylene and the scintillators PPO (2:5-diphenyloxazole) and POPOP [1:4-di-(5-phenyloxazol-2-yl)benzene]. It was counted with standard equipment. The tritium content of a sample was thus compared with that of the original material, and the exchange followed. Good first-order exchange rate constants (λ) were obtained (Tables 4, 5, and 6).

Materials.—(a) Potassium hydrogen sulphate of highest available commercial purity was used. Both the crystalline and fused products were employed. (b) Pure dichloroacetic acid decomposes with time. An aged sample, diluted with water, gave a faint white precipitate with silver nitrate. "Purified" commercial samples also reacted in this way. Reasonably anhydrous material (0.05M-water by Karl Fischer titration), which gave no precipitate with silver nitrate, was prepared by a preliminary drying ($CaSO_4$) followed by vacuum distillation at 1–2 mm. Aged samples were redistilled at this pressure before use. (c) Trifluoroacetic acid was as supplied by Columbia Organic Chemicals Ltd. (d) *p*-Nitroaniline, *o*-nitroaniline, 4-chloro-2-nitroaniline, diphenylamine, and *p*-nitrodiphenylamine were recrystallised samples of m. p. 148° , 71.6° , 116° , 54° , and 135° respectively. (e) 1:2:3-Trimethoxybenzene, m. p. 46° , was prepared by Olivero and Bargellini's method¹¹ from pyrogallol. It was tritiated by

⁷ Satchell, *J.*, 1958, 1916.

⁸ Gold and Satchell, *J.*, 1955, 3609.

⁹ Satchell, *J.*, 1956, 3911.

¹⁰ Satchell, to be published.

¹¹ Olivero and Bargellini, *Gazzetta*, 1948, 78, 372.

dissolving it in an acidified 24.4 moles % ethanol-water mixture, of known $^{12}H_0$, containing tritiated water. After an appropriate interval, based on the expected exchange rate at 25°, the mixture was neutralised with sodium hydroxide and diluted with water, thus precipitating the product. This was well washed with water and dried. Tests for incomplete methylation were negative, and tritiated material dissolved in ethanol-water and immediately re-isolated suffered a negligible change in activity. The observed counting rate indicated that exchange equilibrium was incompletely established at the 4- and the 6-position. Exchange at the 5-position should, therefore, have been negligible, as was confirmed by the linearity of the first-order plots.

TABLE 1(a). *Acidity function in dichloroacetic acid-water mixtures as determined by (a) p-nitroaniline, (b) diphenylamine, (c) o-nitroaniline, (d) 4-chloro-2-nitroaniline, and (e) p-nitrodiphenylamine.*

CHCl ₂ ·CO ₂ H (M) ...	0.05	0.12	0.24	0.48	1.21	2.42	4.84
H ₀ by (a)	1.50	1.18	0.95	0.75	0.61	0.60	0.60
H ₀ by (b)	1.52	1.21	0.99	0.76	0.56	0.35	-0.05
H ₀ by (c)	—	—	—	—	0.66	0.64	0.64
CHCl ₂ ·CO ₂ H (M) ...	7.26	8.47	9.68	10.16	10.89	12.13	
H ₀ by (a)	0.38	0.17	-0.35	—	—	—	—
H ₀ by (c)	0.50	—	-0.20	-0.39	-0.74	—	—
H ₀ by (d)	—	0.40	-0.10	-0.22	-0.56	-0.74	—
H ₀ by (e)	—	—	—	-0.97	-1.26	-1.57	—

TABLE 1(b). *Effect of added water on the acidity of nearly anhydrous dichloroacetic acid (0.05M-H₂O) as indicated by (a) 4-chloro-2-nitroaniline and (b) p-nitrodiphenylamine.*

Total H ₂ O (M) ...	0.05	0.14	0.24	0.61	1.05	1.84	3.52	5.05
H ₀ by (a)	-0.74	-0.74	-0.73	-0.72	—	-0.70	-0.65	-0.60
H ₀ by (b)	-1.57	-1.57	-1.56	—	-1.54	—	-1.46	-1.40

