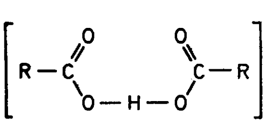
Hypophosphite Solutions in Carboxylic Acids

By **James H. Clark**, Department of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD
John Emsley * and **Trevor B. Middleton**, Department of Chemistry, King's College, Strand, London WC2R 2LS

Hypophosphite salts are very soluble in carboxylic acid solvents and a study of these solutions by various physical and spectroscopic methods (i.r., and ^{1}H and ^{31}P n.m.r.) shows that strong, but not very strong, hydrogen bonding is the principal solute–solvent interaction of the anion. An unusual feature of the solutions is the sensitivity of $J_{HP}(H_2PO_2^-)$ to the solvent medium and it is suggested that this parameter is a guide to the location of the proton of the hydrogen bond.

CARBOXYLATES are very soluble in the parent acid solvent, and the hydrogen bond which forms between a carboxylic acid and its conjugate base (1) is generally much stronger than that which holds together the acid dimers themselves.[1] Certain acids of phosphorus also form cyclic hydrogen-bonded dimers, $(R_2PO_2H)_2$.[2] Strong hydrogen bonding might therefore be expected between a carboxylic acid and a phosphinate anion (2).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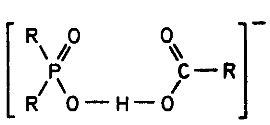

(2)

The high solubility of anhydrous sodium hypophosphite in glacial acetic acid is not reported in the literature.[3] This observation, and the very viscous solutions produced, reminescent of fluoride solutions in glacial acetic acid,[4] prompted us to investigate the systems MH_2PO_2–RCO_2H in the expectation of finding very strong hydrogen bonding of type (2) as was found in MF–RCO_2H systems.[5] However, unlike fluoride dissolution, hypophosphite dissolution in glacial acetic acid is not exothermic, the first indication that the hydrogen bonding is not as strong. Even so, the high solubility of NaH_2PO_2 in glacial acetic acid is not something that one would predict for a non-aqueous solvent with such a low relative permittivity ($\varepsilon = 6.22$).

EXPERIMENTAL

The carboxylic acids (formic, acetic, propionic, butyric, and trifluoroacetic) were high purity commercial reagents dried over molecular sieves before use. Sodium hypophosphite was commercial reagent grade, dried at 120 °C before use. Potassium hypophosphite was prepared by neutralizing the acid with K_2CO_3 and the crystals from the solution were dried at 100 °C *in vacuo* for several hours before use.

Hydrogen-1 n.m.r. spectra were recorded on a Perkin-Elmer R10 spectrometer operating at 60 MHz and were referenced to $SiMe_4$. Phosphorus-31 n.m.r. spectra were recorded on a JEOL JNM PS-100 spectrometer operating at 40.48 MHz with H_3PO_4 as external reference and [$^2H_6$]-acetone as external lock. All spectra were recorded within 24 h of sample preparation and at ambient temperatures.

The i.r. spectra of liquid films (CsBr optics) were obtained from Perkin-Elmer 621 and 457 machines, and peaks were measured against the polystyrene peak at 1 601.4 cm^{-1}.

RESULTS AND DISCUSSION

Sodium Hypophosphite in Glacial Acetic Acid.—Conventional physical property measurements of density, conductance, and freezing point depression were made on this system. Stirring together anhydrous NaH_2PO_2 and hot glacial CH_3CO_2H for several hours produced a viscous solution with a concentration at 20 °C of 734 g NaH_2PO_2 per kg CH_3CO_2H, *i.e.* 8.34 molal. On standing such a solution will crystallise slowly, but completely, to form the disolvate $NaH_2PO_2\cdot2CH_3CO_2H$, with m.p. 35 °C. An 8.3 molal solution corresponds to a 1 : 2 ratio of NaH_2PO_2 : CH_3CO_2H. A saturated solution of NaH_2PO_2 in water at 20 °C is *ca.* 13 molal, corresponding to a NaH_2PO_2 : H_2O mole ratio of *ca.* 1 : 4.[3]

The density of NaH_2PO_2 solutions in CH_3CO_2H varies linearly according to the equation $\rho(\text{g cm}^{-3}) = 1.040 + 0.049m$, where m is the molality.

