390. *The Kinetics of Hydrogen-isotope Exchange Reactions. Part VII.** *Aromatic Hydrogen Exchange in the Solvent Systems* $ZnCl_2$–$CH_3{\cdot}CO_2H$ *and* $ZnCl_2$–HCl–$CH_3{\cdot}CO_2H$.

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The rate of the acid catalysed hydrogen-isotope exchange between *p*-deuteroanisole and the solvent systems named in the Title has been measured at 25°. The rate parallels, to a close approximation, the extent of ionisation of indicators such as 4-chloro-2-nitroaniline and *p*-nitrodiphenylamine in these systems. The ionisation process of these compounds is, therefore, considered to involve only hydrogen transfer. The details of the exchange mechanism are discussed.

VERY little work has been done on hydrogen-isotope exchange caused by suitable Lewis and Brønsted acids working together, and there exist only three such previous studies which concern the exchange of aromatic hydrogen.[1] The first two [1a, 1b] show that the presence of aluminium chloride facilitates the exchange between hydrogen chloride and benzene. The third [1c] demonstrates that the exchange between toluene and dissolved stannic chloride–hydrogen chloride mixtures is of first order in each component. This meagre information, and the fact that the function of such dual-acid systems in promoting hydrogen exchange is likely to be connected with their other catalytic rôles, notably that in the Friedel–Crafts reaction,† encourages further study. The systems $ZnCl_2$–$CH_3{\cdot}CO_2H$ and $ZnCl_2$–HCl–$CH_3{\cdot}CO_2H$ were chosen here, the acetic acid functioning both as a potential Brønsted acid and as the solvent for the other components.

Recent work [2] on aromatic hydrogen exchange, with systems containing only Brønsted acids, has shown that the rate of reaction is governed by the H_0 acidity function for the medium. In work with dual-acid catalysts it is, therefore, natural to look for a similar correlation with indicator ionisation. Thus the work has two aspects: the measurement, in the present media, of the ionisation of indicators commonly used in acidity-function studies (preceding paper) and the measurement of the hydrogen-isotope exchange rates between them and some suitable aromatic compound, now described.

Experimental.—*Materials.* *p*-Deuteroanisole,[3] anhydrous acetic acid,[3] anhydrous hydrogen chloride, and stock solutions of the last in the second, were prepared as previously described,[4] as were the stock solutions of zinc chloride.[5]

Hydrogen-exchange Experiments.—These were conducted essentially as for sulphuric acid–acetic acid media.[3] The anisole concentration was *ca.* 0·08M and tests showed there to be no loss of it from the reaction mixtures. Good first-order plots were obtained in all cases.

DISCUSSION AND RESULTS

$ZnCl_2$–$CH_3{\cdot}CO_2H$ *Solvent System.*—In pure acetic acid *p*-deuteroanisole undergoes hydrogen exchange negligibly slowly at ordinary temperatures.[3] The addition of zinc chloride to the solvent enhances its acidity,‡ and at salt concentrations above 2M or so, the exchange rate at 25° becomes conveniently measurable. The first-order [2] exchange rate constants, λ, for zinc chloride concentrations between 1·90 and 3·19M are given in Table 1. Their logarithms, plotted against values of the logarithms of the ionisation ratios for the indicator *p*-nitrodiphenylamine for the same range,‡ yield a straight line of slope 1·14.

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* Part VI, *J.*, 1956, 3911. † See following paper. ‡ See preceding paper.

[1] (*a*) Kenner, Polanyi, and Szego, *Nature*, 1935, **135**, 267; (*b*) Klit and Langseth, *Z. phys. Chem.*, 1936, *A*, **176**, 65; (*c*) Comyns, Howald, and Willard, *J. Amer. Chem. Soc.*, 1956, **78**, 3989.

[2] Gold and Satchell, *J.*, 1955, 3609, 3619; Mackor, Smit, and van der Waals, *Trans. Faraday Soc.*, 1957, **53**, 1309.

[3] Satchell, *J.*, 1956, 3911.

[4] Satchell, *J.*, 1958, 1916.

[5] Bethell, Gold, and Satchell, preceding paper.

A similar plot, using the ionisation data for 4-chloro-2-nitroaniline, has a slope of 0·93. It is clear that the rate of aromatic exchange in these solutions is directly related to the extent of ionisation of indicator bases of the type used by Hammett in his studies on acidity. In this, the observed behaviour is exactly analogous to that found in aqueous solution.[2]

TABLE 1. *First-order exchange rate constants, λ, for* p-*deuteroanisole in solutions of zinc chloride in acetic acid at* 25°.

