# 580. *Dielectric Studies of Carboxylic Acid–Pyridine Complexes in Benzene.*

## By Mansel Davies and Lucjan Sobczyk.

Dielectric studies of the 1 : 1 complexes of pyridine with acetic, mono-chloroacetic, and trichloroacetic acid have been made in benzene solution over the frequency range 5 c./sec. to 1700 Mc./sec. Equivalent con-ductances, dipole moments, and relaxation times for the solutes are deduced. It is shown that the very small conductances arise from minute concen-trations of complex ions; the dipole moments indicate the nature of the bonding and especially its ionic form for the trichloroacetate; the relaxation times fit rigid dipole structures for the complexes. No evidence is found for a proton-jumping process in these instances.

THE structures of acid–base complexes in non-polar solvents are of considerable interest. It has been established that in some cases the acidity and basicity of organic compounds change markedly from one solvent to another.[1] The acid–base interaction can also vary with the components from a weak hydrogen-bonding process to the formation of ion-pairs, whose degree of dissociation plays a determinative role in the electrolytic conductance. The interaction complex has the nature of an ion-pair when the components are of strongly acidic and basic character whether or not there is appreciable dissociation: dipole-moment measurements have shown this.[2] For weaker acids and bases there is probably an equilibrium

$$X^-H \ldots Y \rightleftharpoons X^- \ldots [H^-Y]^+ \qquad \cdots \cdots \cdots \text{(I)}$$

Instances of this condition have been revealed by spectroscopic studies.[3] This system is of particular interest as the energy can be represented by a curve with two minima; in each configuration there is a hydrogen-bond, but the donor–acceptor relationship is inter-changed with the transfer of the proton. The theoretical representation of such systems has been considered by a number of authors.[4]

An aspect which does not appear to have been widely considered [5] is the possibility of measuring, dielectrically, the relaxation time for the proton in such a situation. As there is an appreciable change in polarity with the displacement of the proton, its

[1] M. M. Davis and Pabo, *J. Amer. Chem. Soc.*, 1960, **82**, 5081; Pearson and Vogelsong, *J. Amer. Chem. Soc.*, 1958, **80**, 1038.

[2] Hulett, Pegg, and Sutton, *J.*, 1955, 3901; Sobczyk and Syrkin, *Roczniki Chem.*, 1956, **30**, 881; Maryott, *J. Res. Nat. Bur. Standards*, 1948, **41**, 1.

[3] Blinc, Hadzi, and Novak, *Z. Elektrochem.*, 1960, **64**, 567; Hadzi, *Vestnik Slovensk. Kem. Drustva*, 1958, **5**, 21; C. L. Bell and Barrow, *J. Chem. Phys.*, 1959, **31**, 1158; Barrow, *Spectrochim. Acta*, 1960, **16**, 799.

[4] Lippincott, Finch, and Schneider in " Hydrogen Bonding," ed. D. Hadzi, Pergamon Press, London, 1957; Coulson, *Research*, 1957, **10**, 149; Sokolov, *Doklady Akad. Nauk S.S.S.R.*, 1948, **60**, 825.

[5] Loveluck, *J. Phys. Chem.*, 1960, **64**, 695.

oscillation should be seen as a dielectric absorption centred at a frequency characteristic of the process. This was one of the features sought in the present study.

When the components XH and Y do not interact in any other way the equilibrium (1) represents the essentials of the acid–base function in its simplest form. Accordingly, its study in non-polar or aprotic solvents should eliminate solvation effects.[6] The systems reported here are in the condition where the simple AB complex is the only species shown by conventional stoicheiometric assessment. Previous dielectric studies of organic salts in non-polar solvents [7] have shown how the ionic conductance, the dipole moment, and the dipole relaxation times reveal the molecular and electrical state of the solute. Similar information was now sought for the acid–base complex.

