Monatshefte für Chemie 119, 1207—1221 (1988)

Monatshefte für Chemie
Chemical Monthly

IR-Spectroscopic Investigations on Solute—Solvent Interactions

Part 1: Solvation of Triethylphosphine Oxide in Aprotic and CH-Acidic Solvents

Ulrich Mayer*, **Helmuth Hoffmann**, and **Robert Kellner**

Department of Inorganic Chemistry, Technical University of Vienna,
A-1060 Vienna, Austria

(Received 3 December 1987. Accepted 25 January 1988)

A systematic study has been carried out on the solvent and concentration dependence of the P = O stretching vibration ν(PO) of the model compound *Et*$_3$PO in various aprotic and several CH-acidic solvents. Evidence has been found for the existence of dipole-dipole complexes in concentrated solutions of *Et*$_3$PO in solvents of low acceptor numbers. In dilute solutions, however, the P = O stretching band generally occurs as a single symmetrical peak which shows that only one kind of solvate species is present in solution. In CH-acidic solvents *Et*$_3$PO is present in the form of hydrogen bonded complexes. Informations about the structure of these complexes have been obtained by means of spectrophotometric titrations. It has been shown that the wavenumbers ν°(PO) obtained by extrapolation of ν(PO) values to zero concentration are linearly related to the acceptor numbers of the solvents, previously derived from ^{31}P-chemical shift measurements. The existence of this linear relationships proves that both parameters are linearly related to the strength of the intermolecular interactions and are virtually free from unspecific contributions such as magnetic anisotropy or vibrational coupling effects. The results of the present study show that the P = O stretching vibration of *Et*$_3$PO represents an ideal probe for the investigation of solvent effects and solvation mechanisms.

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

Infrarotspektroskopische Untersuchungen über Substrat-Lösungsmittel-Wechselwirkungen. Teil 1: Solvatation von Triethylphosphinoxid in aprotischen und CH-aciden Lösungsmitteln

Es wurde die Konzentrations- und Lösungsmittelabhängigkeit der P = O-Valenzschwingung ν(PO) der Modellverbindung *Et*$_3$PO in verschiedenen aprotischen und CH-aciden Lösungsmitteln systematisch untersucht. In hinreichend verdünnten Lösungen tritt die P = O-Valenzschwingung als einzelne symmetrische

Bande auf, was beweist, daß nur eine einzige Solvatform vorliegt. In Lösungsmitteln niedriger Akzeptorzahl konnte bei höheren Konzentrationen die Existenz von Dipol-Dipol-Komplexen nachgewiesen werden. In CH-aciden Lösungsmitteln liegt Et_3PO in Form von Wasserstoffbrückenkomplexen vor. Aussagen über die Struktur dieser Komplexe konnten mit Hilfe spektrophotometrischer Titrationen erhalten werden. Die durch Extrapolation auf Konzentration null erhaltenen Wellenzahlen ν°(PO) hängen linear von den aus den ^{31}P-chemischen Verschiebungen von Et_3PO bereits früher bestimmten Akzeptorzahlen der Lösungsmittel ab. Die Existenz dieser linearen Beziehung beweist, daß beide Parameter frei von störenden Einflußfaktoren (magnetische Anisotropie- und Schwingungskopplungseffekte) sind und tatsächlich linear mit der Stärke der intermolekularen Wechselwirkung variieren. Die Ergebnisse der vorliegenden Studie zeigen, daß die $P=O$-Valenzschwingung von Et_3PO eine hervorragende Sonde zur Untersuchung von Lösungsmitteleffekten und Solvatationsmechanismen darstellt.

Introduction

It is now generally accepted that solvent effects on chemical reactions or physical processes are described best by means of socalled "Linear Energy Relationships" (LERs), equation (1).

$$R(S) = R_0 + a \cdot A(S) + b \cdot B(S) + c \cdot C(S) + \dots \qquad (1)$$

Here, R_0 is a constant, $R(S)$ some solvent sensitive property of the reaction under consideration (e.g. a rate or an equilibrium constant etc.), $A(S)$, $B(S)$, $C(S)$ ... are *solvent*-specific parameters which characterize certain fundamental solvent properties, a, b, c ... are *reactant*-specific coefficients which describe the sensitivity of the reaction towards changes in the solvent parameters A, B, C. The latter are called "Empirical Solvent Parameters" (ESP) and are determined in separate experiments by systematically studying the influence of the solvent on certain molecular properties of selected model compounds.

During the past 40 years, numerous attempts have been made to describe solvent effects by means of linear multiparameter equations [1, 2]. Most of these attempts have remained unsuccessful because the models and (or) parameters used were incorrect or inadequate. Part of the difficulties which were encountered in the application of LERs came from the fact that most of these equations had been developed and applied on a purely empirical basis. The first attempt to derive "universally" applicable LERs within the framework of thermodynamic principles was undertaken by the present author, who tried to combine the fundamental elements of elementary electrostatic and coordination chemical models [3–5]. A related approach was independently developed by *Koppel* and *Palm* [6]. Since then, these concepts have been widely applied either in original or modified form by many authors for the interpretation of solvent effects on chemical reactions and physical processes [7–9].

