

Dissociation Constants of Carboxylic Acids in Formamide

It has already been shown^{1,2} that the dissociation constants K_a of formic and acetic acid are lower in formamide than in water although the dielectric constant of the former is much larger than that of the latter. The variation of K_a with temperature may, in both solvents, be described by a reduced curve proposed by Harned and Embree³:

$$\log K_a^T - \log K_a^\theta = -p(T - \theta)^2 \quad (1)$$

Here θ is the temperature where the dissociation constant has its maximum value K_a^θ and p is a constant for all carboxylic acids. However, in formamide p is about ten times larger than in water, expressing the fact that K_a changes faster with temperature in the former solvent.

These results have been confirmed by further measurements on monochloroacetic acid⁴. Furthermore, determination of the dissociation constant of the alinium ion in formamide⁵ by the previously used potentiometric and an independent spectrophotometric method has shown: (1) that the standard potentials of the Ag; AgCl electrode used in the potentiometric measurements are reasonably correct up to 40°C; (2) that the dissociation constant of the alinium ion is somewhat larger in formamide than in water but that its temperature dependence is analogous in both solvents.

Therefore it may be concluded that the peculiar behaviour of the carboxylic acids is of a specific nature. We propose here a possible qualitative explanation based on the existence of complexes between the undissociated carboxylic acid molecules and formamide. In the literature some evidence for association species may be found⁶⁻⁷, although their exact structure has not been determined. It is possible to imagine at least two different structures due to hydrogen-bound association (Fig. 1). One possibility is the ring structure, the other a chain-forming association; the former is probably the more stable one. No evidence for such complexes in water is known.

The existence of such association structures will have an immediate effect on K_a . It has been shown² that the standard free energy per molecule of the proton transfer reaction (J) may be split into three independent parts.

$$J = J_{in} + J_q + J_e \quad (2)$$

Here J_{in} is the intrinsic work to transfer (in vacuum) a proton from the acid on a solvent molecule and J_q the total interactional free energy between the undissociated or dissociated solute and the solvent with the exception of J_e , the Born-type interaction between the solvated ions. This last contribution, which depends on the dielectric constant of the solvent, has been considered as the most important term determining J (ref. 8). However, J_q may have a marked influence on the value of J , especially if it contains a large contribution due to the free energy of solution of the undissociated acid. This effect will lead to an increase of J (and a decrease of K_a) with respect to the value calculated from the corresponding quantities in water taking into account only the change of the dielectric constant. (It is not very probable that J_{in} should differ greatly for the same acid in water and formamide.)

From a kinetic point of view and writing:

$$K_a = k_a/k_r \quad (3)$$

where k_a and k_r stand respectively for the specific rate of dissociation and recombination of the formed ions, we may estimate k_a at various temperatures from the known values of K_a and the calculated values of k_r according to the method proposed by Eigen *et al.*^{9,10}. We have found that the approximate values of $\ln k_a$, calculated with the help of Dawson's results^{11,12} on the mobility of various ions in formamide, vary linearly with T^{-1} , with a heat of activation of about 7 kcal mol⁻¹. This last value

corresponds roughly to the rupture of two hydrogen bonds. The values of k_a in formamide are several orders of magnitude smaller than the value calculated for acetic acid in water by Eigen⁹. This is further evidence for the existence of a cyclic association between formamide and the carboxylic acid. The transfer of a proton from the carboxylic group to the solvent molecule leaves the proton trapped inside the complex and no real dissociation occurs. This will only take place if the cyclic structure is disrupted and the protonized solvent molecule can separate from the acid. (The existence of trapped protons due to the occurrence of complexes between undissociated acid and solvent molecules has been found recently by Grunwald *et al.*¹³ in nuclear magnetic resonance investigations of benzoic acid in methanol.)

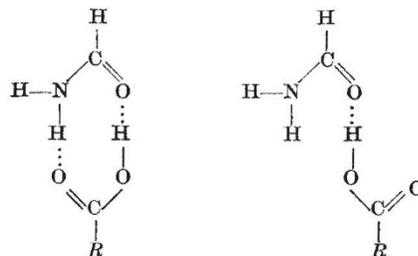


Fig. 1

All this leads to the conclusion that, besides purely electrostatic interactions between the formed ions, other effects should be taken into account in order to explain acidic dissociation. One of these may be a strong interaction between an undissociated acid molecule and the solvent. This effect has escaped attention up to now probably because most non-aqueous solvents which have been studied, had a low dielectric constant so that the influence of complex-formation and the electrostatic effect were in the same direction as compared with water.

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Photochemical Effect in the Reactions of Atoms produced by the Discharge Method

RECENT work¹ has shown that the reactivity of active nitrogen can be increased by diluting the nitrogen with inert gas prior to its passage through the condensed discharge tube. During a more detailed investigation of the effect of inert gas on the reactivity of active nitrogen with nitric oxide and other gases it was found that the