

544. *Hydrogen Bonding in Aqueous Solutions of Maleic Acid.*

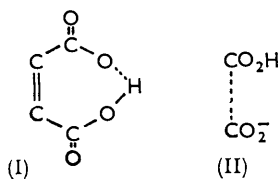
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Interproton distances required to account for the observed values of the dissociation constants, K_1 and K_2 , for maleic and fumaric acid are calculated on the assumption that only electrostatic and dipole interaction is significant. Agreement with reasonable dimensions of the molecules shows that the values of K_1 and K_2 for maleic acid do not require assumption of hydrogen bonding.

Infrared spectral evidence suggests that the acid maleate ion is, but maleic acid itself is not, internally hydrogen-bonded in approximately 1M-aqueous solution.

THE first and the second dissociation constant for maleic acid have frequently been regarded as anomalous and recently it has been thought necessary to introduce the concept of hydrogen bonding in the acid ion (I) to explain the experimental values,^{1,2} and measurement of the dissociation constants in water and heavy water have been made in order to determine the relative strengths of the hydrogen and deuterium bonds.³ Such hydrogen bonding occurs in the crystal⁴ but evidence for its occurrence in solution is necessarily indirect.

The ratio of the dissociation constants of a dibasic acid was first studied quantitatively by Bjerrum⁵ and later by Kirkwood and Westheimer.⁶ It was shown that K_1/K_2 was always greater than four and approached this value as the separation of the carboxyl groups increased. Deviations from this value could be accounted for in terms of electrostatic interaction between the carboxylate ion and the un-ionized carboxyl groups in the structure (II). Naturally this interaction becomes greater as the two carboxyl groups approach one another.



In this paper we give the results of a calculation of electrostatic effects which show that the postulate of hydrogen bonding is not necessary for an explanation of the values of K_1 and K_2 in maleic acid. Some infrared spectral evidence is then presented which suggests that in aqueous solutions, admittedly more concentrated than those in which dissociation constants are determined, maleic acid is not internally hydrogen-bonded but that the acid maleate ion is.

¹ Hunter, *Chem. and Ind.*, 1953, **17**, 155.

² McDaniel and Brown, *Science*, 1953, **118**, 370.

³ Dahlgren and Long, *J. Amer. Chem. Soc.*, 1960, **82**, 1303.

⁴ Shahat, *Acta Cryst.*, 1952, **5**, 763.

⁵ Bjerrum, *Z. phys. Chem.*, 1923, **106**, 219.

⁶ Kirkwood and Westheimer, *J. Chem. Phys.*, 1938, **6**, 506.

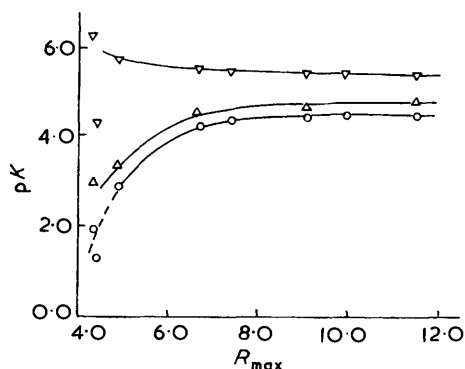
CALCULATION

By using equations developed by Kirkwood and Westheimer it is possible to predict the separation distance of the two carboxyl groups required to produce a given value of ΔpK . These interprotonic distances (R) have been estimated for maleic and fumaric acids in both water and heavy water, the experimental values obtained by Dahlgren and Long³ being used. The acids are considered as spherical molecules and the results are given in the Table.

Acid	Solvent	pK_1	pK_2	R	$R_{max.}$	Bjerrum's value
Maleic	H ₂ O	1.910	6.332	3.63	4.32	0.8
„	D ₂ O	2.535	6.711	3.68	—	—
Fumaric	H ₂ O	3.095	4.602	5.12	6.74	—
„	D ₂ O	3.557	5.025	5.16	—	—

The Table also includes the value of R calculated by application of Bjerrum's original treatment to maleic acid and the probable maximum value of R , $R_{max.}$. This was calculated by using Kirkwood and Westheimer's assumption that the protons were located 1.45 Å from the carboxyl carbon atoms on the extension of the terminal C-C bonds.⁶

