

**IR-Spectroscopic Investigations
on Solute—Solvent Interactions
Part 2: Solvation of Triethylphosphine Oxide
in Hydroxylic Solvents**

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An IR-spectroscopic study has been carried out on the solvation state of the model compound Et_3PO in the solvents methanol, ethanol, propanol, 2-propanol, butanol, 1,2-ethanediol, 1,3-propanediol, water, acetic acid, and formamide. With the exception of formamide (where only one solvate species was detected) the spectra show the presence of two basic types of solvate complexes, which derive from hydrogen bonded complexes with *primary* coordination numbers of one and two, respectively. In water there is evidence that higher coordinated solvates (with *primary* solvation numbers of two and three) are formed. Detailed informations about the structure of these complexes were obtained by spectrophotometric titrations, which show that extensive outer-sphere interactions are taking place in the neat solvents. For solvents, where only one kind of solvate species is present, an excellent correlation was found between solvent acceptor numbers and the wavenumbers $\nu(PO)$ of the P=O stretching vibration of Et_3PO . By contrast, acceptor numbers of protic solvents usually represent average values, which are determined by the relative concentrations and ^{31}P -chemical shifts of the individual solvates present in solution. By means of the wavenumbers $\nu(PO)$ of these solvates and the linear correlation mentioned above, it has become possible to calculate refined acceptor number values termed "Individual Acceptor Numbers", which characterize the acceptor properties of protic solvents as a function of the solvation numbers of the substrates under consideration. It is shown, that the use of these individual acceptor numbers in linear energy relationships allows a significantly improved unified description of solvent effects on chemical reactions and physical processes in aprotic and protic solvents.

(Keywords: IR-Spectroscopy; Solvent effects; Solvation mechanisms; Acceptor number; Triethylphosphine oxide)

Infrarotspektroskopische Untersuchungen über Substrat-Lösungsmittel-Wechselwirkungen. Teil 2: Solvatation von Triethylphosphinoxid in hydroxyliischen Lösungsmitteln

Es wurden IR-spektroskopische Untersuchungen über den Solvationszustand der Modellverbindung Et_3PO in den Lösungsmitteln Methanol, Ethanol, Propanol, 2-Propanol, Butanol, 1,2-Ethandiol, 1,3-Propandiol, Wasser, Essigsäure und Formamid durchgeführt. Mit Ausnahme von Formamid (wo nur eine Solvatform festgestellt werden konnte) zeigen die Spektren die Präsenz von zwei Grundtypen von Solvatkomplexen an, die Wasserstoffbrückenkomplexen mit den *primären* Koordinationszahlen eins und zwei zugeordnet werden können. Bei Wasser gibt es Hinweise für die Existenz von Solvatkomplexen mit den *primären* Solvationszahlen zwei und drei. Detaillierte Informationen über die Struktur der verschiedenen Solvatkomplexe konnten mit Hilfe spektrophotometrischer Titrationen erhalten werden, die beweisen, daß in den reinen Lösungsmitteln starke Outer-Sphere-Wechselwirkungen wirksam sind. Für Lösungsmittel, in denen nur *eine* Solvatform vorliegt, konnte eine ausgezeichnete lineare Beziehung zwischen den Wellenzahlen $\nu(PO)$ der $P=O$ -Valenzschwingung von Et_3PO und den Akzeptorzahlen der Lösungsmittel nachgewiesen werden. Dagegen stellen die Akzeptoren hydroxyliischer Lösungsmittel üblicherweise Mittelwerte dar, die durch die relativen Konzentrationen der einzelnen Solvatspezies und deren charakteristischen ^{31}P -chemischen Verschiebungen bestimmt sind. Aus den charakteristischen Wellenzahlen $\nu(PO)$ der einzelnen Solvate können mit Hilfe der oben erwähnten linearen Korrelation „verbesserte“ Akzeptorzahlparameter errechnet werden, für die wir die Bezeichnung „Individuelle Akzeptorzahlen“ vorschlagen und die die Akzeptoreigenschaften protischer Lösungsmittel als Funktion der Solvationszahlen der betrachteten Substrate beschreiben. Es wird gezeigt, daß die Verwendung dieser individuellen Akzeptorzahlen in linearen Energiebeziehungen eine wesentlich verbesserte einheitliche Beschreibung von Lösungsmittelleffekten auf chemische Reaktionen und physikalische Prozesse in aprotischen *und* protischen Lösungsmitteln ermöglicht.

Introduction

In Part 1 of this series we have reported on IR-spectroscopic investigations on solutions of the model compound Et_3PO in aprotic and CH-acidic solvents [1]. In these solvents the $P=O$ stretching vibration at sufficiently low concentrations occurs as a single, symmetrical band, which suggests that only one kind of solvates is present in solution. This is further supported by the fact that an excellent linear relationship was found between the wavenumbers $\nu^\circ(PO)$ of the $P=O$ stretching vibration and the acceptor numbers AN of the solvents previously determined from ^{31}P -chemical shift measurements [1]. Solvent AN have been widely used in linear energy relationships for the interpretation of solvent effects on chemical reactions and physical processes. Whereas good results are usually obtained for aprotic solvents, the situation is less satisfactory with protic solvents, where differences between calculated and experimental values are frequently observed, suggesting that this phenomenon might be due to the coexistence of different solvate complexes in solution [2, 3].