*Experimental.*—Measurements of the permittivity ($\varepsilon'$) and dielectric loss factors ($\varepsilon''$) were made over two frequency ranges. From 5 c./sec. to 320 kc./sec. the capacitance and reactance of a rhodium-flashed quartz-insulated Tinsley dielectric cell were read directly with a Thompson bridge [8] (whose scales had been calibrated) to a few parts per thousand. For frequencies from 200 to 1700 Mc./sec. the General Radio slotted-line equipment was used.[9]

Chemicals of analytical grade were used as starting materials. Benzene was dried over sodium. Solutions were prepared from freshly distilled samples whose conductances ranged from $0.8$ to $1.6 \times 10^{-13}$ ohm$^{-1}$ cm.$^{-1}$.

Acetic acid was fractionally crystallized to constant m. p. $16.6°$.

Chloroacetic and trichloroacetic acid were crystallized from chloroform and dried over $P_2O_5$ in a vacuum desiccator.

Pyridine was dried over KOH and fractionally distilled; it had b. p. $115.3°$.

All manipulations to prepare solutions were made in a dry-box. The cell for low-frequency measurements was filled and sealed there to exclude moisture. Precautions were taken in filling the slotted-line cell so as to reduce contact with moist air to a minimum. The 1:1 molar ratio of the components was maintained in all cases.

## RESULTS AND DISCUSSION

*Low-frequency Results.*—In the low-frequency range (to 320 kc./sec.) the energy dissipation is found to be due solely to the small electrolytic conductance. Accordingly these results can be treated apart from those at higher frequencies. The specific conductance ($\kappa$) is derived from the loss factor ($\varepsilon''$) and the frequency ($f$, c./sec.): $\varepsilon'' = 1.80 \times 10^{12} \kappa/f$. A typical evaluation is shown in Table 1.

### TABLE 1.

$[CCl_3 \cdot CO_2H, C_5H_5N]$ in benzene: $2.58 \times 10^{-2}$ M. Temp. $= 20.2°$.

| $f$ (c./sec.) | 17.5 | 52.6 | 175 | 526 | 1590 | 5260 |
|---|---|---|---|---|---|---|
| $\varepsilon'$ | $2.42_4$ | $2.45_6$ | $2.46_8$ | $2.47_7$ | $2.47_7$ | $2.47_7$ |
| $\varepsilon''$ | 2.91 | $0.98_6$ | 0.293 | 0.103 | $3.33 \times 10^{-2}$ | $9.97 \times 10^{-3}$ |
| $10^{11}\kappa$ (ohm$^{-1}$ cm.$^{-1}$) | 2.91 | 2.94 | 2.90 | 2.98 | 2.94 | 2.93 |

$\kappa$ (solution) $= 2.93 \pm 0.03 \times 10^{-11}$; $\kappa$ (solvent) $= 10 \times 10^{-14}$.
$\lambda$ (equivalent conductance of solute) $= 1.13 \pm 0.02 \times 10^{-6}$.

Even for these low solution conductances the solvent correction is almost negligible. Our lowest benzene value at 20° ($\kappa = 8.0 \times 10^{-14}$ ohm$^{-1}$ cm.$^{-1}$) compares favourably with the value in Landolt–Börnstein's " Tabellen." It should be emphasized that the deduction of these low values from the frequency-dependence of $\varepsilon''$ eliminates uncertainties (electrode polarization, etc.) in direct resistance measurements. Dust can contribute significantly to these low solvent conductances.

[6] M. M. Davies *et al.*, *J. Res. Nat. Bur. Standards*, 1949, **42**, 595; 1958, **60**, 569; 1961, **65**, *A*, 209; Shatenshtein, *Izotopnyj obmen i zameshtchene wodoroda v organitcheskikh soedinenyakh*, *Izd. Akad. Nauk*, Moscow, 1960; R. P. Bell, " The Proton in Chemistry," Cornell Univ. Press, New York, 1956; Sobczyk and Syrkin, *Roczniki Chem.*, 1957, **31**, 349.
[7] M. Davies and Williams, *Trans. Faraday Soc.*, 1960, **56**, 1619.
[8] Thompson, *Proc. Inst. Elec. Engineers*, 1956, **103**, *B*.
[9] Williams, *J. Phys. Chem.*, 1959, **63**, 534.

