

The Nature of the Co-ordinate Link. Part IX. The Dissociation Constants of the Acids $p\text{-R}_3\text{M}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ (M = C, Si, Ge, and Sn and R = Me and Et) and the Relative Strengths of $d_\pi\text{-}p_\pi$ -Bonding in the M-C_{ar} Bond.*

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The strengths of the above acids have been determined (Table 1) to estimate the relative amounts of double bonding in the M-C_{ar} bond, and hence obtain some indication of how $d_\pi\text{-}p_\pi$ bonding depends on the atom M. This is important in complex chemistry because the transition metals can form $d_\pi\text{-}p_\pi$ bonds with donor atoms from the first transition series, as occurs in complex cyanides, carbonyls, isonitrile complexes, nitro-complexes, etc. Our measurements indicate that, in the above acids, $d_\pi\text{-}p_\pi$ bonding occurs when M = Si, Ge, and Sn. Also, other things being equal, the amounts of $d_\pi\text{-}p_\pi$ bonding appear to be roughly independent of the principal quantum number or size of the atom M.

In previous parts of this series we developed the idea that the co-ordinate bonds between acceptor metal atoms with filled d -orbitals and donor atoms with vacant or potentially vacant d - or p -orbitals have partial double-bond character. The π -type component of the bond is formed by overlap of a filled d -orbital of the metal with a vacant d - or p -orbital of the donor atom. It is a donor π -type bond for which electrons are provided by the metal, and may be called a dative π -bond. In Parts V and VI (Chatt and Wilkins, *J.*, 1952, 273,

* Part VIII, *J.*, 1953, 2363.

4300) we attempted to estimate the relative amounts of $d_{\pi}-d_{\pi}$ bonding in the P-Pt, As-Pt, and Sb-Pt bonds by examining the equilibria between *cis*- and *trans*-(Et_3Q) $_2\text{PtCl}_2$ where Q = P, As, and Sb. Our measurements indicated that the strength of the Q-Pt bond is more than 5 kcal. greater in the *cis*- than in the *trans*-isomers. If we attribute this enhanced strength to greater $d_{\pi}-d_{\pi}$ bonding in the *cis*-isomers, which would be expected on theoretical grounds, our experiments also indicated that the strength of π -type bonding changed very little throughout the series Q = P to Q = Sb. It is well known that the familiar $p_{\pi}-p_{\pi}$ double bonding, as in ethylene and carbon dioxide, is practically limited to atoms of principal quantum number 2, and so it seemed surprising that the change in principal quantum number of atom Q in the above series had so little effect on the strength of $d_{\pi}-d_{\pi}$ bonding. It seems that $d_{\pi}-d_{\pi}$ bonding is roughly independent of the relative sizes of the atoms forming the bond.

There is an element of speculation in the interpretation of the above work and so we have sought another system where dative π -type bonding involving a d -orbital might occur, to see whether it does in fact occur and how the strength of π -type bonding changes with increasing difference in size of the atoms bound. We studied the series $p\text{-R}_3\text{M}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$

FIG. 1. Schematic atomic-orbital representation of the dative π -bond between silicon and an aromatic system.

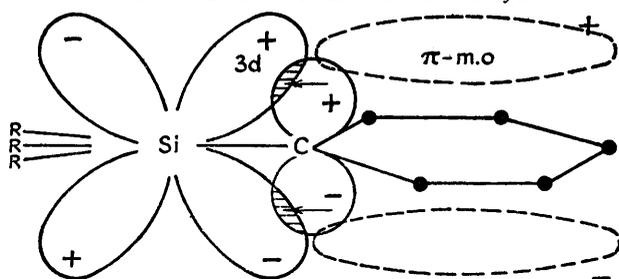
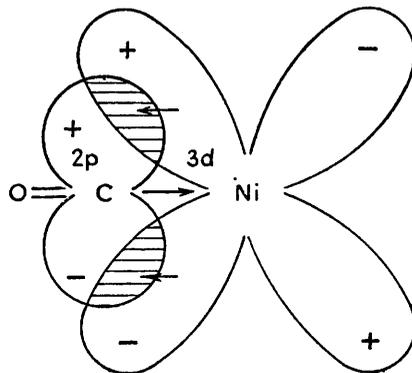
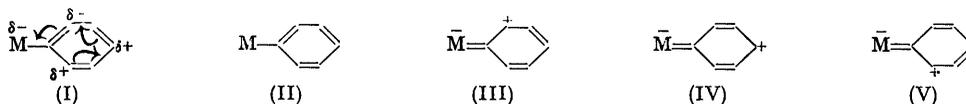


Fig. 2. Schematic atomic-orbital representation of the dative π -bond between nickel and carbon in nickel carbonyl.



(where M = C, Si, Ge, and Sn, and R = Me and Et). In this series the acid strengths should be a sensitive indication of the strength of the M-C_{ar} π -type of bonding, since the electrons forming the dative π -bond must be supplied by the aromatic system. The dative π -bond would be formed by donation of electrons from a π -molecular orbital of the aromatic system into a vacant low-energy d -orbital of the atom M. A schematic representation of the orbitals forming this π -type bond is shown in Fig. 1. Other equivalent representations of the M-C_{ar} bond are (I) and as a resonance hybrid of the canonical forms (II), (III), (IV), and (V). This π -type bond is similar to the π -type bond between a transition metal and ligands containing bivalent carbon as donor, except that the electrons are provided by a d -orbital of the metal atom, and received into a p -orbital of the carbon atom, e.g., Ni-C in nickel carbonyl (Fig. 2).