The molal conductance over the range 0—4 molal concentration shows the same behaviour as KF–CH_3CO_2H [4] in that the conductance falls with concentration in very dilute solutions, rises in the range 0.1—1.3 molal, then falls as the concentration increases further. This behaviour is consistent with ion-pairing, triple ions, and high viscosity respectively. The values are reported in Table 1, the conductances being measured with a Radiometer (Copenhagen) instrument.

The apparent molecular weight of NaH_2PO_2 in CH_3CO_2H varies as shown in Table 2. These results show dissociation at low concentrations, and a molecular weight close to the formula weight of 88 at *ca.* 1 molal concentrations. The drop in molecular weight above 2 molal concentration is due to the non-ideality of these solutions. (At even higher concentrations the disolvate,

TABLE 1

Conductance of NaH_2PO_2 in glacial acetic acid

[NaH_2PO_2] (molality)	Conductance/ S cm^2 mol^{-1}
0.0107	0.0831
0.111	0.0678
0.265	0.134
0.564	0.366
1.105	0.770
1.446	0.803
2.002	0.718
2.50	0.577
2.87	0.484
3.51	0.339
3.94	0.248

TABLE 2

Apparent molecular weight of NaH_2PO_2 in glacial acetic acid

$[NaH_2PO_2]$ (molality)	Apparent M
0.0102	48.9
0.098	66.6
0.233	69.0
0.496	69.2
1.107	86.4
1.470	80.8
2.106	73.2
2.67	68.0
3.13	59.4
3.95	52.2

rather than the solvent, is the solid phase that separates from solution.)

^1H *N.M.R. Spectra.*—Both NaH_2PO_2 and KH_2PO_2 solutions in several carboxylic acids have been investigated. The chemical shift of the hydroxy-proton of the acid medium, δ(OH), and the coupling constant, $J_{HP}(H_2PO_2^-)$, show changes that can be related to the hydrogen bonding. Changes of δ(OH) with molality are shown in the Figure.* For all systems there is a linear relationship, and this enables an extrapolation to a 1 : 1 $MH_2PO_2 : RCO_2H$ ratio. With the assumption that a 'solution' of this composition would have structure (2) the values of δ(OH) may be considered as representative of the chemical shift of the hydrogen-bonding proton, δ(OHO), and these are listed in Table 3. To a first approximation the data seem to be independent of cation.

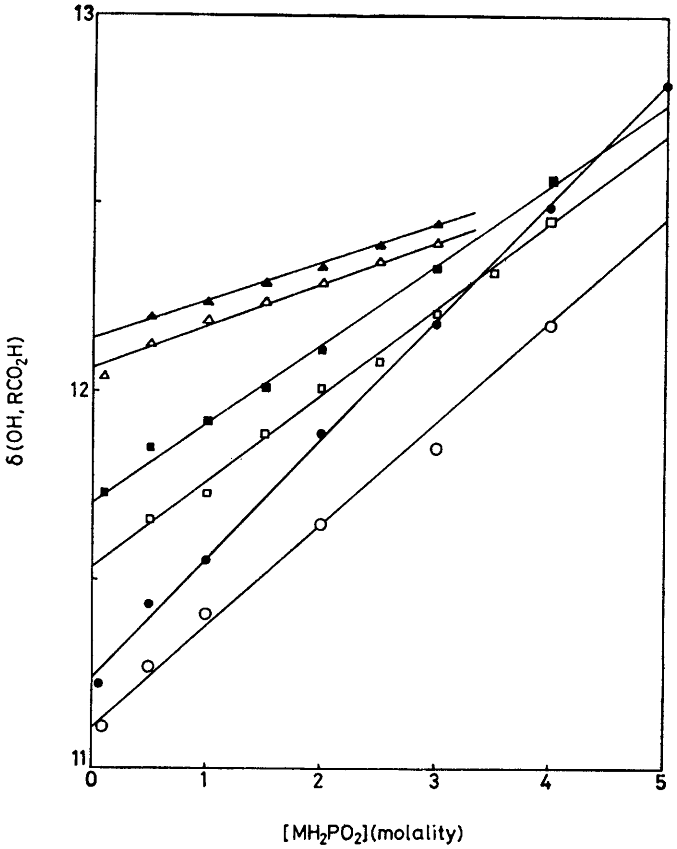
In a previous publication[5] we have shown that the extrapolation method gave values for δ(OHF) and δ(OHO) in good agreement with those obtained by a different method. The exception is HCO_2H, where an inert, *i.e.* non-hydrogen bonding, solute cannot be found to permit a correction factor to be applied to the observed shift so as to allow for the shift of δ(OH, RCO_2H) which occurs on dilution.[6]