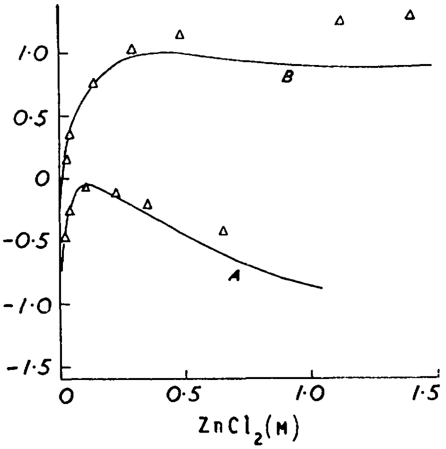
$ZnCl_2$ (M)	1·90	2·07	2·68	3·19
$10^7\lambda$ (sec.$^{-1}$)	3·10	4·05	8·15	16·6
$-\log I$	0·78	0·69	0·40	0·14

I = Ionisation ratio for *p*-nitrodiphenylamine.

TABLE 2. *First-order exchange rate constants, λ, for* p-*deuteroanisole in acetic acid containing both zinc chloride and hydrogen chloride at* 25°.

(i) HCl = 0·05M							
$ZnCl_2$ (M)	0·015	0·040	0·101	0·220	0·350	0·650	
$10^7\lambda$ (sec.$^{-1}$)	3·24	5·81	7·90	7·22	6·04	3·71	
(ii) HCl = 0·42M							
$ZnCl_2$ (M)	0·024	0·048	0·144	0·290	0·480	1·12	1·48
$10^7\lambda$ (sec.$^{-1}$)	13·6	21·9	57·0	105	139	177	201

$ZnCl_2$–HCl–$CH_3\cdot CO_2H$ *Solvent System.*—In this system the presence of hydrogen chloride enhances the acidity produced by a given amount of zinc chloride, and the plots of log I against zinc chloride concentration, at constant hydrogen chloride concentration, are more complex in shape than those found in the presence of zinc chloride alone.* The Figure shows the results of two series of experiments conducted at different constant hydrogen chloride concentrations. In it both log λ and log I for *p*-nitrodiphenylamine in these solutions * are plotted; the exchange rates and the ionisation ratios again follow very similar trends. The parallelism is not exact at high zinc chloride concentrations, but the marked similarity in the shapes and relative dispositions of the ionisation and exchange curves for different hydrogen chloride concentrations is evidence that in this system also the exchange rate and the extent of ionisation of indicators like *p*-nitrodiphenylamine are closely connected.



Correlation of exchange rates with indicator ionisation in acetic acid containing both hydrogen chloride and zinc chloride.

Δ = 6 + log λ. A = log I at [HCl] = 0·05M. B = log I at HCl = 0·42M.

Nature of the Ionisation Process in These Media.—The aromatic hydrogen-isotope exchange in these systems is doubtless acid-catalysed—all the solvent components are acids. Since such hydrogen exchange can, by its very nature, only reflect a Brønsted

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* See preceding paper.

acidity, it seems very likely in view of the direct relation which exists between the exchange rates and the extent of the ionisation of basic indicators that the ionisation process, for the indicators concerned, also involves only proton transfer. Free zinc chloride may be present in solution, but direct interaction between it and the indicators can only play a minor rôle in their ionisation. The chemical formulation of the active acidic species is discussed in the preceding paper.

Mechanism of the Exchange Reaction.—As has been mentioned, in aqueous solutions of mineral acids the rate of aromatic hydrogen exchange parallels the ionisation of indicator bases in the same way as in the present media. The detailed mechanism in aqueous solution has been discussed previously.[2] We consider it to be represented, in essentials, by the scheme:

$$\mathrm{RD} + \mathrm{H}^+ \underset{\text{Fast}}{\rightleftharpoons} \underset{\pi_1}{\mathrm{RDH}^+} \xrightarrow[\text{Slow}]{} \underset{\pi_2}{\mathrm{RHD}^+} \xrightarrow[\text{Fast}]{} \mathrm{RH} + \mathrm{D}^+$$

in which RD represents a deuterated aromatic molecule, π_1 and π_2 are " outer " complexes present in small concentration, and the deuterium content of the system is taken as negligible compared with that of protium.