When $\varepsilon''$(effective) exceeds 0·1 some drift in the measured $\varepsilon'$ factor occurs. This is due to slight imperfection of the quadrature in the bridge. The more correct $\varepsilon'$ value is well established at the higher frequencies.

*Dipole Moments.*—The low-frequency results are summarized in Table 2. Significant results follow from the linear dependence upon the concentrations of the AB complexes of $\Delta\varepsilon' = \varepsilon'$(solution) $- \varepsilon'$(solvent). The gradients of the plots of $\Delta\varepsilon'$ against concentration give the best values of $\mu$(complex) and their constancy emphasizes that a single

TABLE 2.

(a) $[CH_3 \cdot CO_2H, C_5H_5N]$ in benzene; at $21 \cdot 8° \pm 0 \cdot 4°$.

| Concn. (mole/l.) | 0·171 | 0·268 | 0·343 | 0·535 |
|---|---|---|---|---|
| $\Delta\varepsilon'$ | 0·23$_3$ | 0·32$_0$ | 0·52$_8$ | 0·66$_1$ |
| $10^9\lambda$ (eq. cond.) | 6·3$_7$ | 9·0 | 26·3 | 54·2 |

(b) $[CH_2Cl \cdot CO_2H, C_5H_5N]$ in benzene; at $20 \cdot 5° \pm 0 \cdot 5°$.

| Concn. ($10^{-2}$ mole/l.) | 6·46 | 7·45 | 8·70 | 12·92 | 14·9 | 17·4 | 25·84 | 29·8 | 32·9 |
|---|---|---|---|---|---|---|---|---|---|
| $\Delta\varepsilon'$ | 0·18$_0$ | 0·22$_0$ | 0·24$_6$ | 0·35$_8$ | — | 0·49$_8$ | 0·80$_8$ | 0·85$_8$ | 0·96 |
| $10^7\lambda$ (eq. cond.) | 0·65 | 0·71 | 1·23 | 3·3$_0$ | 3·8$_8$ | 8·0$_3$ | 29·1 | 37·1 | 64·$_6$ |

(c) $[CCl_3 \cdot CO_2H, C_5H_5N]$ in benzene; at $20 \cdot 2° \pm 0 \cdot 3°$.

| Concn. ($10^{-2}$ mole/l.) | 1·01$_5$ | 1·29 | 1·94$_5$ | 2·03 | 2·03$_5$ | 2·58 | 3·89 | 4·06 | 4·07 |
|---|---|---|---|---|---|---|---|---|---|
| $\Delta\varepsilon'$ | 0·08$_9$ | 0·10$_5$ | 0·148 | 0·15$_8$ | 0·13$_8$ | 0·19$_3$ | 0·27$_9$ | 0·30$_3$ | 0·27$_7$ |
| $10^7\lambda$ (eq. cond.) | 2·5$_5$ | 3·6$_0$ | 7·7$_1$ | 7·3$_4$ | 6·4$_4$ | 11·3 | 30·$_9$ | 32·$_6$ | 23·$_3$ |

effective dipole species is present in each case, to within the significance of the $\Delta\varepsilon'$ values, *e.g.*, within $\pm 1\%$ or less at the higher concentrations for $(CH_2Cl \cdot CO_2H, C_5H_5N)$. The values so deduced for the effective dipole moments, by Guggenheim's version [10] of the Debye equation, agree well with those (given in parentheses) previously measured for the pyridine complexes, namely: from (a) $2·97 \pm 0·15$ (2·93); from (b) $4·57 \pm 0·10$ (4·67); from (c) $7·68 \pm 0·20$ D (7·78 D).

