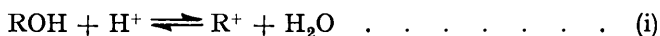


### 768. *The Strengths of Arylmethanols as Secondary Bases.*

By V. GOLD.

The relative strengths of four unsubstituted arylmethanols as secondary bases are shown to be in agreement with values calculated by simple molecular-orbital theory. The calculations are based on the assumption that  $\pi$ -electron energies make the most important structure-sensitive contribution to the free energy of ionisation and that the  $\pi$ -electron energy of di- and tri-phenylcarbonium ions may be calculated in the same way as if the conjugated systems were perfectly coplanar. It is inferred that in the series benzyl alcohol–diphenylmethanol–triphenylmethanol  $\pi$ -electron energies, and not steric strains, decide the relative strengths of secondary bases.

ARYLMETHANOLS have a tendency to ionise in strongly acidic solutions as secondary bases,<sup>1</sup> according to the formal equation :



The best known example of this equilibrium is the ionisation of triphenylmethanol and its derivatives in sulphuric acid solutions. The concept of the acidity function<sup>1,2</sup>  $J_0$  allows the strengths of different secondary bases to be expressed in a quantitative fashion over a considerable range of values in terms of the constant  $K_{\text{ROH}}$ , which governs the equilibrium (i). On this basis, comparative measurements for a number of arylmethanols have recently been reported<sup>3</sup> (though with different symbols). It has been pointed out<sup>4</sup> that there is quantitative disagreement between some of these measurements and the less extensive results of another investigation<sup>5</sup> but, in any case, the data appear to be adequate for the following consideration of the gross structural factors which govern the strengths of unsubstituted arylmethanols as secondary bases.

The standard free-energy change in reaction (i) (and hence the related equilibrium constant  $K_{\text{ROH}}$ ) may, in principle, depend on a number of things. Changes in resonance energy and steric compression energy on going from the alcohol to the carbonium ion are likely to be the most important structure-sensitive factors.<sup>6</sup> In view of the bulkiness of the carbonium ions it is probable that changes in the free energy of solvation would play only a minor rôle. An exact analysis of the problem is obviously impossible at present. In their discussions of it Deno *et al.*<sup>6,7</sup> concluded that the release of steric strain on formation of the carbonium ion was the important variable term, and that the change in resonance energy accompanying ionisation was the same for di- and tri-arylmethanols. As no theoretical estimate of any of the factors appears to have been attempted, we have now used a simple molecular-orbital calculation to assess the importance of  $\pi$ -electron energies and to see if a correlation exists between the change in resonance energy and the constant

<sup>1</sup> Gold and Hawes, *J.*, 1951, 2102.

<sup>2</sup> Gold, *Chem. and Ind.*, 1955, 172; *J.*, 1955, 1263.

<sup>3</sup> Deno, Jaruzelski, and Schriesheim, *J. Amer. Chem. Soc.*, 1955, **77**, 3044.

<sup>4</sup> Gold and Satchell, *J.*, 1956, 1635.

<sup>5</sup> Williams and Bevan, *Chem. and Ind.*, 1955, 171.

<sup>6</sup> Cf. Deno, Jaruzelski, and Schriesheim, *J. Org. Chem.*, 1954, **19**, 155.

<sup>7</sup> Deno and Schriesheim, *J. Amer. Chem. Soc.*, 1955, **77**, 3051.

$K_{\text{ROH}}$ . The method of calculation is analogous to that described for hydrocarbon acids<sup>8</sup> and primary bases<sup>9</sup> and for the ionisation of triphenylmethyl halides.<sup>10</sup>

In calculating the  $\pi$ -electron energies of the carbonium ions it was assumed that the twisting out of coplanarity which is due to the bulk of the phenyl group does not cause the resonance energy to fall greatly below the value applicable to a coplanar system. On this basis, if the changes in the constant  $K_{\text{ROH}}$  are entirely governed by changes in  $\pi$ -electron energies, we should have :

$$-RT \ln K_{\text{ROH}} = (E_{\pi})_{\text{R}^+} - (E_{\pi})_{\text{ROH}} + \text{Constant} \quad \dots \quad (\text{ii})$$

where  $E_{\pi}$  represents the contribution from the  $\pi$ -electron energies to the enthalpies of the hypothetical planar molecules indicated by the second subscript. The value of  $(E_{\pi})_{\text{ROH}}$  was obtained by considering each of the aryl groups attached to the exocyclic carbon atom to contribute an isolated conjugated system. The results of the calculation for a few typical secondary bases are tabulated.

