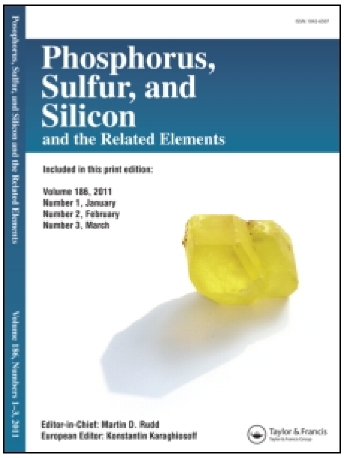

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HYDROGEN BONDING BETWEEN TERTIARY PHOSPHINES AND ALCOHOLS

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HYDROGEN BONDING BETWEEN TERTIARY PHOSPHINES AND ALCOHOLS

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The hydrogen bond between several alcohols, in particular benzyl alcohol and isopropanol, as donors, and a number of tertiary phosphines, as well as a smaller number of tertiary arsines, as acceptors was investigated by means of ir spectroscopy in the temperature range +40° to −20°C. Toluene was used as a solvent. The equilibrium constant K, the hydrogen bond enthalpy $-\Delta H$ and the entropy $-\Delta S$ were determined. The equilibrium constants as well as the $-\Delta H$ values are essentially dependent on the basicity of the phosphines. There is no evidence of any steric influence. In the systems with aliphatic phosphines, the highest equilibrium constants are about 20, the lowest values are near unity. Aromatic phosphines possess a lower affinity of interaction with the alcohols. $-\Delta H$ varies for the different systems between 1.2 and 3.5 kcal·mole^{-1}. Investigating the acceptor power of arsines we found both K and $-\Delta H$ one order of magnitude lower than in the case of phosphines.

INTRODUCTION

Many acylation reactions may be catalysed by tertiary amines, but tertiary phosphines may also be used. There is no doubt, that the catalytic power of the phosphines is a consequence of their ability to act as a proton acceptor in hydrogen bonds. Although the behaviour of amines in hydrogen bonding is the subject of a number of publications (e.g. Refs. 1-5), only little attention has been paid[6] so far to the H bond properties of the tertiary phosphines. It is the purpose of this paper, to give a quantitative description of this problem. We base our information on ir spectroscopic measurements, performed in systems of alcohols and tert. phosphines in toluene as a solvent.

RESULTS AND DISCUSSION

In Figures 1 and 2 for benzyl alcohol and isopropanol, respectively, as donors, the values of ln K are plotted vs. T^{-1}. The slope of the curves allows us to calculate the association enthalpy $-\Delta H$. Both, $-\Delta H$ and ΔS are summarized in Table I. All abbreviations are explained in the legend of this table.

Further, Figure 3 shows $-\Delta H$ as a function of pK_a and Figure 4 gives the relation between $-\Delta H$ and $\Delta\nu_{OH}$: the context of $\Delta\nu_{OH}$ and pK_a may be easily obtained using Figures 3 and 4.

In Figures 1 and 2 we can observe several groups of curves, which concern phosphines of similar behaviour. Thus in Figure 1 four groups may be distinguished.

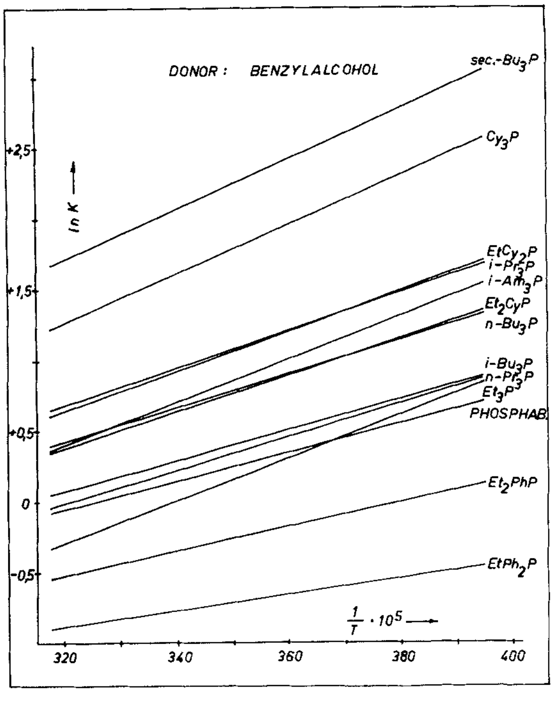

FIGURE 1 Relation between ln K and T^{-1} in hydrogen bonded systems formed by tert. phosphines (see Table I for abbreviations) and benzyl alcohol.

