286. *Co-catalysis. Part II.* The Relative Efficiencies of Halogenated Acetic Acids as Friedel–Crafts Co-catalysts.*

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The rate of loss of carboxylic tritium from acetic, chloroacetic, dichloroacetic, and trifluoroacetic acid to solvent *m*-xylene has been studied, using stannic chloride as catalyst. The general kinetic form is reported, and compared with that observed previously. At the same stannic chloride concentration, and under the simplest kinetic conditions, the order of reactivity is acetic > chloroacetic > dichloroacetic > trifluoroacetic. This result, and previous data, are discussed in relation to Friedel–Crafts co-catalysis. It is concluded that, in the absence of complications due to solvation, the effectiveness of any Brønsted–Lewis acid pair depends primarily on the stability of the complex anion which they form, and this stability, for a given Lewis acid, itself depends on the electron density on that atom of the anion deriving from the Brønsted component, which co-ordinates with the metal.

The diverse reactions which may be broadly defined as of the Friedel–Crafts type include a sub-group whose members require, not only the usual Lewis acid catalyst, but also an additional Brønsted acid co-catalyst. Alkylation with olefins, *cis–trans*-transformation, cationic polymerisation, and electrophilic aromatic substitution by hydrogen are all reactions which, when effected with the aid of Lewis acids, seem on the basis of the present, admittedly restricted, evidence, to require also a co-catalyst whose rôle is to supply protons. Certainly substitution by hydrogen must do so.

As is well known, the immense bulk of Friedel–Crafts literature contains very little systematic quantitative work. Even the comparisons of the various Lewis acids have usually been qualitative, though some general agreement about relative reactivities has been reached.[1] However, the few existing data that bear on the effectiveness of different Brønsted co-catalysts are still contradictory.

Two qualitative studies of this matter have been reported,[2,3] both in connection with cationic polymerisation reactions, and recently we have presented some more quantitative results concerning aromatic hydrogen exchange.[4] We there compared the efficiencies of hydrogen chloride, water, acetic acid, and trifluoroacetic acid as co-catalysts for stannic chloride, in toluene solution. The present report deals with a similar, more detailed, survey of the reactivity of the series of related acids: acetic, chloroacetic, dichloroacetic,

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* The paper in *J.*, 1960, 4388, is regarded as Part I.

[1] Baddeley, *Quart. Rev.*, 1954, **8**, 355; Pepper, *ibid.*, 1954, **8**, 88.

[2] Plesch, *Sci. Proc. Roy. Dublin Soc.*, 1950, **25** 154.

[3] Russell, " Cationic Polymerisation and Related Complexes," Heffer, Cambridge, 1953, p. 144.

[4] Part I, Satchell, *J.*, 1960, 4388.

and trifluoroacetic. The results are below compared with conclusions drawn from the polymerisation studies.

EXPERIMENTAL

Materials.—Stannic chloride was purified as previously described.[4] The anhydrous toluene, acetic acid, trifluoroacetic acid, (*carboxy*-^{3}H)acetic acid, and (*carboxy*-^{3}H)trifluoroacetic acid were previous samples.[4] Pure, dry *m*-xylene was prepared by refluxing the Hopkin and Williams product over calcium hydride for several hours before fractionally distilling it. A fraction with b. p. 139·5° was taken. "AnalaR" chloroacetic acid was used as such. [*carboxy*-^{3}H]Chloroacetic acid was prepared by shaking an ether solution of the "AnalaR" acid with tritiated water, separating the phases, and drying and evaporating the ether layer. A final distillation gave a tritiated product, b. p. 189°. Tests [4] showed that probably not more than 2% of the tritium was on the α-carbon atom. Pure dichloroacetic acid and the corresponding anhydride were prepared as previously described.[5] [*carboxy*-^{3}H]Dichloroacetic acid was prepared by addition of a slight deficit of active water to the anhydride. Reaction was rapid at room temperature. Distillation at 0·05 mm. yielded an active product, b. p. 41°. Tests for carbon-bound tritium were not made, but the kinetic experiments, which yielded good plots for tritium loss from this acid, show that contamination of this kind cannot have been serious. Tritiated water was supplied by the Atomic Energy Authority.

