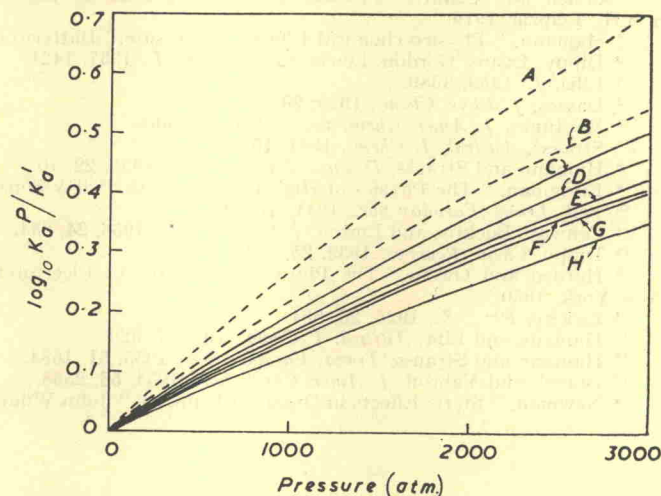


The individual benzoic acids may now be considered (Figure). The graph of  $\log K_a^P/K_a^1$  for *p*-methylbenzoic acid completely overlies that for benzoic acid. Evidently a *p*-methyl constituent has little effect on the change in ionic-solvation free energies with increased pressure.

If the compressibility of the organic acid ions does not change with molar volume the effect of pressure should increase inversely with the size of the ions.<sup>16</sup> The present values of  $K_a^P/K_a^1$  for benzoic acid in water are for equal pressures rather less than Hamann and Strauss's values<sup>16</sup> for acetic and formic acids. The values of  $\Delta V^1$  for *m*- and *p*-nitrobenzoic acids are in turn slightly less than that for benzoic acid.

Variation in strengths of benzoic acids with increasing pressure at 25°.

- A, Benzoic and *p*-methylbenzoic acid in ethanol-water.
- B, Salicylic acid in ethanol-water.
- C, Benzoic acid in water.
- D, *o*-Nitrobenzoic acid in water.
- E, 3,5-Dimethyl-4-nitrobenzoic acid in water.
- F, *p*-Nitrobenzoic acid in water.
- G, *m*-Nitrobenzoic acid in water.
- H, Salicylic acid in water.

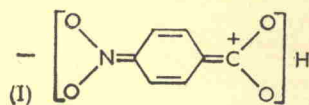


The effect of pressure on salicylic acid is less than that for any other acid on which data are available. It has been suggested<sup>17</sup> that an internal hydrogen bond is formed between the carboxyl and the hydroxyl group which stabilizes the salicylate anion with respect to the free acid. This accounts for the high dissociation constant. Internal hydrogen bonding in the anion would lower the energy of hydration by drawing off part of the charge on the carboxylate group, and by hindering the access of water molecules. The low decrease in compressibility on ionization is in agreement with a low degree of hydration.

Hamann<sup>2</sup> estimated the volume contraction on the formation of one hydrogen bond to be  $-3.4 \text{ cm}^3 \text{ mole}^{-1}$ . Table 14 gives the difference between the volume contractions for benzoic and salicylic acids as  $-3.4 \text{ cm}^3 \text{ mole}^{-1}$  for both water and ethanol-water. Although no significance can be attached to the exact agreement in volume figures the results do support the hydrogen bond explanation for the low  $\Delta V$  for salicylic acid.

Newman<sup>18</sup> considered that the high acid dissociation constant for *o*-nitrobenzoic acid was due to the decrease in the resonance energy of the free acid form, caused by steric interaction of the nitro- and the carboxyl group. The present results suggest that high pressures increase this interaction slightly.

3,5-Dimethyl-4-nitrobenzoic acid has a dissociation constant at 25° only slightly greater than that of benzoic acid, whereas the constant for *p*-nitrobenzoic acid is greater by a



factor of about 6. The use of 10% ethanol as a solvent would account for only a small part of this difference. Part of the decreased acid strength may be due to the increased positive induction effect of the two methyl groups, but a greater decrease is probably due to the steric interaction of the methyl groups with the nitro-group. The anion of *p*-nitrobenzoic acid is stabilized by the resonance structure (I) which can make a maximum contribution to the energy

of the anion only if the nitro-group can become coplanar with the benzene ring.<sup>18</sup> The methyl groups hinder the formation of this planar arrangement. As the pressure effect for the acid is similar to that for *p*-nitrobenzoic acid the interaction between the methyl and the nitro-group cannot be altered appreciably by pressure.

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