The results in the column headed  $(\Delta E_{\pi} - \alpha)\beta^{-1}$  are expressed in terms of the characteristic energy parameter  $\beta$  (the resonance integral) of the molecular-orbital theory. It is known empirically that  $\beta$  has a value of about  $-18$  kcal./mole when, as in our case, no correction is applied in the calculation for changes in compressional energy<sup>11</sup> and overlap is neglected.

The calculation may be compared with experiment by plotting the available experimental values of  $\text{p}K_{\text{ROH}}$  against  $(\Delta E_{\pi} - \alpha)$ . According to the measurements by Deno, Jaruzelski, and Schriesheim<sup>3</sup> the  $\text{p}K_{\text{ROH}}$  values for triphenylmethanol, diphenylmethanol,

R	$(E_{\pi})_{\text{R}^+}$	$(E_{\pi})_{\text{ROH}}$	$(\Delta E_{\pi} - \alpha)\beta^{-1}$
Ph·CH <sub>2</sub> .....	$7\alpha + 8.72\beta$	$6\alpha + 8.00\beta$	0.72
Ph <sub>2</sub> CH .....	$13\alpha + 17.30\beta$	$12\alpha + 16.00\beta$	1.30
Ph <sub>3</sub> C .....	$19\alpha + 25.79\beta$	$18\alpha + 24.00\beta$	1.79
1-C <sub>10</sub> H <sub>7</sub> ·CH <sub>2</sub> .....	$11\alpha + 14.49\beta$	$10\alpha + 13.68\beta$	0.81
2-C <sub>10</sub> H <sub>7</sub> ·CH <sub>2</sub> .....	$11\alpha + 14.42\beta$	$10\alpha + 13.68\beta$	0.74
9-Anthrylmethyl .....	$15\alpha + 20.24\beta$	$14\alpha + 19.31\beta$	0.93
( <i>p</i> -C <sub>6</sub> H <sub>4</sub> Ph) <sub>3</sub> C .....	$37\alpha + 51.01\beta$	$36\alpha + 49.15\beta$	1.86
( <i>p</i> -C <sub>6</sub> H <sub>4</sub> Ph) <sub>2</sub> CPh .....	$31\alpha + 42.61\beta$	$30\alpha + 40.77\beta$	1.84
9-Fluorenyl .....	$13\alpha + 17.72\beta$	$12\alpha + 16.38\beta$	1.34
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Ph·CH <sub>2</sub> .....	$13\alpha + 17.14\beta$	$12\alpha + 16.38\beta$	0.76
<i>m</i> -C <sub>6</sub> H <sub>4</sub> Ph·CH <sub>2</sub> .....	$13\alpha + 17.10\beta$	$12\alpha + 16.38\beta$	0.72
9-Phenyl-9-fluorenyl .....	$19\alpha + 26.22\beta$	$18\alpha + 24.38\beta$	1.84
1-C <sub>10</sub> H <sub>7</sub> ·CPh <sub>2</sub> .....	$23\alpha + 31.54\beta$	$22\alpha + 29.68\beta$	1.86
( <i>m</i> -C <sub>6</sub> H <sub>4</sub> Ph) <sub>3</sub> C .....	$37\alpha + 50.95\beta$	$36\alpha + 49.15\beta$	1.80

and 9-fluorenyl are 6.63, 13.3, and 14.0 respectively. From the value for 2:4:6-trimethylbenzyl alcohol (17.38) and a consideration of the effect of methyl substitution in di- and tri-phenylmethanol it is estimated that the  $\text{p}K_{\text{ROH}}$  value for benzyl alcohol lies in the range 22—27 (see Appendix I). These results are plotted in Fig. 1. A relation, which is linear within the limits of error, is found to exist between  $\Delta E_{\pi}$  and  $\text{p}K_{\text{ROH}}$ , the slope of the line leading to the value  $\beta = -22 \pm 3$  kcal./mole, *i.e.*, close to the value to be expected if the basic assumption of the calculation—that resonance energy is the dominant structural influence governing the strengths of these secondary bases—is correct. The agreement does not constitute a proof but is taken as circumstantial evidence for the correctness of the assumptions.

The proximity of the points for diphenylmethanol and 9-fluorenyl may be regarded as particularly significant since in the latter case the ion is planar, whereas it need not be so in the former. If the model used by Deno *et al.*<sup>6</sup> (according to which only one ring conjugates with the exocyclic carbon atom in di- and tri-arylcarbonium ions, the other ring or rings being unable to share in the conjugation because of their unfavourable orientation) were correct, this agreement would be out of place.

This simple resonance theory would probably be inapplicable to arylmethanols containing more bulky groups, such as naphthyl and anthryl groups perhaps, and measurements

<sup>8</sup> Wheland, *J. Chem. Phys.*, 1934, **2**, 479.

<sup>9</sup> Gold and Tye, *J.*, 1952, 2184.