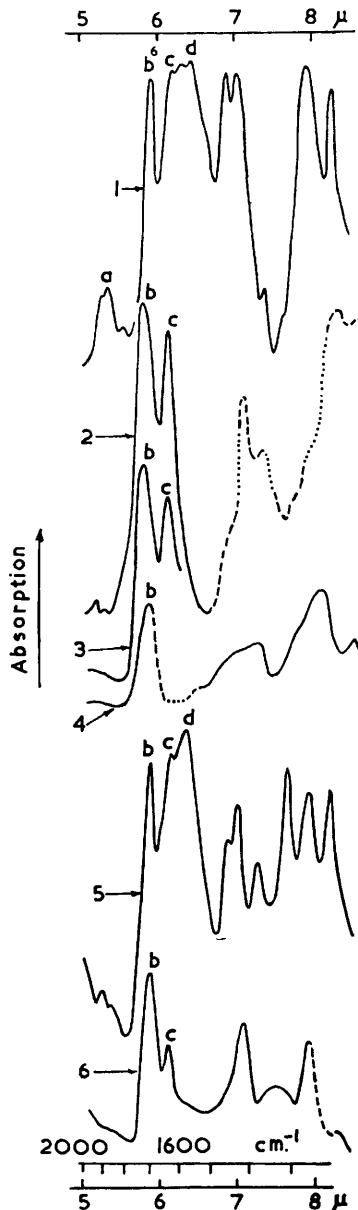
FIG. 1. Dissociation constant as a function of $R_{max.}$. \circ pK_1 , ∇ pK_2 , \triangle pK of monoethyl ester. The acids shown are, in order of increasing $R_{max.}$, maleic, oxalic, malonic, succinic, glutaric, adipic, pimelic, and suberic.



It can be seen that application of Bjerrum's original equation to maleic acid gives much too low a result, as is to be expected. On the other hand, the application of Kirkwood and Westheimer's equations leads to perfectly reasonable results, the difference between R and $R_{max.}$ being comparable to that found by these authors for a number of other dibasic acids. The change in ΔpK between H₂O and D₂O is seen on this interpretation as the result of only a very small increase (*ca.* 0.05 Å) in interprotonic distance. Such an increase is not unexpected.

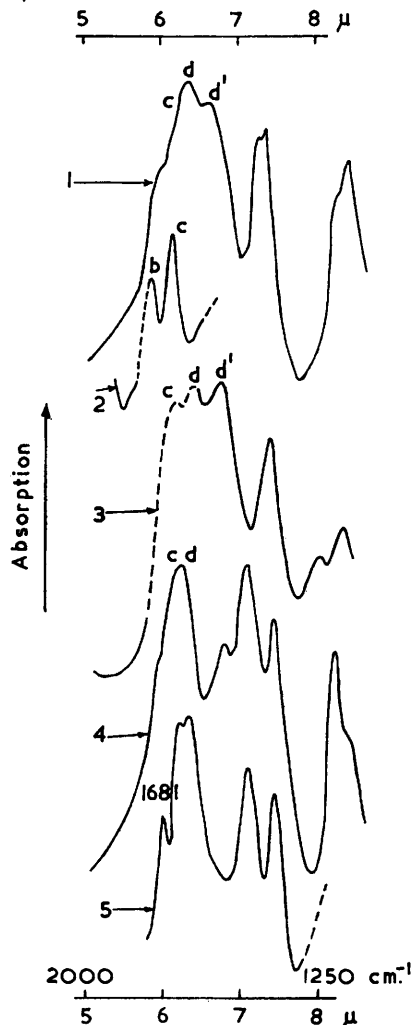
Electrostatic interaction of the type postulated here should have very little effect on K_1 but should produce a considerable drop in K_2 . On the other hand, hydrogen bonding should cause an increase in K_1 over the expected value due to the stabilisation of the acid anion if internal hydrogen bonding were more important in the acid anion than in the free acid. For the same reason a decrease in K_2 should occur. A decision as to which of the effects are operating might therefore be possible from an examination of K_1 for maleic acid. The dissociation constants for a series of acids are shown in Fig. 1 where they are plotted against the structural distance $R_{max.}$ defined above. It must be emphasised that calculation of this distance depends purely on the geometry of the molecules concerned. It can be seen that the values of both K_1 and K_2 change little at values of $R_{max.}$ greater than about 7 Å. The value of K_2 for maleic acid is low, but K_2 values for both malonic acid and succinic acid are also falling slightly as $R_{max.}$ decreases. In any case, a low value of K_2 is to be expected. K_1 for maleic acid appears to lie on a smooth curve with acids of the type HO₂C·[CH₂]_n·CO₂H as would be expected if dipole interaction were

FIG. 2. Infrared spectra of maleic acid and deuteromaleic acid, as solid and in various solvents, between 5 and 8 μ . The broken line indicates regions of solvent absorption exceeding 70% and the dotted lines indicate complete extinction by solvent.