Both approaches rest on the view that solvent effects were primarily determined by the interplay of polar and coordinating properties of the solvents which one attempts to characterize by means of empirical solvent parameters. Evidently, the main difficulty is, to find suitable model compounds or parameters, respectively, which, in the ideal case, should characterize *one and only one* of the fundamental solvent properties mentioned above. In practice this requirement is very difficult to meet, since solvent effects on any molecular property of any model compound usually involve the combined influence of several factors which are not easy to separate. In the analysis of solvent effects by means of LERs, the imperfections of the parameters used manifest themselves by non-statistical deviations from the regression lines defined by equation (1). Such deviations can indeed be frequently observed for individual solvents or even certain groups of solvents [8].

One of the main obstacles to a solution of this problem is our present lack of knowledge about the solvation state of the various model compounds used for the definition of empirical solvent parameters. Although a large number of such parameters has been published, virtually no systematic measurements have been carried out so far concerning the elucidation of solvation mechanisms.

Another, equally important problem, which has also been largely ignored so far, is the possible falsification of empirical solvent parameters by additional effects, which are not necessarily proportional to the strength of the intermolecular interactions. Typical examples are the falsification of NMR-frequencies (which are frequently used as ESP) by magnetic anisotropy contributions or the falsification of vibrational frequencies by various kinds of coupling effects. Again, the detection of such interfering mechanisms requires a detailed knowledge about the solvation state of the corresponding model compounds.

The various problems associated with the proper application of LERs have prompted us several years ago to start with systematic NMR- and IR-spectroscopic investigations on the solvation of various model compounds which have been used for the definition of empirical solvent parameters.

The present work is concerned with IR-spectroscopic investigations on the solvation of the model compound triethylphosphine oxide (Et_3PO). This compound had been introduced already several years ago by the present author in an attempt to set up an empirical scale of solvent electrophilic properties based on the observation that the ^{31}P-NMR frequency of Et_3PO is strongly dependent on the solvating power of the solvents [10]. The latter was characterized by the socalled "Acceptor Number", AN, which is readily obtained from the measured ^{31}P-chemical shifts (extrapolated to zero concentration and referred to *n*-hexane) according to equation (2):

$$AN = 2.348 \cdot \delta^{31}P \ (AN = 0 \text{ for } n\text{-hexane}) \qquad (2)$$

Although NMR-spectroscopy has been widely applied for the characterization of solvent effects, its applicability for the study of solvation mechanisms is limited since fast exchange processes between different solvate species, which may simultaneously exist in solution, usually lead to signal averaging. By contrast, such species should in principle be detectable by means of IR-spectroscopic measurements provided that suitable model compounds with suitable "indicator" bands are available. As will be shown below, Et_3PO meets a number of requirements which make it ideally suited for the investigation of solvation mechanisms.

The present paper is concerned with IR-spectroscopic studies on the solvation state of Et_3PO in aprotic and CH-acidic solvents, results for hydroxylic solvents will be communicated in Part 2 of this series [11].

Experimental

IR-spectra were recorded with a Perkin-Elmer 180 grating spectrometer. The accuracy and the reproducibility of the wavenumber measurements was regularly checked by means of a polystyrene test spectrum. Solution spectra were usually recorded at 5 different concentrations in the range ~ 0.005–0.7 mol/l at slit widths of 2–3 cm^{-1} by means of demountable or permanently sealed liquid cells equipped with KBr, NaCl or CaF_2-windows. In solvents, which show very low transmittances in the P=O stretching region the number of data points had to be reduced and spectra were recorded only for the more concentrated solutions. The position of the band maxima is considered to be accurate to $\pm$ 0.2 cm^{-1}. In view of the high hygroscopicity of Et_3PO all manipulations were carried out in a glove box filled with dry nitrogen. Solvents were purified and dried according to standard procedures [12]. The water content was checked by *Karl Fischer* titration and was usually not higher than 10^{-3} mol/l.

Results

Fig. 1 shows the IR-spectrum of a 0.05 molar solution of Et_3PO in CCl_4 (4000–1100 cm^{-1}) and CS_2 (1100–500 cm^{-1}), respectively. Wavenumbers ν(PO) of the P=O stretching vibration of Et_3PO in different solvents and at different concentrations are listed in Table 1 together with values ν°(PO) [obtained by extrapolation of ν(PO) values to zero concentration] and corresponding acceptor numbers (AN) of the solvents. Fig. 2 shows the concentration dependence of ν(PO) for a number of representative solvents. Band profiles for solutions of Et_3PO in *n*-hexane at different concentrations are represented in Fig. 3. Results of spectrophotometric titrations of Et_3PO with $CHCl_3$, CH_2Cl_2 and 1,2-dichloroethane (*DCE*) are shown in Figs. 4–7.