TABLE 3

N.m.r. spectral data

		^1H N.m.r.			^{31}P N.m.r.	
Solute	Solvent	$\delta(OHO)_{1:1}$ [a]	$^1J_{HP}$ [b]	$\delta^0(H_2PO_2)$ [c]	$^1J_{HP}$ [d]	$\delta^{0.5}(H_2PO_2)$ [d]
NaH_2PO_2	H_2O		526		518	7.24
KH_2PO_2			529			
NaH_2PO_2	HCO_2H	16.5	570	7.36	564	11.33
KH_2PO_2		17.5	571	7.31		
NaH_2PO_2	CH_3CO_2H	14.8	535	7.12	537	6.60
KH_2PO_2		14.9	544	7.40		
NaH_2PO_2	$CH_3CH_2CO_2H$	13.6	534	7.16	531	5.91
KH_2PO_2		13.3	535	7.23		
NaH_2PO_2	$CH_3(CH_2)_2CO_2H$	13.1	533	7.15	529	5.50
KH_2PO_2		13.1	534	7.20		
NaH_2PO_2	CF_3CO_2H		600 ± 10		630 ± 50	8 ± 2 [e]

[a] Corrected for dilution effects, see text. [b] ±5 Hz; corrected to infinite dilution. [c] Corrected to infinite dilution. [d] Based on 0.5 molal concentrations. [e] Very broad bands, $\Delta\nu_{\frac{1}{2}}$ *ca.* 250 Hz.



δ(OH, RCO_2*H*) *vs.* $[MH_2PO_2]$: (○) NaH_2PO_2–HCO_2H; (●) KH_2PO_2–HCO_2H; (□) NaH_2PO_2–CH_3CO_2H; (■) KH_2PO_2–CH_3CO_2H; (△) NaH_2PO_2–$CH_3CH_2CO_2H$; (▲) KH_2PO_2–$CH_3CH_2CO_2H$

The results are shifts that are generally less than those observed for bicarboxylate hydrogen-bonding protons, *e.g.* $[MeCO_2–H–O_2CMe]^-$ where δ(OHO) is 15.7 p.p.m.[5] and $[CF_3CO_2–H–O_2CCF_3]^-$ where it is 18.8 p.p.m.[7] The lower shifts of Table 3 suggest asymmetric, and possibly weaker, hydrogen bonding systems between $H_2PO_2^-$ and RCO_2H, depicted as either $[H_2PO_2 \cdots HO_2CR]^-$ or $[H_2PO_2–H \cdots O_2CR]^-$. The results in Table 3 for δ(OHO) indicate a difference between HCO_2H and the other acid homologues.

Formic acid, being a stronger acid, might transfer its proton to the hypophosphite ion $[H_2PO_2–H \cdots O_2CH]^-$ whereas the others prefer the alternative asymmetric hydrogen bond arrangement. The values of δ(P*H*) and

* Except for the systems NaH_2PO_2–$CH_3CH_2CH_2CO_2H$ and KH_2PO_2–$CH_3CH_2CH_2CO_2H$, whose points and plot overly those of the corresponding propionic acid systems.