Since these species are usually subject to fast chemical exchange processes, they cannot be detected by NMR-spectroscopic measurements, which means that acceptor numbers for protic solvents might be average values, which depend on the relative concentrations and ^{31}P -chemical shifts of the various solvates present in solution. As has been shown in the preceding paper [1], such species, however, can be easily identified IR-spectroscopically by means of the $\text{P}=\text{O}$ stretching vibration of Et_3PO , which responds very sensitively to changes in the solvent environment and therefore represents an ideal probe for the elucidation of solvation mechanisms.

The present paper is concerned with IR-spectroscopic investigations on the solvation state of the model compound Et_3PO in various hydroxylic solvents, formamide and several binary solvent mixtures.

Results

Table 1 lists the wavenumbers $\nu(\text{PO})$ for various concentrations of Et_3PO in formamide and several hydroxylic solvents (S). Wavenumbers $\nu^\circ(\text{PO})$ obtained by extrapolation of $\nu(\text{PO})$ -values to zero concentration are compiled in Table 2 together with the corresponding wavenumber differences $\Delta \nu^\circ(\text{PO}) = \nu^\circ(\text{PO}) (n\text{-hexane}) - \nu^\circ(\text{PO}) (\text{S})$; the value $\nu^\circ(\text{PO}) (n\text{-hexane}) = 1192.1 \text{ cm}^{-1}$ has been determined previously [1]. Figures 1–8 show the IR-spectra of Et_3PO in the $\text{P}=\text{O}$ stretching region at different concentrations in the solvents methanol, ethanol, propanol, 2-propanol, butanol, 1,2-ethanediol, 1,3-propanediol, acetic acid, and water. Results of spectrophotometric titrations of Et_3PO with methanol, ethanol, and acetic acid in the solvents cyclohexane, *n*-hexane, and CCl_4 , respectively, are shown in Figs. 9–12.

Experimental conditions were the same as those described in Part I of this series [1].

Table 1. Wavenumbers $\nu(\text{PO})$ (cm^{-1}) of Et_3PO at different concentrations in various hydrogen bonding solvents

Solvent	c (mol/l)	$\nu(\text{PO})$ (cm^{-1})	$\nu(\text{PO})$ (cm^{-1})
2-propanol	1.50	~ 1157	~ 1136
2-propanol- d_8	1.50	na	1136.2
	0.90	na	1135.0
	0.54	na	1134.3
	0.22	na	1134.2
	0.086	na	1134.2

Table 1 (continued)

Solvent	c (mol/l)	$\nu(\text{PO})$ (cm^{-1})	$\nu(\text{PO})$ (cm^{-1})
Formamide	0.701	—	1 133.2
	0.221	—	1 132.5
	0.070	—	1 132.2
Ethanol	1.505	1 157.5	1 130.1
	0.999	1 157.5	1 129.2
	0.504	1 157.0	1 128.7
	0.159	1 158	1 127.6
	0.050	1 158	1 127.0
<i>n</i> -propanol	1.502	1 157.7	1 130.5
	1.004	1 158.2	1 128.7
	0.500	1 158.2	1 127.7
	0.160	1 158	1 126.5
	0.050	1 158	1 126.5
<i>n</i> -butanol	1.502	1 157.8	1 131.5
	1.000	1 157.9	1 129.4
	0.502	1 158.1	1 127.8
	0.159	1 158	1 126.9
	0.050	1 158	1 126.0
Methanol	1.498		1 127.8
	0.999		1 127.2
	0.499	~ 1 154 (sh)	1 126.8
	0.158		1 126.6
	0.050		1 125.5
1,3-propanediol	0.499		1 120.8
	0.158	~ 1 150 (sh)	1 120.3
	0.050		1 119.5
1,2-ethanediol	1.503		1 120.3
	0.500	~ 1 150 (sh)	1 119.4
	0.158		1 118.7
	0.051		1 117.5
Water	1.500		1 104.5
	0.999		1 103.3
	0.502	~ 1 125 (sh)	1 102.5
	0.159		1 101.9
	0.051		1 101.5
Acetic acid	1.497		1 097.3
	1.004		1 096.8
	0.503	~ 1 130 (sh)	1 096.2
	0.158		1 095.7
	0.050		1 095.5