Discussion

Triethylphosphine oxide has a number of unique properties which make it especially suitable as a model compound for the investigation of solvent effects and solvation shell structure. It is still the only model compound known to date which is sufficiently soluble in all kinds of solvents ranging from inert media like hydrocarbons to highly reactive solvents such as trifluoromethane sulfonic acid or concentrated sulfuric acid.

The molecule has a comparatively simple structure which largely excludes ambiguities in the molecular interpretation of solvent effects as opposed to many other popular model compounds, which usually contain different functional groups and (or) large polarizable organic residues which may be subject to specific interactions with solvent molecules.

The most prominent feature of the molecule is the presence of the highly polarizable P=O "double" bond, which makes it particularly sensitive towards changes in the solvent environment. The polarization of the P=O band is accompanied by two major effects: (1) an increase in the ^{31}P-resonance frequency (which has been used for the definition of the AN parameter) and (2) a pronounced bathochromic shift of the P=O stretching vibration, which may therefore be used as an alternative probe for the investigation of solvent effects. As has been pointed out in the introduction, IR-spectroscopic measurements have the great advantage that they allow to distinguish between different solvate species present in equilibrium, but in practice the applicability of this method is often limited by unfavourable absorption characteristics of the model compounds under consideration.

Fig. 1 shows the IR-spectrum of *Et*$_3$PO in the solvent CCl_4 or CS_2, respectively. In CCl_4 the P=O stretching vibration occurs as a very intense, sharp and symmetrical band at 1 178 cm^{-1} *. The region between 1 220 and 1 050 cm^{-1} is entirely free from other absorptions. Since most solvents fortunately have transmission windows in this region, bathochromically shifted P=O stretching bands can usually be easily detected even in highly dilute solutions**. Theoretical investigations show that the P=O stretching vibration is also largely uncoupled [13, 15], which means that changes in the intermolecular interaction energies are directly reflected in corresponding changes in the P=O stretching frequency which is therefore ideally suited for the investigation of solvation

---

* A complete band assignment of both the infrared and *Raman* spectrum based on a normal coordinate analysis will be given elsewhere [13].

** Interference of bathochromically shifted P=O bands with CH_3-rocking and C—C stretching vibrations occuring below 1 050 cm^{-1} is observed only with very strong acceptor solvents [14].

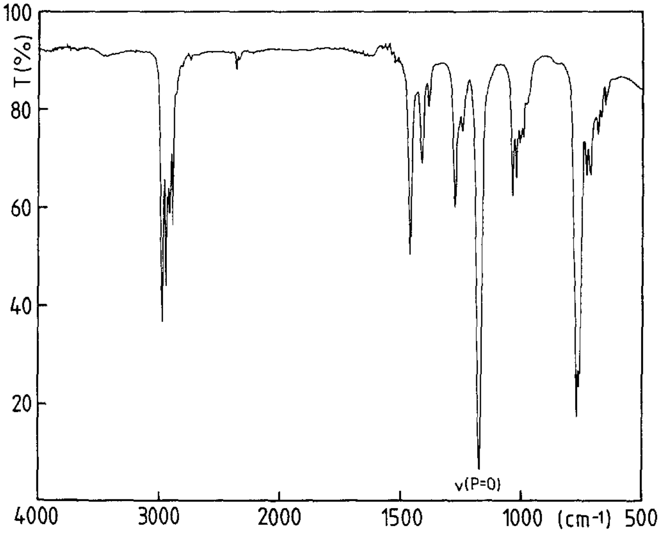

Fig. 1. Infrared spectrum of a 0.05 molar solution of Et_3PO in CCl_4 (4000–1100 cm^{-1}) and CS_2 (1100–500 cm^{-1}), respectively

mechanisms. This also applies to a number of other symmetrical and asymmetrical tertiary phosphine oxides which have recently been tested in our laboratory [16].

Fig. 2 reveals that the P=O stretching vibration of Et_3PO is strongly dependent on the solvent and to a lesser degree also on the concentration. Values ν°(PO) obtained by extrapolation of ν(PO) values to zero concentration are listed in Table 1. As expected, ν°(PO) values decrease with increasing solvating power of the solvents, i.e. increasing AN (Table 1).

In more strongly solvating solvents like nitromethane or dimethylsulfoxide the ν(PO) values increase with increasing concentration of Et_3PO and vice versa. The sign of the concentration dependence changes in the region between 1170 and 1175 cm^{-1}, which coincides with the P=O stretching wavenumber of molten Et_3PO observed at 1172.5 cm^{-1}. This observation proves that the polarization state of the molecule and in particular of the P=O bond is due to the reaction field of the medium, which in turn is determined by the reaction field contributions of *both* solvent *and* solute molecules, thus explaining the characteristic concentration dependencies observed in Fig. 2.