$\delta(PH)$ do not serve to distinguish these two hydrogen bonding types, but we believe that $J_{HP}(H_2PO_2^-)$ can be used to discriminate them.

Hydrogen-1 and ^{31}P n.m.r. data were collected for NaH_2PO_2 solutions in glacial acetic acid over the concentration range 0.5—5 molal. Nearly linear relationships of $\delta(PH)$, $\delta(PH)$, and J_{HP} with concentration were found and these can be described by the equations (1)—(3), where m is the molality.

$$\delta(PH) = 11.55 + 0.22m \qquad (1)$$

$$\delta(PH) = 6.65 - 0.24m \qquad (2)$$

$$J_{HP} = 537.2 - 2.45m \qquad (3)$$

The chemical environment having most influence on $J_{PH}(H_2PO_2^-)$ appears to be the extent of protonation of the hypophosphite oxygens. At one extreme there is the protonated acid cation $H_2PO_2H_2^+$ which is responsible for the coupling constant of 671 Hz observed for H_3PO_2 in H_2SO_4 as the solvent.[8] At the other extreme there is the anion $H_2PO_2^-$ in an inert medium. The value of 518 Hz for $J_{HP}(H_2PO_2^-)$ in water[9] is hardly likely to represent the coupling constant of the isolated $H_2PO_2^-$, but it can be taken as representative of the hypophosphite ion in a hydrogen-accepting role, water acting as the donor, of the type $[H_2PO_2 \cdots HOH]^-$. The acid itself, H_2PO_2H, has a value of 573 Hz for J_{HP}.[10] Using these values as guidelines to the proton's proximity to $H_2PO_2^-$ it can be seen from Table 3 that NaH_2PO_2 in CF_3CO_2H gives us J_{HP} 600 Hz, indicating protonation to $H_2PO_2H_2^+$ to a significant extent in this strongest of carboxylic acids; pK_a (H_2O ref.) $H_2PO_2H = 1.1$, $CF_3CO_2H = 0.25$, $H_2SO_4 = -3$.[11]

In HCO_2H, the strongest of the unsubstituted aliphatic acids, J_{HP} is *ca.* 570 Hz, almost the same as H_2PO_2H itself. This suggests that in HCO_2H as the solvent H_2PO_2H is a weaker acid than in water and $H_2PO_2^-$ becomes protonated; the hydrogen bonding complex can be seen as $[H_2PO_2\text{-}H \cdots O_2CH]^-$. The other carboxylic acid homologues, being weaker acids, do not protonate the anion and behave more like water, *i.e.* $[H_2PO_2 \cdots H\text{-}O_2CR]^-$.

Spectroscopic examinations of hydrogen-bonding systems rarely depend on observing long-range effects. Notable exceptions have been the ^{13}C spin-relaxation studies on long-chain alcohols,[12] the ^{35}Cl n.q.r. studies on chlorocarboxylic acids,[13] and ^{19}F n.m.r. studies of *p*-fluorophenol hydrogen-bonded complexes.[14] If the coupling constant $J_{PH}{}^{0.5}(H_2PO_2^-)$ (at 0.5 molal concentration) is to be included in this category then clearly it will be necessary to refine the method by observing it under as wide a range of environments as possible. Nevertheless the information it supplies is not inconsistent with the interpretation offered here.

The I.r. Spectra.—These show that the hydrogen bonding may best be described as strong but not very strong, on the basis of $\Delta\nu_s(OH)$.[15] The i.r. spectra have been observed on NaH_2PO_2 solutions, $NaH_2PO_2 \cdot 2CH_3CO_2H$, and a solid corresponding to the monosolvate $NaH_2PO_2 \cdot CH_3CO_2H$.

