743. *Co-catalysis. Part III.*[1] *A Comparison of Aliphatic and Aromatic Carboxylic Acids as Friedel–Crafts Co-catalysts for Stannic Chloride.*

By D. P. N. SATCHELL.

Brønsted co-catalytic efficiencies, in relation to stannic chloride, are found to be in the order *o*-toluic acid > pivalic acid ~ benzoic acid > phenylacetic acid > *m*-nitrobenzoic acid. These are held to support previous generalisations about co-catalytic behaviour.

A possible parallelism between carboxylic acid–Lewis acid interaction and carboxylic anhydride–Lewis acid interaction is pointed out.

IN Part II[1] we made use of the aromatic hydrogen exchange reaction to compare the co-catalytic powers of a series of halogen-substituted acetic acids and, in the light of other, previous evidence, made the tentative generalisation that co-catalytic ability ultimately depended on the electron-availability on those atoms of the anion provided by the

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[1] Part II, Satchell, *J.*, 1961, 1453.

Brønsted component which co-ordinate with the Lewis acid. Thus with stannic chloride the order of co-catalytic efficiency is

$$HCl > H_2O > CH_3{\cdot}CO_2H > CH_2Cl{\cdot}CO_2H > CHCl_2{\cdot}CO_2H > CF_3{\cdot}CO_2H$$

Results for some further aliphatic, and also some aromatic, carboxylic acids are now reported and are discussed in the light of the foregoing generalisation.

The acids studied were benzoic, *o*-toluic, *m*-nitrobenzoic, pivalic, and phenylacetic. The experiments with each co-catalyst, though of the same design, were not so extensive as those reported in previous Parts. Use was made of the fact that the exchange rate constant at low co-catalyst concentrations is little dependent on this concentration. Thus, exchange rates were determined for each acid at an arbitrary low acid concentration and at one, or sometimes two, stannic chloride concentrations. The observed exchange rates are collected in Table 1, together with the corresponding acid dissociation constants, and data for acetic acid for comparison.[1]

TABLE 1. *Rate constant for tritium exchange between aliphatic and aromatic carboxylic acids and* m-*xylene catalysed by stannic chloride, at 25°.*

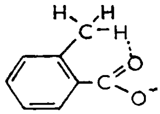
λ = observed first-order exchange rate constant. K = acid dissociation constant in water at 25°. Brønsted acid concentration ~0·08M.

Acid	[SnCl$_4$]	$10^4\lambda$ (min.$^{-1}$)	K	Acid	[SnCl$_4$]	$10^4\lambda$ (min.$^{-1}$)	K
$CH_3{\cdot}CO_2H$ [1]	0·172	62·2	$1{\cdot}8 \times 10^{-5}$	$CH_2Ph{\cdot}CO_2H$	0·344	197	$6{\cdot}0 \times 10^{-5}$
	0·344	140		$Ph{\cdot}CO_2H$	0·172	119	$6{\cdot}8 \times 10^{-5}$
$CF_3{\cdot}CO_2H$ [1]	0·344	8·51	>1		0·344	265	
$CMe_3{\cdot}CO_2H$	0·172	123	$9{\cdot}6 \times 10^{-6}$	*o*-$C_6H_4Me{\cdot}CO_2H$	0·344	383	$1{\cdot}3 \times 10^{-4}$
	0·344	288		*m*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$	0·344	124	$3{\cdot}5 \times 10^{-4}$

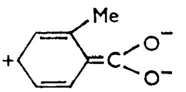
It is at once apparent that co-catalytic power is not simply related to conventional acid strength. This result supports the conclusions of Part I.[2]

A qualitative estimate of the relative electron availabilities on the oxygen atoms of the different co-catalyst anions is easiest for the series of structurally related acids *o*-toluic, benzoic, and *m*-nitrobenzoic. The *m*-nitrobenzoate ion will be expected to have a lower electron availability than the benzoate ion, because of the $-I$ effect of the *m*-nitro-group. Also, the benzoate ion might arguably be expected to have a lower availability than the *o*-toluate ion, for the *ortho*-substituent will certainly have a $+I$ effect. This substituent has been considered previously to have one, or both, of two other effects of relevance. Some authors[3] have considered the possibility of six-membered hydrogen-bonded ring structures of the form (I). These, if real, would tend to localise the charge on a carboxylic-oxygen atom, and so reinforce the $+I$ effect. Such structures as a partial explanation of "*ortho*"-effects are, however, at present out of favour. Their existence is, of course, not essential to the present argument: the $+I$ effect remains. The *o*-methyl group will also very probably have a steric effect which will tend to reduce the conjugation of the carbonyl group with the benzene ring. This will reduce the importance of structures such as (II) for the *o*-toluate ion in comparison with the benzoate ion. However, these

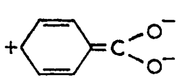
(I)



(II)



(III)



triply charged species are likely to be of rather minor importance in determining the overall resonance hybrid, especially in media of such low dielectric constant (~2) as were used in the present experiments (see previous Parts). It seems reasonable, therefore, to expect

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

[3] "Determination of Organic Structures by Physical Methods," ed. Braude and Nachod, New York, 1955, p. 631.

any differences in the electron density of the *o*-toluate and benzoate ions to be due mainly to the $+I$ effect of the methyl group, and thus to anticipate a greater electron availability for the oxygen atoms of the former than for those of the latter.