In most solvents and at most concentrations the P=O stretching vibration appears as a single symmetrical band which indicates that only

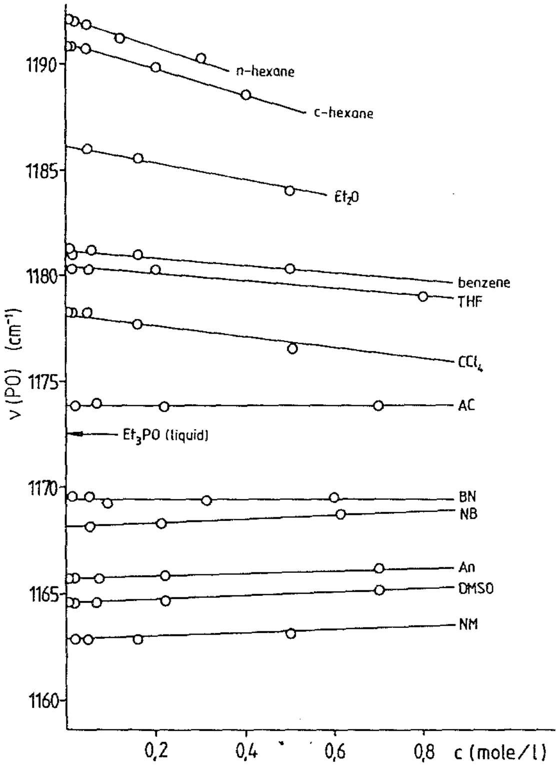

Fig. 2. Wavenumbers ν(PO) of the P=O stretching vibration of *Et*$_3$PO as a function of concentration in various aprotic solvents

one kind of solvate species is present in solution. In carbon tetrachloride and diethylether, however, the bands are asymmetric and considerably broadened at the low wavenumber side, which indicates the formation of dipole-dipole aggregates in the more concentrated solutions. The existence of such aggregates is clearly visible from Fig. 3, which shows the P=O stretching region of *Et*$_3$PO in *n*-hexane. At very low concentrations the band is symmetrical and located at ~ 1 192 cm^{-1}. At higher concentrations first a shoulder and then a new peak appear at lower wavenumbers. The peak at 1 184.5 cm^{-1} is most probably due to an *Et*$_3$PO-dimer. Detailed ^{31}P-NMR [17] and IR-spectroscopic measurements [16] reveal that in addition higher aggregates are formed even at comparatively low concentrations, as is also indicated by the asymetric band profile of solution no. 3 in Fig. 3 (exactly the same features can be observed for solutions of *Et*$_3$PO in cyclohexane [14]). Recent systematic IR-spec-

Table 1. *Wavenumbers* ν(PO) *(cm^{-1}) of Et$_3$*PO *at different concentrations in various aprotic and* CH-*acidic solvents; wavenumbers* ν°(PO) *obtained by extrapolation of* ν(PO) *values to zero concentration and solvent acceptor numbers (AN)*

Solvent	c (mol/l)	ν(PO) (cm^{-1})	ν°(PO) (cm^{-1})	AN
n-hexane	0.300	1 190.3*	1 192.1	0.0
	0.119	1 191.2*		
	0.0476	1 191.8*		
	0.0189	1 192.0		
	0.00753	1 192.1		
	0.00301	1 192.0		
Cyclohexane	0.401	1 188.5*	1 191.0	0.0
	0.201	1 189.8*		
	0.0499	1 190.7*		
	0.0125	1 190.9		
	0.0040	1 190.9		
Diethyl ether	1.137	1 181.5	1 186.2	3.9
	0.899	1 183.5		
	0.500	1 184.0		
	0.159	1 185.6		
	0.0499	1 186.0		
Benzene	0.501	1 180.3	1 181.2	8.2
	0.158	1 181.0		
	0.0498	1 181.2		
	0.0160	1 181.0		
	0.00507	1 181.3		
Tetrahydrofuran	0.800	1 179.0	1 180.4	8.0
	0.201	1 180.3		
	0.0501	1 180.3		
	0.0125	1 180.3		
Carbon tetrachloride	1.498	1 174.4	1 178.2	8.6
	0.509	1 176.6		
	0.158	1 177.7		
	0.0489	1 178.3		
	0.0162	1 178.3		
	0.00483	1 178.2		
Acetone (AC)	0.697	1 173.8	1 173.8	12.5
	0.221	1 173.8		
	0.0698	1 173.9		
	0.0221	1 173.8		
	0.00701	(1 173.5)		

