# H—D EXCHANGE OF COMPLEX ACIDS WITH AROMATIC HYDROCARBONS*

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Received November 4th, 1974

H—D exchange rates were studied of catalytic systems $TiCl_4$-RCOOH (R = $CF_3$, $CCl_3$, $CHCl_2$, $CH_3$, $CH_3CH_2$), $SnCl_4$-RCOOH (R = $CH_3$, $(CH_3)_2CH$, $(CH_3)_3C$), and carboxylic acids alone with symmetric aromatic hydrocarbons benzene, *p*-xylene, and mesitylene. The exchange rates in the systems with $TiCl_4$ and $SnCl_4$ increase with the increasing strength of the carboxylic acids. Relative exchange rate constants in the $TiCl_4$-containing systems were by 3—4 orders of magnitude larger than in the systems with $SnCl_4$. The acidity of the systems, characterized by the logarithm of the rate constant of the exchange reaction, has made it possible to estimate the catalytic activity of these systems in oligomerization, alkylation, and isomerization reactions.

In the previous study[1] the formation of complexes of $TiCl_4$ and $SnCl_4$ with carboxylic acids was investigated by means of infrared spectroscopy and proton magnetic resonance. It was found that the magnitude of the $\nu$(O—H) vibration shift of the carboxylic acid towards lower wavenumbers, due to the complex formation, and the shift of the acidic proton resonance band towards higher magnetic fields were proportional both to the complex acid strength and to the aromatic solvent basicity. These spectroscopic quantities can be used in estimating the relative acidity of those systems only which contain weak non-halogenated carboxylic acids, where the equilibrium is shifted considerably towards the complex formation. However, the acidity of the systems manifests itself markedly in their ability to exchange the acidic proton with hydrogens of rather weakly ionized substances, *e.g.*, hydrocarbons. The rates of H—D and H—T exchange were used in evaluating the relative acidity of the systems $SnCl_4$–protonic acid in toluene and in *m*-xylene[2-4]. The proton exchange in the presence of $SnCl_4$ was found to be always faster than with the protonic acid alone, and the rates were decreasing in the sequence of the acids investigated: HCl > $(CH_3)_3CCOOH$ > $CH_3COOH$ > $CH_2ClCOOH$ > $CHCl_2COOH$ > $CF_3COOH$.

This paper summarizes the results on the H—D exchange rate measurements in the catalytic systems $SnCl_4$, $TiCl_4$–carboxylic acids and carboxylic acids alone with benzene, *p*-xylene, and mesitylene. The aim of this study has been to compare the relative acidity of these systems on the ground of the electrophilic exchange reaction rate determination, and to obtain in this way an estimation of their catalytic activity in proton-initiated reactions.

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* Part II in the series Catalytic Systems Lewis Acid–Brönsted Acid; Part I: This Journal *40*, 326 (1975).

## EXPERIMENTAL

*Chemicals.* The origin and purification of all chemicals was described in Part I. Benzen $C_6D_6$ (99·8% D) was obtained from Institut für Physikalische Stofftrennung, Leipzig, DDR, and was not subjected to further purification. Deuterated acids $CF_3COOD$, $CCl_3COOD$, and $CH_3COOD$ were prepared by mixing the anhydrides with the stoichiometric amount of $D_2O$ (99·8%) and by fractionation after boiling under reflux. Deuterated acids $CCl_2HCOOD$, $(CH_3)_2CHCOOD$, and $(CH_3)_3CCOOD$ were prepared by a multiple exchange of the acids with $D_2O$; after the exchange, water was distilled away *in vacuo.* Water-free acids were obtained by a slow distillation at the normal pressure; the fractions of the tabulated boiling point were used in the exchange studies. The purity of the acids and their isotopic content was also checked by measuring infrared spectra of their heptane solutions.