When we started this work there was considerable doubt whether any of the above M-C_{ar} bonds had an order greater than unity (see Remick, *Record Chem. Prog.*, 1950, 11,



57). However, a number of recently published studies of silylbenzene derivatives containing electron-repelling groups substituted in the benzene ring, show that the Si-C_{ar} bond has partial double-bond character (Soffer and De Vries, *J. Amer. Chem. Soc.*, 1951, 73, 5817; Benkeser and Krysiak, *ibid.*, 1953, 75, 2421; Freiser, Eagle, and Speir, *ibid.*, p.

2821, 2824). The present work shows that the Si-C_{ar} bond has some double-bond character, at least in the anion *p*-R₃Si·C₆H₄·CO₂⁻ and therefore very probably in the acid; also that the Ge-C_{ar} and Sn-C_{ar} bonds are very closely similar in this respect to the Si-C_{ar} bond.

If all the M-C_{ar} bonds were purely σ-bonds, then only the electrostatic or inductive effects of the atoms M could influence the strengths of the acids *p*-R₃M·C₆H₄·CO₂H. In these circumstances the acid strengths should lie in the order of the electronegativities of the atoms M. Since carbon is much more electronegative than any of the other atoms M, *p*-R₃C·C₆H₄·CO₂H should be the strongest of this series of acids.

Since there are no 2*d*-orbitals, carbon has no vacant low-energy *d*-orbitals and so cannot form dative π-bonds, unless there are very weak dative π-bonds involving 3*d*-orbitals; thus the R₃C-C_{ar} bond should be purely of σ-type, or nearly so. Silicon, germanium, and tin have vacant *d*-orbitals in their valency shells, hence they might form strong dative π-bonds with the aromatic carbon atom, and so the M-C_{ar} bond could have definite double-bond character when M = Si, Ge, and Sn, but not C. In this event the electron withdrawal from the π-molecular orbitals of the aromatic system in forming the dative π-bond (a negative mesomeric effect) would enhance the strengths of the acids containing silicon, germanium, and tin.

The strengths of the above acids were measured in 60·1% aqueous ethanol by Kilpi's absolute differential method (*ibid.*, 1952, 74, 5296), modified to obtain more accurate relative values of *K_a* by using a differential titration technique and quinhydrone electrodes.

The strength of *p*-Me₃Si·C₆H₄·CO₂H relative to benzoic acid has been measured previously in 50% (by volume) aqueous ethanol. Roberts, McElhill, and Armstrong (*ibid.*, 1949, 71, 2923) first reported these acids to have p*K* values of 5·85 and 5·75 respectively, later corrected to 5·80 ± 0·01 and 5·80 ± 0·01 (Roberts and Regan, *ibid.*, 1953, 75, 4102); but their method was not one which would allow of such great accuracy. In 10⁻⁵ M-aqueous solution, using a spectroscopic method, Benkeser and Krysiak (*loc. cit.*) found values of p*K* 4·27 ± 0·02 and 4·20 ± 0·04. In 60·1% (by weight) aqueous ethanol we find, by Kilpi's method, that *p*-Me₃Si·C₆H₄·CO₂H is very slightly stronger than benzoic acid (see Table 1) with p*K* values of 5·955 ± 0·002 and 5·979 ± 0·009 (the "errors" are standard deviations). Since previous evidence points to *p*-trimethylsilylbenzoic acid's being slightly weaker than benzoic acid, we have also compared potentiometrically the pH of solutions of the acids identical in every respect, except that they contained the two different acids. At the half-titration point in 60·1% ethanol and an ionic strength of 5·2 × 10⁻³ the silyl acid is definitely the stronger and differs from benzoic acid by about 0·025 p*K* unit. It may be that the difference in the relative strengths of the two acids found by ourselves and by Benkeser and Krysiak is due to the use of different solvents (cf. Halford, *ibid.*, 1931, 53, 2944).

TABLE 1. The thermodynamic dissociation constants (*K_a*) of *p*-R₃M·C₆H₄·CO₂H in 60·1% (by weight) aqueous ethanol at 25°.

M	Electro- negativity *	10 ⁶ <i>K_a</i> (R = Me)	10 ⁶ <i>K_a</i> (R = Et)	M	Electro- negativity *	10 ⁶ <i>K_a</i> (R = Me)	10 ⁶ <i>K_a</i> (R = Et)
C	2·5	0·70	0·71	Ge	1·7	1·07	1·08
Si	1·8	1·11	1·13	Sn	1·7	1·05	1·17 †

Under the same conditions benzoic acid has a strength, 10⁶*K_a* = 1·05, and *p*-Me₃Si·CH₂·C₆H₄·CO₂H, 10⁶*K_a* = 0·46.

* According to Pauling ("Nature of the Chemical Bond," Cornell Univ. Press, 1945, p. 64).