na not accessible because of interference with solvent bands

sh shoulder, approximate value

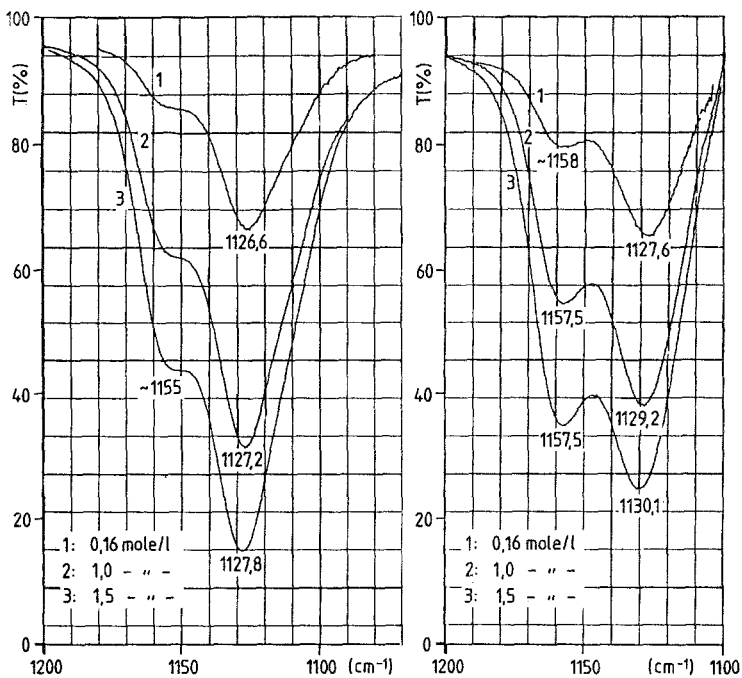


Fig. 1. P=O stretching bands of Et_3PO in $MeOH$

Fig. 2. P=O stretching bands of Et_3PO in $EtOH$

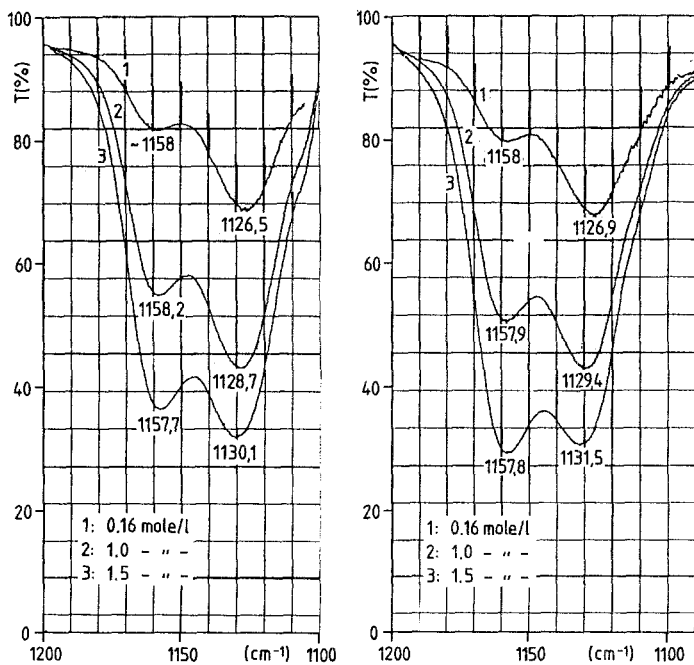


Fig. 3. P=O stretching bands of Et_3PO in $n-PrOH$

Fig. 4. P=O stretching bands of Et_3PO in $n-BuOH$

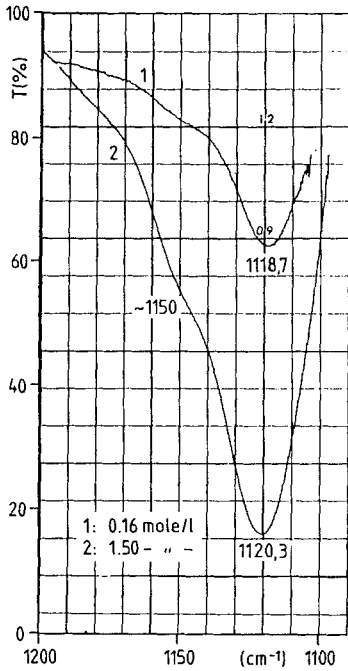


Fig. 5. P=O stretching bands of Et_3PO in 1,2-ethanediol

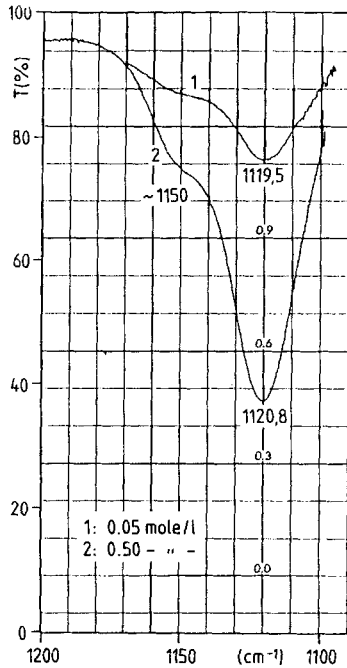


Fig. 6. P=O stretching bands of Et_3PO in 1,3-propanediol

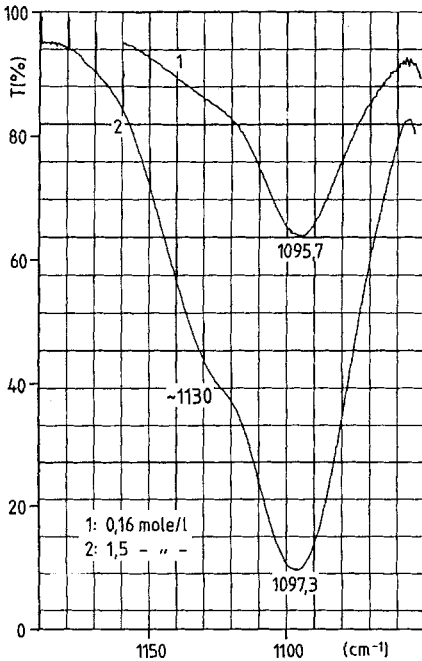


Fig. 7. P=O stretching bands of Et_3PO in acetic acid

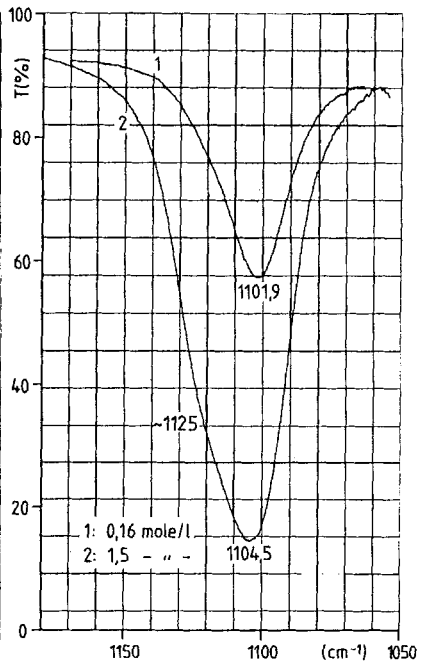


Fig. 8. P=O stretching bands of Et_3PO in water

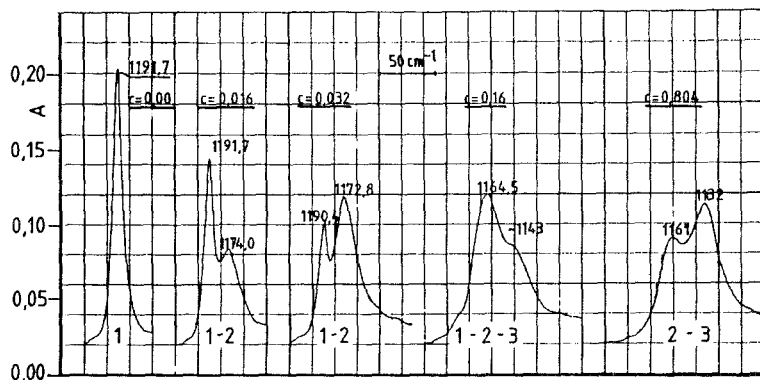


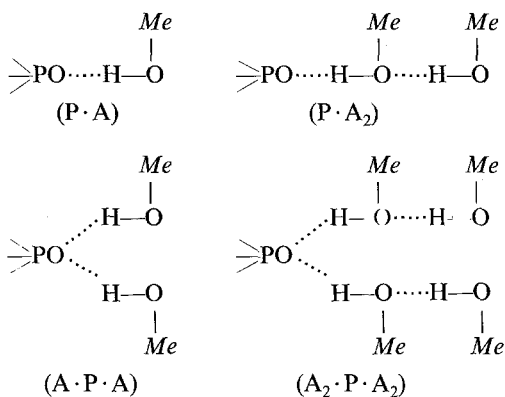
Fig. 9. Changes in the P=O stretching region on titration of Et_3PO ($c = 0.02$ mol/l) with $MeOH$ in cyclohexane; c = concentration of $MeOH$ added

Discussion

Spectra of Et_3PO in pure hydroxylic solvents (Figs. 1–8) generally show two distinct bands or shoulders, respectively, in the P=O stretching region, which indicate the presence of at least two different solvate species. This is in contrast to the situation in aprotic and CH-acidic solvents, where only one kind of species was observed at sufficiently low concentrations [1]. On dilution the proportion of the low wavenumber species generally increases as compared to the high wavenumber species, indicating that the former represents a higher solvated form of Et_3PO : In order to clarify the nature of the complexes present in the pure solvents, solutions of Et_3PO in “inert” or weakly coordinating solvents like hexane or CCl_4 were titrated with increasing amounts of the acceptor component. Figure 9 shows the results for the titration of Et_3PO with $MeOH$ in cyclohexane: addition of somewhat less ($c = 0.016$ mol/l) than the stoichiometric amount of $MeOH$ produces a new band (band 2) located around 1174 cm^{-1} with a simultaneous decrease in intensity of the band of the “free” Et_3PO -molecule (band 1) observed at 1192 cm^{-1} . Further addition of $MeOH$ leads to changes in relative intensities of band 1 and band 2 and at $c = 0.16$ mol/l to the appearance of a third band (band 3) as a shoulder around 1143 cm^{-1} , which develops into a well pronounced peak at $c = 0.8$ mol/l, the solubility limit of $MeOH$ in cyclohexane. From the observed changes in intensities and peak separations, it can be safely concluded that bands 2 and 3 belong to Et_3PO — $MeOH$ complexes with *primary* solvation numbers of 1 and 2, respectively*. As can be seen from