*Procedures.* Mixing of the catalytic systems containing $TiCl_4$ and $SnCl_4$ was carried out with the help of syringes in test tubes with ground-in stoppers. After no more HCl was evolved in the systems with $TiCl_4$, the mixture was transferred into a tube for $^1$H-MR measurements. The rate of the H—D exchange was followed by measuring the intensity of the acid proton resonance bands of the catalytic systems and of the protons of aromatic hydrocarbons. In the case of *p*-xylene and mesitylene the methyl band of the aromatic hydrocarbons served as the internal standard, in the case of benzene, tetramethylsilane was added. The samples (with the exception of those with a very slow exchange rate) were kept at a constant temperature (25°C or 50°C) during the entire exchange period in the spectrometer probe. With very slowly exchanging samples, about 10 ml of the solution was divided into ten ampules which were then sealed. Thermostated ampules were then opened only before the $^1$H-MR spectra measurements. In the systems with $TiCl_4$ the exchange of acidic protons with $C_6D_6$ was measured, in the other systems the exchange of acidic deuteron with aromatic hydrogens was followed. In order to obtain exchange rates suitable for $^1$H-MR measurements, weak acids were combined with more basic aromatic compounds and strong acids with less basic aromatic compounds: the acids $CHCl_2COOD$, $CCl_3COOD$, and $CF_3COOD$ with mesitylene; $CF_3COOD$ and complex systems containing $SnCl_4$ with *p*-xylene; complex systems containing $TiCl_4$ with deuterated benzene; mixtures $D_2SO_4 + CF_3COOD$ with normal benzene. Molar ratios of the components carboxylic acid: Lewis acid: aromatic hydrocarbon were kept constant in the systems exchanging with mesitylene and *p*-xylene; this ratio, however, could not be kept constant in the systems with $TiCl_4$ and $D_2SO_4 + CF_3COOD$ because of a limited solubility. The rate constant of the exchange reaction, formally of the first order, was determined both from the measured half-life of the exchange ($k = \ln 2/t_{1/2}$) and from the linear dependence $-\ln(1 - F) = kt$, where $F = (A_t - A_0)/(A_\infty - A_0)$ (ref.[5]) in which $A_0$ is the concentration of the exchangeable hydrogen (deuterium) atoms in the aromatic hydrocarbon or in the acid at $t = 0$, $A_t$ that one at a time $t$ during the measurement, and $A_\infty$ that one after reaching the equilibrium.

$^1$H-MR *spectra* were measured using a NMR spectrometer Tesla BS 487 at 80 MHz. Infrared spectra of the solutions of acids in benzene, *p*-xylene, and mesitylene were measured in KBr cells using a UR-10 spectrometer (Zeiss, Jena).

## RESULTS AND DISCUSSION

The rates of the H—D exchange with benzene, *p*-xylene, and mesitylene, characterized, by the rate constants *k*, for the catalytic systems $TiCl_4$, $SnCl_4$–carboxylic acids, and some halogenoacetic acids are summarized in Table I. The rates ought to be a measure of the acidity of the catalytic systems and acids. It was shown in the system $H_2SO_4$-$CF_3COOH$ exchanging with deuterated benzene, toluene, and *p*-xylene that log *k* is directly proportional to the acidity of the system as defined by the Hammett acidity function $H_0$ (ref.[6]). The exchange rates found in the systems $TiCl_4$--$RCOOH$-$C_6D_6$ characterize the overall acidity of the system. Therefore, they do not provide an accurate measure of the acidity of the complexes $RCOOH.TiCl_4$ which are evidently the most acidic particles in the system. In the interaction of $TiCl_4$ with acids not only the complexes $RCOOH.TiCl_4$ are formed, but also carboxylates $RCOOTiCl_3$ and $(RCOO)_2TiCl_2$ (ref.[1]). Of those namely the former preserves a certain electron-acceptor ability. Weak complexes of these carboxylates with non-reacted carboxylic acid, as well as the non-reacted acid itself, contribute somewhat to the overall acidity of the system. With a given initial ratio $TiCl_4$ : $RCOOH$ the amount of the complex $RCOOH.TiCl_4$ formed and the amount of carboxylate is substantially dependent on the nature of the acid. Thus, *e.g.*, it was found[1] that in the systems with $CH_3CH_2COOH$ and $CH_3COOH$ at the component ratio $TiCl_4$ : : $RCOOH = 1$ the reaction between $TiCl_4$ and the acid was quantitative and the acid was mostly consumed to form the complex, to a lesser extent to form the carboxyl-