† This value may be slightly in error because this acid was exceptionally difficult to purify, and purity could not be guaranteed.

The results listed in Table 1 show that the orders of acid strengths in the *p*-R₃M·C₆H₄·CO₂H series of acids do not lie in the order of the electronegativities of M, but that the acids containing silicon, germanium, and tin are much stronger than *p*-R₃C·C₆H₄·CO₂H. This indicates clearly that dative π-bonding occurs in the bonds Si-C_{ar}, Ge-C_{ar}, and Sn-C_{ar}, and that it is enough to overcome the positive inductive effect due to the greater electropositive character of silicon, germanium, and tin relative to carbon. Where the silicon atom is not conjugated with an aromatic system the positive inductive effect of silicon is evident

from the low acid strength of $p\text{-Me}_3\text{Si}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ (see Eaborn and Parker, *J.*, 1954, 939) and silylacetic acids (Sommer *et al.*, *J. Amer. Chem. Soc.*, 1949, 71, 1509), also from the enhanced basic strengths of aliphatic amines such as $\text{Me}_3\text{Si}\cdot\text{CH}_2\cdot\text{NH}_2$ ($K_b = 8.5 \times 10^{-4}$) relative to $\text{Me}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$ ($K_b = 3.9 \times 10^{-4}$) (Noll, Daubert, and Speier, *ibid.*, 1951, 73, 3871). The electron-releasing and -attracting properties of the silicon triad are therefore exactly opposite in character to those of the halogens.

The strengths of the acids containing silicon, germanium, and tin are not appreciably different, hence if there is any change in inductive effect in this series its effect on the acid strength is exactly compensated by a change in the mesomeric effect, *i.e.*, in the strength of dative π -bonding. However, since the electronegativities of silicon, germanium, and tin are approximately equal, the inductive effect probably changes little throughout this triad. We conclude, therefore, that the double-bond character of the Si-C_{ar} , Ge-C_{ar} , and Sn-C_{ar} bonds in this series of compounds is approximately constant in spite of the great changes in relative sizes of the atoms bound. This finding is in accordance with the recent theoretical prediction by Craig, Maccoll, Nyholm, Orgel, and Sutton (*J.*, 1954, 332) that $d_{\pi}\text{-}p_{\pi}$ bonding should be more or less independent of the relative sizes of the bonded orbitals, especially when the d -orbital is considerably more diffuse than the p -orbital. It should be emphasised, however, that the amount of π -bonding will be greatly dependent on the electron-attracting or -releasing effects of substituents attached to the benzene nucleus or to the silicon, germanium, or tin atoms.

EXPERIMENTAL

Microanalyses are by Messrs. W. Brown and A. G. Olney of these laboratories.

Preparation of the Acids.—*p-tert.*-Butylbenzoic acid was prepared by oxidation with hypochlorite of *p-tert.*-butylacetophenone (Price and Lincoln, *J. Amer. Chem. Soc.*, 1951, 73, 5836). It had m. p. 168.5–169° (Price and Lincoln give 166°) (Found : C, 74.3; H, 8.0%; equiv., 178. Calc. for $\text{C}_{11}\text{H}_{14}\text{O}_2$: C, 74.1; H, 7.9%; equiv., 178).

p-(1 : 1-Diethylpropyl)benzoic acid. This acid is much more difficult to obtain than *p-tert.*-butylbenzoic acid but was finally obtained in small yield by oxidation with hypochlorite of *p*-(1 : 1-diethylpropyl)acetophenone. Acetyl chloride (30.4 g., 1.0 mol.) was added with stirring to a suspension of anhydrous ferric chloride (78 g., 1.2 mols.) in carbon tetrachloride (200 c.c.) at 3°, followed by the dropwise addition of 1 : 1-diethylpropylbenzene (Schreiner, *J. prakt. Chem.*, [2], 1910, 82, 296) at 30–40° (ice cooling). After being stirred for 5 hr. at 40° the reaction mixture was hydrolysed with dilute hydrochloric acid and extracted with ether. The ethereal extract was dried (Na_2SO_4) and the ether distilled off, leaving a black viscous residue. This was refluxed for 2 hr. with a solution of Girard P reagent (70 g.) in ethanol (720 c.c.) and glacial acetic acid (72 c.c.), and the mixture then poured into cold water (4.5 l.) containing sodium hydroxide (40 g.). The aqueous solution was filtered, all the ether-soluble material was extracted and then the aqueous portion was acidified with concentrated sulphuric acid (60 c.c.). The acid solution was kept overnight and extracted again with ether. The dried ethereal extract on distillation gave crude *p*-(1 : 1-diethylpropyl)acetophenone (12.5 g.), b. p. 173–174°/12 mm. (Found : C, 81.3; H, 10.1, 9.6. $\text{C}_{15}\text{H}_{22}\text{O}$ requires C, 82.5; H, 10.2%). It was further purified through the semicarbazone which was thrice recrystallised from light petroleum-benzene with no attempt to separate the geometrical isomers. The semicarbazone had m. p. 160–180° from different preparations presumably depending on the isomeric composition of the product (Found : C, 69.9; H, 8.7; N, 15.3. Calc. for $\text{C}_{16}\text{H}_{22}\text{ON}_3$: C, 69.8; H, 9.15; N, 15.3%). The semicarbazone (0.25 g.), oxidised by heating in a sealed tube with 40% nitric acid at 200°, yielded terephthalic acid (0.07 g.), identified by its infra-red spectrum.