General Experimental Arrangements.—These followed the previous pattern and involved a dry-box technique.[4] All experiments were at 25°. Repetitions with different samples of reagents showed the kinetic data to be reproducible and not significantly due to adventitious impurities (*e.g.*, water).

A yellow colour, indicative of complex formation, is present in solutions of stannic chloride in *m*-xylene. The colour intensity decreases with the addition of quantities of the acetic acids. A spectrophotometric analysis of this phenomenon was not attempted in the present work (see Part I).

Radioactive Assay.—This was by a scintillation procedure, previously described.[4]

RESULTS AND DISCUSSION

Attention is first drawn to the relative simplicity of the systems here studied as examples of co-catalysed reactions. Only three components are involved: the two acids, and the aromatic hydrocarbon to which tritium is lost by the Brønsted acid. To simplify the exchange kinetics the aromatic compound was used in excess of the other two components, and it could conveniently act as solvent for them. Other types of co-catalysed reaction (*e.g.*, polymerisation) almost always involve an additional, non-reacting component to function as solvent.

Part I dealt with the system HX–$SnCl_4$–toluene, where HX was severally water, acetic acid, trifluoroacetic acid, or hydrogen chloride. Exchange rates, at a given stannic chloride concentration, were in the order hydrogen chloride > water > acetic acid > trifluoroacetic acid. This fact, together with the other kinetic details, led to the general conclusion that it was the ability of the Brønsted acid co-catalyst to form an ionic complex with the Lewis acid which, in the absence of deactivating solvent effects, determined co-catalytic efficiency. It was pointed out that trifluoroacetic acid would be expected to form a stable ionic complex with difficulty, or not at all (there was, however, spectral evidence for some variety of interaction), and the neglible exchange rate found with this co-catalyst was in keeping with the appreciable exchange rate for acetic acid—a compound known to form stable complexes with stannic chloride.[6,7] These two particular results made it appear likely that the series of structurally related acids, acetic, chloroacetic, dichloroacetic, and trichloro(or trifluoro)acetic, would show decreasing co-catalytic activity, in spite of their increasing conventional acid strength. This is the subject now examined.

[5] Satchell, *J.*, 1960, 1752.
[6] Usanovich and Kalabanovskaya, *Zhur. obshchei Khim.*, 1947, **17**, 1235.
[7] Satchell, *J.*, 1958, 3910.

Some physical evidence,[8] based on viscosity and other data, is held to indicate that, while acetic acid and chloroacetic acid form complexes with stannic chloride, dichloroacetic and trichloroacetic acids do not, or do so only negligibly. One might perhaps, therefore, predict for the series not only decreasing co-catalytic activity, but also a sudden fall in activity when the disubstituted acid is reached; however, this effect is not, in fact, observed (see below).

Some preliminary experiments were conducted in toluene (the aromatic solvent used in the previous work) with chloroacetic acid as co-catalyst. As expected, the observed exchange rate was less than for acetic acid, and in consequence too small for convenient measurement.[4] A change had therefore to be made to a more reactive aromatic compound. Mesitylene proved difficult to purify, different samples giving different colours on the addition of stannic chloride. (The random results obtained by Comyns, Howald, and Willard[9] in experiments with this compound are therefore not thought surprising.) A trial run also showed the exchange rate at quite a low stannic chloride concentration to be very fast. Mesitylene was therefore abandoned.

m-Xylene proved a suitable compound. Purification provided samples giving reproducible kinetic data. The *meta*-isomer was chosen since the others tend to rearrange to it under acidic conditions, and so complication of that kind was avoided. Data obtained for the different acids in exchange with *m*-xylene, at 25°, are tabulated. As will be seen, xylene has a convenient reactivity in the present context. Also the rather small spread of the exchange rates obtained with the four acids enabled it to be used with them all.