TABLE 2. *Acidity function in potassium hydrogen sulphate-water mixtures as determined by (a) p-nitroaniline, (b) diphenylamine, and (c) o-nitroaniline.*

KHSO ₄ (M)	0.25	0.50	1.00	1.50	2.00	2.25	
H ₀ by (a)	0.96	0.66	0.35	0.15	-0.03	-0.14	
H ₀ by (b)	—	0.70	0.38	0.15	-0.01	—	
H ₀ by (c)	—	0.67	0.34	0.12	-0.04	-0.15	

TABLE 3. *Acidity function in trifluoroacetic acid-water mixtures as determined by (a) o-nitroaniline, and (b) diphenylamine.*

CF ₃ ·CO ₂ H (M)	0.99	2.16	4.04	5.39	6.73	
H ₀ by (a)	0.09	-0.12	-0.28	-0.42	-0.64	
H ₀ by (b)	0.24	-0.07	-0.19	-0.37	—	

TABLE 4. *Rate of loss of tritium from [4: 6-³H]1 : 2 : 3-trimethoxybenzene in aqueous potassium hydrogen sulphate at 25°.*

KHSO ₄ (M)	0.50	1.00	2.00	2.50
10 ⁷ λ (sec. ⁻¹)	1.84	4.41	10.5	14.4

TABLE 5. *Rate of loss of tritium from [4: 6-³H]1 : 2 : 3-trimethoxybenzene in aqueous dichloroacetic acid at 25°.*

CHCl ₂ ·CO ₂ H (M)	0.12	0.24	1.21	2.42	4.84	7.24	12.13
10 ⁷ λ (sec. ⁻¹)	0.34	0.48	1.51	2.40	6.0	11.0	12.30

TABLE 6. *Rate of loss of tritium from [4: 6-³H]1 : 2 : 3-trimethoxybenzene in aqueous trifluoroacetic acid at 25°.*

CF ₃ ·CO ₂ H (M)	0.99	2.16	4.04	6.73
10 ⁷ λ (sec. ⁻¹)	4.80	12.2	49.8	137

RESULTS AND DISCUSSION

Acidity Functions.—(a) *Dichloroacetic acid-water mixtures.* The only previous data for this system are those of Bell and Brown.⁴ They used one indicator, *p*-nitroaniline,

¹² Satchell, *J.*, 1957, 3524.

and dichloroacetic acid concentrations below 5M. The results given in Table 1 were obtained with five indicators, and cover the composition range from *ca.* 0.05M to the almost anhydrous acid (12.1M-acid, 0.05M-water). The region close to the pure acid was studied in some detail.

Several points of interest emerge. In the dilute acid region (below 5M) the values for *p*-nitroaniline agree only moderately well with Bell and Brown's. 0.99 being used as pK_a of *p*-nitroaniline, the present values lie *ca.* 0.1 unit above Bell and Brown's at 4M and fall off more slowly at lower acidities. The data for *o*-nitroaniline agree well with the new values for *p*-nitroaniline. The same is true for diphenylamine at acid concentrations below 0.5M. However, above this point diphenylamine indicates a continued rise in acidity and does not show the H_0 plateau exhibited by *p*- and *o*-nitroaniline between *ca.* 1M and 3M. These findings support Paul and Long's suggestion² that appreciable salting-in of indicators by the organic acid is responsible for the H_0 plateau, and that indicators of different structural type should show specific effects. Thus *p*- and *o*-nitroaniline behave much the same, whereas diphenylamine exhibits divergent behaviour when the acid concentration becomes appreciable.

The more concentrated region (above 5M) has been covered with the indicators *o*-nitroaniline, 4-chloro-2-nitroaniline, and *p*-nitrodiphenylamine. Above *ca.* 5M there is no agreement at all between the data produced by these indicators, though between 7M and 11M their trends are similar. Some change in behaviour is expected⁷ in view of the alteration in the character of the medium, from one of high to one of low dielectric constant, which is occurring. Changes in the relative basicities of the indicators are expected,⁷ and in the effectively anhydrous solvent 4-chloro-2-nitroaniline gives $H_0 = -0.74$ in comparison with -1.57 given by *p*-nitrodiphenylamine. Similar discrepancies occur in the literature concerning anhydrous trifluoroacetic acid.¹³ Too much weight is not, however, to be attached to the absolute values of H_0 in the nearly anhydrous region, since determinations seemed somewhat dependent on impurities other than water.

