Succinamic Acids. Part I. Hydrogen-bonding Equilibria in Succinanilic Acids

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Spectroscopic evidence shows that *N*-alkylsuccinanilic acids form two types of hydrogen bonded associates. The usual cyclic dimeric acid is in equilibrium with polymeric associates which become more significant at high concentrations of the acid. The presence of an intramolecularly hydrogen-bonded monomeric acid could not be detected either by spectroscopic means or by abnormal heats of association of the acids.

THE bifunctional nature of succinamic acids (I) can lead to complex association equilibria in non-polar aprotic solvents. Thus, in solutions of succinamic acids ($R^1 = R^2 =$ alkyl) Antonenko [1] claims to have detected at least three types of hydrogen-bonded species involving hydrogen bonding of the carboxy-group to both amide and carboxy-functions of the succinamic acid.

$$R^1R^2N{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$$

(I)

In connection with a kinetic study of the formation of the aniline and anhydride from succinanilic acids (I; $R^1 =$ alkyl, $R^2 =$ aryl) in a non-polar solvent, an investigation of the associations of these acids was undertaken. The results of this investigation are reported here.

EXPERIMENTAL

The alkylsuccinanilic acids were prepared by mixing equimolar quantities of the *N*-alkylaniline with succinic anhydride in benzene solution. The solution was left overnight, and the succinanilic acid was precipitated by the addition of light petroleum. The acids were recrystallized from light petroleum–benzene mixtures; *N*-methyl, m.p. 94—95° (lit.,[2] 91—92°); *N*-ethyl, m.p. 97—98° (lit.,[2] 92—93°); *N*-isopropyl, m.p. 95—96°.

3,*N*-Dimethylsuccinanilic acid was prepared in a similar manner, but during the reaction a large (*ca.* 50%) amount of 2,*N*-dimethylsuccinanilic acid crystallized from the solution. Addition of light petroleum to the filtered solution gave essentially pure 3,*N*-dimethylsuccinanilic acid. This was recrystallized from light petroleum–benzene, m.p. 85—86° (lit.,[3] 77—78°).

Carbon tetrachloride (AnalaR) was dried over molecular sieve (B.D.H. type 4A).

Unless otherwise stated, spectra were recorded at ambient temperature with a Grubb–Parsons G.S.4 spectrometer. Measurements were carried out in the 4000—3000 cm.$^{-1}$ region with cells having either sodium chloride or quartz optical surfaces. Measurements of carbonyl absorptions were carried out by use of cells with sodium chloride optical surfaces.

The variation with temperature of the intensity of the hydroxy-group stretching bands at *ca.* 3540 cm.$^{-1}$ was studied with a 4-cm. quartz cell fitted with an electric heating jacket. The temperatures of solutions were measured with a thermocouple immersed in the solutions.

RESULTS

Spectroscopic Data.—The i.r. spectra of solutions of *N*-ethylsuccinanilic acid in carbon tetrachloride, recorded in the regions 4000—3000 and 2000—1600 cm.$^{-1}$ under various conditions, are shown in Figures 1 and 2 respectively.

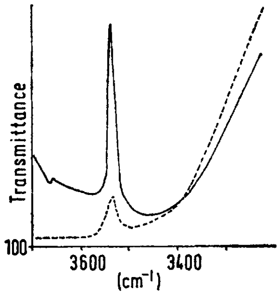

FIGURE 1 The i.r. spectra of *N*-ethylsuccinanilic acid for CCl_4 solutions in the 4000—3000 cm^{-1} region. (Solid line $2{\cdot}3 \times 10^{-2}$M, broken line 6×10^{-4}M)

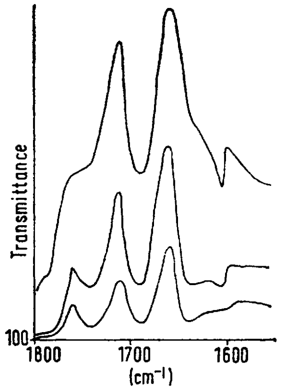

FIGURE 2 The i.r. spectra of *N*-ethylsuccinanilic acid for CCl_4 solutions in the 2000—1600 cm^{-1} region

These spectra are typical of those obtained with other succinanilic acids.

The characteristic features of the spectra between 4000 and 3000 cm.$^{-1}$ are the single sharp absorption at *ca.* 3540 cm.$^{-1}$ and the broad absorption which occurs below 3500 cm.$^{-1}$. These absorptions correspond to the stretching frequencies of an unbonded hydroxy-group and the bonded hydroxy-group of the cyclic acid dimer (II) respectively.[4] As would be expected for a mixture of monomer and dimer or polymer, the relative intensity of the unbonded absorption

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[1] N. S. Antonenko, *Zhur. obshchei Khim.*, 1965, **35**, 425

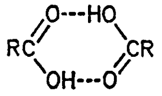
[2] K. V. Auwers, *Annalen*, 1896, **292**, 188, 192.