TABLE I

Comparison of Exchange Rates in Systems $TiCl_4$, $SnCl_4$-Carboxylic Acids

| Acid | Aromatic hydrocarbon (Ar) | Molar ratio RCOOH/Ar | Rate constant[b] $k$, $h^{-1}$ | log $k'$[c] |
|---|---|---|---|---|
| $CF_3COOH + TiCl_4$[a] | benzene-$d_6$ | 0·66 | 2·1 | 3·3 |
| $CCl_3COOH + TiCl_4$ | benzene-$d_6$ | 0·66 | 8·3 | 3·9 |
| $CHCl_2COOH + TiCl_4$ | benzene-$d_6$ | 0·66 | $2{\cdot}1 . 10^1$ | 4·3 |
| $CH_3COOH + TiCl_4$ | benzene-$d_6$ | 0·66 | $5{\cdot}8 . 10^{-1}$ | 2·8 |
| $CH_3CH_2COOH + TiCl_4$ | benzene-$d_6$ | 0·66 | $4{\cdot}6 . 10^{-1}$ | 2·7 |
| $CH_3COOD + SnCl_4$[a] | *p*-xylene | 4·32 | 1·8 | 0·26 |
| $(CH_3)_2CHCOOD + SnCl_4$ | *p*-xylene | 4·32 | $4{\cdot}6 . 10^{-1}$ | −0·33 |
| $(CH_3)_3CCOOD + SnCl_4$ | *p*-xylene | 4·32 | $3{\cdot}5 . 10^{-1}$ | −0·45[d] |
| $CF_3COOD$ | *p*-xylene | 4·32 | $9{\cdot}3 . 10^{-4}$ | −3·0 |
| $CF_3COOD$ | mesitylene | 4·73 | 9·3 | −3·0 |
| $CHCl_2COOD$ | mesitylene | 4·73 | $5{\cdot}8 . 10^{-2}$ | −5·2 |
| $D_2SO_4 + CF_3COOD$[e] | benzene | 3·26 | $1{\cdot}4 . 10^1$ | 4·1 |

[a] Molar ratio $RCOOH/TiCl_4 = 1$, $RCOOH/SnCl_4 = 2$; [b] values of *k* are usually average values of at least two measurements not differing mutually by more than 10%; [c] rate constant related to *p*-xylene (equation (*1*)); [d] measured at 50°C, $k^{50}$ recalculated to $k^{25}$ using the activation energy of exchange 9·1 kcal/mol obtained in the systems $SnCl_4$-$CH_3COOD$ and $(CH_3)_2CH$. .COOD in *p*-xylene; [e] 3M-$D_2SO_4$ in $CF_3COOD$.

ate, releasing simultaneously HCl. In the systems with $CHCl_2COOH$ and $CCl_3COOH$ the amount of the acid which reacted with $TiCl_4$ was 80% and 54%, respectively. There was more carboxylate than the complex among the products and the ratio complex/carboxylate was but slightly higher in the system with $CHCl_2COOH$. In the system $TiCl_4$–$CF_3COOH$ under the same conditions only 15% of the acid reacted, mainly to form carboxylate (more than 90%); thus the concentration of the complex with $TiCl_4$ was approximately by more than an order of magnitude lower than in the systems with chloroacetic acids. The concentration of the complexes in the systems with $TiCl_4$ thus decreases in the acid order $CH_3CH_2COOH > > CH_3COOH > CHCl_2COOH > CCl_3COOH \gg CF_3COOH$. It can be seen from Table I that the increasing exchange rates follow the same order, with the exception of the last system: the lower exchange rate in the system with $CF_3COOH$ is due to a considerably lower concentration of the complex. It may be assumed, therefore, that in the above mentioned series of acids the acidity of the complexes increases.