The present results for dichloroacetic acid imply that, at least for aqueous solutions, the H_0 scale for this weak acid is not useful: it is not independent of the indicator used in its determination.

A final point of interest concerns the almost anhydrous region. Bruckenstein and Kolthoff¹⁴ have shown that with acetic acid, indicators which are partly ionised in the anhydrous solvent become more so on the addition of small quantities of water—a base in this medium. They explain the phenomenon by the formation of triple and quadruple ions, involving protonated water molecules. Although these authors did not carry their experiments so far, there must come a time, as more water is added, when its effect as a base in lowering the overall acidity of the medium begins to outweigh its effect in promoting ion association. Thus, with suitable indicators, an acidity maximum should be observed in acetic acid. Since the dielectric constants of acetic and dichloroacetic acids are not very different, a similar phenomenon might be expected in the latter. The relevant data in Table 1(b), although not very accurate, imply that no maximum exists, although the decrease in acidity on addition of water is at first very slow. The reason for the absence of the marked effects shown in acetic acid is probably to be found in the greater strength of the substituted acid. The addition of water will have a much more pronounced effect on the acidity, and its rôle as a base will, therefore, quickly become dominant.

(b) *Potassium hydrogen sulphate-water mixtures.* The previous data here are again those of Bell and Brown,⁴ who used *p*-nitroaniline, and acid concentrations up to 2.7M. The values for *p*-nitroaniline have now been redetermined, and measurements made with diphenylamine and *o*-nitroaniline over the same concentration range (Table 2). The previous authors found an H_0 plateau above *ca.* 1M. In the present study no such region has been found, but rather a general increase in acidity with concentration. Furthermore,

¹³ Kilpatrick and Hyman, *J. Amer. Chem. Soc.*, 1958, **80**, 77; Van Dijke Tiers, *ibid.*, 1956, **78** 4165.

¹⁴ Bruckenstein and Kolthoff, *J. Amer. Chem. Soc.*, 1956, **78**, 10.

all three indicators give values which are in very reasonable mutual agreement. The behaviour now exhibited is that expected from aqueous solutions of a relatively weak inorganic acid. It is concluded that the H_0 scale for solutions of potassium hydrogen sulphate is useful, for it seems very likely that other indicators will also give values in agreement with these now obtained. The position of this acid, among weak acids in general, no longer appears anomalous. In Fig. 1 the data are compared with those for hydrogen fluoride and phosphoric acid in the same concentration region.² Potassium hydrogen sulphate takes its proper place, being slightly stronger than phosphoric acid.

(c) *Trifluoroacetic acid-water mixtures.* Randles and Tedder³ studied this system using *o*- and *p*-nitroaniline and 4-chloro-2-nitroaniline. Measurements with *o*-nitroaniline give values in reasonable agreement with theirs (Table 3). Diphenylamine gives data which are, on the average, 0.09 unit more positive, but which, in contrast to the behaviour shown in dichloroacetic acid, show no marked tendency to decrease rapidly with increasing acid concentration. The change in indicator structure involved thus has less effect on the reproducibility of the H_0 scale in this case.

