Effect of intramolecular hydrogen bonding on the relative acidities of substituted salicylic acids in benzene solution[1]
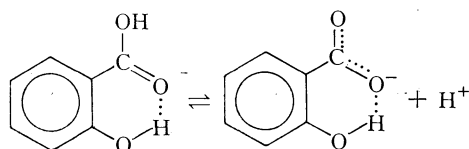
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Received November 17, 1966

The relative acidities of fifteen 4- and 5-substituted salicylic acids were determined in benzene solution by potentiometric titration. The potentials at half neutralization (h.n.p.) relative to that of salicylic acid were considered to measure the acidities of the substituted acids relative to the parent acid. These potentials, designated by Δ_{hnp}, gave a significantly better correlation with Hammett's sigma constants in an equation of the form proposed by Jaffe, $\Delta_{hnp} = \rho_1\sigma_1 + \rho_2\sigma_2$, than in a simple Hammett equation, $\Delta_{hnp} = \rho_1\sigma_1$. In these equations the subscripts 1 and 2 refer to the position of a substituent relative to the carboxyl group and to the phenolic group respectively. The value of ρ_2/ρ_1 was found to be 0.4, indicating that the electronic effect of a substituent on the acid strength via the phenolic hydrogen-bonded path is almost half as large as the direct effect through the carboxyl group. These results, together with the fact that in aqueous solution there is very little if any transmission via the phenolic group, are discussed in terms of intramolecular hydrogen bonding of salicylic acids in benzene and in water.

Salicylic acid is a much stronger acid than the other monohydroxybenzoic acids because an intramolecular hydrogen bond stabilizes the salicylate anion more than it does the un-ionized acid. In *m*- and *p*-

hydroxybenzoic acids the phenolic group is not in a position to chelate with the carboxyl group, so the acidities of these acids are not "abnormal". This interpretation was first clearly expressed in modern terms by Baker (1) and has become so widely accepted that it is a common feature in all textbooks which deal with the strengths of organic acids.

Jaffe (2) pointed out that, according to the above interpretation, substituents in the 4- and 5-positions of salicylic acids should influence the acidity of the carboxyl group by two paths: a "direct" one through the carboxyl group, and an "indirect" one through the phenolic group via the intra-

molecular hydrogen bond. These should be expressed quantitatively by the Hammett relationship (3) in the form of eq. [1] for the direct effect and eq. [2] for the indirect one.

[1] $$\mathrm{Log}\ (K/K_0) = \rho_1\sigma_1$$

[2] $$\mathrm{Log}\ (K/K_0) = \rho_2\sigma_2^-$$

In these equations K and K_0 are the ionization constants of substituted and unsubstituted salicylic acids respectively, σ_1 is Hammett's sigma constant for the substituent with reference to the carboxyl group, σ_2^- is the sigma constant for the same substituent with reference to the phenolic group, and ρ_1, ρ_2 measure the susceptibility of the ionization constants to electronic influences via the direct and indirect routes respectively. Jaffe proposed (2) that the direct and indirect effects should be additive so that the overall effect of a substituent in the 4- or 5-position would be given by eq. [3].

[3] $$\mathrm{Log}\ (K/K_0) = \rho_1\sigma_1 + \rho_2\sigma_2^-$$

However, in a recent paper Dunn and Kung (4) showed that the ionization constants of sixteen 4- and 5-substituted salicylic acids in water at 25° are not correlated significantly better by eq. [3] than by eq. [1] (taking the 95% confidence level as the lower limit of significance).