1, Solid maleic acid. 2, Maleic acid in dioxan. 3, Maleic acid in methanol. 4, Maleic acid in water. 5, Solid maleic dideuterioacid. 6, Maleic dideuterioacid in deuterium oxide.

FIG. 3. Infrared spectra of potassium hydrogen maleate and potassium deuterium maleate, as solid and in various solvents, between 5 and 8 μ .



1, Solid potassium hydrogen maleate. 2, Potassium hydrogen maleate in dioxan. 3, Potassium hydrogen maleate in water. 4, Solid potassium deuterium maleate. 5, Potassium deuterium maleate in deuterium oxide.

becoming more important with decreasing carboxyl separation and the C=C bond had had little effect. The acid dissociation constants of the monoesters of various dibasic acids lie on a similar curve ⁷ and in this case dipole interaction between ethoxycarbonyl and carboxyl groups appears to be the only explanation for the increase of K_1 as the separation distance falls.

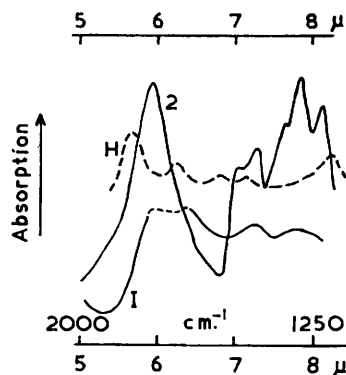
Calculations by Westheimer and Benfey ⁸ suggest that hydrogen bonding is an appreciable but not dominant factor leading to a high K_1/K_2 ratio for maleic acid. They suggest that the maximum effect of hydrogen bonding would be to increase K_1/K_2 by a factor of about 28 over the statistical value. Their result rests on the assumption that an ethoxycarbonyl group has the same effect as a carboxyl group on the ionisation of an adjacent carboxyl group. This assumption may not be justified at very low separations.

We conclude that calculations based on dissociation-constant data for dibasic acids shed little light on the nature of the acid maleate ion in solution. For some of the substituted succinic acids investigated by Ebersson, ⁹ where K_1/K_B and K_1/K_2 ratios are extremely high, it seems necessary to postulate hydrogen bonding. For maleic acid these ratios can be satisfactorily accounted for by electrostatic interaction although the calculations are of such an approximate nature that hydrogen bonding cannot be ruled out. To throw further light on this problem we have measured the infrared spectra of solutions of maleic acid and its salts in both water and heavy water.

EVIDENCE FROM INFRARED SPECTRA

Experimental.—The infrared absorption spectra of maleic acid, of potassium hydrogen maleate, and of sodium hydrogen fumarate, and also of the corresponding deuterated compounds,

FIG. 4. Infrared spectra of sodium hydrogen fumarate, as solid (1) and in aqueous solution (2), between 5 and 8 μ . Curve H is for the solid, as found by Hadži and Novák.¹²



have been measured in the solid and in aqueous (or D_2O) solution. Some spectra were also measured in dioxan and in methanol. A Grubb-Parsons double-beam GS2 spectrometer was used. Particular attention was paid to the region 5–8 μ , and the spectra in that region are shown in Figs. 2, 3, and 4. Solids were mounted in potassium bromide discs (1.0–1.3 mg. in $\frac{1}{2}$ -in. diam. disc with about 200 mg. of potassium bromide). We are indebted to Mrs. B. S. Crawford for the preparation and infrared examination of these discs. The solutions were either 1M or saturated, and they were mounted in capillary thickness between silver chloride plates. The spectra shown are difference spectra, the solvent contribution being balanced out by careful adjustment of a similar cell in the blank beam. Exact balance at capillary thickness is only achieved by trial, and the results were confirmed by observation of difference spectra with both too little and too much solvent compensation. Broken lines in the spectra indicate uncertainty in the region of strong solvent absorption. The dioxan solution of maleic acid was 1M and was measured at 0.1 mm., that of potassium hydrogen maleate about 0.1M,

⁷ Walker, J., 1892, **61**, 696.