FIG. 1. *Acidity functions for weak acids (a) HF, (b) H₃PO₄, (c) KHSO₄.*

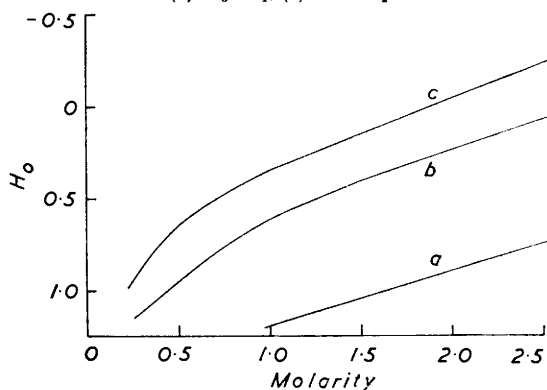
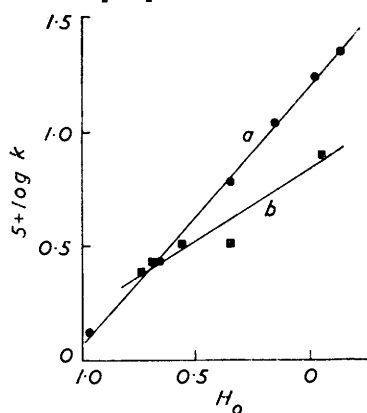


FIG. 2. *Decomposition of paraldehyde in weak acids (a) KHSO₄, (b) CHCl₂-CO₂H.*



Previous Studies of Acid Catalysis in Solutions of Weak Acids.—There have been only two such studies in which correlations between rates and H_0 were to be expected. These concern (a) the decomposition of paraldehyde, and (b) the hydrolysis of sucrose.

(a) The paraldehyde decomposition was studied by Bell and Brown⁴ who used aqueous solutions of potassium hydrogen sulphate and of dichloro- and trichloro-acetic acids. They showed that in the common aqueous mineral acids the rate of decomposition is controlled by H_0 but that for the above three acids the rate appeared to increase faster than H_0 required. However, for potassium hydrogen sulphate a plot (Fig. 2) of their rate constants against the amended acidity data gives a very good straight line of slope 1.12, in close agreement with that found for the other mineral acids. The mechanism of the paraldehyde decomposition in aqueous hydrogen sulphate is thus identical with that obtaining in solutions of the other inorganic acids, and there is no discrepancy in need of explanation, either in terms of salt effects or of additional reaction paths.

For dichloroacetic acid the decomposition rates do not correlate badly with the amended H_0 data for *p*-nitroaniline, apart from the last point. They increase *less* rapidly than the data for diphenylamine demand (Fig. 2). Bearing the lack of generality of the acidity scale for dichloroacetic acid in mind, we see that there is no clear evidence of a lack of dependence of rate on H_0 . The reaction mechanism in this medium seems very likely to be much the same as in aqueous solutions of inorganic acids.

It is thus only trichloroacetic acid for which any problem remains. Here there exists

a real divergence between existing H_0 data and reaction rate. Further discussion is deferred.

(b) The rate of hydrolysis of sucrose, which correlates with H_0 in aqueous mineral acids, also fails to do so in aqueous trichloroacetic acid, the only weak acid in which the reaction has been studied.⁵

Aromatic Hydrogen Isotope Exchange.—(a) *Status of the reaction.* The acid-catalysed decomposition of paraldehyde can be accomplished by Lewis, as well as by Brønsted acids.¹⁵ The fact that the reaction is, in essence, only an electronic rearrangement, suggests that it may be particularly prone to catalysis by a variety of paths. The acid-catalysed hydrolysis of sucrose is complex, and may also be particularly susceptible to catalysis by more than one route. Both these reactions must involve electrophilic attack on oxygen when the catalyst is a Brønsted acid.

Aromatic hydrogen isotope exchange was chosen for this study because the acid-catalysed process is relatively simple, and must involve Brønsted acids. The electrophilic attack is also on carbon, rather than on oxygen. The reaction is thus of a different type from the two previously studied in these solvents.