<sup>10</sup> Streitwieser, *J. Amer. Chem. Soc.*, 1952, **74**, 5288.

<sup>11</sup> Lennard-Jones, *Proc. Roy. Soc.*, 1937, *A*, **158**, 280; Coulson and Altmann, *Trans. Faraday Soc.*, 1952, **48**, 293.

of the basic strength of the corresponding alcohols may yield quantitative information regarding the  $\pi$ -electron energies of twisted conjugated systems.

In view of the apparent success of this treatment, it remains to inquire whether the experimental data on which the model used by Deno *et al.* was based may have an alternative explanation. The evidence adduced falls into two main groups. First, it was noted that there was an almost constant difference between  $pK$  for  $Ar_3C\cdot OH$  and  $pK$  for  $Ar_2CH\cdot OH$  for a number of substituted phenyl groups  $Ar$ . This indicates that two substituent groups in diphenylmethanol exert the same influence on the  $pK_{ROH}$  value as three of the same kind in triphenylmethanol. A similar relation was also noted for single substituent groups in di- and tri-phenylmethanol. Secondly, there is a similarity in absorption spectra between several pairs of correspondingly substituted di- and tri-aryl-carbonium ions.

The interpretation of the absorption spectra will have to await more detailed knowledge concerning the electron systems of twisted conjugated systems, but the substituent effects may be qualitatively explained also in terms of our model.

Consider the effect of a single electron-attracting group  $X$  in the di- and in the tri-phenylcarbonium ion. The electron-withdrawal of  $X$  from the exocyclic carbon atom will

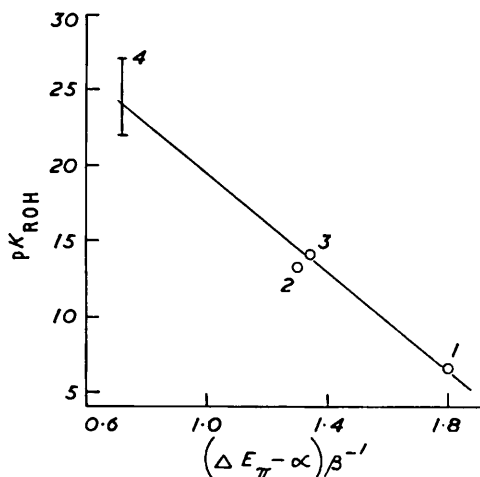


FIG. 1.

- 1, Triphenylmethanol.
- 2, Diphenylmethanol.
- 3, 9-Fluorenone.
- 4, Benzyl alcohol.

be partially compensated by electron-release from the unsubstituted phenyl group(s), which, according to the situation, can act as "electron sources" or "sinks." In this way the effect of  $X$  is "diluted" by being spread over the other rings and will, in first approximation, be inversely proportional to the total number of rings, as observed by Deno and Schriesheim.<sup>7</sup>

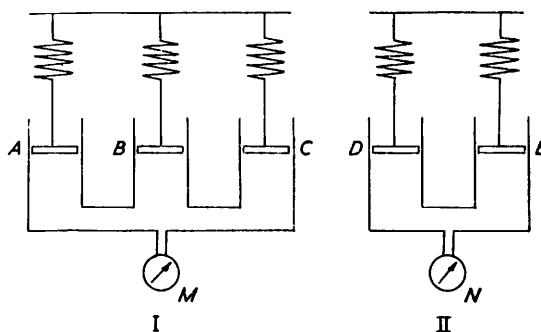
It has also been observed that two identical substituent groups in diphenylmethanol effect the same change in  $pK$  for diphenylmethanol as three of the same kind in  $pK$  for triphenylmethanol, and the following is suggested as a tentative explanation of this. The inductive effect of a substituent group in a highly polarisable system of many mobile electrons is more appropriately described as a change in electrical potential at a certain carbon atom in the molecule than as the migration of a certain amount of charge from the substituent group to that atom. Thus, the presence of a group  $X$  in the ring of the phenyl-carbonium ion will cause a change in the electrical potential (or "pressure" of electrons) at the  $\alpha$ -carbon atom. It is this potential (and not the net electric charge) which parallels the inductive contribution to the ionisation tendency of the molecule. On going from the mono- to the di-phenylcarbonium ion (and, analogously, to the triphenylcarbonium ion), the potential at the exocyclic carbon atom will be similarly affected by the substituent only if both rings exert the same effect. To a first approximation and for groups of moderate inductive strength, this may be expected to be the case if the rings are identically substituted. When one of the rings remains unsubstituted we have the case of the

"dilution" effect discussed above. How correct or useful this picture of the inductive effect may be in general cannot be judged on the evidence considered so far. To clarify the basic concepts involved, a crude mechanical analogue of the model is described in Appendix II.

