

**851.** *The Effectiveness of Brønsted-Lewis Acid Combinations under Friedel-Crafts Conditions, investigated by Hydrogen Isotope Exchange.*

By D. P. N. SACHELL.

Experiments are reported on the rate of hydrogen exchange between toluene, containing dissolved stannic chloride, and various Brønsted acids. Exchange rates for different acids, at the same stannic chloride concentration, are in the order  $\text{HCl} > \text{H}_2\text{O} > \text{AcOH} \gg \text{CF}_3\text{CO}_2\text{H}$ . Thus the reaction rate is not simply related to the conventional strength of the Brønsted acid. Rather, it is considered to be determined by the extent to which stannic chloride and Brønsted acid can form an ionic complex, and by the number, and nature, of the species available to solvate this complex. These factors are discussed, together with other details of the reactions, for which mechanisms are proposed.

A simple and convenient preparation of tritium-labelled hydrogen chloride is described.

HYDROGEN isotope exchange involving acids is a process which, of necessity, includes the transfer of protons. The study of hydrogen exchange reactions is therefore one way of throwing light on the protonating powers of different acidic solvents. Since the nature of the acidic properties possessed by the dual-acid systems \* which are frequently used in Friedel-Crafts reactions and in cationic polymerisations is still imperfectly understood, a study of the hydrogen exchange occurring under similar conditions seemed attractive: any information gained about the mechanism must also increase knowledge of the nature of the acidic species.

Few reports exist concerning hydrogen exchange under the influence of dual-acids in otherwise aprotic (*i.e.*, typical Friedel-Crafts) conditions. There have been three previous studies.<sup>1</sup> The first two <sup>1a,b</sup> show that the presence of aluminium chloride facilitates the exchange between hydrogen chloride and benzene. The third <sup>1c</sup> indicates that the rate of exchange between toluene and dissolved stannic chloride-hydrogen chloride mixtures is of the first order in each component. The results are few and the authors do not speculate about the mechanism, though they give evidence for some complex formation between the solvent (toluene) and the Lewis acid. The nature of the complex is not detectably affected by the addition of hydrogen chloride.

The type of system chosen by these previous workers, in which the compound exchanging hydrogen with the acid components acts also as the solvent, so that no further diluent species is present, is the simplest devisable, and therefore also the most suitable for

\* Lewis acid together with some Brønsted acid co-catalyst.

<sup>1</sup> (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.

initial study. We decided, in consequence, to study first the toluene-stannic chloride-hydrogen chloride system in greater detail, and then to proceed to systematic variations of the hydrocarbon, the Lewis acid, and the Brønsted acid component. Some variations of the Brønsted acid are reported below. Because water also can act as a co-catalyst,<sup>2</sup> the experiments were performed with carefully dried reagents in a dry atmosphere.

#### EXPERIMENTAL

*Materials.*—"AnalaR" toluene was refluxed over calcium hydride for several hours and then distilled. Commercial stannic chloride was fractionally distilled, in a nitrogen atmosphere, at reduced pressure. Gaseous protium chloride was prepared by addition of the concentrated aqueous acid to concentrated sulphuric acid and washed with the latter. Tritium chloride was prepared by bubbling dry protium chloride through two successive 1 ml. portions of concentrated (ca. 98% by weight) sulphuric acid rich in tritium. Tests showed that for a moderate bubbling rate, through fine jets, exchange equilibrium between the gas and sulphuric acid was at least 50% attained. The method is simple and can be used to prepare dry hydrogen chloride samples with a wide range of activities. Pure tritium chloride cannot, of course, be prepared in this way. Tritiated sulphuric acid was prepared by addition of a calculated quantity of tritiated water to solid sulphur trioxide at 0°. The sulphur trioxide was distilled from oleum into a tared flask, forming part of an all-glass apparatus. Tritiated water was supplied by the Atomic Energy Authority, in ampoules of 1 ml., with a nominal activity of 0.2 curie/ml. Anhydrous acetic acid was prepared by adding the calculated quantity of acetyl chloride to pure, almost anhydrous, acid of known (Karl Fischer) water content. The reaction between acetyl chloride and water in acetic acid at room temperature is fast, and of known rate.<sup>3</sup> After an appropriate interval an excess of dry silver acetate was added to remove chloride. The mixture was then refluxed and finally the anhydrous acid, b. p. 118°, was distilled off. This method is quick and convenient; that involving the addition of acetic anhydride, followed by a period of heating, is inferior because in the present state of knowledge the period of heating must be somewhat arbitrary. [*carboxy*-<sup>3</sup>H]Acetic acid was prepared by the addition of the calculated quantity of active water to acetic anhydride containing dissolved hydrogen chloride. After a suitable interval<sup>3</sup> an excess of silver acetate was added to remove chloride. A short period under total reflux was followed by distillation, the dry acid boiling at 118°. To show<sup>4</sup> that no tritium found its way into the methyl group during the preparation, a sample of the active product was added to water and just neutralised, and the silver salt precipitated with silver nitrate. The solid was filtered off, washed with water, dried, and suspended in toluene. Gaseous hydrogen chloride was then passed through the toluene suspension for about 15 min. Considerable, though not quantitative, conversion into free acetic acid, occurs during this process.<sup>5</sup> The resulting suspension was filtered, and an aliquot part taken for counting. Assay showed that the methyl group contained a negligible amount of tritium.