These moments suffice to establish a qualitative difference between the acetic and the trichloroacetic acid complex. We accept Smyth's planar representation [11] of the carboxylic group with $\mu(C{=}O) = 2·70$ D as shown in Fig. 1. This leads to $\mu(CH_3 \cdot CO_2H)$ (calc.) = 1·62 D; the observed value for the monomer acid is near 1·7 D. If the pyridine moment (2·22 D), which lies along the N–*para*-C axis, is merely added along the H–O line, the molecular complex would have a moment of 2·16 D (cf. 2·93 D observed for the acetic acid complex). Clearly the O–H $\cdots$ N interaction leads to greater polarity. Infrared spectra of such hydrogen bonds, and especially the changes in $\nu$(OH) and the intensity, show that this is due largely to stretching of the O–H bond and an increase in its ionic character.

Calculation shows that if the total O–H $\cdots$ N moment is increased from 3·73 D (above) to 4·71 D then the moment of the complex is reproduced. Let us further accept the simplest model for the dipole moment (1·51 D) of the O–H group: $r$(O–H) = 0·96 Å; $e$ (effective charge at the O and H centres) = $1·57 \times 10^{-10}$ e.s.u. An adequate estimate [12] of $r$(O–H) in the complex is 1·02 Å, which leads to an effective charge = $2·35 \times 10^{-10}$ e.s.u. The model thus suggests an increase of some 50% in the ionicity of the (O–H) bond on formation of the complex with pyridine, which is at best an approximate, but not an unreasonable, result.

Using Smyth's value for the $Cl_3C$ group moment in the above model leads, from $\mu$(complex) = 7·78 D, to a total moment in the O–H $\cdots$ N line of 8·65 D. If the change in $r$(O–H) is restricted to the 6% previously assumed, this dipole would need to carry a charge of $6·3 \times 10^{-10}$ e.s.u. in the complex, *i.e.*, in excess of the electronic change. Thus the dipole moment of the trichloroacetic acid–pyridine complex is sufficient to establish the qualitative result that the O–H $\cdots$ N system acquires an ion-pair character and that the

[10] Guggenheim, *Trans. Faraday Soc.*, 1951, **47**, 573.
[11] Smyth, " Dielectric Behaviour and Molecular Structure," McGraw Hill Co., New York, 1955, p. 306.
[12] M. Davies and Sutherland, *J. Chem. Phys.*, 1938, **6**, 755.

hydrogen moves significantly from the oxygen. The approximate estimate of the O–H $\cdots$ N moment as 8·65 D could be accommodated without change of the pyridine moment if an (O⁻H⁺) ion-pair arose with $r$(OH) = 1·34 Å. This would place the proton approximately at the centre of the O–N separation. The neglect of polarizability in these estimates only serves to reduce the " ionicity " deduced and the qualitative conclusion that the hydrogen is transferred in the trichloroacetic acid–pyridine complex cannot be avoided.

*Ionic Conductance.*—Since the ionic dissociation of the complex is of the form, AB = A⁺ + B⁻, the viscosity of benzene would suggest $\lambda_\infty$ values for complete dissociation of the order of 100. The $\lambda$ values found indicate that at most some $10^{-7}$ part of the solute
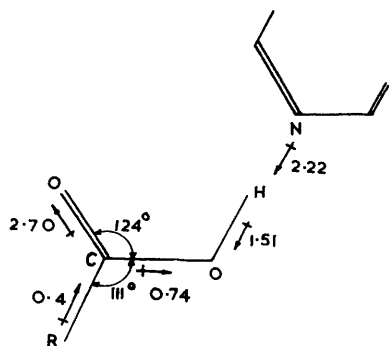


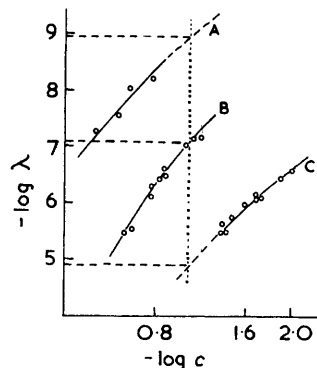FIG. 1. Assumed polar configurations of interacting components.



