

were carried out on this substance. In all cases the products were found to be α -amino, β -naphthol and 5-aminotetrazole.

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¹ Morgan and Reilly, *J. Chem. Soc.*, **103**, 808, 1494 (1913); **105**, 436 (1914); **109**, 155 (1916). Reilly and Madden, *J. Chem. Soc.*, **127**, 2936 (1925); **134**, 815 (1929). Reilly and MacSweeney, *Proc. Roy. Irish Acad.*, **39**, B, 497 (1930).

² Thiele, *Ann.*, **270**, 46 (1892).

³ Hantzsch and Vagt, *Ann.*, **339**, 314 (1900).

⁴ Hofmann and Hock, *Ber.*, **43**, 1866 (1910).

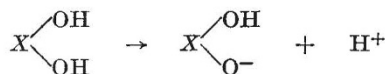
⁵ Hofmann and Hock, *Ber.*, **43**, 682 (1910).

⁶ Norris-Shreve, Carter and Willis, *Ind. Eng. Chem.*, **36**, 472 (1936).

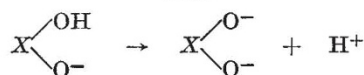
Relationships Between some Dissociation Constants

In these Laboratories the fungistatic properties of ethylenic and acetylenic compounds have been studied recently¹. Our results indicated that biological activity was connected with the presence of substituents that attract electrons strongly, and led us to a consideration of the dissociation constants of compounds which donate protons (that is, acids as defined in the broadest sense), since these constants form a basis for a comparison of the affinity for electrons of radicals and groups. During the course of this work, relationships were found between certain dissociation constants, which constants are conveniently expressed as $\Delta F (= -RT \cdot \log_e K)^2$ for the reaction $RH \rightarrow R^- + H^+$ taking place in dilute aqueous solution at 25° C. Although the relationships summarized below are of general application, space here does not permit them to be illustrated by long lists of examples, and so, as far as possible, only the values of ΔF (calories) for the seven acids, H_3PO_4 (I) + 2,900; $H_2PO_4^-$ (II) + 9,800; HPO_4^{2-} (III) + 16,900; H_2SO_3 (IV) + 2,400³; HSO_3^- (V) + 9,800³; HSO_4^- (VI) + 2,300 and $HOCl$ (VII) + 10,100^{4,5}, have been used in this discussion

(1) The values of ΔF for the two reactions



and



differ by 7 kgm. cal. Compare (I) and (II); (II) and (III); and (IV) and (V).

(2) The addition of a doubly bonded oxygen atom to the atom attached to a dissociating hydroxyl group decreases the value of ΔF by 7 kgm. cal.; for example, (V) and (VI). One of the two effects (1) and (2) in reverse should cancel out the other, and indeed (IV) and (VI) do agree within the limits of the experimental error.

(3) In the reaction $-Y-H \rightarrow -Y^- + H^+$, the combination of an additional proton with Y or the replacement of an atom directly attached to Y by another higher in atomic number by one unit decreases ΔF by 14 kgm. cal.; compare (III) and (VI). The difference, 14 kgm. cal., is so large that accurate measurement of both dissociation constants is usually difficult. However, the effect (3) can be reduced by

combining it with (1) or (2), and the difficulty then disappears. The dissociation constant of a hydroxylic acid should, in fact, be unaltered if the atom attached to the hydroxyl group is moved back one place in the periodic table (ΔF changed by -14 kgm. cal.), and either: (a) two oxygen atoms are linked to the replacing atom by semi-polar double bonds ($+2 \times 7$) as in (V) and (VII); or (b) one oxygen atom ($+7$) is attached and an extra proton is put on this oxygen atom ($+7$) (examples are the pairs (I) and (IV) and (II) and (V)); or (c) two protons are added to oxygen atoms already attached to the replacing atom ($+2 \times 7$); (I) and (VI).

(4) In the reaction $-Y-H \rightarrow -Y^- + H^+$, the replacement of Y by an atom one higher in atomic number apparently decreases ΔF by 21 kgm. cal., at any rate when Y is carbon or nitrogen. This difference between the ΔF values is so large that it cannot be measured directly. However, ΔF for $AOH \rightarrow AO^- + H^+$ is greater than ΔF for $ANH_3^+ \rightarrow ANH_2 + H^+$. A comparison can be made with more than twenty different groupings for A , and the difference in the ΔF values is always close to 7 kgm. cal. This figure may be regarded as the net result of an increase in ΔF of 2×14 kgm. cal. due to the removal of two protons (effect 3) and a decrease of 21 kgm. cal. for the replacement of nitrogen by oxygen. This fourth effect is interesting because it suggests a means by which ΔF for carbon-hydrogen links can be estimated. For the dissociation of nitric acid, ΔF seems to be roughly $-1,000$ cal.⁶ From this by calculation for effects (3) and (4), ΔF for nitromethane should be $+13,000$ cal. The estimation of ΔF for nitromethane from that of nitramide ($+9,000$ cal.) leads to a figure of $+16,000$ cal. The experimental value of ΔF is $+15,000$ cal. The effect on the dissociation constants of pyridinium ions produced by substituents can now be used to throw light on problems of substitution in benzene derivatives.

This and other matters arising out of the discovery of these relationships will be discussed when a fuller account of this work is prepared for publication elsewhere.

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¹ Brian, P. W., Grove, J. F., and McGowan, J. C., *Nature*, **158**, 876 (1946).

² Most of the values given for ΔF have been calculated from the dissociation constants shown in Landolt-Bornstein's "Physikalisch-Chemische Tabellen", Berlin (1923) and Supplements (1927), (1931) and (1936).

³ Tartar, H. V., and Garretson, H. H., *J. Amer. Chem. Soc.*, **63**, 808 (1941).

⁴ Holst, G., *Chem. Abst.*, **35**, 2784 (1941).

⁵ Hagiwara, H., *Chem. Abst.*, **35**, 20 (1941).

⁶ Redlich, O., *Z. phys. Chem.*, **A**, **182**, 42 (1938).

Nature of the Tryptophanase Complex

IN a previous communication¹ we described the preparation of a cell-free extract of tryptophanase from *Esch. coli* and its resolution into a coenzyme fraction and an apoenzyme.

The effect of various inhibitors was studied, as summarized below, and afforded information as to possible components of the enzyme complex.

Mepacrine. The inhibitory effect of mepacrine on the growth and tryptophanase activity of *Esch. coli* has already been announced² by Dawson, and this inhibition is antagonized by riboflavin.