Trifluoroacetic acid, b. p. 71°, was the product from fractional distillation of a sample containing added anhydride. Tritium-labelled acid was prepared by the controlled addition of active water to a slight excess of trifluoroacetic anhydride, followed by fractional distillation. The acetyl chloride and the acetic and the trifluoroacetic anhydrides were all redistilled samples.

All the products were stored in an anhydrous atmosphere (see below).

*General Experimental Arrangements.*—Most of the operations during which the absence of moisture was desirable, were carried out in a large, two-compartment dry-box. The various solutions were prepared in one compartment, and the thermostating devices, in which the reaction flasks were placed, were in the other compartment, where sampling was also carried out. The compartments were not directly connected, and by this separation of the operations it was hoped to keep radioactive contamination to a minimum. The box as a whole was occasionally flushed with dry nitrogen, the effluent gas being bubbled through water. Negligible activity was detected in this water. The 25° thermostat comprised a beaker containing paraffin oil and a hollow copper coil through which water was pumped from an external bath. The paraffin was thereby maintained at 25° ± 0.1°. For a few experiments a small lagged

<sup>2</sup> Evans and Lewis, *J.*, 1957, 2975.

<sup>3</sup> Satchell, *J.*, 1960, 1752.

<sup>4</sup> Butler and Gold, unpublished work.

<sup>5</sup> Jeffery and Satchell, unpublished work.

beaker of paraffin oil was maintained at  $50^\circ \pm 0.5^\circ$  by an electrical heating coil, controlled by an external Variac. In the experiments at  $50^\circ$  some of the reaction mixture escaped from the reaction vessels in spite of the ground-glass stoppers (see below), so little work was done at this temperature. The reagents for making up reaction mixtures were stored permanently in the dry-box. For the experiments with hydrogen chloride the reagents included stock solutions of protium and tritium chloride in dry toluene, these being prepared externally by bubbling the gas through the solvent under anhydrous conditions, with minimum exposure of the resulting solution to the atmosphere. The acid content of these solutions was found by thoroughly extracting a portion with water and titrating the combined extracts for chloride. The analyses were repeated from time to time, hydrogen chloride being little soluble in toluene and liable to escape.

The reaction vessels were thick-walled Pyrex test-tubes, of approximately 10.5 ml. capacity, fitted with ground-glass stoppers. The tubes were filled with the appropriate volumes of the various reagents inside the box. The total volume of a reaction mixture was kept close to 10 ml., so that the volume left between the liquid surface and the stopper was small. This procedure helped to ensure that in the experiments with hydrogen chloride most of this gas was in the liquid phase. The filled tubes were transferred to the thermostat and allowed to reach bath-temperature; then an initial sample was taken for assay, followed by others at appropriate intervals.