If co-catalytic ability is related to this electron availability, as we suggest, then the predicted order of efficacy will be *o*-toluic > benzoic > *m*-nitrobenzoic. This is the order found experimentally (see Table). In view of the fairly clear-cut nature of the argument for these acids this result seems rather strong support for the proposed generalisation.

Another series of structurally related acids is available in pivalic (trimethylacetic), acetic, and phenylacetic acid. The oxygen atoms of the pivalate ion will have greater electron densities than those of the acetate ion, in view of the substitution of the t-butyl for the methyl group on the carboxylic-carbon atom. Thus the co-catalytic power of pivalic acid would be expected to exceed that of acetic acid, as found (see Table). This result is again good support for the proposed generalisation.

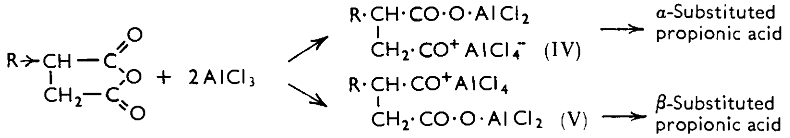
Phenylacetic acid proves to be a slightly better co-catalyst than acetic acid. In view of what has been described [4] as the "dual" nature of the phenyl group, *i.e.*, the ability to supply or withdraw electrons as the occasion demands, it is difficult to predict the relative electron availabilities for the acetate and phenylacetate ions in the present context. If it were possible to prove that electron withdrawal was dominant here, then phenylacetic acid, as a better co-catalyst than acetic acid, would provide an exception to the generalisation proposed. There seem, however, no strong grounds on which to regard it as such. Indeed, the success of the rule in correlating co-catalytic efficiency suggests that, in fact, the phenyl group is supplying electrons in this reaction.

A final interesting comparison is that between the aromatic and the aliphatic series, *i.e.*, between benzoic and acetic acid. Benzoic is the better co-catalyst, being nearly as effective as pivalic acid (see Table). The reason is, perhaps, the possibility of some (though very small) contribution from structures with extended conjugation such as (III) which are not possible for the acetate ion. It is again very difficult to predict the relative electron availabilities for these two anions. The experimental findings might be taken to indicate that the benzoate ion has the greater electron density on oxygen.

It will be noticed that the effects discussed, in this paper, are small: the total change in rate from *m*-nitrobenzoic to *o*-toluic is by a factor of only 3. However, this is to be expected in view of previous results: very large changes in electron density seem required to affect materially the catalytic efficiency.

In general, it seems that all the results so far assembled can be reasonably fitted into a single pattern and, on the whole, the new work tends to support the generalisations made in previous Parts. It will be interesting to see if further experiments lead to a refutation or whether, in fact, the prediction of co-catalytic power is, in principle at least, a straightforward problem under the conditions considered, and for similar systems.

Finally, it is noteworthy that Berliner, in his review [4] of the aluminium chloride-catalysed, Friedel–Crafts acylation by substituted succinic anhydrides, concluded that the direction of cleavage of unsymmetrically substituted anhydrides (which can give two isomeric ketones) is similarly controlled by the electrophilic character of the Lewis acid and the substituent's influence on the electron availability on carboxylic oxygen. The mechanism is considered to be of the annexed type. While the proportions of the products



are doubtless determined by factors other than the relative amounts of (IV) and (V), nevertheless a study of the available data [4] for media of low dielectric constant, such as were

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[4] Berliner, in "Organic Reactions," Wiley & Sons, Inc., New York, 1949, Vol. V, pp. 232 *et seq.*

used in our experiments (*i.e.*, benzene, toluene, xylenes, etc.), shows that they may be reasonably rationalised by assuming (*a*) that the preferential formation of (IV) or (V) is the dominant effect in product determination, (*b*) that electron-repelling substituents (R) favour initial attack on the nearest carbonyl to yield (IV) [rather than (V)], and that electron-withdrawing substituents have the opposite effect.

For media of higher dielectric constant such as nitrobenzene, Berliner points out that rationalisation requires the introduction of an additional, medium effect. The extension of the above generalisations to such systems is in any case problematical, for the relative importance of the different steps in the mechanism may well be altered. However, for media of low dielectric constant, there appear some grounds for thinking that there is an analogy between the mechanisms of Friedel–Crafts co-catalysis by carboxylic acids, and Friedel–Crafts acylation by carboxylic anhydrides: they both seem strongly influenced by electron availability on carboxylic oxygen.

Experimental.—*Materials.* The *m*-xylene and stannic chloride were prepared as previously described. Pivalic acid was prepared by fractionation of a commercial sample: a cut of b. p. 163° was taken. [*carboxy*-^{3}H]Pivalic acid was prepared by a method used for [*carboxy*-^{3}H]dichloroacetic acid.[1] Phenylacetic acid had m. p. 77°. [*carboxy*-^{3}H]Phenylacetic acid was prepared by dissolving a small quantity in dry ether and shaking the solution with active water; separation of the phases was followed by drying ($CaCl_2$) and evaporation under a vacuum, which left the active solid, m. p. 76°. " AnalaR " benzoic acid, *o*-toluic acid, and *m*-nitrobenzoic acid had m. p. 122°, 102—103°, and 142° respectively. [*carboxy*-^{3}H]Benzoic acid, [*carboxy*-^{3}H]-*o*-toluic acid, and [*carboxy*-^{3}H]-*m*-nitrobenzoic acid were prepared as was [*carboxy*-^{3}H]phenylacetic acid, and had m. p. 121°, 101·5°, and 141°, respectively.

Methods. These have been described previously.[1,2]

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