Table 1 (continued)

Solvent	c (mol/l)	ν(PO) (cm^{-1})	ν°(PO) (cm^{-1})	AN
Triethylphosphine oxide	neat (melt)	1 172.5		13.0 (Ref. [17])
Benzonitrile (BN)	0.584	1 169.5	1 169.5	15.5
	0.311	1 169.4		
	0.0959	1 169.3		
	0.0538	1 169.5		
	0.0105	1 169.6		
Acetonitrile (An)	0.702	1 166.1	1 165.7	18.9
	0.223	1 165.8		
	0.0701	1 165.7		
	0.0226	1 165.7		
	0.00716	1 165.7		
Dimethylsulfoxide (DMSO)	0.701	1 165.2	1 164.5	19.3
	0.221	1 164.7		
	0.0699	1 164.6		
	0.0224	1 164.5		
	0.00686	1 164.6		
Nitromethane (NM)	0.502	1 163.1	1 162.8	20.5
	0.157	1 162.9		
	0.0495	1 162.8		
	0.0182	1 162.8		
	0.00619	(1 162.3)		
1,2-dichloroethane (DCE)	0.499	1 168.1	1 167.4	16.7
	0.159	1 167.7		
	0.0505	1 167.6		
	0.0168	1 167.4		
	0.00634	1 167.3		
Dichloromethane	0.701	1 162.1	1 161.3	20.4
	0.222	1 161.6		
	0.0720	1 161.5		
	0.0224	1 161.3		
	0.00671	(1 161.0)		
Chloroform	0.501	1 153.3	1 154.1	25.1
	0.160	1 153.8		
	0.0496	1 154.1		
	0.0151	1 154.0		
	0.0053	1 154.1		

* Second band or shoulder, respectively, at lower wavenumbers

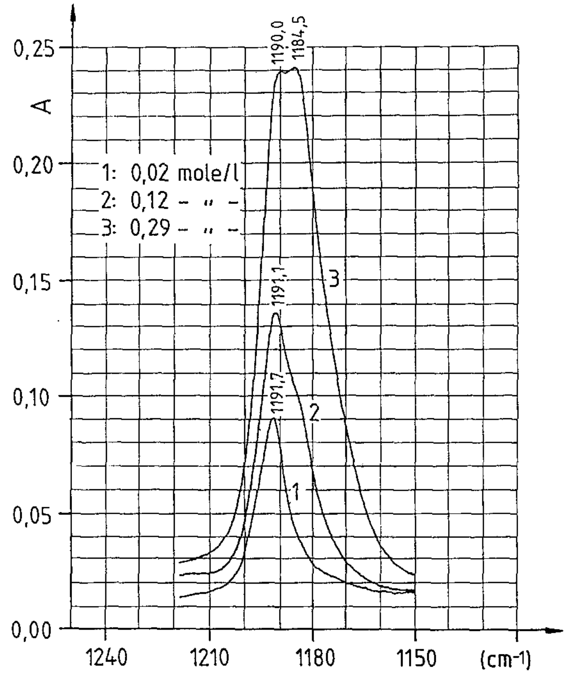

Fig. 3. P=O stretching bands of Et_3PO in *n*-hexane

troscopic measurements have shown that (contrary to existing views) the formation of both homo- and hetero-dipole-dipole complexes of *well defined stoichiometry* is a very general phenomenon in noncoordinating solvents [18]. We shall report on these investigations shortly.

Symmetrical or nearly symmetrical bands were also observed in the solvents $CHCl_3$ and CH_2Cl_2. Since these molecules are known to form hydrogen bonded complexes with donor molecules, we have tried to clarify the solvation state of Et_3PO in these solvents by means of spectrophotometric titrations. Fig. 4 shows the titration of Et_3PO with $CHCl_3$ in *n*-hexane: Addition of increasing amounts of $CHCl_3$ to a solution of Et_3PO in *n*-hexane leads to the successive evolution of two new bands located around 1 178 cm^{-1} (band 2) and 1 163 cm^{-1} (band 3) with a simultaneous decrease in intensity of the band at 1 192 cm^{-1} (band 1) characteristic of the "free" Et_3PO-molecule. From the observed changes in intensity and peak separations it follows that bands 2 and 3 are due to 1 : 1 and 1 : 2 Et_3PO—$CHCl_3$ complexes, respectively. At higher $CHCl_3$-concentrations, both bands are shifted to lower wavenumbers, which, in principle, could be interpreted as the result of either a medium effect or