[3] B. R. Baker, R. E. Schaub, and J. H. Williams, *J. Org. Chem.*, 1952, **17**, 116.

[4] L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Methuen, London, 2nd edn., p. 165.

increased on dilution. The quantitative relationship between the intensity of this band and concentration of the acid will be discussed later.

In the region 2000—1600 cm.$^{-1}$ dilute carbon tetrachloride solutions of the acids absorbed at *ca.* 1760, 1710, and 1660 cm.$^{-1}$. The bands at 1760 and 1660 cm.$^{-1}$ can be assigned to unbonded carboxy and amide I stretching frequencies respectively, and that at 1710 cm.$^{-1}$ corresponds to the carbonyl frequency in an acid cyclic dimer of the type (II).[4]



(II)

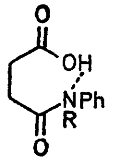
$$R_2N\cdot CO\left[CH_2\cdot CH_2\cdot CO\cdot OH\cdots\cdots NR_2\cdot CO\right]_n CH_2\cdot CH_2\cdot CO_2H$$

(III) a; $n = 1$
b; $n \geqslant 1$

In solutions which were almost saturated a shoulder appeared on the band at 1710 cm.$^{-1}$, with an apparent maximum at *ca.* 1740 cm.$^{-1}$. In Nujol mulls of the acids the carboxy-absorption was a poorly resolved doublet centred at *ca.* 1730 cm.$^{-1}$. Antonenko[1] has assigned a band at 1725 cm.$^{-1}$ in the spectrum of *NN*-diethylsuccinamic acid (I; $R^1 = R^3 = Et$) to the acid carbonyl of open dimers of the acid in which the acid group is hydrogen-bonded to the amide group of another acid. Thus the absorption at 1730 cm.$^{-1}$ in the solid acids and at 1740 cm.$^{-1}$ in solution could be due to formation of such associates. We have been able to show that in mixtures of acetic acid and *N*-methylacetanilide in carbon tetrachloride solution an absorption occurs at 1748 cm.$^{-1}$ which does not occur in the spectra of the components alone. This would add weight to the assignment of the band at 1730—1740 cm.$^{-1}$ to the stretching of a carboxy-group bonded to amide. However, although Antonenko refers to such species (IIIa) as dimers, the rapid disappearance of these bands on dilution suggests that these are in fact polymeric in nature (*e.g.* IIIb).

The i.r. spectra of succinanilic acids in carbon tetrachloride show that these acids form at least two types of hydrogen-bonded associates. We were unable to detect any absorptions which could be attributed to the formation of an intramolecularly bonded monomeric acid, such as that reported by Antonenko for the succinamic acids. The evidence for such a species was the appearance of a band at 1580—1590 cm.$^{-1}$ in tertiary succinamic acids. In the succinanilic acids the *N*-phenyl absorption occurs in this region, but the phenyl absorption of *N*-methylsuccinanilic acid in chloroform solution was found to be much broader than the phenyl absorption of *N*-methylacetanilide. Thus it is possible that the band which Antonenko attributes to intramolecular hydrogen bonding in monomeric succinamic acids also occurs in succinanilic acids [as in (IV)]. However, the broadening of the phenyl absorption is not in itself sufficient evidence for an intramolecularly bonded succinanilic acid.

It would be expected that bonding of the carboxy-group to amide would lower the frequency of the carboxy-stretching. However, in dilute carbon tetrachloride solutions the only carboxy-absorptions noted were those for the unbonded monomer and cyclic dimer (II). Thus unless absorption of the intramolecularly hydrogen bonded monomer fortuitously coincides with the absorption attributed to unbonded monomer or cyclic dimer there is little evidence from spectroscopic measurements for such a species.



(IV)

It was thought possible that measurements of association constants might provide evidence for or against such a species. Consequently the association constants and the thermodynamic functions for the equilibria have been measured.