The ketone was recovered from the semicarbazone by acid hydrolysis and oxidised (5 g.) at 60–70° by vigorous stirring with a solution of potassium hypochlorite [200 c.c.; Price and Lincoln (*loc. cit.*)]. When all the ketone had dissolved (1½ hr.) the excess of hypochlorite was destroyed with sodium hydrogen sulphite, and the solution acidified to free the *p*-(1 : 1-diethylpropyl)benzoic acid. This was extracted from the aqueous solution with ether and extracted in turn from the ethereal solution by sodium carbonate solution. The oil obtained on acidification was taken up in ether, and the ethereal solution dried and evaporated to leave an oily residue which solidified overnight; yield 3 g. To obtain a solid sample of this acid at this stage was one of

the main difficulties in the preparation. All attempts to prepare the acid by other possible synthetical routes gave small quantities of oils. The crude product, recrystallised 12 times from aqueous ethanol, gave the pure acid, m. p. 58—60° (Found: C, 76.5; H, 9.3. $C_{14}H_{20}O_2$ requires C, 76.3; H, 9.2%). It is very soluble in all organic solvents.

The acids containing silicon, germanium, and tin were obtained by the following series of reactions:



In the first preparations only a moderate excess of magnesium was used, but in the last two ($p\text{-Me}_3\text{Ge}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ and $p\text{-Et}_3\text{Sn}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$) we used a very large excess of magnesium (30 mols.) which gave an improved yield (see Gilman and McGlumphy, *Bull. Soc. chim.*, 1928, 43, 1322; Skelly, M.Sc. Thesis, Queen's University, Belfast, 1952, p. 86). The bromo-compounds, $p\text{-R}_3\text{M}\cdot\text{C}_6\text{H}_4\cdot\text{Br}$, are colourless liquids; the triethyl acids, $p\text{-Et}_3\text{M}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, are low-melting solids, very soluble in all solvents except water, and difficult to purify. The trimethyl derivatives of higher melting point are readily purified. All the acids are white crystalline solids.

p-Trimethylsilylbenzoic acid. When prepared as above (Roberts, McElhill, and Armstrong, *J. Amer. Chem. Soc.*, 1949, 71, 2923) this acid had m. p. 116.5—117.5° (Roberts *et al.* give 117—118°) (Found: C, 62.2; H, 7.2%; equiv., 192. Calc. for $C_{10}H_{14}O_2Si$: C, 61.8; H, 7.3%; equiv., 194).

p-Triethylsilylbenzoic acid. *p*-Bromophenyltriethylsilane (Grüttner and Cauer, *Ber.*, 1918, 51, 1283) (15.5 g.) in ether (25 c.c.) was converted into the Grignard reagent by use of magnesium (1.9 g.) in ether (10 c.c.) and refluxing the solution for 2 hr. It was then poured on solid carbon dioxide and kept overnight. The product was hydrolysed by dilute hydrochloric acid, extracted with ether, and worked up in the same way as for *p*-(1:1-diethylpropyl)benzoic acid. The oily crude *p*-triethylsilylbenzoic acid slowly solidified and was recrystallised twice by freezing it at -75° from its solution in light petroleum (b. p. 40—60°). It had m. p. 47.0—47.5° (Found: C, 66.5; H, 8.5%; equiv., 236. $C_{13}H_{20}O_2Si$ requires C, 66.1; H, 8.5%; equiv., 236). Its *p*-nitrobenzyl ester had m. p. 83.5—84.0° (Found: C, 65.4; H, 6.5; N, 3.7. $C_{20}H_{25}O_4NSi$ requires C, 65.4; H, 6.9; N, 3.8%).

p-Triethylsilylbenzoic acid (0.95 g.) was heated in a sealed tube at 100° for 10 hr. with bromine (0.658 g.). The acid product was *p*-bromobenzoic acid, m. p. 255°, confirmed by forming its *p*-nitrobenzyl ester, m. p. 140.5—141°.

p-Bromophenyltrimethylgermanium. Trimethylbromogermanium (Lengel and Dibeler, *J. Amer. Chem. Soc.*, 1952, 74, 2683; Dennis and Patnode, *ibid.*, 1930, 52, 2779) (17 g.) in benzene (50 c.c.) was added gradually to a Grignard reagent prepared from magnesium (4 g.) in ether (30 c.c.) and *p*-dibromobenzene (38 g.) in ether (120 c.c.). After refluxing for 3 hr., the product was hydrolysed with ammonium chloride solution, the ether layer was separated and dried, and the ether removed by distillation. The residue, which was fractionated up a 9'-column packed with Dixon rings, yielded *p*-bromophenyltrimethylgermanium (8.8 g.), b. p. 118°/20 mm. (Found: C, 39.5; H, 4.7. $C_9H_{13}BrGe$ requires C, 39.5; H, 4.8%).