The systems $RCOOD$–$SnCl_4$ with the component ratio 2 : 1 exchange deuterium for hydrogen with a sufficient rate only with more basic aromatic hydrocarbons, as, *e.g.*, with *p*-xylene. The exchange rate in the system $CH_3COOD$–$SnCl_4$ was – with the molar ratios of all components preserved – considerably higher than in the systems with isobutyric and pivalic acid (Table I). Small additions of $D_2O$ speeded up the exchange in these systems. However, neither the addition of 1 mmol of $D_2O$ in the system with isobutyric acid increased the exchange rate to the rate in the system with anhydrous $CH_3COOD$. These results, together with the results obtained for the systems with $TiCl_4$, contradict the opinion of Satchell[4] that the exchange rate in complex systems increases with the basicity of the carboxylic acid. His conclusions have been based on a higher exchange rate in the tritium-labelled system $SnCl_4$–$(CH_3)_3CCOOH$ in comparison with the system $SnCl_4$–$CH_3COOH$. The acidity of the complex $2\,CH_3COOD.\,SnCl_4$ in comparison with the complex containing pivalic acid (which has a lower dissociation constant than acetic acid) is even higher than the measured exchange rates show, as its equilibrium concentration is by about 10% lower than the concentration of the complex $2\,(CH_3)_3CCOOD.\,.SnCl_4$. This is because the equilibrium constant of the former complex formation is of the order of $10^1$, while that one of the latter complex is of the order of $10^2$ (ref.[1,7]). In the systems $SnCl_4$–halogenated acetic acids which form complexes to a negligible extent only, the exchange rate is higher than with the pure acids. However, it does not reach the rates obtained with the complexes of non-halogenated acids and the relative increase of the rate after the $SnCl_4$ addition decreases with the increasing strength of the acid. This can be explained, in agreement with the results of Satchell[3], by the decreasing tendency of forming complexes with $SnCl_4$.

The rate of exchange of pure carboxylic acids could be measured well in the systems. $CF_3COOD$, $CCl_3COOD$, and $CHCl_2COOD$–mesitylene. The acids $CHF_2COOD$ and $CH_2ClCOOD$ showed a very low solubility in mesitylene and the exchange rate of acetic acid was too slow. Table II shows that the rate of exchange increases with the increasing strength of the acid, characterized, *e.g.*, by its dissociation constant in water. The exchange rate between a carboxylic acid and an aromatic hydrocarbon also increases with the increasing ratio acid/aromatic hydrocarbon. In the system $CF_3COOD$–mesitylene an approximately linear dependence was found between $\log k$ and the acid molar concentration over the concentration range $3-10$M.

It follows from the studies of infrared spectra of acid solutions that the acid dimers do not exhibit an interaction with aromatic compounds which could be verified experimentally. However, their dissociation to monomers or to linear oligomers occurs the more extensively the stronger is the acid and the more basic is the aromatic hydrocarbon. The acid monomer is then solvated by the aromatic compound and this leads to a decrease of the wave-number of the monomer $\nu(O—H)$ vibration. Again, this decrease is the larger the stronger is the acid and the more basic is the aromatic hydrocarbon. The dimer-to-monomer dissociation increases with the decreasing concentration of the acid in the aromatic hydrocarbon, but even in the system $CF_3COOH$–mesitylene during the dilution of the acid an absolute increase of the monomer concentration does not take place. Contrarily, with the increasing concentration of the acid up to 3M the absolute concentration of the monomer increases. The monomer concentration solely is not, however, the decisive factor influencing the exchange rate, as, *e.g.*, in 1M solutions of $CF_3COOH$ in *p*-xylene the monomer concentration is only 1·3-times smaller than in mesitylene (assuming the extinction coefficient of the monomer is the same in both aromatic compounds). On the other hand, the rate of exchange in *p*-xylene is lower by four orders of magni-

TABLE II

Comparison of Molecular Spectroscopic Data with Exchange Rates in Systems Halogenoacetic Acid–Aromatic Hydrocarbon

| Acid | $k'^a$ | | $\nu(O—H)$ of monomer acid, $cm^{-1}$ | | $E$, $\nu(O—H)^b$ | $K_{diss.}{}^c$ in water 25°C |
|---|---|---|---|---|---|---|
| | mesitylene | *p*-xylene | mesitylene | *p*-xylene | mesitylene | |
| $CF_3COOD$ | 1 | $1{\cdot}16 . 10^{-4}$ | 3 320 | 3 350 | 8·0 | $5{\cdot}9 . 10^{-1}$ |
| $CCl_3COOD$ | $4{\cdot}63 . 10^{-2}$ | — | 3 330 | 3 350 | 5·7 | $1{\cdot}2 . 10^{-1}$ |
| $CHCl_2COOD$ | $6{\cdot}26 . 10^{-3}$ | — | 3 355 | 3 375 | 1·0 | $5{\cdot}1 . 10^{-2}$ |