The first group contains the compounds sec. Bu_3P and Cy_3P, the second one is formed by the substances Et Cy_2P, i-Pr_3P, Et_2CyP and n-Bu_3P, the third one includes the phosphines i-Bu_3P, n-Pr_3P, Et_3P and phosphabic, and the aromatic phosphines form another

TABLE I

Thermodynamic data of hydrogen bonding in systems by tert. phosphines as acceptors and benzyl alcohol or isopropanol as donors

Donor: Benzyl alcohol								
Acceptor →	Et_3P	n-Pr_3P	i-Pr_3P	n-Bu_3P	i-Bu_3P	sec. Bu_3P	i-Am_3P	Cy_3P
$-\Delta H$ (kcal·mole^{-1})	3.1	2.9	2.7	2.4	2.1	3.5	3.0	3.4
$-\Delta S$ (e.u.)	10.4	9.3	7.3	6.9	6.7	7.9	9.0	8.5
	Et_2CyP	$EtCy_2P$	Et_2PhP	$EtPh_2P$	Phosphab	$EtPh_2PO$	Cy_2PH	$CyPH_2$
$-\Delta H$ (kcal·mole^{-1})	2.5	2.8	1.8	1.2	2.0	5.0	1.4	0.5
$-\Delta S$ (e.u.)	7.3	7.8	6.7	5.6	6.6	10.7	4.7	4.6
Donor: Isopropanol								
Acceptor →	Et_3P	n-Pr_3P	i-Pr_3P	sec. Bu_3P	i-Am_3P	Et_2CyP		
$-\Delta H$ (kcal·mole^{-1})	2.1	2.0	2.4	3.0	2.5	2.4		
$-\Delta S$ (e.u.)	7.6	7.3	7.9	8.4	8.4	7.8		

The meaning of the abbreviations used throughout this paper is as follows: Et = ethyl, Pr = propyl, Bu = butyl, Am = amyl, Cy = cyclohexyl, Ph = phenyl, Phosphab. = phosphabicycloheptane.

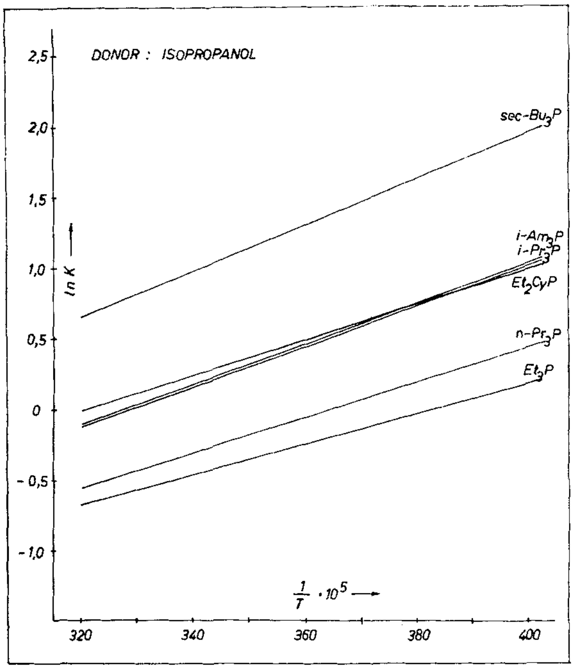

FIGURE 2 Relation between ln K and T^{-1} in hydrogen bonded systems formed by tert. phosphines (see Table I for abbreviations) and isopropanol.

group. It may be perceived, that the belonging of the several phosphines to the different groups is essentially determined by the +I effect of their substituents. The enthalpy values, with that of the system Et_3P/ benzyl alcohol as an exception, behave analogously to the equilibrium constants. The equilibrium constant of this exceptional system seems to be controlled by basicity, but $-\Delta H$ and $-\Delta S$ are greater than would be expected on the basis of proportionality between $-\Delta H$ and K.