p-Trimethylgermanylbenzoic acid. The above bromo-derivative (8.8 g., 1 mol.) in ether (100 c.c.) was added during 1 hr. to magnesium (23 g., 30 atom propn.) in ether (60 c.c.). The mixture was boiled under reflux during the addition, and afterwards for another 2½ hr., then carbonated. The acid was isolated in the same way as triethylsilylbenzoic acid. The crude *p*-trimethylgermanylbenzoic acid (3.2 g.) recrystallised five times from light petroleum (b. p. 80—100°) gave the pure material (1.0 g.), m. p. 119.5—121° (Found: C, 50.3; H, 5.9%; equiv., 238. $C_{10}H_{14}O_2Ge$ requires C, 50.3; H, 5.9%; equiv., 239).

p-Bromophenyltriethylgermanium was prepared in the same way as its trimethyl homologue, but from triethylchlorogermanium (Kraus and Flood, *J. Amer. Chem. Soc.*, 1932, 54, 1635), in 27% yield. The crude *p*-bromo-compound had b. p. 156°/14 mm. (Found: C, 46.8, 47.05; H, 6.0, 6.0; $C_{12}H_{18}BrGe$ requires C, 45.6; H, 6.1%).

p-Triethylgermanylbenzoic acid. This was prepared in the same way as *p*-triethylsilylbenzoic acid. The Grignard reagent, from the crude *p*-bromo-compound (5.0 g.) and magnesium (0.6 g.) in ether (11 c.c.), yields ultimately the crude *germanylbenzoic acid* as a sticky oil. Recrystallised twice by freezing (-75°) from light petroleum (b. p. 40—60°) it gave the pure acid (0.75 g.), m. p. 45—46° (Found: C, 56.0; H, 7.1%; equiv., 278. $C_{13}H_{20}O_2Ge$ requires C, 55.6; H, 7.2%; equiv., 281).

p-Bromophenyltrimethyltin. Prepared in exactly the same way as its germanium analogue, from trimethylbromotin (70 g.) and the Grignard reagent from *p*-dibromobenzene (107 g.),

magnesium (11 g.), and ether (400 c.c.), the *product* (36.5 g.) had b. p. 124°/15 mm. (Found : C, 33.6; H, 3.9. $C_9H_{13}BrSn$ requires C, 33.8; H, 4.1%).

p-Trimethylstannylbenzoic acid. Carbonation of the Grignard reagent from *p*-bromophenyltrimethyltin (36.5 g.), magnesium (3.1 g.), and ether (65 c.c.) gave the crude *acid* (4 g.). This was recrystallised twice from aqueous alcohol, then six times from light petroleum (b. p. 80—100°) giving the pure acid (1.3 g.), m. p. 131—132° (Found : C, 42.6; H, 5.0%; equiv., 284. $C_{10}H_{14}O_2Sn$ requires C, 42.15; H, 4.95%; equiv., 285).

p-Bromophenyltriethyltin. Obtained in analogous manner to *p*-bromophenyltrimethylgermanium, in 32% yield, the compound had b. p. 165.5°/14 mm. (Found : C, 40.1; H, 5.4. $C_{12}H_{18}BrSn$ requires C, 39.8; H, 5.3%).

p-Triethylstannylbenzoic acid. Carbonation of the Grignard reagent from *p*-bromophenyltriethyltin (10.8 g., 1 mol.), magnesium (23 g., 30 atom propns.), and ether (160 c.c.) yielded the crude *acid* (2.5 g.). Twice recrystallised by freezing (−75°) from light petroleum (b. p. 40—60°) it had m. p. 44.5—46.5° (Found : C, 47.9; H, 6.2%; equiv., 324. $C_{13}H_{20}O_2Sn$ requires C, 47.75; H, 6.2%; equiv., 327). This acid is slowly decomposed even by cold aqueous sodium carbonate and so the alkaline extraction must be carried out rapidly. Its high solubility in organic solvents and tendency to hydrolyse made its purification difficult. When treated with bromine in a sealed tube at 100° for 4 hr., it gave *p*-bromobenzoic acid, m. p. and mixed m. p. 254.5—255°.

Dissociation Constants.—The acids $p-R_3M \cdot C_6H_4 \cdot CO_2H$ are too insoluble in water for the determination of their acid strengths by direct pH measurements in that medium and so we chose aqueous ethanol containing 60.1% (by weight) of ethanol as solvent. In such solvents no standards of pH have been established and the conventional methods of determining acid strengths in water are available only as approximate methods. However, two closely related absolute methods of determining acid strength have been developed, one by Kilpi (*Z. physikal. Chem.*, 1935, 173, 223; *loc. cit.*) and the other by Grunwald (*ibid.*, 1951, 73, 4934). We tried both methods, and for our purpose found Kilpi's method as modified by R. Näsänen (*Suomen Kem.*, 1948, B, 21, 5) most suitable. The method depends upon determining the slope of the titration curve at the first inflection point in the titration with strong base of a solution of the weak acid containing a little of some strong acid. Previous workers have done this by titrating the solution in a cell containing a standard calomel or silver chloride electrode and one sensitive to changes in $[H^+]$. They add exactly equal increments of alkali, and note the small increment in potential of the cell. In Näsänen's method the concentration dissociation constants K'_a are calculated from the three maximum increments in potential. The accuracy of the method was limited by the accuracy with which the potential changes and the volumes of added alkali can be measured. By using a differential titration technique with two quinhydrone electrodes and a micrometer syringe, it is possible to measure the potential changes on each addition to 0.02 mv and volumes of 0.1 c.c. to better than 1 in 500, *i.e.*, to about the same accuracy as the other experimental operations. The limitation in the absolute accuracy of the method is now set by the unknown but small diffusion potential which develops between the cell compartments on each addition of titrating reagent. The repeatability and relative accuracy of the method is, however, excellent since the differential titration allows the checking of the zero after each addition and the elimination of any stray potentials which develop during an experiment. The method also has the advantage that rigorous exclusion of carbon dioxide is unnecessary. In some preliminary experiments we deliberately added a little sodium carbonate, and showed that the evaluation of the dissociation constants was not affected by it.