* The term *primary* solvation (or primary coordination) number specifies the number of acceptor molecules (here $MeOH$) *directly* bonded to the oxygen atom of the Et_3PO -molecule via hydrogen bonds.

Fig. 9, both bands are progressively shifted to lower wavenumbers with increasing concentration of *MeOH*. Since medium effects are not to be expected at such low *MeOH* concentrations, these shifts must be caused by the formation of various types of outer-sphere complexes as depicted in the following scheme**.



Experimentally, only a small part of these complexes can be *directly* observed. Actually, this is not too surprising in view of the fact, that the relative concentrations of the various species, which are to be expected theoretically, will certainly differ considerably for coordination chemical and thermodynamic reasons. Furthermore, peak separations are expected to decrease rapidly with increasing total solvation numbers, which means that peaks are no longer resolved particularly in view of the comparatively large half-widths of the bands. Fortunately, we have been able to obtain more detailed informations about the mechanism of outer-sphere-complex formation by analogous investigations on the model compound Me_3PO , where the spectra are much better resolved [4]. From the results of this study and the bathochromic band shifts observed in Fig. 9 the following conclusions can be drawn: the peak around 1174 cm^{-1} is undoubtedly due to the $\text{Et}_3\text{PO} \cdot \text{MeOH}$ ($\text{P} \cdot \text{A}$) complex, the peak at 1164.5 and the shoulder at 1143 cm^{-1} can be assigned to the species

** Symbol "P" denotes a phosphine oxide molecule (here Et_3PO) and "A" an acceptor molecule (here MeOH). The position of A (left and right from P) allows to distinguish between complexes with *primary* solvation numbers of 1 and 2. Thus, $\text{A} \cdot \text{P} \cdot \text{A}$ symbolizes a complex, where both MeOH molecules are directly coordinated to the oxygen atom of P, whereas $\text{P} \cdot \text{A}_2$ denotes a complex, where the second MeOH molecule is outer-sphere coordinated to the oxygen atom of the first one and so forth.