*Sampling and Counting Procedure.*—In all experiments the Brønsted acid component carried the tritium initially, and this species was usually kept in at least a 60—70-fold deficit compared with the number of exchanging sites in the solvent.<sup>6</sup> Hence the activity in the acid fell eventually to a low level. To assay the tritium remaining in the acid, at various times, use was made of the fact that acidic hydrogen atoms are very rapidly exchangeable with those of water, whereas those in toluene are only very slowly exchangeable.<sup>7</sup> In practice a small volume (0.1 ml.) of reaction mixture was pipetted into a stoppered tube, containing 5 ml. of "AnalaR" toluene and 1 ml. of water. The tube was shaken vigorously for a few minutes. This process both arrests the exchange being studied and removes all the rapidly exchangeable tritium from the toluene layer to the aqueous layer, the exchanging hydrogen atoms in the water being in great excess. During the shaking, besides the tritium, some, if not all, of the Brønsted and the Lewis acid components from the sample would also be transferred to the aqueous phase. The sample was therefore kept small enough to avoid quenching complications which could arise from such a source, and small also to avoid materially increasing the space above the liquid in the reaction vessel.

After the layers had been allowed to separate, a portion (usually 0.5 ml.) of the (lower) aqueous layer was pipetted off for counting, care being taken not to contaminate the inside of the pipette with the toluene layer, the outside being wiped finally with absorbent tissue. (In fact, a small amount of contamination would not be important since the sample had in any case been 50-fold diluted in the toluene layer.) The counting was by a scintillation technique, the water sample being added to 20 ml. of a (50 : 50 vol.%) toluene-alcohol mixture containing 1.5 g. of PPO per l. The Ekco N612 scintillation unit and N630F scaler had a tritium efficiency of ca. 5%, and activity levels were arranged to give initial counts of 500—1000 per sec. There were no complications due to quenching, and duplicate sampling showed an overall reproducibility of  $\pm 6\%$ .

Rate constants were calculated from the usual first-order law for tritium exchange.<sup>7</sup> Good plots were obtained in all cases (except where mentioned below). The constants were reproducible to  $\pm 8\%$ .

*Experiments with Water Present.*—A few experiments were carried out with water as the Brønsted acid component, both alone and in conjunction with hydrogen chloride. For these experiments a stock solution of active water in toluene was prepared, with the known solubility of water in toluene<sup>8</sup> in mind. The first-order plots obtained were not linear. The results are discussed below.

*Ultraviolet Spectra.*—These were taken with a Beckman spectrophotometer and 1 cm. path quartz cells, fitted with ground stoppers. The cells were filled in the dry-box. The spectrophotometer cell compartment was controlled (thermostat) at  $25^\circ$ .

<sup>6</sup> Gold and Satchell, *J.*, 1956, 2743.

<sup>7</sup> Gold and Satchell, *Quart. Rev.*, 1955, 9, 51.

<sup>8</sup> Tarassenkov and Poloshinzewa, *Zhur. obshchei Khim.*, 1931, 1, 71; *Ber.*, 1932, 65 184.

## RESULTS AND DISCUSSION

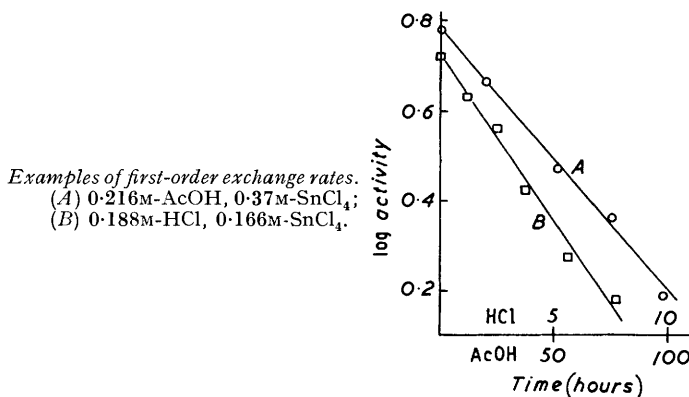
*Hydrogen Chloride-Stannic Chloride-Toluene System.*—The exchange rate was determined for various hydrogen chloride concentrations between 0.038 and 0.375M and for stannic chloride concentrations between 0.042 and 0.332M. There is no detectable exchange over long periods in the absence of stannic chloride.<sup>1c</sup> The results are given in Table I. Fig. 1 shows a typical first-order plot. All the experiments for this system were at 25°. It will be seen that at fixed hydrogen chloride concentration the first-order exchange rate constant

TABLE I. Exchange in hydrogen chloride-stannic chloride-toluene at 25°.