FIG. 2. log $\lambda$–log $c$ plots for acid–pyridine complexes in benzene.
A, CH₃·CO₂H. B, CH₂Cl·CO₂H.
C, CCl₃·CO₂H.

is present as free ions. Accordingly, the concentration-dependence of $\lambda$ indicates only the behaviour of a negligible fraction of the solute.

Nevertheless, interesting conclusions can be drawn on the nature of such ionic dissociation as does occur. If it were solely of the form written above, (monomer complex) = (free ions), then for small dissociation $\lambda = \lambda_\infty K c^{-\frac{1}{2}}$ where $K$ measures the dissociation equilibrium. At the lowest concentrations, however, all three solutes show $\lambda c^{\frac{1}{2}}$ approaching zero at least as rapidly as $c$, whilst at higher concentrations it increases even more rapidly than $c$ itself. This leads to the conclusion that the simple ionization process envisaged above plays no significant part in the observed conductance.

Rutgers and de Smet's model [13] for the conductance in such " weak salt " solutions assumes the presence of ion-pairs AB, and other aggregates $(AB)_m$, $(AB)_n$, etc., each such species dissociating slightly into univalent ions. At $c$ g.equiv./l. the equivalent conductance is then calculated to be of the form

$$\lambda c = Ac^{\frac{1}{2}} + A_m c^{m/2} + A_n c^{n/2} + \cdots$$

We have already seen that for the acid–pyridine complexes $A = \lambda_\infty K = 0$. A plot of log $\lambda$ against log $c$ (Fig. 2) defines a mean effective degree for the ionizing complexes: $m = 5\cdot9$ for [CH₃·CO₂H–C₅H₅N]; $m = 7\cdot6$ for [CH₂Cl·CO₂H,C₅H₅N]; $m = 5\cdot2$ for [CCl₃·CO₂H,C₅H₅N]. Thus the ionization process can be represented as of the form:

$$6AB \rightleftharpoons (AB)_6 \rightleftharpoons A^-(AB)_2 + HB^+(AB)_3$$
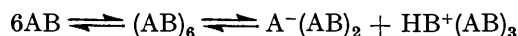
The electrostatic energy of a free ion A⁻ in benzene ($\varepsilon' = 2\cdot28$) is so large (especially when the charge is localized on one or two atoms in the ion) that ion–dipole interactions probably lead to its protection by a number of other solute molecules or ion-pairs. The

[13] Rutgers and de Smet, *Trans. Faraday Soc.*, 1952, **48**, 635.

concentration range available for significant measurement is too small for further analysis along these lines to be worth while.

A rough comparison of the conductivities of the three complexes can be made by considering their (partly extrapolated) λ values at a common concentration. At log $c = \bar{2}\cdot9$ the values of $-\log λ$ in Fig. 2 are proportional to the p$K$'s of the acids (see Fig. 3). This merely indicates that the tendency to form the $A^-(AB)_s$ ion decreases, as would be expected, with increasing p$K$ of the HA acid. Also approximately linearly dependent on the acid p$K$ is the observed dipole moment of the AB monomeric complex (see Fig. 3).

*High-frequency Results.*—In the megacycle region the effect of the minute ionic conductance (inversely dependent on the frequency) is negligible and the permittivity (ε′)