$Et_3PO \cdot MeOH \cdot MeOH$ ($P \cdot A_2$) and $A \cdot P \cdot A_2$, respectively. The 1:2 primary complex, $A \cdot P \cdot A$, appears to be present only in relatively low concentrations and therefore cannot be directly observed. The peaks at 1161 and 1132 cm^{-1} probably result from the species ($P \cdot A_2 + P \cdot A_3$) (or perhaps $P \cdot A_2 + P \cdot A_4$) and $A_2 \cdot P \cdot A_2$, respectively. Note that the positions of these two peaks differ from those observed in pure methanol by only 5–7 cm^{-1} . A detailed IR-spectroscopic and thermodynamic analysis of this and related systems will be given elsewhere [4].

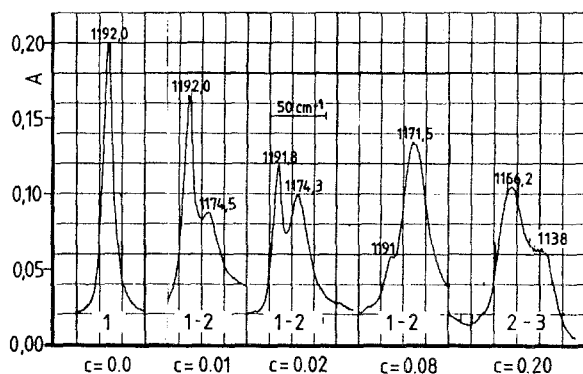


Fig. 10. Changes in the P=O stretching region on titration of Et_3PO ($c = 0.02$ mol/l) with $EtOH$ in n -hexane; c = concentration of $EtOH$ added

Similar results were obtained in the titration of Et_3PO with $EtOH$ in n -hexane (Fig. 10): the peaks or shoulders, respectively, at 1174.5, 1171.5, 1166.2 and 1138 cm^{-1} can be attributed to the species or mixtures $P \cdot A$, ($P \cdot A + P \cdot A_2$), $P \cdot A_2$ and $A_2 \cdot P \cdot A_2$, respectively.

In order to test the influence of the "inert" solvent used, the interaction of Et_3PO with $EtOH$ was also studied in CCl_4 (Fig. 11). The absorption spectra show the same pattern of peaks as observed in n -hexane. The peaks at 1164 and 1155 cm^{-1} can be assigned to the species $P \cdot A$ and $P \cdot A_2$, respectively, the maximum at 1131.5 cm^{-1} to the complex $A_2 \cdot P \cdot A_2$, the peaks at 1159.1 and 1136.5 cm^{-1} correspond to mixtures of ($P \cdot A + P \cdot A_2$) and ($A \cdot P \cdot A_2 + A_2 \cdot P \cdot A_2$), respectively. Owing to the stronger solvating power of CCl_4 , complex formation under comparable conditions is less complete than in n -hexane and peak positions of corresponding complexes are shifted to lower wavenumbers (about 10 cm^{-1} for $P \cdot A$ and $P \cdot A_2$ and about 6 cm^{-1} for $A \cdot P \cdot A_2$ and $A_2 \cdot P \cdot A_2$).

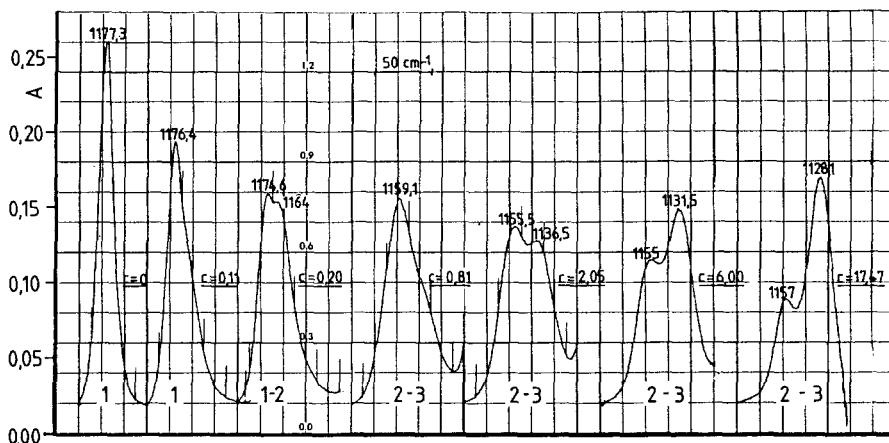


Fig. 11. Changes in the P=O stretching region on titration of Et_3PO ($c = 0.2 \text{ mol/l}$) with $EtOH$ in CCl_4 ; c = concentration of $EtOH$ -added

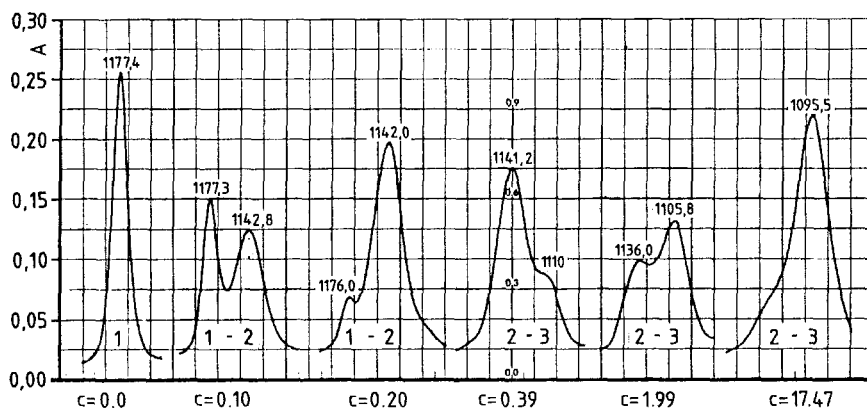


Fig. 12. Changes in the P=O stretching region on titration of Et_3PO ($c = 0.2 \text{ mol/l}$) with acetic acid in CCl_4 ; c = concentration of acetic acid added