$\lambda$  = observed first-order exchange rate constant; square brackets represent molarity.

[HCl] .....	0.038	0.075	0.1125	0.188	0.375	0.375	0.375	0.375	0.188
[SnCl <sub>4</sub> ] .....	0.166	0.166	0.166	0.166	0.166	0.332	0.083	0.042	0.322
10 <sup>6</sup> $\lambda$ (sec. <sup>-1</sup> ) .....	38	41	44	48	66	130	34	17	91

is closely proportional to the stannic chloride concentration, but at fixed stannic chloride concentration it is rather little affected by the total concentration of hydrogen chloride. In fact the rate only increases by a factor of 1.7 for a ten-fold increase in hydrogen chloride concentration, and a change of this magnitude can probably be attributed to a salt effect in a medium of such low dielectric constant.<sup>3</sup> The behaviour observed would be expected

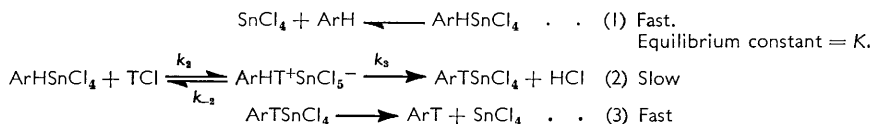


for a reaction of first-order in *both* stannic chloride and tritium chloride; for the first-order exchange rate (at any given stannic chloride concentration) would, of course, not depend on the quantity of tritium chloride present, and an increase in the total hydrogen chloride concentration, at constant tritium chloride concentration, would not increase the number of tritium chloride-toluene collisions and so would have no direct effect on the rate. If, however, the exchange mechanism involved two hydrogen chloride molecules (only one of which need carry tritium), then the rate would be expected to depend on the total hydrogen chloride concentration because the number of effective collisions would then be related to the square of this quantity. The absence of dependence on total hydrogen chloride is therefore good evidence that only one molecule is required. As noted by Comyns, Howald, and Willard,<sup>1c</sup> when stannic chloride is added to toluene the solution becomes pale yellow and the ultraviolet and visible spectra reveal increased absorption below 4300 Å though no new peak is observed. Since both toluene and stannic chloride absorb negligibly above 3100 Å, the effect is presumably due to complex formation between them. The intensity of absorption at 3800 Å (a convenient, arbitrary wavelength) is closely proportional to the stoichiometric stannic chloride (Table 2). This is expected whatever the position of the equilibrium producing the complex, for the toluene is in great excess. The spectra are not detectably affected by the addition of hydrogen chloride.<sup>1c</sup>

TABLE 2. Intensity of absorption of solutions of stannic chloride in toluene at 25°.

(a) Stannic chloride alone.					
[SnCl <sub>4</sub> ] .....	0.054	0.108	0.216	0.270	0.432
log (I <sub>0</sub> /I) at 3800 Å .....	0.230	0.461	0.915	1.10	1.83
log (I <sub>0</sub> /I) at 4200 Å .....	0.040	0.079	0.158	0.192	0.318
(b) 0.270M-Stannic chloride with added acetic acid.					
[AcOH] .....	0.0	0.30	0.53	0.80	1.37
log (I <sub>0</sub> /I) at 3800 Å .....	1.10	0.69	0.44	0.245	0.106
(c) 0.270M-Stannic chloride with added trifluoroacetic acid.					
[CF <sub>3</sub> ·CO <sub>2</sub> H].....	0.0	0.22	0.65	1.10	
log (I <sub>0</sub> /I) at 3800 Å .....	1.10	1.06	0.94	0.84	

In the light of the foregoing, the following mechanism is suggested:



The position of the pre-equilibrium (1) is not decided by the data now available. Since the second step is slow this mechanism accounts for the observed orders:

$$\begin{aligned}
 \text{Rate} &= Kk_2k_3/(k_{-2} + k_3)[\text{ArH}][\text{SnCl}_4][\text{TCl}] \\
 &= k[\text{SnCl}_4][\text{TCl}]
 \end{aligned}$$

The ion-pair intermediate  $\text{ArHT}^+\text{SnCl}_5^-$  will be present in low concentration. In view of previous results<sup>9</sup> for the zinc chloride-hydrogen chloride-acetic acid system, there may perhaps be a further, partly ionised, form of this intermediate, with the aromatic molecule solvating an incipient proton, thus  $\text{ArHT}^{\delta+}\text{SnCl}_5^{\delta-}$ . Such a species easily fits in the above scheme.