FIG. 3. Dependence of (——) log λ and (— —) μ for complexes on p$K$ for the acidic component.
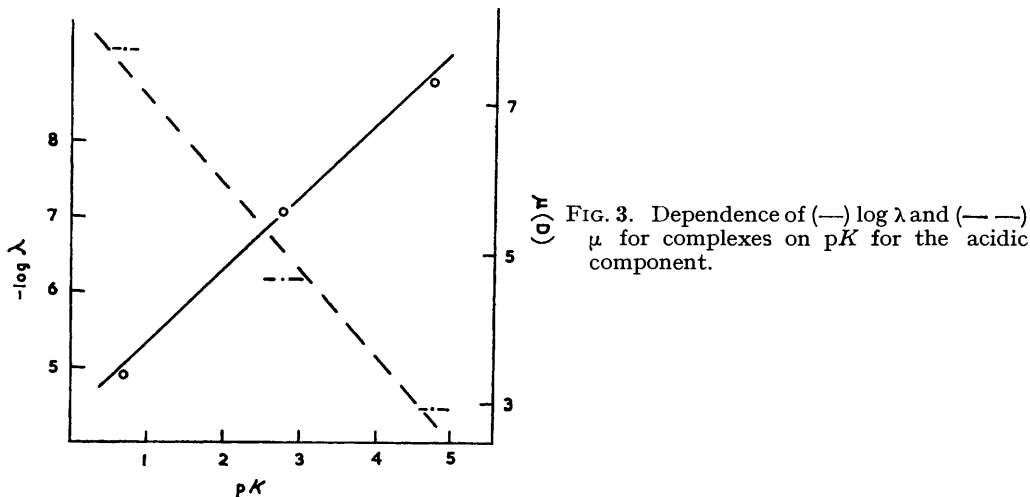
varies as the time of oscillation of the field approaches that characterising the rate of reorientation of the polar molecules, *i.e.*, the dipole relaxation time τ. The dependence of the dielectric absorption (ε″) on frequency for a dilute solution was given by Debye in terms of $\tan δ = ε″/ε′$:

$$\Delta \tan δ = \frac{(ε′ + 2)^2}{ε′} \cdot \frac{\pi Nμ^2 c}{6750kT} \frac{ωτ}{1 + ω^2τ^2}, \qquad (2)$$

where $ω = 2\pi f$ (c./sec.), $c$ = molarity, and $\Delta \tan δ = \tan δ$ (solution) $- \tan δ$(solvent). For benzene in the frequency range of the present measurements tan δ is of the order

TABLE 3.

| $f$ ($10^6$ c./sec.) | ε′ | $10^3\Delta \tan δ$ | $10^{12}τ$ (sec.) | $f$ ($10^6$ c./sec.) | ε′ | $10^3\Delta \tan δ$ | $10^{12}τ$ (sec.) |
|---|---|---|---|---|---|---|---|
| [CH$_3$·CO$_2$H,C$_5$H$_5$N] in benzene; $c = 3\cdot15$ | | | | [CH$_2$Cl·CO$_2$H,C$_5$H$_5$N] in benzene: $c = 2\cdot48$ | | | |
| $\times 10^{-1}$ M; $t = 20\cdot2°$; $μ = 2\cdot93$ D. | | | | $\times 10^{-1}$ M; $t = 20\cdot8°$; $μ = 4\cdot67$ D. | | | |
| 251 | $2\cdot69_5$ | 9·0 | 37·5 | 251 | $2\cdot99_0$ | $22\cdot_1$ | $45\cdot_3$ |
| 451 | $2\cdot69_9$ | 15·7 | $36\cdot_3$ | 451 | $2\cdot99_2$ | $39\cdot_6$ | $45\cdot_7$ |
| 601 | $2\cdot65_6$ | 19·9 | $35\cdot_4$ | 601 | $2\cdot96_2$ | $49\cdot_2$ | $(43\cdot_2)$ |
| 895 | $2\cdot65_3$ | 30·2 | $36\cdot_9$ | 895 | $2\cdot93_2$ | $75\cdot_6$ | $46\cdot_2$ |
| 1696 | $2\cdot50_8$ | 57·4 | $(41\cdot_2)$ | 1696 | $2\cdot87_9$ | 124 | $46\cdot_4$ |

| $f$ ($10^6$ c./sec.) | ε′ | $10^3\Delta \tan δ$ | $10^{12}τ$ (sec.) |
|---|---|---|---|
| [CCl$_3$·CO$_2$H,C$_5$H$_5$N] in benzene: $c = 3\cdot65 \times 10^{-2}$ M; $t = 20\cdot5°$; $μ = 7\cdot78$ D. | | | |
| 251 | $2\cdot53_1$ | $12\cdot_6$ | $65\cdot_2$ |
| 451 | $2\cdot49_4$ | $21\cdot_2$ | $62\cdot_4$ |
| 601 | $2\cdot48_0$ | $27\cdot_4$ | $62\cdot_5$ |
| 895 | $2\cdot46_4$ | $38\cdot_3$ | $62\cdot_2$ |
| 1696 | $2\cdot41_0$ | $58\cdot_0$ | $65\cdot_1$ |

$1 \times 10^{-3}$ or less. Some of the results for the acid–pyridine solutions are shown in Table 3.