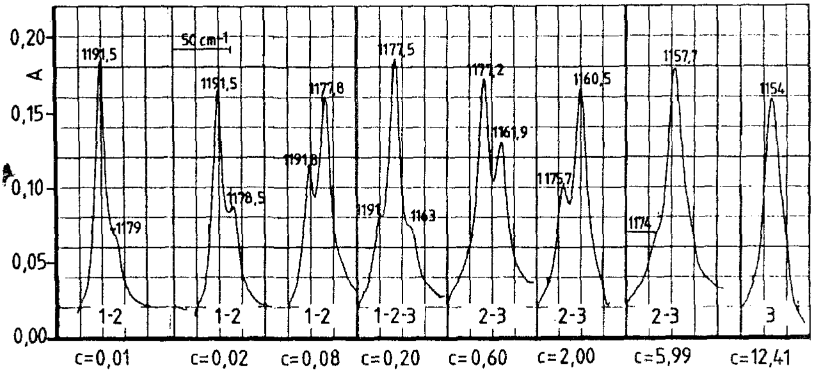

Fig. 4. Changes in the P=O stretching region on titration of *Et*$_3$PO ($c = 0.02$ mol/l) with CHCl$_3$ in *n*-hexane; c = concentration of CHCl$_3$ added

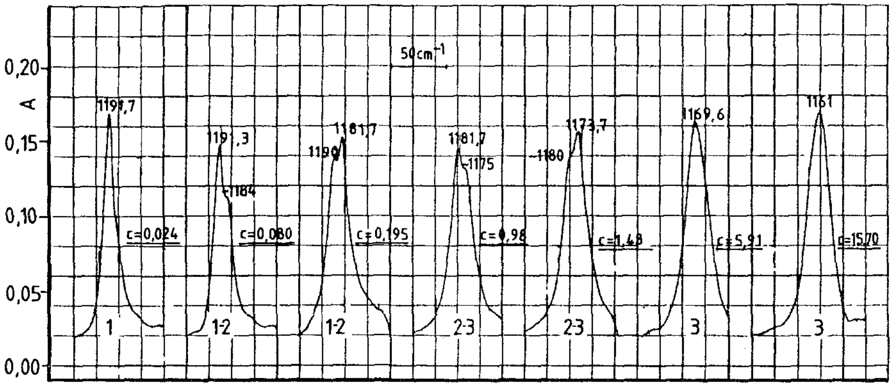

Fig. 5. Changes in the P=O stretching region on titration of *Et*$_3$PO ($c = 0.02$ mol/l) with CH$_2$Cl$_2$ in *n*-hexane; c = concentration of CH$_2$Cl$_2$ added

outersphere-interactions. Recent investigations [19] on the solvation state of CHCl$_3$ in various solvents have shown that chloroform (contrary to several literature reports) has no proclivity for self-association or outer-sphere interactions, which means that the observed bathochromic band shifts would stem from a medium effect.

Similar results were obtained for the spectrophotometric titration of *Et*$_3$PO with CH$_2$Cl$_2$ in *n*-hexane (Fig. 5). Addition of CH$_2$Cl$_2$ again leads to the appearence of two new bands located at 1 182 cm^{-1} (band 2) and ~ 1 174 cm^{-1} (band 3), which, for the same reasons as indicated above, can be attributed to a 1 : 1 and 1 : 2 *Et*$_3$PO—CH$_2$Cl$_2$ complex, respectively. As with CHCl$_3$, both bands are shifted to lower wavenumbers with

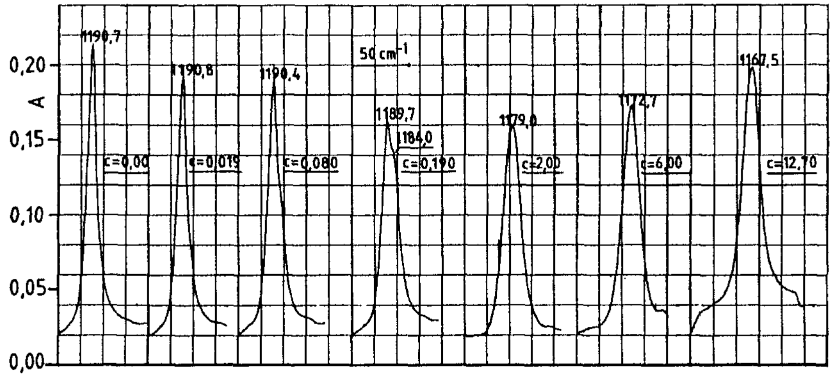

Fig. 6. Changes in the $P{=}O$ stretching region on titration of Et_3PO (c = 0.02 mol/l) with 1,2-dichloroethane in cyclohexane; c = concentration of 1,2-dichloroethane added

increasing CH_2Cl_2-content, suggesting that both complexes are subject to a medium effect.