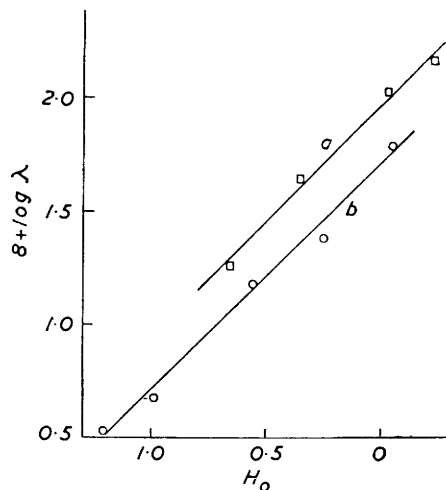


FIG. 3. *Hydrogen isotope exchange in weak acids (a) KHSO_4 , (b) $\text{CHCl}_3\text{-CO}_2\text{H}$.*

In aqueous solutions of the mineral acids the exchange rate follows H_0 for all the aromatic compounds so far studied,¹⁶ including trimethoxybenzene.¹⁰ Correlation is exhibited also in solutions of such acids in anhydrous acetic⁹ and trifluoroacetic acid.¹⁷ Whether the mechanism, under these conditions, involves a rapid pre-equilibrium followed by a rate-determining rearrangement of the conjugate acid of the aromatic compound or, alternatively, a slow proton transfer, is still debated.⁵

(b) *Potassium hydrogen sulphate-water mixtures.* Four different mixtures were studied covering the range 0.5—2.5M. The first-order exchange rate constants are collected in Table 4. Plotted against the appropriate H_0 values* (Fig. 1) they produce a good straight line of slope 1.02 (Fig. 3). This correlation is to be expected in view of the behaviour of the paraldehyde decomposition previously discussed. It seems that potassium hydrogen sulphate-water mixtures will prove suitable media for experiments

* For these acid mixtures, as for the others discussed below, measurements were made of the effect of the dissolved trimethoxybenzene on the value of H_0 . In all cases the acidity was decreased. For potassium hydrogen sulphate solutions the change was negligible. For the other solutions the change was larger (though in no case greater than 0.1 unit) but sufficiently constant for no significant error to be introduced by using the data given in Tables 1 and 3.

¹⁵ Bell and Skinner, *J.*, 1952, 2955.

¹⁶ Gold and Satchell, *J.*, 1955, 3619; see also refs. 8 and 9.

¹⁷ Mackor, Smit, and van der Waals, *Trans. Faraday Soc.*, 1957, **53**, 1309.

of the Zucker-Hammett design,⁵ always provided that general acid-catalysed reaction rates do not fortuitously correlate with H_0 also. This point remains to be established.

(c) *Dichloroacetic acid-water mixtures*. Seven mixtures, with acid contents ranging from 0.1 to 7.3M, were used, and the rate was also measured in the anhydrous solvent. The rate constants are collected in Table 5, and plotted against H_0 , as measured by diphenylamine, in Fig. 3. The correlation is fairly good. The rate in the anhydrous solvent is also roughly what one might expect on the basis of the data in Table 1. There is clearly no marked departure from correlation with indicator ionisation. This finding is again in keeping with the behaviour of paraldehyde. The fact that the exchange rates in aqueous dichloroacetic acid and potassium hydrogen sulphate are not quite the same at the same value of H_0 was rather to be expected in view of previous work.¹⁸

(d) *Trifluoroacetic acid-water mixtures*. Acid catalysis in this system does not appear to have been studied previously. Four mixtures were used varying from 1.0 to 6.7M-acid, *i.e.*, covering the H_0 plateau region. The exchange rate constants are given in Table 6. In this system, as found previously for trichloroacetic acid, the reaction rate increases faster than existing H_0 data demand. These, while admittedly very limited, indicate some generality for the function, so it appears likely that some additional, and probably synchronous, mechanism, involving catalysis by the un-ionised organic acid molecule operates for hydrogen exchange in trifluoroacetic acid solutions, and possibly also for the hydrolysis of sucrose and the decomposition of paraldehyde in trichloroacetic acid solutions.

Whether any such mechanism is important for these reactions in dichloroacetic acid is not yet possible to decide. There is still no need to postulate one. In any case, it will be rendered less prominent by the fact that the hydrogen atom of dichloroacetic acid is less electrophilic than those of trichloro- and trifluoro-acetic acids.

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¹⁸ Gold and Satchell, *J.*, 1955, 3622.