The data have two main features: (i) The observed kinetic pattern, common in outline to all the acids. (ii) The relative co-catalytic activity.

(i) *The Kinetic Form.*—This is as previously found for the $CH_3{\cdot}CO_2H$–$SnCl_4$–toluene system.[4] (*a*) There is no observable exchange over long periods in the absence of stannic chloride. (*b*) The exchange rates are in all cases roughly proportional to the stannic chloride concentration. (*c*) At the lowest co-catalyst concentrations the exchange rate is rather little affected by changes in the concentration of this species. (*d*) At higher co-catalyst concentrations (when this species has a concentration comparable with, or greater than, the stannic chloride concentration) the rate falls, though to different extents with the different acids (this effect is discussed below). For a detailed attempt at a mechanistic interpretation of this general kinetic behaviour, see Part I.

TABLE 1. *Exchange between acetic acid and* m-*xylene catalysed by stannic chloride at* 25°.

$[SnCl_4]$	0·086	0·172	0·344	0·344	0·344	0·344
[AcOH]	0·175	0·175	0·175	0·088	0·525	1·85
$10^4\lambda$ (min.$^{-1}$)	28·5	62·2	144	141	126	14·7

In all Tables, λ = first-order exchange rate constant, and square brackets represent molarity.

TABLE 2. *Exchange between chloroacetic acid and* m-*xylene catalysed by stannic chloride at* 25°.

$[SnCl_4]$	0·344	0·344	0·260	0·177	0·177
$[CH_2Cl{\cdot}CO_2H]$	0·053	0·106	0·053	0·053	1·11
$10^4\lambda$ (min.$^{-1}$)	40·6	32·9	27·6	21·0	8·63

TABLE 3. *Exchange between dichloroacetic acid and* m-*xylene catalysed by stannic chloride at* 25°.

$[SnCl_4]$	0·177	0·260	0·344	0·344	0·344	0·344
$[CHCl_2{\cdot}CO_2H]$	0·048	0·048	0·024	0·048	0·288	1·08
$10^4\lambda$ (min.$^{-1}$)	9·6	12·8	21·0	19·3	10·4	6·1

(ii) *Relative Co-catalytic Efficiency.*—Since at co-catalyst concentrations well below that of the stannic chloride, the reaction rate is insensitive to changes in co-catalyst concentration, it seems most legitimate to compare co-catalyst activities in this range. Table 5

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[8] Usanovich, Sumarokova, and Glushchenko, *Zhur. obshchei Khim.*, 1951, **21**, 981.

[9] Comyns, Howald, and Willard, *J. Amer. Chem. Soc.*, 1956, **78**, 3989.

TABLE 4. *Exchange between trifluoroacetic acid and* m-*xylene catalysed by stannic chloride at* 25°.

$[SnCl_4]$	0·34	0·68
$[CF_3 \cdot CO_2H]$	0·08	0·08
$10^4\lambda$ (min.$^{-1}$)	8·51	17·3

TABLE 5. *Relative rates of exchange at* 0·344M-*stannic chloride for different acids.**

K = acid dissociation constant at 25°.

HX	$10^4\lambda$ (min.$^{-1}$)	K
$CH_3 \cdot CO_2H$	140	$1·8 \times 10^{-5}$
$CH_2Cl \cdot CO_2H$	40·6	$1·5 \times 10^{-3}$
$CHCl_2 \cdot CO_2H$	19·3	$5·1 \times 10^{-2}$
$CF_3 \cdot CO_2H$	8·51	>1

* The comparisons are at arbitrary low acid concentrations, the rate being slightly dependent on acid concentration.