Apparatus.—The cell and electrode assembly are shown in Fig. 3. The solution to be titrated was placed in the cell, and stirred by passing through *C* a stream of nitrogen saturated with solvent vapour at the temperature of the experiment. Electrode *D* was a bright platinum disc 1 cm. in diameter separated from the rest of the cell by a coarse sintered-glass disc *G* through which the solution passed easily. The small electrode compartment containing *D* had a capacity of 0.5 c.c. when the cell was filled to the working level, and could be flushed out with nitrogen by turning tap *A* and closing tap *B*. Electrode *E* was a piece of bright platinum foil 2" × 1" curved into a half-cylinder to fit the cell. The titrating reagent was added from an "Aglä" micrometer syringe *F*, fitted with a long capillary nozzle which just dipped into the liquid in the cell. The cell was maintained at 25.00° ± 0.02°. Potential differences between the electrodes were measured with a Tinsley Vernier Potentiometer.

Materials.—*Ethanol.* "AnalaR" ethyl alcohol was used after boiling out of carbon dioxide and oxygen under nitrogen. Absence of traces of acetaldehyde and acetic acid was proved by testing with 2 : 4-dinitrophenylhydrazine and also by spectroscopy. The ethanol used had a transmission greater than 60% determined against water in 1 cm. quartz cells at 215 m μ .

Water. Distilled water was redistilled from potassium permanganate then passed through a Bio-demineralite ion-exchange resin.

Solvent. This was a mixture of the above water and ethanol of such composition that it had a specific gravity at 25° of $88,936 \pm 5 \times 10^{-5}$. This corresponds to a composition of $60.10 \pm 0.02\%$ of ethanol by weight ("Handbook of Chemistry and Physics," 33rd edn., Chemical Rubber Publ. Co., Cleveland, Ohio, 1951—1952, p. 1771). The acid strength of benzoic acid was checked in every new batch of solvent. This solvent was used to prepare the following solutions. Additional ethanol was added to the perchloric acid and sodium hydroxide solutions to compensate for the water in the concentrated solutions of these substances.

Perchloric acid. A standard solution (ca. 0.05N) was prepared from "AnalaR" acid, without further purification.

Sodium perchlorate. "AnalaR" grade was recrystallised from water and dried for at least 12 hr. at 150°, then made up into a standard solution of approximately 8×10^{-2} moles/l.

Sodium hydroxide. A standard solution (ca. 0.05N) was prepared, free from carbonate, by removing the clear supernatant liquid from a saturated solution of "AnalaR" sodium hydroxide and diluting as necessary.

Quinhydrone. "AnalaR" grade was added as solid to the titration cell when required.

Procedure.—40 c.c. of a solution of the weak acid of known concentration (ca. $1.0 \times 10^{-2}M$) were accurately pipetted into the cell. To this was added 0.2 c.c. of the perchloric acid solution

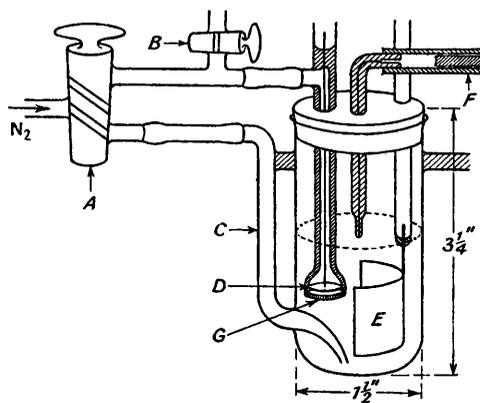


FIG. 3. Cell and electrode assembly used to measure the acid dissociation constants.

and enough sodium perchlorate solution (ca. 1 c.c.) to adjust the ionic strength to about 3.0×10^{-3} . Quinhydrone (ca. 0.05 g.) was added and the solution stirred by nitrogen until all had dissolved, then the small cell compartment containing the electrode *D* was flushed out a number of times. The potential difference between the electrodes was now measured with nitrogen passing through *C*. This initial potential was usually about 0.2 mv and will be called the "zero potential." An exactly measured addition (ca. 0.1 c.c.) of the standard alkali was now run in, causing a change in potential difference of ca. 10 mv which remained constant to 0.02 mv for several minutes before diffusion through the sintered-glass disc became apparent as a drifting potential. The cell compartment was flushed out and the "zero potential" re-determined. The differential titration was now continued with exactly equal additions of alkali, each causing a greater potential change, until at least one addition of alkali had been made after the addition causing the maximum potential change. The solution was then back-titrated with the standard perchloric acid in 0.1 c.c. additions in exactly the same manner. These two titrations were used to give two values of the concentration constants K' . A typical example is given in Table 2, together with a typical calculation.