The disolvate has four broad bands in the region above 1 800 cm^{-1}, at *ca.* 1 900, 2 550, 2 900, and 3 400 cm^{-1}. The three highest bands are visible as shoulders on the main peak of the very broad band ν_s (OH; CH_3CO_2H liquid), and although the shoulders become more prominent in $NaH_2PO_2 \cdot 2CH_3CO_2H$ they would still seem to be related to acetic acid hydrogen-bonding to itself. The band at 1 900 cm^{-1} is consequently chosen as $\nu_s(OH)$ of the hydrogen bond between the hypophosphite anion and the acetic acid. The shift $\Delta\nu_s(OH)$ is therefore *ca.* 1 600 cm^{-1}, which is 2.5 times that of acetic acid dimer (hydrogen-bond energy 30 kJ mol^{-1}) and represents a hydrogen bond that is of medium strength and supporting the formula $[H_2PO_2 \cdots H\text{-}O_2CCH_3]^-$ rather than (2).

The spectrum of the monosolvate $NaH_2PO_2 \cdot CH_3CO_2H$ shows a complete lack of resolution in the region above 2 000 cm^{-1}. This material could not be grown as a definite phase and was produced from the disolvate by prolonged pumping, a method that is obviously not reliable. Pumping eventually removes all the acid, something that cannot be achieved with the very strong hydrogen-bonded systems $KF \cdot CH_3CO_2H$ and $CH_3CO_2K \cdot CH_3CO_2H$.

The out-of-plane bending mode, $\gamma(OH)$, was not obscured by other bands, unlike the in-plane mode $\delta(OH)$. It was observed to move to higher frequencies as the concentration of NaH_2PO_2 in CH_3CO_2H increased, going from 930 cm^{-1} in the pure solvent to 1 000 cm^{-1} in the disolvate. This again is a feature of increasing hydrogen-bond strength. In carboxylic acids this mode increases from *ca.* 650 cm^{-1} in the monomer to 950 cm^{-1} in acid dimers to *ca.* 1 300 cm^{-1} in bicarboxylates.[16]

The PH_2 vibrational modes appear unaffected by solution in CH_3CO_2H. Although they are almost submerged by the broad hydrogen-bonding bands, in some instances they appear as clearly recognizable peaks at 2 280—2 450, ν_s and ($\nu_{as}PH_2$); 1 140, $\delta(PH_2)$; 1 090, $\rho_w(PH_2)$; and 820 cm^{-1} ($\rho_r PH_2$).[17] Slight changes of <10 cm^{-1} occur when NaH_2PO_2 is dissolved in CH_3CO_2H, but one noteable change is that $\rho_r(PH_2)$ is resolved into a doublet.

The PO_2 vibrational modes, on the other hand, might have been expected to show changes due to hydrogen bonding. These bands, however, do not shift but become broader. They are still centred at 1 190, $\nu_{as}(PO_2)$; 1 050, $\nu_s(PO_2)$; and 480 cm^{-1}, $\delta(PO_2)$.[17] The bending mode is resolved into a well defined doublet, a change in symmetry occasioned by the hydrogen-bonding differences between the two oxygen atoms.

Summary.—Although NaH_2PO_2 and KH_2PO_2 are unexpectedly very soluble in carboxylic acids, there are no grounds for attributing this to an unusually strong hydrogen bonded anion pair of type (2). Although very strong hydrogen bonds are formed between two carboxylate groups, and two phosphate groups in some instances,[18] the mixed acid system carboxylate–hypophosphite does not participate in a single minimum potential-well type of hydrogen bond. The same state of affairs was found with the mixed acetate–trifluoroacetate anion whose hydrogen bond was of the normal, weak kind, whereas the hydrogen bonds of the biacetates and bistrifluoroacetates were both very strong.[5] Evidence presented in this paper suggests that the mixed carboxylate–hypophosphite hydrogen-bond potential-well has double minima, although the lower energy may be nearer either oxygen depending upon the acidities.

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