Table 3 shows the $\tau$ values calculated from equation (2). The essential constancy in each instance confirms the earlier indications that the solutes are single rigid-dipole molecules. The degree of conformity to the simple Debye equation for a single relaxation time is shown for the trichloroacetate complex in Fig. 4 where $\Delta \tan \delta$ (calc.) (for $\mu = 7{\cdot}78$ D; $\tau = 63{\cdot}5 \times 10^{-12}$ sec.; $c = 3{\cdot}65 \times 10^{-2}$M) is plotted with the observed points. One consequence of this agreement is that no evidence of any " proton-jumping " process can
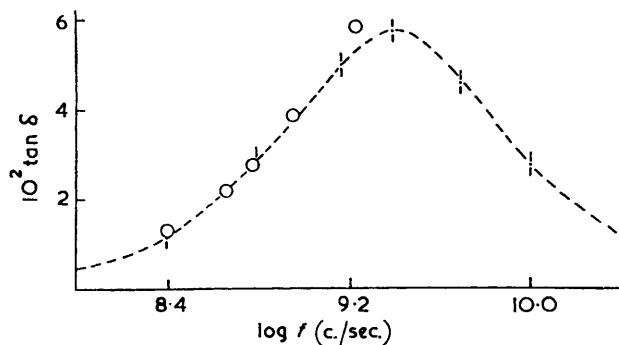


FIG. 4. $[CCl_3 \cdot CO_2H, C_5H_5N]$ in $C_6H_6$; $t = 20{\cdot}5°$; $c = 3{\cdot}65 \times 10^{-2}$M. Circles $\bigcirc$ = observed $\tan \delta$ (solute); vertical lines are calculated from Debye equation for $\mu = 7{\cdot}78$ D, and $\tau = 63{\cdot}5 \times 10^{-12}$ sec.

be seen in the dielectric properties for the frequency range up to 1700 Mc./sec. It cannot be excluded at other frequencies in the present cases even though the $\Delta \tan \delta$ values quantitatively fit those for the rigid-dipole relaxation; in other instances, more favourable to the process energetically, it might well play a significant role.

The mean $\tau$-values given by Table 3 provide the sequence (in $10^{-12}$ sec.): $36{\cdot}_5$, $(+9{\cdot}4)$, $45{\cdot}_9$, $(+17{\cdot}6)$, $63{\cdot}_5$. This shows an increment of approximately $9 \times 10^{-12}$ sec. per atom of chlorine replacing hydrogen in the acid. Such an increment is to be expected from the Debye relation $\tau = 3v\eta/kT$, where $v$ is the volume of the molecule and $\eta$ is the viscosity of the medium. Although the absolute values of $\tau$ predicted by this relation are often up to four times greater than those observed, the proportionality to the molecular volume is often well maintained, especially for rigid-molecular dipoles of similar type in the same solvent. Comparison of the $\tau$ values with those for a number of ion-pairs [7] (*e.g.*, tri-n-butylamine picrate, $220 \times 10^{-12}$ sec.) in media of closely similar viscosities shows that, within the uncertainties in estimating $v$, the observed $\tau$'s are all proportional to the molecular volumes. It could be that the rigid character of the dipole involves, in addition to the O–H $\cdots$ N bonding, a weak interaction between the acid-carbonyl group and the $\alpha$-hydrogen of pyridine which has been suggested by Sobczyk and Syrkin.[2]