Fig. 6 shows the titration of Et_3PO with 1,2-dichloroethane (*DCE*) in the solvent cyclohexane. 1,2-dichloroethane is traditionally considered as a weakly polar and very weakly coordinating solvent which has been widely used in coordination chemical studies. Inspection of Fig. 6 reveals that, evidently, even *DCE* forms a complex with Et_3PO which can be identified as a shoulder around 1184 cm^{-1} at a *DCE*-concentration of 0.19 mol/l. Contrary to $CHCl_3$ and CH_2Cl_2, however, no second band could be detected at higher *DCE*-concentrations. The band at 1184 cm^{-1} is most probably due to a $Et_3PO \cdot DCE$ 1 : 1 complex.

In order to test the influence of the "inert" solvent used on the formation and detectability of the various complexes discussed above, the titration of Et_3PO with $CHCl_3$ was also carried out in the solvent CCl_4. Carbon tetrachloride is usually considered as a typical non-polar, non-coordinating solvent, which has been widely used in IR-spectroscopic investigations because of its excellent transmittance properties. Inspection of Fig. 7 readily shows that the spectra are much less well resolved than in hexane. Evidence for the formation of two different complexes is actually found only in two mixtures, namely at $c(CHCl_3)$ = 1.99 and 5.95 mol/l, where the presence of these complexes is indicated by the appearance of shoulders or peaks, respectively. Clearly, hydrocarbons are much better solvents for the detection and investigation of weak complexes [18] than CCl_4, which is by no means that inert as is usually believed. The latter point also manifests itself by the high acceptor number or low $\nu^\circ(PO)$ value, respectively, of this solvent (Table 1).

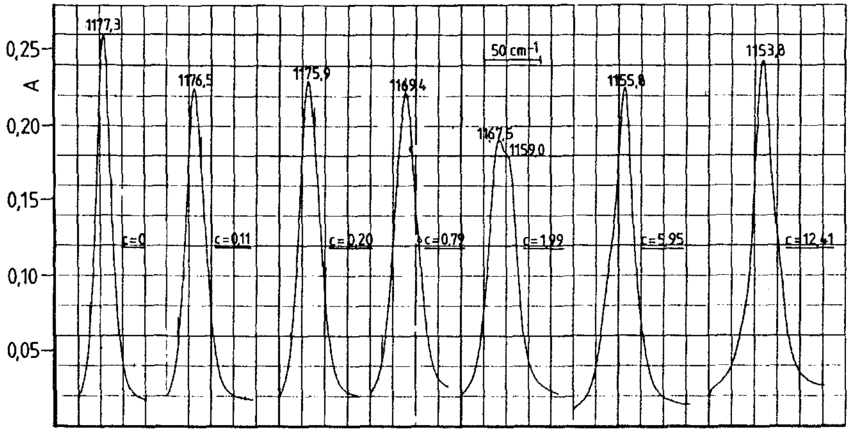

Fig. 7. Changes in the P=O stretching region on titration of *Et*$_3$PO ($c = 0.20$ mol/l) with $CHCl_3$ in CCl_4; c = concentration of $CHCl_3$ added

Analysis of Figs. 4 and 5 provides two additional important informations: (1) Peak separations $\Delta\nu\,(1 \rightarrow 2)$ and $\Delta\nu(2 \rightarrow 3)$ for bands 1,2 and 2,3 are approximately equal for each of the systems studied ($CHCl_3$: $\Delta\nu = 15 \pm 1\,\mathrm{cm}^{-1}$, CH_2Cl_2: $\Delta\nu = 9 \pm 1\,\mathrm{cm}^{-1}$). This means that hydrogen bond formation between *Et*$_3$PO and the first acceptor molecule has practically no effect on the basicity of the second lone pair of the oxygen atom.

(2) The peak separations $\Delta\nu(1 \rightarrow 2)$ between the P=O stretching bands of *Et*$_3$PO and its 1 : 1 *Et*$_3$PO·*A* complex (*A* = acceptor molecule) observed in Figs. 4, 5 and 6, provide a quantitative measure of the relative acidities (intrinsic acceptor strengths) of the isolated, monomeric acceptor molecules*. The knowledge of these values is very important for solution chemists, since the relative acidities (relative acceptor strengths) of *neat* protic solvents (the socalled "bulk acidities") do not always conform to the relative acidities shown by the corresponding isolated, monomeric molecules. As will be shown in Part 2 of this series this is especially true for highly associated media [11]. From the peak separations $\Delta\nu(1 \rightarrow 2)$ observed in Figs. 4, 5 and 6 it follows that the relative intrinsic acceptor strengths increase in the series *DCE* ($\Delta\nu \sim 7\,\mathrm{cm}^{-1}$) < CH_2Cl_2 $\Delta\nu(\sim 10\,\mathrm{cm}^{-1})$ < $CHCl_3$ ($\Delta\nu \sim 14\,\mathrm{cm}^{-1}$). The relatively high value for *DCE* shows that its acceptor properties are by no means negligible.

---

* Such intrinsic acidities should actually be determined in the gas phase; unfortunately these values are usually not easily accessible.