#### APPENDIX I. $pK_{\text{ROH}}$ value for benzyl alcohol.

The approximate estimate (22—27 units) is based on the following three, largely independent, lines of reasoning: (i) If we assume the difference in  $pK_{\text{ROH}}$  values between diphenylmethanol and benzyl alcohol to be the same<sup>6</sup> as that between dimesitylmethanol and 2:4:6-trimethylbenzyl alcohol, we obtain  $pK$  24.1 for benzyl alcohol. (ii) The effects of *o*- and *p*-methyl substituents on the  $pK_{\text{ROH}}$  value of diphenylmethanol are known.<sup>3</sup> We now assume that the effect of a *p*-methyl group in benzyl alcohol is the same as that of two *p*-methyl groups in diphenylmethanol, and that the effect of two *o*-methyl groups in benzyl alcohol is twice that exerted by two methyl groups (in the 2:2'-positions) in diphenylmethanol. This leads to the value  $pK$  22.0 for benzyl alcohol. A similar consideration of the effect of methyl substituents in triphenylmethanol leads to a higher value ( $\sim 27$ ). Since triphenylmethanol differs from benzyl alcohol in structure rather more than does diphenylmethanol, the lower value is preferred. (iii) The effectiveness of substituent groups in the ring on dissociation constants of aromatic acids is largely determined by the distance of the acidic group from the aromatic

FIG. 2.



ring and its manner of attachment (see ref. 12, Figs. 36 and 39). On this basis, the methyl groups in 2:4:6-trimethylbenzyl alcohol might each be expected to have an effect similar in magnitude to that of a *p*-methyl group in aniline. (*o*-Methyl groups in aniline are not comparable because of the peculiar steric inhibition of resonance which arises in this structure. In acids where this *ortho*-effect is absent, as in phenols, the effects of *ortho*- and *para*-substituents are roughly equal.) This procedure leads to  $pK = 18.8$  for benzyl alcohol. However, this value must be too low, as the calculation ignores the hyperconjugative effect of the methyl group. This is likely to be stronger in the phenylcarbonium ion than in the anilinium ion. The difference in the effects on a dissociation constant which a substituent group exerts from the *meta*- and the *para*-position is a measure of the conjugative effect of that group. In aniline this difference amounts to 0.4 unit for the methyl group and 0.5 unit for chlorine, *i.e.*, methyl and chlorine substituents have very similar effects. In triphenylmethanol and in diphenylmethanol the differential effect of chlorine substitution, in all *para*-positions on the one hand and in one *meta*-position in each ring on the other, amounts to 3.3 units,<sup>3</sup> *i.e.*, in these *para*-substituted arylmethanols there appears to be an additional base-strengthening effect of  $\sim 2.8$   $pK$  units, due to conjugation. If the effect of the methyl group is again about the same as that of chlorine, and if three methyl groups in benzyl alcohol have three times the effect of a chlorine atom in the *para*-position of each ring in diphenylmethanol, the calculated value of  $pK$  for benzyl alcohol is  $\sim 27$ .

#### APPENDIX II. Mechanical analogue of inductive effect in system of mobile electrons.

The three benzene rings in the triphenylcarbonium ion are compared to three cylinders which are attached to a common manifold (Fig. 2, I). The cylinders are closed by weightless and frictionless pistons, and the system is filled with an ideal gas. The upward motion of the

<sup>12</sup> Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall, New York, 1941.

pistons is limited by springs (obeying Hooke's law) under compression. Similar systems with two cylinders (Fig. 2, II) or one cylinder represent the di- and the mono-phenylcarbonium ions respectively. The pressure at  $M$  and  $N$  is the analogue of the electrical potential at the exocyclic carbon atom.

The introduction of an electron-repelling substituent group into one of the rings may be likened to placing a *small* weight  $w$  on one of the pistons (say,  $A$ ). This will cause compression of the gas and of the springs attached to  $B$  and  $C$ , a slight release of the compression of the spring attached to  $A$ , and an increase of the pressure registered by the manometer  $M$  which is attached to the manifold. If the volume of the manifold is small compared with that of the pistons, the following statements—which correspond to the substituent effects discussed in the last two paragraphs of the paper—follow from Boyle's law and Hooke's law: (1) If a weight  $w$  is placed on  $A$ , and an equal weight  $w$  on  $D$ , then the pressure changes at  $M$  and  $N$  are in the ratio 2 : 3, *i.e.*, they are inversely proportional to the number of cylinders. (2) Three equal weights  $w$  placed respectively on  $A$ ,  $B$ , and  $C$  change the pressure at  $M$  as much as two of the same weights, placed at  $D$  and  $E$  respectively, change the pressure at  $N$ .

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