In acetic acid, where ionic species exist largely as ion-pairs, an anion will presumably be associated with the outer complexes during the slow step, and the solvent acids will be largely undissociated. The analogous kinetic formulation is therefore as follows:

$$\mathrm{RD} + \mathrm{HA}_i \underset{\text{Fast}}{\rightleftharpoons} \underset{\pi_1}{\mathrm{RDH}^+\mathrm{A}_i^-} \xrightarrow[\text{Slow}]{} \underset{\pi_2}{\mathrm{RHD}^+\mathrm{A}_i^-} \xrightarrow[\text{Fast}]{} \mathrm{RH} + \mathrm{DA}_i$$

If k represents the rate constant of the slow step, $K_a^{\mathrm{RDH^+A_i^-}}$ the equilibrium constant of the first step, and X the transition state, then, for a single acid HA_i, the Brønsted rate equation is:

$$\text{Rate} = k(\mathrm{RD})(\mathrm{HA}_i)/K_a^{\mathrm{RDH^+A_i^-}}.f_{\mathrm{X}} \quad \quad (1)$$

where parentheses represent activity, and f an activity coefficient. For more than one acid, if f_{X} and k are assumed to be independent of the particular anion involved, then

$$\text{Rate} = \frac{k(\mathrm{RD})}{f_{\mathrm{X}}} \sum_i (\mathrm{HA}_i)/K_a^{\mathrm{RDH^+A_i^-}} \quad \quad (2)$$

The first-order exchange rate constant, λ, is then

$$\lambda = \frac{kf_{\mathrm{RD}}}{f_{\mathrm{X}}} \sum_i (\mathrm{HA}_i)/K_a^{\mathrm{RDH^+A_i^-}} \quad \quad (3)$$

The indicators being assumed also to exist largely as ion-pairs in the ionised condition, then the expression for I is [4]

$$I = \sum_i (\mathrm{HA}_i)f_{\mathrm{B}}/K_a^{\mathrm{BH^+A_i^-}}.f_{\mathrm{Y}} \quad \quad (4)$$

where B is a given indicator, Y the ion-pair $\mathrm{BH^+A_i^-}$, and $K_a^{\mathrm{BH^+A_i^-}}$ the ionisation constant for ion-pair formation. If the values of f_{Y} for different ion-pairs be taken as equal, then

$$I = \frac{f_{\mathrm{B}}}{f_{\mathrm{Y}}} \sum_i (\mathrm{HA}_i)/K_a^{\mathrm{BH^+A_i^-}} \quad \quad (5)$$

In equations (3) and (5) the activity coefficient ratios refer to species of similar structure and might be expected to vary in roughly the same way with medium composition. The equilibrium constants $K_a^{\mathrm{BH^+A_i^-}}$ and $K_a^{\mathrm{RDH^+A_i^-}}$ are for ion-pair formation between a given acid, HA_i, and the bases B and RD. If their ratio for different acids may, as a first approximation, be taken to be constant, then λ would be expected to follow the trend of I, as is found experimentally. The assumption concerning the constancy of the equilibrium constant ratio is only necessary if more than one acid is active. This is very probably the case in the solutions containing both hydrogen chloride and zinc chloride, and therefore it is not very surprising that in these solutions the correlation is not exact. As has been previously pointed out,[4] it is probably the fact that such ratios are not constant which is the major cause for the lack of exact parallelism observed for the ionisation of different indicators under such conditions. However, it is clear that the type of mechanism suggested for aqueous exchange remains satisfactory in acetic acid.

The only likely alternative mechanism is that depicted in the following scheme, in which there is a rate-determining attack by the acid species, *i.e.*, $k_1 \ll k_{-1}$ or k_2.

$$\mathrm{HA} + \mathrm{RD} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{RDH^+A^-} \xrightarrow{k_2} \mathrm{RH} + \mathrm{DA}$$

If it is assumed that the activity coefficients of the transition states of each step are the same, and of value f_Z, then

$$\text{Rate} = [k_1k_2/(k_{-1} + k_2)](\mathrm{RD})(\mathrm{HA})/f_Z \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If there is more than one acid active, and if the ratio $k_2/(k_{-1} + k_2)$ $(= \phi)$, and also f_Z, be considered independent of the acid involved, then

$$\text{Rate} = (\mathrm{RD})\phi[\sum_i k_{1_i}(\mathrm{HA}_i)]/f_Z \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Or

$$\lambda = \phi f_{\mathrm{RD}}[\sum_i k_{1i}(\mathrm{HA}_i)]/f_Z \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

For λ to parallel I on this basis, the ratio f_{RD}/f_Z must show similar variations to the ratio f_B/f_Y, and the product $k_{1i} . K_a^{\mathrm{BH^+A}_i^-}$ must be approximately constant for different acids. On the whole these conditions seem rather less likely to be satisfied than those for the previous mechanism, especially since the proton of the attacking acid may be solvated, and then Y and Z will not represent similar molecular aggregates. However, it is obviously not possible to make a definite decision at present.

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