The observed participation of only a single Brønsted acid molecule in complex formation with the Lewis acid, for the hydrogen exchange, agrees with the findings by Evans and Lewis<sup>10</sup> for a related system, namely, dimerisation of diphenylethylene in benzene catalysed by stannic chloride-hydrogen chloride. These authors do not comment on the possibility of complex formation between stannic chloride and the solvent. For the protonation of the ethylene they suggest either a termolecular process between it, hydrogen chloride, and stannic chloride or a bimolecular step involving the ethylene and  $\text{HSnCl}_5$  formed in a pre-equilibrium. In the light of the present results for toluene the latter alternative seems correct,  $\text{HSnCl}_5$  being present in small concentration, stabilised by solvation by benzene.

TABLE 3. Exchange rates in the presence of water at 25°.

λ calculated for initial rates.				
[SnCl <sub>4</sub> ]	[H <sub>2</sub> O]	[HCl]	10 <sup>6</sup> λ (sec. <sup>-1</sup> )	
0.166	0.018	—	27 (average of 3 results)	
0.166	0.016	0.03	20	
0.166	0.015	0.04	26	

To make certain that measurable effects due to water had been excluded, some experiments were performed in which water was deliberately added. In the absence of hydrogen chloride, stannic chloride and water do, in fact, produce exchange, though the plots here obtained have not been linear, the reaction slowing up with time. The initial rate was less than that found for the same concentration of hydrogen chloride. Addition of water to a hydrogen chloride run decreased the exchange rate. The results are in Table 3. In view of these findings (particularly the non-linear plots) and since the hydrogen chloride exchange rates were reproducible with different samples of reagents, and on different occasions, it is

<sup>9</sup> Bethell, Gold, and Satchell, *J.*, 1958, 1918.

<sup>10</sup> Evans and Lewis, *J.*, 1959, 1946.

concluded that effects due to the presence of water are certainly not dominant (if present at all) in the data of Table 1.

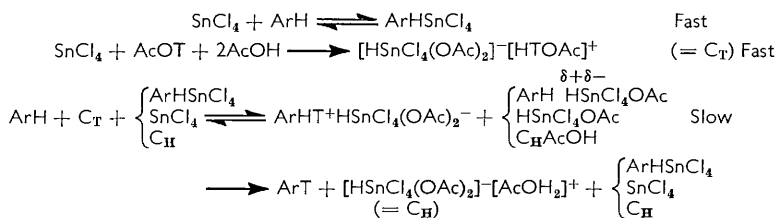
TABLE 4. *Exchange in the system acetic acid-stannic chloride-toluene at 25°.*

[SnCl <sub>4</sub> ].....	0.19	0.37	0.73	0.37	0.37	0.37	0.37	0.19
[AcOH] .....	0.216	0.216	0.216	0.108	0.216	0.430	0.860	1.8
10 <sup>6</sup> λ (sec. <sup>-1</sup> ) .....	1.7	3.7	7.4	3.5	3.7	3.9	4.2	0.38

We comment below on the fact that the initial exchange rate for catalysis by water is not so very different from that for catalysis by hydrogen chloride in spite of the widely differing acidities. It is not yet known why plots were not linear for the water reaction, though it is possible that the stannic chloride-water complex is little soluble in toluene, and tends to come out of solution.

*Acetic Acid-Stannic Chloride-Toluene System.*—Exchange rates were measured for 0.108–1.8M-acetic acid and 0.19–0.73M stannic chloride. The rate constants obtained at 25° are in Table 4. Fig. 1 shows a typical first-order plot. The measured first-order rate is reasonably proportional to stoichiometric stannic chloride concentration, and largely independent of total acetic acid concentration over a considerable range, increasing very slightly, though eventually falling with large further addition of acetic acid. These results are best considered together with those obtained from absorption spectra.