contains such a comparison. The catalytic efficiency is seen to be in the order, acetic > chloroacetic > dichloroacetic > trifluoroacetic, with acetic about sixteen times more effective than trifluoroacetic. The observed order is, therefore, as expected, and its qualitative explanation is presumably along the lines previously adumbrated. The co-catalytic process involves, of necessity,[4] the formation of an ionic complex, and the stability of the complex anion will be a determinant of the extent of its own formation. If it is assumed the main determinant, then of the four co-catalysts that possessing the anion which will form the most stable co-ordinate bond with stannic chloride will be the most effective, and that possessing the anion least able to co-ordinate will be the least effective. Thus [4,8] acetic and trifluoroacetic acid would be expected to be the best and worst co-catalyst respectively, as found. This result, in view of their very different conventional acidities, and in the light of a comparison of the protonation equilibria, (i) $B + HX \rightleftharpoons BH^+X^-$ and (ii) $B + HX + SnCl_4 \rightleftharpoons BH^+SnCl_4X^-$ (where B represents the aromatic solvent, and HX the Brønsted component), shows that it must be the satisfaction of the electron-demand of the Lewis acid which plays the dominant rôle in determining complex-formation. Factors which determine the position of equilibrium (i) (which represents the conventional acidity of HX) must be less important.

It will be recalled that, on the basis of the Russian work [8] on the gross physical properties of mixtures of stannic chloride with the chloroacetic acids, a sharp loss of activity after chloroacetic was expected. This is not observed. The relative activities are acetic : chloroacetic : dichloroacetic : trifluoroacetic, 1 : 0·29 : 0·14 : 0·06. Clearly, complex formation must be easier in the exchanging systems than in mixtures of stannic chloride and dichloroacetic acid alone. It is, of course, the presence of the aromatic compound which facilitates complex formation by its solvation, on one way or another, of the acidic hydrogen atoms produced—a rôle dichloroacetic acid itself is presumably little able to play.

The Discussions of this and previous work [4,10] lead to the postulation of a variety of forms for the Brønsted–Lewis complexes, or dual-acids. For Brønsted species such as hydrogen chloride the two most likely forms in solution will be $B \cdots H^{\delta+} \cdots {}^{\delta-}SnCl_5$ and $[BH]^+[SnCl_5]^-$, where B is the solvent. The second, fully ionic complex, being the species which leads directly to reaction (see Part I), will be present in very small amount. Rather similar structures must obtain for acids such as dichloroacetic, discussed above, which themselves solvate their own complexes with difficulty. For acids such as acetic, with greater electron-availability for the anion, the complexes not only require less solvation but may be solvated by the Brønsted component itself. Hence all the following species are probably present in solution: $H_2SnCl_4(OAc)_2$, $[HSnCl_4(OAc)_2]^-[AcOH_2]^+$, $[BH]^+[HSnCl_4(OAc)_2]^-$, together with more highly solvated forms.

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[10] Bethell, Gold, and Satchell, *J.*, 1958, 1918.

As a whole, the exchange experiments indicate that the order hydrogen chloride > water > acetic acid > chloroacetic acid > dichloroacetic acid > trifluoroacetic acid obtains for the effectiveness of the different co-catalysts. The total reactivity spread is a factor of approximately 430. While the mechanisms of catalysis by these acids are undoubtedly different in detail (see Part I, and below) it is probably the stability of the dual-acid anion which, in all cases, determines the extent to which, and thus the rate at which, protons (or tritons) are transferred between the complex acid and the aromatic species. Put another way, the anion stability may be considered to control the extent of formation of the BH^+X^- type of complex, which leads directly to reaction. It is the superficially anomalous position of hydrogen chloride in the reactivity sequence which provides the clue to the fact that it must be the electron density of the co-ordinating atom of the Brønsted acid anion that determines the stability of the complex anion. Thus the chloride ion will have a greater electron density than the oxygen atom of the hydroxide ion, which, in turn, will have a greater electron density than the oxygen atoms of the acetate ion, and so on down the series. This general point will be further supported in Part III.