Association Constants of the Succinanilic Acids.—The spectroscopic data given above shows that the association equilibrium of succinanilic acids in carbon tetrachloride solution can be most rigorously expressed by (1):

$$(\mathrm{M})_n\cdots(\mathrm{M})_3 \overset{(\mathrm{M})}{\rightleftharpoons} (\mathrm{M})_2 \underset{K_{\mathrm{p}}(\mathrm{M})}{\rightleftharpoons} \mathrm{M} \underset{K_{\mathrm{D}}(\mathrm{M})}{\rightleftharpoons} \mathrm{D} \qquad (1)$$

where M represents the monomeric succinanilic acid (I), D represents the cyclic dimer (II), and $M_2\cdots M_n$ represents polymers of structure (III). The amount of polymeric associates at the concentrations used is small, and the system can be regarded as a simple association [equation (2)].

$$2\mathrm{M} \underset{K_D}{\rightleftharpoons} \mathrm{D} \qquad (2)$$

It was assumed that the sharp absorption at 3534 cm.$^{-1}$ was due solely to unbonded hydroxy-stretching and that Beer's law was obeyed by this absorption. Allowances were made for the absorbance of the dimer in this region. The absorbance (α) of the hydroxy-group is given by (3)

$$\alpha = \varepsilon_{\mathrm{F}}\,.\,C_{\mathrm{F}}l \qquad (3)$$

where ε_{F} and C_{F} are the extinction coefficient and concentration of the unbonded hydroxy-groups respectively, and l is the cell path length. For equilibrium (2) the concentration of monomer [M] is related to the total concentration of acid species (A_{T}) by (4),

$$[\mathrm{M}] = \frac{(8K_{\mathrm{D}}A_{\mathrm{T}} + 1)^{\frac{1}{2}} - 1}{4K_{\mathrm{D}}} = C_{\mathrm{F}} \qquad (4)$$

and the absorbance is thus given by equation (5).*

$$\alpha = \frac{\varepsilon_{\mathrm{F}}l([8K_{\mathrm{D}}A_{\mathrm{T}} + 1]^{\frac{1}{2}} - 1)}{4K_{\mathrm{D}}} \qquad (5)$$

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* It should be noted that a relationship of the same form as equation (5) relates the absorbance of the unbonded carboxy-groups in polymers of type (III) to A_{T}, provided it is assumed that the association constants K_{p} are all the same.

Upon rearranging equation (5) and squaring both sides, one obtains

$$\frac{2K_D\alpha}{\varepsilon_F{}^2 l} + \frac{1}{\varepsilon_F} = \frac{lA_T}{\alpha} \qquad (6)$$

Thus a plot of $A_T/(\alpha/l)$ *vs.* (α/l) should be linear, having a slope of $2K_D/\varepsilon_F{}^2$ and an intercept of $1/\varepsilon_F$.

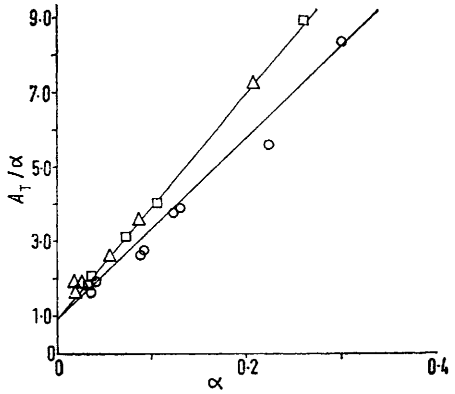

FIGURE 3 Variation of A_T/α with α for *N*-methyl-, (○), *N*-ethyl- (□), and *N*-isopropyl- (△) succinanilic acids at 20°

Typical plots of this type are shown in Figure 3 for *N*-methyl-, -ethyl-, and -isopropyl-succinanilic acids. Owing to the low solubilities of succinanilic acid and 2,*N*-dimethylsuccinanilic acid in non-polar solvents these compounds could not be studied.

Association constants for use in temperature studies were more conveniently obtained by use of equation (7), using the ε_F values obtained as described above.

$$K_D = [D]/[M]^2 = \frac{A_T - [M]}{2[M]^2} = (A_T - \alpha/\varepsilon_F l)/2(\alpha/\varepsilon_F l)^2 \qquad (7)$$

Enthalpies and entropies of association of the acids in carbon tetrachloride were obtained from plots log K_D *vs.* $1/T$ (Figure 4) in the usual manner. These quantities are given in the Table.