The differential technique must have introduced a liquid junction potential and perhaps a systematic error. This potential was so small that attempts to measure it by replacing the large platinum electrode by a silver chloride electrode and using solutions and reagents all $3 \times 10^{-3}M$ in potassium chloride, but containing no sodium perchlorate, failed. The stability and sensitivity of this arrangement were not sufficient to allow us to determine even the sign of the diffusion potential. Any systematic error introduced, therefore, seems unlikely to cause an absolute error greater than 1% in K_a . This would not alter the relative accuracy of the determinations which is correctly indicated by the standard deviations.

Calculation.—The calculation was made by Näsänen's method (*loc. cit.*). Our potential changes and volumes are, however, about 1% greater and smaller respectively than those which would have been obtained with Kilpi's electrode assembly. This 1% is the ratio of the volumes of the two cell compartments, which should therefore be made as small as possible. The two

TABLE 2. *The titration of one sample of p-trimethylsilylbenzoic acid.*

Titration with alkali			Back-titration with acid		
E.M.F. of cell (mv)			E.M.F. of cell (mv)		
zero	after addn. of Δv	increment	zero	after addn. of Δv	increment
-0.20	9.11	9.31	+0.18	9.45	9.27
-0.22	10.98	11.20	+0.32	10.76	10.44
-0.09	10.98	11.07	+0.31	10.89	10.58
-0.11	9.44	9.55	+0.47	9.64	9.17

Quantities relating to the inflection point : $V^* = 41.6$ c.c., $10^2\Delta v = 9.88$ c.c., $10^2C = 5.086M$, $10^2C_A = 1.210M$, $10^2I = 2.519$.
 Quantities relating to the inflection point : $V = 42.0$ c.c., $10^2\Delta v = 9.88$ c.c., $10^2C = 4.810M$, $10^2C_A = 1.199M$, $10^2I = 2.768$.

From which are calculated : $dE/dm = 11.64$; $10^4P = 6.138$; $10^6K' = 1.502$; $10^6K = 1.103$.
 From which are calculated : $dE/dm = 10.915$; $10^4P = 6.130$; $10^6K' = 1.512$; $10^6K = 1.119$.

• For the meaning of the symbols see below.

errors are however compensating, and cancel out to within experimental error in calculating P (see below). The following symbols and quantities enter into the calculations : C , concentration of titrating reagent; C_A , concentration of weak acid; dE/dm , slope of titration curve in mv per addition (Δv) of alkali or acid at the inflection point [it is calculated from the three greatest potential increments observed during each titration (Näsänen, *loc. cit.*)] ; I , the ionic strength of the solution under investigation at the inflection point; K , the thermodynamic dissociation constant of the weak acid; K' , the concentration dissociation constant of the weak acid; $k = (2.303 RT)(nF)^{-1} = 59.16$; V , total volume of solution in the main cell compartment when the titration is at the inflection point; Δv , the volume of one addition of titrating reagent; x , hydrogen-ion concentration. Other relations used are :

$$\left(\frac{\partial F}{\partial m}\right)_x = \frac{\Delta v C}{V}; \quad \frac{dpH}{dm} = \frac{1}{k} \cdot \frac{dE}{dm}; \quad P = \left(\frac{\partial F}{\partial m}\right)_x \left(\frac{dpH}{dm}\right)^{-1}$$

where F is a function of the ion concentrations (cf. Näsänen, *loc. cit.*). The constant K' of the weak acid is obtained from the following two equations by successive approximations :

$$K' = (0.4343P - x)(x + K')^2(xC_A)^{-1} \quad \text{and} \quad x = [K'C_A(1 - K'x^{-1})(1 + K'x^{-1})^{-3}]^{\frac{1}{2}}$$

In our experiments a good initial estimate of x is given by $x = 0.215P$ and a first estimate of K' by $K' = x^2(C_A)^{-1}$. By using these estimates a good value of K' was quickly obtained.

The thermodynamic constants K were calculated from K' by the Debye-Hückel limiting law which appears to be applicable in aqueous alcohol up to ionic strengths of 0.006 (Grunwald and Berkowitz, *J. Amer. Chem. Soc.*, 1951, **73**, 4939). By using 43.4 for the dielectric constant of 60.1% aqueous ethanol (Akerlof, *J. Amer. Chem. Soc.*, 1932, **54**, 4125) the limiting law for 60.1% (by weight) aqueous ethanol at 25° becomes :

$$-\log f_{\pm} = 1.24I^{\frac{1}{2}}$$

Results.—Complete sets of determinations showing the best and worst agreement are given in Table 3 and the results for all the acids are summarised in Table 4.