Fig. 12 shows the titration of Et_3PO with CH_3COOH in CCl_4 . It is well known, that CH_3COOH in the liquid state and in non-coordinating solvents exists predominantly in the form of stable cyclic dimers. Consequently, some authors have suggested, that the interaction of bases B with CH_3COOH might lead directly to the formation of outer-sphere complexes of type $B \cdot A_2$. By contrast, Fig. 12 shows, that reaction of stoichiometric amounts of CH_3COOH and Et_3PO ($c = 0.2 \text{ mol/l}$) in CCl_4 leads almost quantitatively to a simple 1 : 1 complex ($P \cdot A$) with a peak at

1142 cm^{-1} . Further addition of CH_3COOH produces a shoulder around 1108 cm^{-1} which must be assigned to a simple 1:2 primary complex, $\text{A}\cdot\text{P}\cdot\text{A}$. This is in contrast to the situation with methanol (Fig. 9) where formation of the outer-sphere complex $\text{P}\cdot\text{A}_2$ is clearly favoured over formation of $\text{A}\cdot\text{P}\cdot\text{A}$. Formation of outer-sphere complexes is indicated only at higher acid concentrations ($c = 1.99 \text{ mol/l}$) by bathochromic shifts of peak positions: the peaks at 1136 and 1105.8 cm^{-1} are most probably due to mixtures of $(\text{P}\cdot\text{A} + \text{P}\cdot\text{A}_2)$ and $(\text{A}\cdot\text{P}\cdot\text{A} + \text{A}\cdot\text{P}\cdot\text{A}_2)$ with species $\text{P}\cdot\text{A}$ and $\text{A}\cdot\text{P}\cdot\text{A}$ dominating, respectively.

From the results of the titration experiments it is possible to draw realistic conclusions about the solvation state of the model compound Et_3PO in pure hydroxylic solvents: in *MeOH*, *EtOH*, *n-PrOH*, and *n-BuOH*, triethylphosphine oxide appears to exist predominantly in the form of two basic types of solvates of structure $\text{P}\cdot\text{A}_n$ and $\text{A}_m\cdot\text{P}\cdot\text{A}_n$ with $n \geq 4$ and $m \leq n$. The very similar positions of corresponding $\text{P}=\text{O}$ bands in dilute solutions of these solvents suggest that differences in hydrogen bonding properties displayed by the bulk solvents stem from differences in the *distribution* of these two types of species rather than differences in intrinsic acidities of the isolated molecules. In fact, at a given concentration, the ratio of the species $\text{A}_m\cdot\text{P}\cdot\text{A}_n/\text{P}\cdot\text{A}_n$ increases in the sequence *n-BuOH* \rightarrow *MeOH*.

Spectra in 1,2-ethanediol and 1,3-propanediol (Figs. 5 and 6) are very similar in type to those of the monofunctional alcohols, except that the two bands occur at somewhat lower wavenumbers indicative of somewhat stronger acceptor properties. The spectra do not provide any definite indication for the formation of chelate complexes but work is now in progress to clarify this question.

Outer-sphere complexes are also formed in acetic acid. According to the present results and recent analogous investigations on Me_3PO [4], the degree of outer-sphere complexation is definitely smaller than in the lower alcohols or water (see below). The peaks at ~ 1130 and 1096 cm^{-1} appear to result primarily from the species $\text{P}\cdot\text{A}_2$ and $\text{A}\cdot\text{P}\cdot\text{A}_2$, respectively, but this assignment should be considered as tentative at present.

The situation in water is much more complex than in the alcohols or in acetic acid. In concentrated solutions again a second band can be observed as a shoulder around 1125 cm^{-1} in addition to the major peak at 1103 cm^{-1} . A comparison of the acceptor numbers of water ($\text{AN} = 54.8$) and acetic acid ($\text{AN} = 52.9$) and the peak positions of the two solvate species (Figs. 7 and 8) reveals that the two solvents show very similar *bulk* acidities towards Et_3PO . This is rather surprising at first sight, since monomeric acetic acid is expected to be a much stronger acceptor than