This phosphine possesses very little steric shielding and therefore the approach between donor and acceptor may be a specially intense one, but simultaneously this approach may demand also a special steric arrangement. Both factors may be the reason for the high values of $-\Delta H$ and $-\Delta S$. Considering the smallness of this association complex, the high value of $-\Delta S$ may be also connected with a special arrangement of the molecules of the solvatation shell. The approximate proportionality between $-\Delta H$ and pK_a values in all other cases is an indication, that steric effects do not play an important role, probably because of the size of the phosphorus atom. Small deviations from a linear ΔH/pK_a relation are not surprising, because the pK_a values are measured using nitromethane as a solvent. In a few cases the pK_a values are only estimated on the base of Taft σ^* constants[9]. Thus the pK_a values may be somewhat uncertain. The presentation of the Badger-Bauer rule for all systems in Figure 4 seems not likely to give significant results, in particular because of the small difference in the values of $-\Delta H$ and the uncertainty of $\Delta\nu_{OH}$.

The association behaviour of the phosphines used is also generally determined by their basicity when isopropanol acts as a donor (Figure 2). Corresponding to the lower acidity of this alcohol, equilibrium constants as well as $-\Delta H$ and $-\Delta S$ values are smaller than in the case of benzyl alcohol. Remarkably the

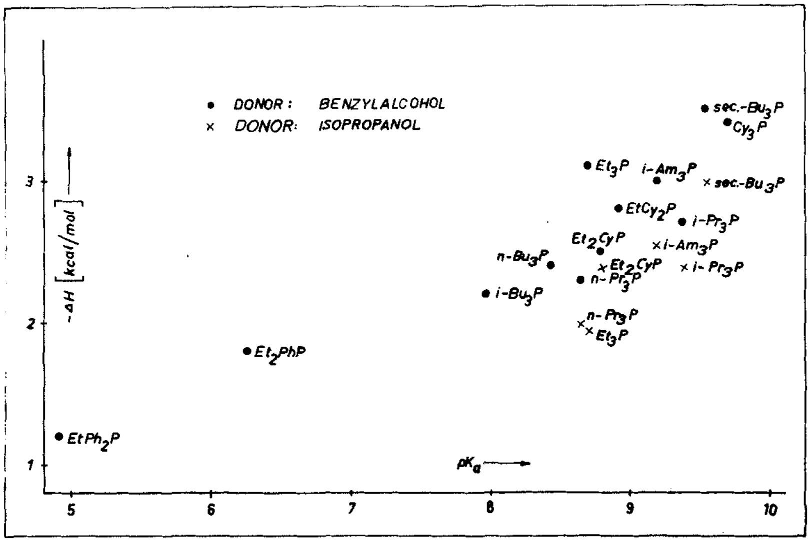

FIGURE 3 $-\Delta H$ *vs.* pK_a of the systems of Figures 1 and 2.