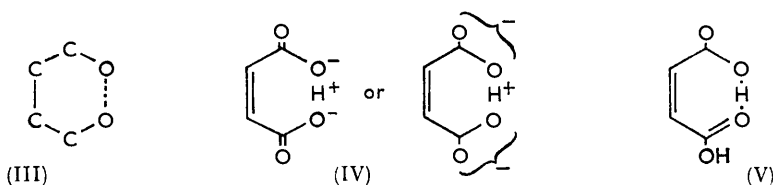
⁸ Westheimer and Benfey, J. Amer. Chem. Soc., 1956, **78**, 5309.

⁹ Ebersson, Acta Chem. Scand., 1959, **13**, 211.

measured at 0.8 mm. thickness. The methanol solution of maleic acid was 0.5M, measured at 0.02 mm.

Results.—The spectra shown in Figs. 2, 3, and 4 cover the carbonyl-stretching and the carboxylate-ion frequencies. The spectra of the solids are subject to the uncertainties of the disc method. Our spectrum of maleic acid agrees with that obtained by Mecke,¹⁰ using the same techniques, and the spectra of the acid and solid potassium hydrogen maleate agree with those obtained by Cardwell, Dunitz, and Orgel,¹¹ who used Nujol mulls. On the other hand, the spectrum of sodium hydrogen fumarate is entirely different from that given by Hadži and Novak¹² who use Nujol and fluorocarbon mulls. They find, for potassium hydrogen fumarate, a strong band at 1756 cm.⁻¹, and their spectrum is shown in Fig. 4. It is possible that the sort of difference that Hadži and Novak find between vitreous and crystalline samples of the acid salt of phenylacetic acid is being observed here.

Discussion.—Both maleic acid⁴ and potassium hydrogen maleate¹³ have planar ring structures (III) in the crystalline state, with O—O distances (2.46 and 2.42 Å, respectively) which are taken to indicate strong (perhaps symmetrical) hydrogen bonds. Cardwell, Dunitz, and Orgel had argued, before X-ray diffraction data were available for potassium hydrogen maleate, that the spectral differences between maleic acid and the acid potassium salt were in favour of the symmetrical structure (IV) for the hydrogen maleate (MH⁻) ion. The band (*b*) at 1704 cm.⁻¹ in maleic acid, which is due to the externally bonded carbonyl group in the unsymmetrical structure (V), is not present in potassium hydrogen maleate but is found as a broad band centred on 1681 cm.⁻¹ in sodium hydrogen fumarate. The broad band extending from 6 to 6.5 μ in maleic acid contains three maxima, of which the first (*c*) at 1632 cm.⁻¹ is probably due to C=C stretching (since it appears with varying intensity but fairly constant frequency in all spectra of maleic acid and potassium hydrogen maleate), and the pair (*d*) at about 1585 and 1562 cm.⁻¹ can be assigned to vibrations of the C=O link involved in the internal hydrogen bond. The absence of band (*b*) and the considerable lessening of intensity of the C=C band (*c*) in potassium hydrogen maleate is consistent with the symmetrical structure of the HM⁻ ion. The C=C absorption is not detected in solid sodium hydrogen fumarate, in agreement with the *trans*-configuration. The absorption (*d*) in maleic acid appears in the acid potassium salt at 1569 cm.⁻¹, and a further band (*d'*) appears at 1488 cm.⁻¹ in the latter. These may also be assigned to C=O/C—O frequencies, possibly coupled with OH deformation, in the symmetrical •C=O•H⁺•O•C=O• group. They may be expected to be not far removed from carboxylate



frequencies¹⁴ at 1610—1550 and 1420 cm.⁻¹. (It is not clear why the carboxylate frequencies do not appear in our spectrum of sodium hydrogen fumarate. The structure of potassium hydrogen fumarate¹⁵ involves an extended chain of hydrogen fumarate [HFum⁻] ions, externally hydrogen-bonded at each end.) Additional evidence that Cardwell *et al.* might have used is the absence of the very broad absorption between 3500 and 2000 cm.⁻¹ from the crystal spectra of potassium hydrogen maleate. This absorption, due to external hydrogen-bonding, is prominent in maleic acid and potassium hydrogen fumarate.