TABLE

Molar extinction coefficients and thermodynamic data for the association of succinanilic acids in carbon tetrachloride

Acid	ε_F ($M^{-1}\cdot cm^{-1}$)	K 30° ($mol^{-1}\cdot l$)	$-\Delta H_{ass}$ ($kJ\cdot mol^{-1}$)	$-\Delta S_{ass}$ ($J\cdot mol^{-1}\cdot K^{-1}$)
N-Me	110 ∓ 10	1350 ∓ 300	42 ∓ 2	75 ∓ 8
N-Et	110 ∓ 10	1010 ∓ 270	42 ∓ 2	80 ∓ 8
N-Pr^i	110 ∓ 10	1020 ∓ 270	34 ∓ 4	54 ∓ 16
3,*N*-Me$_2$		2250 ∓ 400	39 ∓ 4	25 ∓ 12

Although the variation in hydroxy-group absorption intensity is consistent with the equilibrium shown in equation (2), if *two* monomeric species (M′ and M″) were present, and the absorption at ~3540 cm.$^{-1}$ were due only to one of these, a similar relationship would be obeyed. Thus, if the equilibria were as shown in (8) the equation corresponding to (6) would be (9) if M″ only absorbed.

$$M'' \underset{K_1}{\rightleftharpoons} M' \underset{K_2(M)}{\rightleftharpoons} \tfrac{1}{2}D \qquad (8)$$

$$\frac{2K_2\alpha}{\varepsilon_F{}^2 l} + \frac{(K_1 + 1)}{\varepsilon_F} = \frac{lA_T}{\alpha} \qquad (9)$$

Thus a plot of α *vs.* A_T/α would still be linear, but the intercept in this case would be $(K_1 + 1)/\varepsilon_F$ instead of $1/\varepsilon_F$. If K_1 were significant (*i.e.* >0·5) the extinction coefficient ε_F of the absorbing species, the unbonded monomer, would be unusually low. This is not the case, as Harris and Hobbs [5] report values of ε_F for a series of acetic acids as between 90—130.

In addition, the formation of an intramolecularly bonded monomer would have an effect on the heat of association of the acids. The heats of association found for succinanilic acids are in the range −35 to −45 kJ mol^{-1}. These values are approximately those expected for association of an acid intermediate strength between acetic acid ($\Delta H_{ass} = -45$ kJ mol^{-1} [6]) and benzoic acid ($\Delta H_{ass} = -46$ kJ mol^{-1} [7]). If, however, a significant fraction of the monomeric acid were intramolecularly bonded, the apparent heats of association would be expected to be considerably lower, and plots of log K_D *vs.* $1/T$ would be curved. This was not found, and again would suggest that an intramolecularly bonded monomeric acid does not form an appreciable fraction of the monomeric acid. We conclude, therefore, that the predominant species in succinanilic acid solutions are the unbonded monomer, cyclic dimer, and, at high concentrations, an infinite polymer in which the carboxy-groups are intermolecularly bonded to amide groups. Our data suggest that an intramolecular bonded monomer is not a major component of succinanilic acids even in dilute solution, but kinetic data suggests that the dissociation of these acids to anilines and succinic anhydrides [8] involves such a monomer as an intermediate.

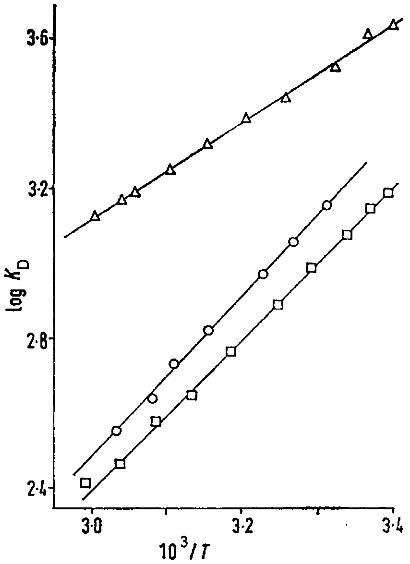

FIGURE 4 Variation of log K_D with $1/T$ for succinanilic acids

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[5] J. T. Harris and M. E. Hobbs, *J. Amer. Chem. Soc.*, 1954, **76**, 419.

[6] H. E. Affsprung, S. D. Christian, and A. M. Melnick, *Spectrochim. Acta*, 1964, **20**, 285.

[7] G. Allen, J. G. Watkinson, and K. H. Webb, *Spectrochim. Acta*, 1965, **22**, 807.

[8] M. J. Gregory, unpublished data.

However, the concentration of the bonded monomer could well be below the spectroscopic limits of detection.

The modest decreases in the heats of association of *N*-isopropyl- and 3,*N*-dimethyl-succinanilic acids, relative to the *N*-methyl- and *N*-ethyl-succinanilic acids, are presumably steric effects. The magnitude of the effect is considerable for a substituent six atoms away from the reactive centre. It is thought that the decrease is associated with a conformational change which occurs in the formation of the dimeric acid from the *N*-methyl and *N*-ethyl-acids, but which is prevented by interactions of the *N*- and 3-substituents in *N*-isopropyl- and 3,*N*-dimethyl-succinanilic acids. The interactions apparent in space-filling models of the compounds are so many that no interaction could be detected which would specifically account for what is a small energy change, in terms of steric interactions.

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