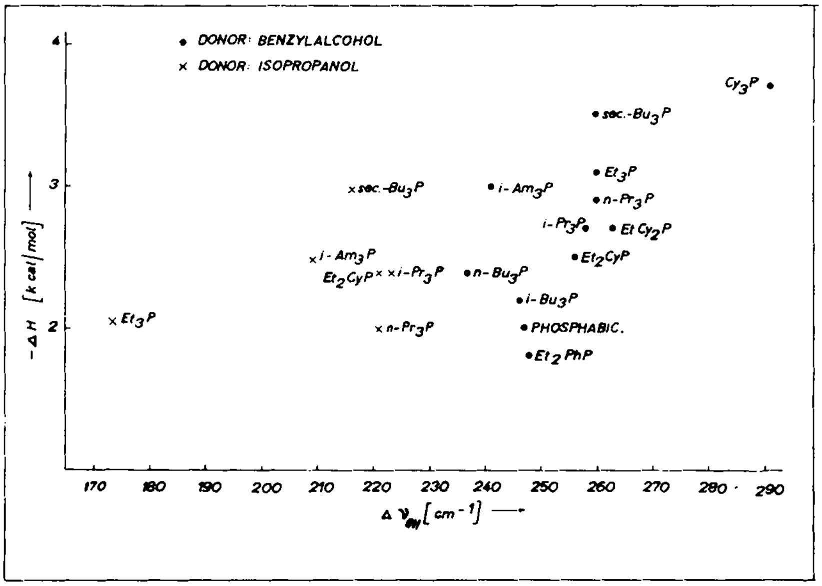

FIGURE 4 $-\Delta H$ *vs.* $\Delta\nu_{OH}$ of the systems of Figures 1 and 2

exceptional position of the compound Et_3P, which we emphasized in the case of benzyl alcohols, is lost. Especially in view of the smallness of the difference of the pK_a's of the substances used here, it is not reasonable to consider a relationship between $-\Delta H$ and pK_a. The predominant influence of a Brönstedt relation is also to be recognized in systems, containing tert. butanol or methanol as a donor. If the same phosphines are used, the association behaviour, characterized by K, $-\Delta H$ and $\Delta\nu_{OH}$, essentially is determined by the acidity of the alcohol (Table II). Even when we use tert. butanol as a donor, steric effects do not play any observable role. There is also no remarkable difference in the half width of the associated OH bands.

But the determination of these values is complicated by the fact, that in all cases the associated OH band is clearly unsymmetrical and can be divided into a smaller short wave and a greater long wave band, both showing a symmetrical profile. This effect is also recognized in some of the systems formed by tert. amines and alcohols. We shall try to explain this special finding at a later time.[10]

Additionally we have measured the change of $\Delta\nu_{OH}$ with temperature. Although this effect should not be used unreservedly to draw conclusions because of the uncertainty of the experimental values, the $\Delta\nu_{OH}$ values increase differently for the various phosphines in the temperature range +40° to −20°C, increases between 5 and 14 cm^{-1} being shown. Certainly this effect is not to be discussed in terms of a Badger–Bauer relation, especially because we found

TABLE II

Thermodynamic data of hydrogen bonding and values of $\Delta\nu_{OH}$ in systems formed by tert. phosphines as acceptors and methanol or tert. butanol as donors

Donor: Methanol				
Acceptor →	$i\text{-}Pr_3P$	sec. Bu_3P	$i\text{-}Am_3P$	Et_2PhP
$-\Delta H$ (kcal $mole^{-1}$)	2.5	3.7	3.0	0.7
$-\Delta S$ (e.u.)	6.9	8.9	8.4	2.4
$\Delta\nu_{OH}$ (cm^{-1})	230	235	222	
Donor: tert. Butanol				
Acceptor as above				
$-\Delta H$ (kcal $mole^{-1}$)	2.3	2.9	2.2	
$-\Delta S$ (e.u.)	7.4	8.2	7.5	
$\Delta\nu_{OH}$ (cm^{-1})	216	202	189	

ln K as a linear function of T^{-1}. Systems of tert. amines and alcohols show, as we shall report before long,[10] a variation of $\Delta\nu_{OH}$ in the same range of temperature up to twice that found in the phosphine systems. The intensity of the association band is very sensitive towards changes in the basicity of the acceptor molecules. In Figure 5 relative integrated absorbancies (referred to the intensity of the associated band of the system n-Pr_3P benzyl alcohol) are plotted *vs.* the basicity of the acceptor. The coefficient of the integrated absorbancies of the associated OH bands are in a strong way dependent on the temperature, as is to be seen from Figure 6. But the number of systems for which we have taken into account this particular question, is too low, to be related to special features of the molecules.