¹⁰ Mecke, D.M.S. Card 5124 (10/59).

¹¹ Cardwell, Dunitz, and Orgel, *J.*, 1953, 3741.

¹² Hadži and Novak, *Nuovo Cimento*, 1955, 2, 716.

¹³ Darlow, in Hadži (ed.), "Hydrogen Bonding," Pergamon Press, 1959, p. 40.

¹⁴ Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, 1954, p. 149.

¹⁵ Gupta, *Acta Cryst.*, 1956, 9, 263.

Forsen¹⁶ has shown that sodium hydrogen maleate, dissolved in dimethyl sulphoxide, shows proton magnetic resonance signals at very low field and has ascribed this to the internal hydrogen bond which is retained in that solvent. Similar chemical shifts were observed by Eberson and Forsen¹⁷ for solutions in dimethyl sulphoxide of the monoacid salts of the racemic $\alpha\alpha'$ -dialkylsuccinic acids which show high K_1/K_2 ratios in 50% aqueous ethanol. Attempts to find the same chemical shifts in aqueous or methanol solutions of these salts were not successful, but this does not provide evidence against the internal hydrogen bond in these solvents since the signal could be lost by rapid proton exchange between the ion and the solvent. For this reason, the infrared spectrum (where the transitions occur in a time which is shorter than in proton magnetic resonance by a factor of 10^6) is likely to be the only means of obtaining evidence about the stability of the internal hydrogen bond in aqueous solution.

Eberson¹⁸ has compared the spectra of the alkylated succinic acids, their monoacid salts, and solutions of these in methanol and in D_2O . The solid spectra support the view that the monoacid salts of the acids with high K_1/K_2 ratio have the internal hydrogen bond, but that those of the low-ratio acids do not. The externally bonded carbonyl band occurs at 1680—1700 cm^{-1} but is considerably weakened in the monoacid salts, to a greater extent with the high-ratio acids than the low. The salts of the high-ratio acids also show in the solids the two broad bands near 1580 and 1480 cm^{-1} which appear to be characteristic of the internally bonded carboxylate groups and correspond to (\bar{d}) and (d') in the spectrum of potassium hydrogen maleate. These bands persisted in methanol and in D_2O solutions (where, however, the species involved would be the deuterated ions).

From Fig. 2 it can be seen that bands (d) of maleic acid are not retained in solutions in dioxan or methanol. Furthermore, band (a) assigned to the O-H stretching frequency of the internal hydrogen bond in maleic acid is not present in these solutions. The carbonyl frequency (b) is prominent at 1724 cm^{-1} in both solvents. In aqueous solution (b) is at 1701 cm^{-1} . The band (c) assigned to C=C stretch is present in the solutions but cannot be discerned in water because it is overlapped by the strong band of water itself at 1640 cm^{-1} . It is reasonably certain, however, that the bands (d) are not present in aqueous solution. This view is reinforced by the deuterated acid D_2M and its solution in D_2O . Bands (b) and (c) remain but (d) disappears in solution.

In the acid salt the situation is different. Fig. 3 shows that in dioxan solutions of potassium hydrogen maleate the carbonyl band (b) appears in medium intensity, the C=C stretching frequency (c) is intensified, and the bands (d) and (d') are absent. In aqueous solution, however, there is no sign of (b), (c) is uncertain because of solvent absorption, and the bands (d) and (d') remain of high intensity. In the case of potassium deuterium maleate the evidence is similar but somewhat less conclusive.

It appears probable therefore that the intramolecular hydrogen bond present in crystalline maleic acid is not sufficiently strong to withstand competition for the hydrogen bond from dioxan, methanol, or water. The acid maleate ion, on the other hand, has a stronger intramolecular hydrogen bond which remains stable in water but appears to be broken by dioxan. The weak band at 1681 cm^{-1} in D_2O solutions of potassium deuterium maleate suggests that the bond in that case may be just so stable that both bonded and non-bonded ions are present in comparable equilibrium concentrations.

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¹⁶ Forsen, *J. Chem. Phys.*, 1952, **31**, 852 (1952).

¹⁷ Eberson and Forsen, *J. Phys. Chem.*, 1960, **64**, 767.

¹⁸ Eberson, *Acta Chem. Scand.*, 1959, **13**, 224.