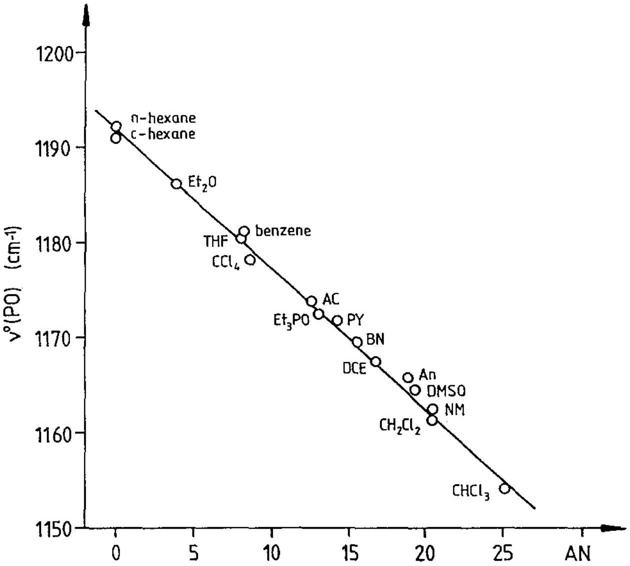

Fig. 8. Relationship between P=O stretching wavenumbers ν°(PO) obtained by extrapolation to zero concentration and solvent acceptor numbers (AN)

Since an increase in solvent AN is expected to cause a weakening of the P=O bond and therefore a decrease in the wavenumber of the P=O stretching vibration, it was particularly interesting to test the relationship between these two parameters. Fig. 8 reveals that they are indeed linearly related to each other. The correlation also includes the solvents $CHCl_3$ and CH_2Cl_2, which were shown to form hydrogen bonded complexes with Et_3PO. From the distribution of the solvate species observed in Figs. 4 and 5 one can conclude that Et_3PO exists predominantly in the form of 1 : 2 Et_3PO-acceptor complexes in these solvents.

$$\nu^\circ(\mathrm{PO}) = 1\,191.85 - 1.451 \cdot \mathrm{AN} \qquad (3)$$

$$r^2 = 0.995, \quad \overline{\delta\nu} = 0.63\,\mathrm{cm}^{-1}$$

The excellent linear relationship between ν°(PO) and AN values, equation (3), proves that both parameters are indeed proportional to the strength of the intermolecular interactions and virtually free from unspecific contributions such as magnetic anisotropy or vibrational coupling effects. Clearly, such a linear relationship can only be expected if only one kind of solvate species is present in solution. Results for hydroxylic solvents where the situation is more complicated will be reported in Part 2 of this series [11].

Acknowledgments

Thanks are due to the *"Fonds zur Förderung der wissenschaftlichen Forschung"* for support of this work through project 5984, to Professor Dr. *R. Kellner* from the Institute of Analytical Chemistry, who provided the Perkin-Elmer 180 IR-spectrometer and to Mr. *F. Danzinger* for technical assistance.

References

[1] *Leffler JE, Grunwald E* (1963) Rates and Equilibria of Organic Reactions. Wiley, New York

[2] *Amis ES, Hinton JF* (1973) Solvent Effects on Chemical Phenomena. Academic Press, New York, London

[3] *Mayer U* (1975) Pure Appl Chem 41: 291

[4] *Mayer U* (1978) Monatsh Chem 109: 421

[5] *Mayer U* (1978) Monatsh Chem 109: 775

[6] *Koppel IA, Palm VA* (1972) In: *Chapman NB, Shorter J* (eds) Advances in linear free energy relationships. Plenum Press, London, New York

[7] *Reichardt C* (1979) Solvent effects in organic chemistry. Verlag Chemie, Weinheim, New York

[8] *Mayer U* (1979) Pure Appl Chem 51: 1697

[9] *Mayer U* (1983) Studies in physical and theoretical chemistry, vol 27: Ions and molecules in solution. Elsevier, Amsterdam, p 219

[10] *Mayer U, Gutmann V, Gerger W* (1975) Monatsh Chem 106: 1235

[11] *Mayer U, Hoffmann H, Kellner R* (1988) Monatsh Chem 119: 1223

[12] *Riddick JA, Bunger WB* (1970) In: *Weissberger A* (ed) Techniques of Chemistry, vol II, Wiley-Interscience, New York, Toronto

[13] *Bauer G, Mayer U* et al (to be published)

[14] *Hoffmann H* Thesis PD, Technical University of Vienna

[15] *Goubeau J, Lentz A* (1971) Spectrochim Acta 27A: 1703

[16] *Mayer U, Danzinger F,* unpublished results

[17] *Rauchbüchl A* Thesis PD, Technical University of Vienna

[18] *Mayer U, Danzinger F* (to be published)

[19] *Mayer U, Schneider B* (to be published)