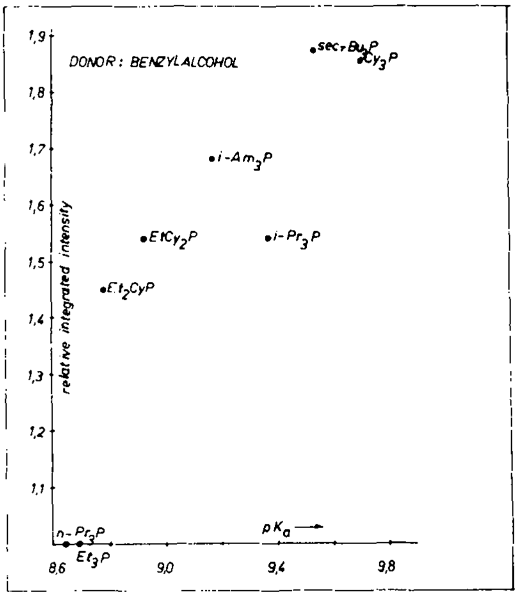

FIGURE 5 Relative integrated absorbance coefficients of the associated OH band of some tert. phosphine/benzyl alcohol systems as a function of pK_a at −23°C.

Somewhat outside our original subject, we have additionally investigated the acceptor behaviour of one primary and one secondary phosphine, as shown in Figure 7. These two substances are extremely sensitive towards oxygen and we conceive the results of the investigation of these substances as a criterion of the reliability of our measuring method with respect to the non-oxidation of phosphines used.

The clear linear relationship between ln K and T^{-1} confirms, in our opinion, that under the experimental conditions used in this work oxidation does not take place.

The strong influence of the acidic PH proton on the acidity of the phosphine used is clearly demonstrated.

Further we investigated the proton acceptor power of three tert. arsines. The absorption in the range of the associated OH band is extremely weak due to the low basicity of the arsines. Therefore we have determined $\Delta\nu_{OH}$ only at 253 K. The results concerning this class of substances are summarized in Table III. As is to be expected, the enthalpy values as well as the entropy values are low, and remarkably in the case of the system n-Pr_3As benzyl alcohol we found a zero enthalpy. Therefore in the context of this association complex we can speak of a pure entropy bond. Our results, obtained for the arsine systems, are seriously in contrast to those given by Choinowski[6] for similar systems. We believe the values reported there are affected by oxidation of the acceptor molecules.

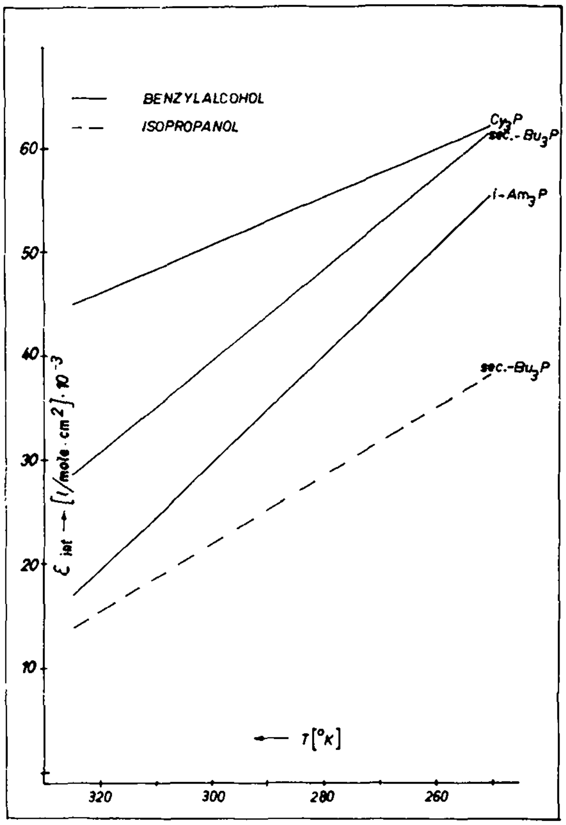

FIGURE 6 Temperature dependence of the absorbance coefficients of the integrated associated OH bands of selected tert. phosphine/benzyl alcohol systems and the system sec.-Bu_3P/isopropanol.