[a] Rate constant related to the system $CF_3COOD$–mesitylene at the same molar ratio RCOOH/ /aromatic hydrocarbon; [b] extinction of the monomer acid band in 1M solution related to the system $CHCl_2COOH$–mesitylene; [c] ref.[12].

tude (Table II). This observation is in agreement with the concept of Gold[8] and others[9] that the slowest step in the exchange is not the formation of the complex with the aromatic hydrocarbon, but rather the exchange within the complex:

$$1/2(\mathrm{AD})_2 + \mathrm{ArH} \xrightleftharpoons{\text{fast}} \mathrm{ArH.AD} \xrightleftharpoons{\text{slow}} \mathrm{ArD.AH} \xrightleftharpoons{\text{fast}} \mathrm{ArD} + \\ + 1/2(\mathrm{AH})_2 \,.$$

The relation between the magnitude of the monomer-aromatic hydrocarbon interaction, characterized by the position of the monomer $\nu$(O—H) vibration band, and the rate of exchange (Table II) has a qualitative character only. As the fraction of the acid monomer : dimer decreases with the increasing concentration of the acid, the linear dependence of log $k$ on the acid concentration shows that the particle actively carrying out the exchange is not an isolated molecule of the acid monomer, but presumably its ionized agglomerate with other acid molecules.

From the point of view of characterizing the catalytic activity of the studied systems in acid-catalyzed reactions, it is useful to mutually compare the acidity of these systems as obtained from the H—D exchange measurements, because the exchange occurs, similarly as isomerisation and alkylation reactions, *via* the formation of a protonized complex with an aromate. The logarithm of the rate constant of the exchange reaction can be approximately regarded as a measure of the acidity, as it exhibits an approximately linear dependence not only on the Hammett acidity function $- H_0$, but also on the basicity of the aromatic hydrocarbon, with a proportionality constant in both cases close to unity[6,9]. It was found by direct measurements of the exchange rates of the system $H_2SO_4$–$CF_3COOH$ (of a known $H_0$) in several aromatic compounds that in *p*-xylene the exchange was $10^3$-times faster than in benzene, and in mesitylene $10^4$-times faster than in *p*-xylene (ref.[6] and Table I). Similar data were obtained on the exchange of $CF_3COOH$ with various aromatic hydrocarbons[9]. They correspond well to the relative basicities of these aromatic compounds as obtained both by means of complex acid HF–$BF_3$ (ref.[10]) and from relative electric conductivities in systems HF–aromatic hydrocarbon[11].

Therefore, the obtained values of log $k$ can be recalculated to relative log $k'$ related to *p*-xylene as to a reference solvent:

$$\log k' = \log k\,(p\text{-xylene}) = \log k\,(\text{benzene}) + 3 = \log k\,(\text{mesitylene}) - 4 \qquad (1)$$

The values of log $k'$ which express also the relative acidity of the systems are given in Table I. For comparison with sulphuric acid, the most often used acidic catalyst, the rate of exchange between $D_2SO_4$ and benzene was measured. It follows from the approximately equal exchange rates with 3M-$D_2SO_4$ in $CF_3COOD$ and the systems $TiCl_4$ with halogenated acetic acids (Table I) that the complexes $TiCl_4$.RCOOH are probably stronger than sulphuric acid, as their concentration in the system was by one or two orders of magnitude lower than the concentration of sulphuric acid. The systems with $SnCl_4$ are substantially less acidic than the systems with $TiCl_4$, and it follows from a comparison with published data[6] that their protonation action can be compared to that one of $0{\cdot}1\text{M-}H_2SO_4$ in $CF_3COOH$.

This comparison of the acidity of catalytic systems, based on log $k$ measurements, is relatively accurate for systems measured at the same molar ratios and under the same conditions. However, it provides only order-of-magnitude estimates of values as far as the differences in acidities are concerned between the systems containing $TiCl_4$ or $SnCl_4$ and sulphuric acid, where the influence of the kinetic effect of the reverse exchange H—D and D—H was neglected[13] and the influence of different concentrations of the catalytic systems was not properly evaluated.

*The authors are indebted to Dr B. Matyska for valuable comments and to Mrs D. Rubášová for her technical help in measuring the infrared spectra.*

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Translated by Z. Herman.