When acetic acid is added to a stannic chloride solution in toluene, the absorption at 3800 Å is reduced, falling eventually to a very low value (Table 2). Since (see p. 4391) the optical density is proportional to total “ free ” (*i.e.*, SnCl<sub>4</sub> and ArHSnCl<sub>4</sub>) stannic chloride, the observed reductions in log (*I*<sub>0</sub>/*I*) can be used to calculate the quantity of stannic chloride removed by the added acetic acid. At the lowest concentrations studied here, one stannic chloride molecule appears to require three acetic acid molecules, and this number does not rise appreciably until most of the stannic chloride has been removed, whereafter the average number of acetic acid molecules needed to secure one stannic chloride molecule begins to increase. Thus, so far as the kinetic results in Table 4 are concerned (apart from the value for 1.8M-acetic acid) the added acetic acid will probably exist largely as SnCl<sub>4</sub>(AcOH)<sub>3</sub>, perhaps partly as C<sub>II</sub> (*i.e.*, [HSnCl<sub>4</sub>(OAc)<sub>2</sub>]<sup>-</sup>[AcOH<sub>2</sub>]<sup>+</sup>). There is, in fact, independent evidence for ready complex formation between acetic acid and stannic chloride, and for the existence of the above species.<sup>11</sup> It is now required to devise an exchange mechanism involving this species which demands the approximate first-order dependence on stoichiometric stannic chloride, and also a zero-order dependence on total acetic acid at low concentrations and a negative order at high concentrations. It is difficult to explain the order in stannic chloride convincingly, but the mechanism given below (which is similar to one devised by Evans and Lewis<sup>2</sup> for a system involving catalysis by stannic chloride and water) is credible:



The three species joined by the braces ({} ) comprise the stoichiometric stannic chloride concentration, and if their efficiency for accepting an acetic acid molecule is roughly the same, then the first-order dependence on total stannic chloride is explained. These species will certainly all accept acetic acid, though the complex C<sub>II</sub> would be expected to do so less readily than the other two. However, this species is in deficit compared with free stannic chloride at all except the highest concentrations of acetic acid, and there the

<sup>11</sup> Satchell, *J.*, 1958, 3910.

changes in dielectric constant may have some compensating effect. At the lower acetic acid concentrations this compound will exist largely as  $\text{SnCl}_4(\text{AcOH})_3$  and hence a zero-order dependence on total acetic acid is to be expected for the tritium exchange rate (a similar argument to that outlined for the hydrogen chloride reaction applies, see p. 4391). When additional acetic acid is present beyond that necessary to produce  $\text{SnCl}_4(\text{AcOH})_3$  a fall in exchange rate is to be expected for at least two reasons. First, the additional acid will provide sites for tritium without increasing the number of effective collisions. Hence the observed exchange rate constant will fall. Secondly, when more than three acetic acid molecules are available for each stannic chloride molecule, then the species  $\text{SnCl}_4(\text{AcOH})_3$  will be further stabilised by effective solvation, and will therefore have less tendency to transfer a proton to an aromatic molecule. The more effective the solvation the less the tendency will be. If the above mechanism is correct, then, even when only three molecules are present per molecule of stannic chloride, the transfer appears to require an additional species to accept the acetic acid molecule that is being freed.

It follows that when sufficient acetic acid is present the exchange rate constant should fall, and the observed rate for 0.19M-stannic chloride in the presence of 1.8M-acetic acid shows that this happens. This particular constant is not very accurate, but its value does imply that the second, as well as the first, of the above-mentioned effects is operating. That this should be so can also be concluded from a comparison of the exchange rate in the present system with that found for the much more reactive compound anisole in pure acetic acid, at the same stannic chloride concentration.<sup>6,11,12</sup>

Other predictions based on the proposed mechanism can be devised, but the present system is somewhat unfavourable for further tests.