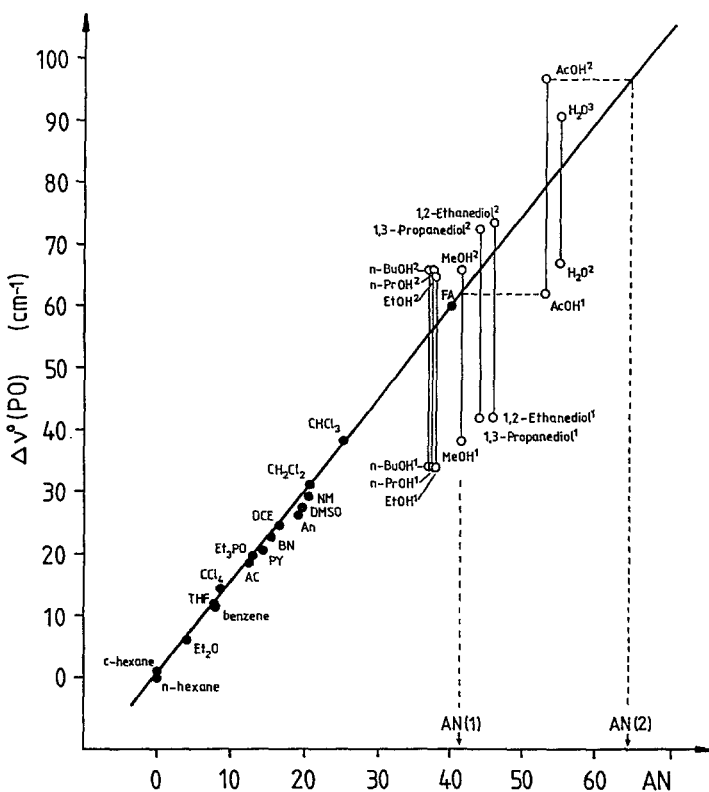


Fig. 13. Wavenumber differences $\Delta\nu^\circ(\text{PO}) = \nu^\circ(\text{PO})(n\text{-hexane}) - \nu^\circ(\text{PO})(\text{S})$ as a function of solvent acceptor numbers AN

monomeric water. This is indeed confirmed by the results of the titration experiments which provide peak separations $\Delta\nu(\text{P} \rightarrow \text{P} \cdot \text{A})$ in cyclohexane or hexane of $\sim 18 \text{ cm}^{-1}$ for $\text{A} = \text{MeOH}$ and EtOH (Figs. 9 and 10) and 42 cm^{-1} for $\text{A} = \text{CH}_3\text{COOH}$ [4]*. From these results follows that the unexpectedly high bulk acidity of water as compared to liquid acetic acid must be ascribed a) to a higher degree of outersphere complexation and b) to the possible formation of solvates with higher primary solvation numbers (probably “dihydrates” and “trihydrates”).

Fig. 13 shows the relationship between solvent acceptor numbers and the wavenumber differences $\Delta\nu^\circ(\text{PO}) = \nu^\circ(\text{PO})(n\text{-hexane}) - \nu^\circ(\text{PO})(\text{S})$

* As has been pointed out in Part 1 [1], these peak-separations may serve as an approximate measure of the intrinsic acidities (acceptor strengths) of the monomeric acceptor molecules.

for the P=O stretching vibration of Et_3PO for aprotic *and* protic solvents (values $\nu^\circ(PO)$ for aprotic solvents are from [1]). The straight line shown corresponds to that given in Part 1 [1], except that the solvent formamide has also been included. Formamide is a strongly polar and strongly hydrogen bonding solvent. Contrary to the alcohols, however, only one P=O stretching band is observed in the spectrum, which according to recent measurements results from an outer-sphere complex with a primary solvation number of two [4]. The existence of this excellent linear relationship, which is described by Eq. (1), shows that both parameters are free from unspecific contributions such as magnetic anisotropy or vibrational coupling effects and may therefore be alternatively used as empirical solvent parameters in all cases where only one kind of solvate is present in solution.

$$\Delta\nu^\circ(PO) = \nu^\circ(PO)(n\text{-hexane}) - \nu^\circ(PO)(S) = -0.11 + 1.484 \cdot AN \quad (1)$$

$$r^2 = 0.997 \quad \overline{\delta\nu} = 0.68 \text{ cm}^{-1}$$

In those cases, where several solvates are present in solution, the acceptor numbers represent average values, which are determined by the concentrations c_1, c_2, c_3, \dots and the individual ^{31}P -chemical shifts $\delta_1, \delta_2, \delta_3, \dots$ of the various species present in solution according to Eq. (2).

$$AN = 2.348(c_1 \cdot \delta_1 + c_2 \cdot \delta_2 + c_3 \cdot \delta_3 + \dots)/(c_1 + c_2 + c_3 + \dots) \quad (2)$$

This equation may be used to define “refined” acceptor number parameters for which we propose the term “*Individual Acceptor Numbers*” and which characterize the acceptor properties of protic solvents as a function of solvation numbers and solvation shell structure. In view of the large variety of solvate species which may *theoretically* exist in solution, the attempt to characterize acceptor properties of protic solvents by such numbers may seem at first sight unrealistic. However, experience fortunately shows that the number of predominant species is usually small, which makes it worth while to attempt at least an approximate solution of this difficult problem. Assuming for the time being, that only two types of basic solvates are usually present in solution, Eq. (2) reduces to Eq. (3), where the quantities AN(1) and AN(2) can be easily calculated from the corresponding peak positions $\nu_1^\circ(PO)$ and $\nu_2^\circ(PO)$ by means of the linear relationship described by Eq. (1).

$$AN = [c_1 \cdot AN(1) + c_2 \cdot AN(2)]/(c_1 + c_2) \quad (3)$$

“Individual Acceptor Numbers” calculated in this way are listed in Table 2; the numbers in parentheses indicate the pertinent *primary*

Table 2. Wavenumbers $\nu^\circ(\text{PO})$ (cm^{-1}) of Et_3PO obtained by extrapolation of $\nu(\text{PO})$ -values (Table 1) to zero concentration, wavenumber differences $\Delta\nu^\circ(\text{PO}) = \nu^\circ(\text{PO})$ (*n*-hexane) $- \nu^\circ(\text{PO})$ (S) and corresponding "Individual Acceptor Numbers", $\text{AN}(i)$ calculated from Eq. (1). The numbers (i) in parentheses indicate the primary solvation numbers of the corresponding solvates