Direct Comparison of Acid Strengths of p-Trimethylsilylbenzoic Acid and Benzoic Acid.—Solutions of $1.029 \times 10^{-2}M$ -benzoic and p -trimethylsilylbenzoic acids in 60.1% (by weight) ethanol were half neutralised with 0.0569N-sodium hydroxide, and then placed in two separate cells with equal amounts of solid quinhydrone. The ionic strength of the solutions was 5.2×10^{-3} . Nitrogen was bubbled through both cells throughout the experiment. The cells were connected by a freshly prepared saturated potassium chloride bridge. The E.M.F. between two platinum foil electrodes (*a*) and (*b*) was measured, first with both electrodes in one cell (benzoic acid), then with electrode (*a*) in p -trimethylsilylbenzoic acid and (*b*) in benzoic acid, and finally with both

electrodes in the silylbenzoic acid. The experiment was repeated with the same solutions, then again with new solutions at the same concentration and using another salt bridge. The results are shown in Table 5.

TABLE 3.

<i>p</i> -Me ₃ Si·C ₆ H ₄ ·CO ₂ H									
10 ³ <i>I</i> *	10 ² <i>C</i> _A	10 ⁴ <i>P</i>	10 ⁶ <i>K</i> '	10 ⁶ <i>K</i>	10 ³ <i>I</i> *	10 ² <i>C</i> _A	10 ⁴ <i>P</i>	10 ⁶ <i>K</i> '	10 ⁶ <i>K</i>
3·013	1·116	5·930	1·521	1·111	3·128	1·314	6·434	1·518	1·104
3·360	1·101	5·937	1·538	1·105	2·519	1·210	6·138	1·502	1·103
2·773	1·333	6·442	1·500	1·110	2·768	1·199	6·130	1·512	1·119

$K = 1·109 \times 10^{-6}$; standard deviation $\pm 0·006$.

<i>p</i> -Me ₃ Ge·C ₆ H ₄ ·CO ₂ H									
10 ³ <i>I</i> *	10 ² <i>C</i> _A	10 ⁴ <i>P</i>	10 ⁶ <i>K</i> '	10 ⁶ <i>K</i>	10 ³ <i>I</i> *	10 ² <i>C</i> _A	10 ⁴ <i>P</i>	10 ⁶ <i>K</i> '	10 ⁶ <i>K</i>
2·188	1·038	5·606	1·462	1·120	3·333	0·858	5·144	1·494	1·075
2·421	1·027	5·583	1·466	1·107	3·049	0·964	5·388	1·456	1·062
2·558	0·899	5·211	1·461	1·095	3·298	0·955	5·346	1·447	1·043
2·776	0·890	5·200	1·471	1·089	3·182	0·657	4·449	1·464	1·061
2·916	0·875	5·032	1·400	1·030	3·348	0·651	4·468	1·491	1·072
3·140	0·866	5·063	1·433	1·038					

$K = 1·072 \times 10^{-6}$; standard deviation $\pm 0·028$.

* The range of ionic strength is limited because lower strengths than those used decrease the sensitivity of the apparatus by increasing the resistance of the cell. Higher strengths would carry the experiments into the region where the Debye-Hückel limiting law is not sufficiently well obeyed.

TABLE 4.

Acid	10 ⁶ <i>K</i>	No. of detmns.	Standard deviation	Acid	10 ⁶ <i>K</i>	No. of detmns.	Standard deviation
C ₆ H ₅ ·CO ₂ H.....	1·050	27	$\pm 0·022$	<i>p</i> -Me ₃ Ge·C ₆ H ₄ ·CO ₂ H ...	1·072	11	$\pm 0·028$
<i>p</i> -Me ₃ C·C ₆ H ₄ ·CO ₂ H	0·699	8	$\pm 0·006$	<i>p</i> -Et ₃ Ge·C ₆ H ₄ ·CO ₂ H ...	1·077	6	$\pm 0·008$
<i>p</i> -Et ₃ C·C ₆ H ₄ ·CO ₂ H	0·712	6	$\pm 0·006$	<i>p</i> -Me ₃ Sn·C ₆ H ₄ ·CO ₂ H ...	1·051	6	$\pm 0·008$
<i>p</i> -Me ₃ Si·C ₆ H ₄ ·CO ₂ H	1·109	6	$\pm 0·006$	<i>p</i> -Et ₃ Sn·C ₆ H ₄ ·CO ₂ H ...	1·172	6	$\pm 0·027$
<i>p</i> -Et ₃ Si·C ₆ H ₄ ·CO ₂ H	1·129	6	$\pm 0·028$	<i>p</i> -Me ₃ Si·CH ₂ ·C ₆ H ₄ ·CO ₂ H	0·464	4	$\pm 0·006$

TABLE 5. Potential differences between the electrodes in mv.

Experiment	1	2	3
Both electrodes in benzoic acid	0·06	0·06	0·21
(a) in the <i>p</i> -trimethylsilylbenzoic acid	0·78	2·20	1·80
Both in <i>p</i> -trimethylsilylbenzoic acid	0·19	0·16	0·10

(a) Was the positive electrode.

Although the relative potentials of the electrodes fluctuate by 0·15 mv these experiments leave no doubt that the silylbenzoic acid is the stronger in 60·1% ethanol. The average difference in *pK* (from these figures) is $0·025 \pm 0·015$.

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