The Kinetics of Hydrogen Isotope Exchange Reactions. Part IV. A Comparison of the Exchange Reactivity of Different Aqueous Acids.*

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The rates of loss of deuterium from *p*-chloro[*o*-^{2}H]phenol in aqueous phosphoric acid and from [*o*-^{2}H]*p*-cresol in aqueous hydrochloric acid have been studied as a function of the acid concentration. The velocities obtained are found to be related to Hammett's acidity function H_0 in a similar way to those for the same compounds in aqueous sulphuric acid (see Part II, *J.*, 1955, 3609), but there are quantitative differences in behaviour between the different acids.

It was shown in Part II that, in sulphuric acid solution, the logarithm of the rate of hydrogen isotope exchange was a linear function of Hammett's acidity function H_0 with a slope close to the theoretical value of -1. If this correlation is, in fact, significant and not just fortuitous in the particular case of sulphuric acid, then the same relation should be obeyed when other acids are used. This point has been tested in the present investigation.

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* Part III, preceding paper.

Experimental.—The reagents and experimental methods used were the same as those described in Part II (*loc. cit.*). The results are tabulated below.

Rate of loss of deuterium from [*o*-^{2}H] p-*cresol in aqueous hydrochloric acid.*

HCl (wt. %)	7·10	11·66	15·16	21·55
$-H_0$ ⁽¹⁾	0·58	0·98	1·31	1·90
$10^7\lambda$ (sec.$^{-1}$) ⁽²⁾	3·95	13·3	38·9	306·0

⁽¹⁾ Taken from Hammett and Paul, *J. Amer. Chem. Soc.*, 1934, **56**, 828. ⁽²⁾ Defined by equation (1), Part II (*loc. cit.*).

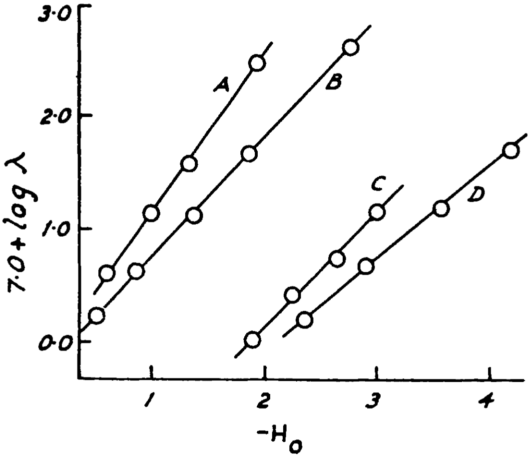
Rate of loss of deuterium from p-*chloro*[*o*-^{2}H]*phenol in aqueous phosphoric acid.*

H_3PO_4 (wt. %)	63·6	68·1	72·7	76·4
$-H_0$ ⁽¹⁾	1·90 ± 0·1	2·25 ± 0·1	2·65 ± 0·1	3·00 ± 0·1
$10^7\lambda$ (sec.$^{-1}$) ⁽²⁾	1·17	2·67	5·6	14·8

⁽¹⁾ Taken from Heilbronner and Weber, *Helv. Chim. Acta*, 1949, **32**, 1513. ⁽²⁾ Defined by equation (1), Part II.

DISCUSSION

The results of this investigation follow the same general pattern as those reported in Part II, in that the rates are again found to depend on Hammett's acidity function, log λ being linearly related to $-H_0$. For *p*-chlorophenol in phosphoric acid and in sulphuric acid, the respective slopes of the graphs are 1·00 and 0·90. For *p*-cresol in hydrochloric acid the slope is 1·42, and in sulphuric acid it is 1·08. From the Figure it can be seen that, because of these differences in slope, the rate constants referring to different acids diverge with increasing acidity. If produced to lower acidities both pairs of lines intersect at H_0 = 0·5—0·0. At the highest acidities, values for log λ obtained with different acids at the same value of H_0 differ by as much as 0·4 unit.



Dependence of exchange rate on acidity.
A, p-*Cresol in* HCl.
B, p-*Cresol in* H_2SO_4.
C, p-*Chlorophenol in* H_3PO_4.
D, p-*Chlorophenol in* H_2SO_4.

Divergences from the theoretical slope and differences in the detailed behaviour of different acids have been reported before in connection with reactions whose velocities are related to H_0, *e.g.*, the hydrolysis of methylal (Long and McIntyre, *J. Amer. Chem. Soc.*, 1954, **76**, 3240, 3243) and of acetic anhydride (Gold and Hilton, *J.*, 1955, 843). The present results bear marked qualitative similarities to these earlier data (which also refer to the same acidity region) and may be usefully compared with them.

For the hydrolysis of methylal, Long and McIntyre found that the plot of log *k* against $-H_0$ showed a slope of ∼1·25 for hydrochloric acid and ∼1·15 for sulphuric acid, and their rates, like ours, are equal at H_0 ∼0·5 but diverge towards high acidities, those in hydrochloric acid being the faster. These authors have given a semiquantitative explanation of the different divergences from unit slope in the various acids in terms of specific salt effects. On this basis, since the deuterium exchange involves a different substrate from the hydrolysis, an exact agreement between the two reactions is hardly to be expected, as this would imply a fortuitous identity of the salt effects in the two cases. However, the observed parallelism indicates a similar behaviour of the relevant activity coefficients in the two acids.

The data on the hydrolysis of acetic anhydride refer to sulphuric acid, hydrochloric acid, and phosphoric acid so that a more complete comparison with our exchange data is possible. Gold and Hilton found that for these three acids the slopes of the log k against $-H_0$ plots were 0·96, 1·33, and 0·86 respectively. For both reactions the hydrochloric acid and phosphoric acid plots lie above that for sulphuric acid. Here again therefore the results show a similar trend and the departures from ideal behaviour in the two cases probably have similar origins.

The rather steep slopes recorded above for the reactions in hydrochloric acid may be partly due (and this suggestion is made with considerable diffidence) to slight inaccuracies in the (rather old) H_0 data (Hammett and Paul, *J. Amer. Chem. Soc.*, 1934, **56**, 828) used in plotting the graphs in all three investigations. If data taken from more recent but less extensive measurements (Braude, *J.*, 1948, 1971; Paul, *J. Amer. Chem. Soc.*, 1954, **76**, 3236) are used, the slopes of the plots are considerably reduced, though not sufficiently to bring them exactly to unity. The three available sources of hydrochloric acid acidity function data disagree above 1M.

For the benzene–sulphuric acid exchange the slope of the log λ–H_0 plot differs from -1 more markedly than do those for the reactions of the substituted phenols in this acid (see Parts II and III). This is to be expected in view of Long and McIntyre's explanation, since this molecule is likely to be salted out by sulphuric acid more strongly than are the substituted phenols (see Long and McDevit, *Chem. Rev.*, 1952, **51**, 119). The behaviour of benzene is therefore consistent with that of the other compounds.

In view of the analogies noted above and the fact that a slope of exactly -1 is the exception rather than the rule for reactions whose rates are related to H_0, it seems legitimate to regard the deuterium exchange rates as indeed being so related.

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