Table 5 contains data on the exchange rates, at the same stannic chloride concentration, brought about by acetic acid, water, and hydrogen chloride. The water reaction probably has a mechanism analogous to that obtaining for acetic acid. Evans and Lewis find that, for dimerisation of diphenylethylene in benzene, the system is well behaved (as previously mentioned, the present system gives non-linear plots) and they conclude that  $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$  is the active acidic species, excess of water producing a decrease in catalytic power, as does an excess of acetic acid in the present exchange. They also found a first-order dependence on total stannic chloride, and suggest a mechanism of the type given above in which the species  $\text{SnCl}_4$  and  $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$  are assumed to provide equally effective solvation for an ion-pair complex between acid and ethylene. As noted previously, Evans and Lewis<sup>10</sup> also studied the dimerisation in hydrogen chloride–stannic chloride–benzene. A comparison of the rates, while not very meaningful in view of the differences in mechanism, shows the rate in the hydrogen chloride system to be about 3.3-fold faster at 30°. A similar comparison for the exchange reaction, at 25°, gives a factor of 1.6 (Table 5). The similarity between the ratios lends a little support to the assumption that the quoted rates for the water exchange have meaning. If they have, then since the acetic acid exchange is about 17-fold slower, at the same stannic chloride concentration, than the rate for water, we reach the tentative and curious conclusion that water is a more powerful co-catalyst than acetic acid.<sup>13</sup>

TABLE 5. *Comparison \* of rate constants at 0.166M-stannic chloride at 25°.*

Brønsted acid.....	HCl	H <sub>2</sub> O	AcOH	CF <sub>3</sub> ·CO <sub>2</sub> H
10 <sup>6</sup> λ (sec. <sup>-1</sup> ) .....	44	27	1.6	v. small

\* Comparisons are at arbitrary, low acid concentrations, the rate being slightly dependent on this concentration.

The more general conclusion from the foregoing results is that the ability of a dual-acid system to transfer protons to a particular base is not simply related to the conventional acid strength of the Brønsted component. It appears rather to be determined by a

<sup>12</sup> Satchell, *J.*, 1956, 3911.

<sup>13</sup> Cf. Plesch, *Sci. Proc. Roy. Dublin Soc.*, 1950, 25, 154.

number of factors related (*a*) to the ability of the co-catalyst to form a complex with the Lewis acid, and (*b*) to the various opportunities for solvation of the very acidic protons so produced, these two phenomena being, in addition, interdependent.

*Trifluoroacetic Acid-Stannic Chloride-Toluene System.*—In view of the considerations noted above, the results obtained with trifluoroacetic acid are especially interesting. There is evidence<sup>14</sup> that neither di- nor tri-chloroacetic acid forms complexes with stannic chloride. This may be attributed either to the drain on the electrons of the carboxylic oxygen atoms due to the chlorine substituents, or to the lack of suitable species to accept a proton (another aspect of the same phenomenon) or to both. Similar effects would be expected for trifluoroacetic acid. If the first reason were important, and no complex were possible, then little exchange would be expected between toluene and this acid, in the presence of stannic chloride. In fact, with trifluoroacetic acid as the Brønsted component very little exchange is obtained at 25°, or at 50°, over a period of some days. It was therefore surprising to find that the addition of trifluoroacetic acid to a solution of stannic chloride in toluene reduces the absorption at 3800 Å. The effect is less marked than for acetic acid (Table 2) but it seems that some form of interaction between trifluoroacetic acid and stannic chloride must take place, which reduces the tendency of the latter to form a complex with the solvent but nevertheless does not lead to a dual-acid capable of initiating exchange. It is perhaps the demand of the exchange process for the existence of a fully ionised form for the complex acid (*e.g.*,  $\text{ArH}_2^+\text{SnCl}_5^-$ ) which in the present case cannot be met.

It will be interesting to learn the effect of trifluoroacetic acid as a co-catalyst for stannic chloride in a Friedel-Crafts reaction or in cationic polymerisation.

The author thanks Dr. I. R. Beattie for advice on dry-box technique.

KING'S COLLEGE, STRAND,  
LONDON, W.C.2.

[Received, April 12th, 1960.]

<sup>14</sup> Usanovitch and Sumarokova, *J. Gen. Chem. (U.S.S.R.)*, 1951, **21**, 1079.

---