Solvent S	$\nu^\circ(\text{PO})$	$\Delta\nu^\circ(\text{PO})$	$\text{AN}(i)$	$\nu^\circ(\text{PO})$	$\Delta\nu^\circ(\text{PO})$	$\text{AN}(i)$
2-propanol	~ 1157	~ 35.1	~ 23.7 (1)	1133.8	58.3	39.4(2)
Formamide	—	—	—	1132.1	60.0	40.5(2)
Ethanol	1158	34.1	23.1 (1)	1127.2	64.9	43.8(2)
<i>n</i> -propanol	1158	34.1	23.1 (1)	1126.2	65.9	44.5(2)
<i>n</i> -butanol	1158	34.1	23.1 (1)	1126.0	66.1	44.6(2)
Methanol	~ 1154	~ 38.1	~ 25.8 (1)	1126.0	66.1	44.6(2)
1,3-propanediol	[1150]	[42.1]	[28.4] (1)	1119.6	72.5	48.9(2)
1,2-ethanediol	[1150]	[42.1]	[28.4] (1)	1118.1	74.0	49.9(2)
Water	[1125]	[67.1]	[45.3] (2)?	1101.5	90.6	61.1(3)?
Acetic acid	[1130]	[62.1]	[41.9] (1)	1095.5	96.6	65.2(2)

[] Approximate values obtained from band shoulders (see Table 1)

solvation numbers. If necessary, this simple approach can be easily refined by taking into account the presence of additional species. Attempts are now being made to analyse the band structures displayed in Figs. 1-8 by deconvolution procedures in order to perhaps detect and locate additional solvate species which might be present in solution but which are not directly observable because of low peak intensities or unfavourable overlapping of bands.

The fact that bases may form different solvate complexes in protic solvents appears to be of fundamental importance for a better understanding of the chemical reactivity of this group of solvents. Measurements, which we have recently carried out for a few other model compounds prove that this is a quite general phenomenon and not restricted to phosphine oxides. In particular, these findings have important consequences for the interpretation of solvent effects by means of empirical solvent parameters and linear energy relationships. We suppose that practically all empirical acidity parameters available today actually represent blends of "individual acidities", which are determined by the distribution of the various solvate complexes formed between the respective model compound and the solvent molecules. Among other factors, these distributions are expected to depend strongly on the basicity of the substrate: strongly basic substrates like phosphine oxides or sulfoxides will tend to form complexes with higher solvation numbers than weakly basic substrates, which means that AN(2) or AN(3) values will probably give better results in linear energy relationships than AN(1) values. An example is given in Fig. 14 which shows the relationship between the ESR-nitrogen coupling constants of the diphenyl nitroxide radical Ph_2NO and experimental acceptor numbers and calculated individual acceptor numbers, respectively. Use of the AN(1)-values for the alcohols and the AN(2)-value for water yields a very satisfactory linear relationship for *both* aprotic *and* protic solvents whereas large deviations are observed for the latter solvents, when the coupling constants are plotted versus either our original (experimental) acceptor numbers or AN(2) and AN(3) values for the alcohols and water, respectively. This result strongly suggests that Ph_2NO forms predominantly "monosolvates" in the alcohols and a "disolvate" in water. As a consequence, these solvents apparently behave as weaker acids towards Ph_2NO than towards Et_3PO , which forms solvates with higher primary solvation numbers (Table 2). The present example shows that the position of solvent points in diagrams of type Fig. 14 may provide valuable informations about solvation numbers of reactants and the distribution of their solvate complexes, which otherwise could not be obtained directly. In many cases, observed reactivities (e.g. rate constants) might actually turn out to be a

blend of "individual reactivities" originating from differently reactive solvates, which exist in equilibrium. Even then, the use of individual acceptor numbers (or equivalent parameters) should offer a chance to give a more correct interpretation of solvent effects. The above conclusions are not confined to the solvation of basic substrates in protic solvents but may

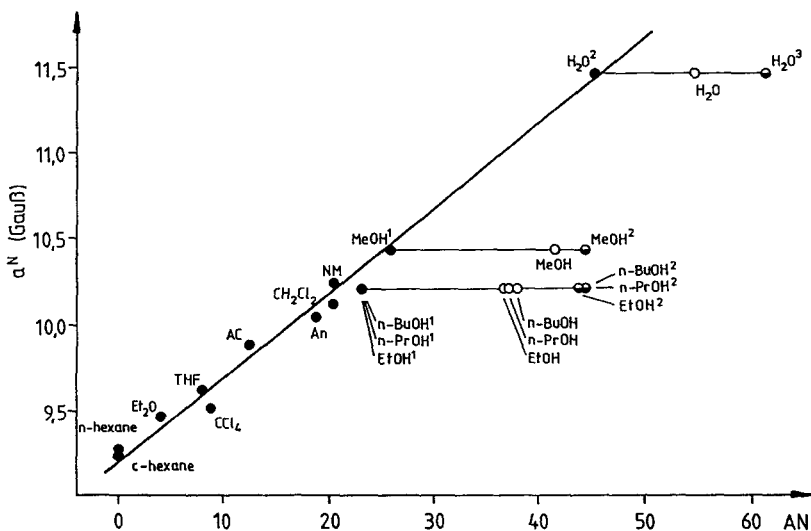


Fig. 14. Relationship between the ESR nitrogen coupling constants a^N of $(C_6H_5)_2NO$ and solvent acceptor numbers or "Individual Acceptor Numbers" AN (i), respectively

be equally well applied to the solvation of acidic substrates (e.g. cations) in basic solvents and solvent mixtures. Surprisingly, this fundamentally important problem appears to have been largely ignored so far by authors concerned with the development of empirical solvent parameters and the application of linear energy relationships.

Work is now in progress in our laboratory to extend these studies to other model compounds, solvents and solvent mixtures.

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