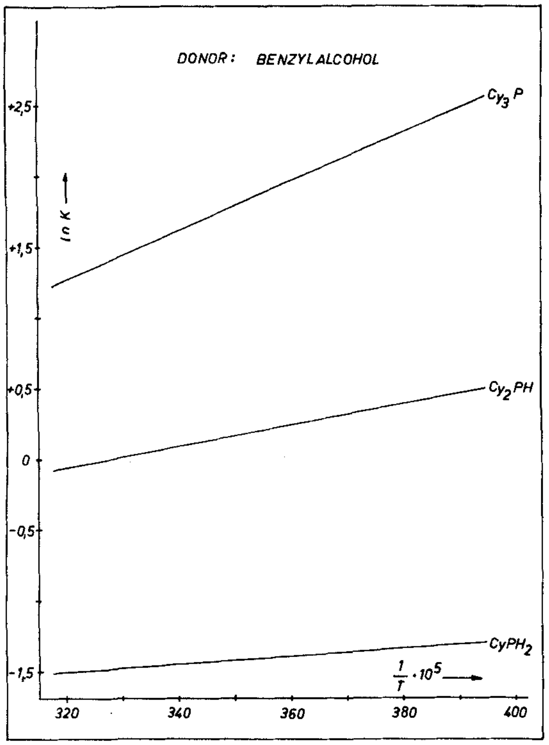

FIGURE 7 ln K/T^{-1} relations of hydrogen bonded systems formed by a primary or a secondary or a tertiary phosphine as an acceptor and benzyl alcohol as a donor.

EXPERIMENTAL

Substances

The phosphines used were taken from the stocks of our Institute. They had been synthesized by a well known procedure, described in Ref. 7. The compounds were always freshly distilled before use. We have paid special regard to the sensitivity of our compounds to oxidation. The preparation of the solutions was therefore carried out using an inert gas apparatus. The absence of PO bonds was controlled by means of ir spectroscopy. The solvent toluene (uvasol quality, Merck) was always freshly distilled from molecular sieve to remove last traces of moisture. The purity of the alcohols used was checked by gas chromatography. The ir spectra were recorded on a Beckman IR 12 spectrophotometer. Normally NaCl cells of 2.6 mm thickness were used. The reference cell contained the same quantity of phosphine as the sample cell. The associated band was recorded with a speed of 16 cm^{-1} min^{-1}, but the free one with a speed of 6.4 cm^{-1} min^{-1}. The concentration of alcohol in the solutions used amounts to about 0.02 mole l^{-1}, thus avoiding the homogeneous association of the alcohols. The quantity of phosphines was chosen in such a way, that on association approximately half of the free OH band disappeared. The temperature adjustment was done using a Peltier apparatus described previously.[8] The equilibrium constants were determined using the base line method and formula given in an earlier publication.[1] The temperature dependence of the absorbance coefficient of the free OH band was always taken into consideration. Concerning the calculation, we assume the formation of only 1:1 associates, and also the equality of the absorbance coefficients of the free OH bands in pure toluene solution as well as in the three component system toluene-phosphine-alcohol. The consistency of the obtained values is an indication of the fulfilment of both assumptions.

Errors

The deviation from the linearity of the transmittance of the IR 12 was constantly found to be less than half of one percent. This uncertainty may lead to an error in K up to 4-5% and may cause an uncertainty of 0.25 kcal $mole^{-1}$ in the association enthalpy $-\Delta H$.

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We are very indebted to Dr. F. Krech, Dr. G. Thomas and Dr. J. Heinicke for preparing the acceptor substances, to Prof. Dr. K. Issleib for his permanent interest in this work and to Dr. J. Shorter for his careful reading of this English version.

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TABLE III

Thermodynamic data of hydrogen bonding and values of $\Delta\nu_{OH}$ in systems formed by tert. arsines as acceptors and benzyl alcohol or phenol as donors

Donor	Acceptor	$-\Delta H$ (kcal/mole)	$-\Delta S$ (e.u.)	$\Delta\nu_{OH}$ (cm^{-1})
benzyl alcohol	n-Pr_3As	0.0	0.8	113
benzyl alcohol	i-Pr_3As	0.5	2.5	122
phenol	i-Pr_3As	1.5	5.4	215
phenol	Cy_3As	1.6	5.7	227