Comparison with Previous Work.—The results and conclusions outlined above are in some conflict with those obtained from studies of cationic polymerisation. The two relevant investigations, which are qualitative, concern the polymerisation of isobutene at low temperatures, and in an inert medium. With titanium tetrachloride Plesch [2] found water to be a better co-catalyst than acetic, chloroacetic, or dichloroacetic acid, which all, in fact, inhibit polymerisation, while trichloroacetic acid is a satisfactory co-catalyst. A more extended series of Brønsted components was studied by Russell,[3] who used stannic chloride as the Lewis acid. He found activities in the order chloroacetic > acetic > nitroparaffins > water. The position assigned to water differs from that given by Plesch. Nevertheless the general order of effectiveness is that of increasing conventional acidity. This result is not in keeping with that now found for hydrogen exchange, and the conclusions of these authors were correspondingly different. However, the isobutene system very unsatisfactory. During polymerisation co-catalyst is removed, for the anion is involved in chain termination.[11] Clearly if the anions of weak acids are more effective chain-terminators than those of strong acids (as is possible), it would not be surprising that strong acids are better co-catalysts, or that weak acids inhibit the reaction. Moreover, studies of polymerisation in general suffer serious disadvantages from a kinetic viewpoint. They are often conducted at a low temperature (as were the above examples) which exaggerates the problem of contamination by water. The systems are frequently inhomogeneous, and the reaction curves seem often sigmoid. These facts, together with the acknowledged complexity of polymerisation processes, render conclusions about relative co-catalytic efficiency drawn from their study subject to reservation. Many additional, secondary effects may be included in such conclusions. More broadly, the detailed nature of the catalytic process for hydrogen exchange and for polymerisation may differ significantly, for while an essential feature, in each case, will no doubt be the formation, at some stage, of a complex between the Lewis and the Brønsted acid, nevertheless these acids may have other, and different, rôles to play in the two reactions. These other rôles are more likely to be prominent for polymerisation than for exchange.

One of these rôles, played by the Brønsted component, and already mentioned, is common to all co-catalysed systems. As previously mentioned, when the Brønsted acid reaches a concentration comparable with, or greater than, that of the Lewis acid, further increase in Brønsted acid concentration decreases the exchange rate. A similar effect has been observed by Dainton and Tomlinson [12] for the polymerisation of α-methylstyrene by H_2O–$SnCl_4$ in ethyl chloride, and by Eastham [13] for the *cis–trans*-isomerisation of but-2-ene by H_2O–BF_3 in ethyl chloride. Part of the explanation of this effect (see Part I)

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[11] Plesch, *J.*, 1950, 543.

[12] Dainton and Tomlinson, *J.*, 1953, 151.

[13] Eastham, *J. Amer. Chem. Soc.*, 1956, **78**, 6040; Eastham and Clayton, *ibid.*, 1957, **79**, 5368.

for the exchange reactions, and doubtless for other co-catalysed processes also, is that when in excess the Brønsted acid can (further) solvate the complex acid which has been formed (by accepting a proton, or in other ways), and so decrease its tendency to protonate a substrate. Since this feature of co-catalysed reactions is always liable to be present, its isolation is an essential pre-requisite of any kinetic analysis of mechanism.

Different systems will be more or less subject to the phenomenon: as the co-ordinating ability of the Brønsted acid decreases, it should tend to disappear. Some confirmation of this can be discovered by comparing the data in Tables 1 and 2. When a very poorly solvating acid, such as hydrogen chloride, is used, the effect does not noticeably intrude (Part I).

In general, we find that the complexities of Friedel–Crafts co-catalysed systems arise from the varied opportunities for solvation of the reactant species—a conclusion apparently in line with the views of Evans and his collaborators.[14]

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[14] Cf., *e.g.*, Evans and Lewis, *J.*, 1957, 2975.