

Intermolecular Hydrogen Bonding between Organic Phosphoryl Compounds and Phenol

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Equilibrium constants of dimeric hydrogen bond complexes between phenol and 15 different organic phosphoryl compounds in carbon tetrachloride have been determined at 5–10 temperatures in the region 20–70°C. The calculated ΔH values lie in the region –7.6 to –12.8 kcal/mole and the ΔS values in the region –14.2 to –27.7 e.u. The exceptional high ΔH and ΔS values of 1-propyl-1-oxo-phospholane, –12.8 kcal, resp. –27.7 e.u., are discussed in relation to the strong catalytic effect of phospholane oxides in the transformation of isocyanates to carbodiimides.

Some years ago Aksnes and Gramstad¹ reported equilibrium constants of 18 dimeric hydrogen bond complexes between phenol and organic phosphoryl compounds in carbon tetrachloride. An approximately linear dependence between the logarithm of the equilibrium constants and the wave number shift, $\Delta\nu_{\text{OH}}$, of the associated phenolic hydroxyl band relative to the free band was observed. The measurements which were performed at two temperatures (20 and 50°C) were not sufficiently accurate to give reliable individual enthalpy and entropy data of the complexes. However, the main trend was that as the wave number shift, $\Delta\nu_{\text{OH}}$, of the complexes increased, a corresponding increase of the negative values of ΔH and ΔS was also observed. Such mutual compensation effects between ΔH and ΔS seem to be common phenomena.² As a first approximation the variation of ΔH and ΔS seemed to be linearly dependent on $\Delta\nu_{\text{OH}}$.^{1,11,12} Since the phosphoryl oxygen occupies a corner of the tetrahedrally shaped molecule, steric interaction was thought to be of minor importance for formation of the dimeric hydrogen bond complexes between phenol and phosphoryl compounds.

In the present paper the measurements of equilibrium constants of dimeric hydrogen bond complexes between phenol and phosphoryl compounds have been extended further. Several cyclic phosphorus esters and phosphine oxides have been included in the study. Reliable individual ΔH and ΔS data have been obtained from measurements of equilibrium constants at 5–10 temperatures in the interval between 20 and 70°C.

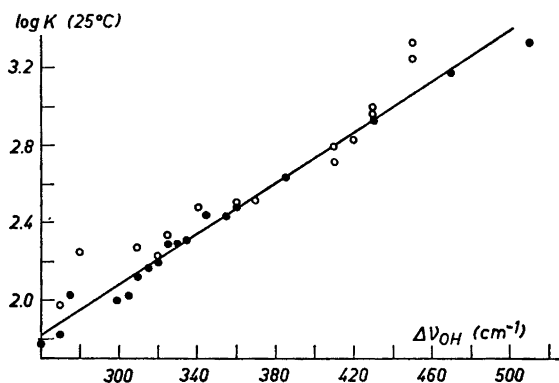


Fig. 1. Plot of $\log K$ for the hydrogen bond complexes between phenol and organic phosphoryl compounds as function of the wave number shift $\Delta\nu$ of phenol. Open circle: Data from this work (Table 1). Filled circle: Data calculated from previous work.¹

RESULT AND DISCUSSION

Data from the present study are summarized in Table 1. In Fig. 1 is plotted $\log K$ as function of $\Delta\nu_{OH}$ for phenol and 33 phosphoryl compounds. The filled circles are calculated from the aforementioned work of Aksnes and Gramstad.¹ The equilibrium constants which that time were calculated at 20° and 50°C are here interpolated to 25°C. The open circles in Fig. 1 are values obtained for compounds studied in this work. The general trend of distribution of the $\log K$ values is still fairly well described as a linear function of $\Delta\nu_{OH}$. However, it is clearly seen that several of the new compounds give a much poorer fit to the line than the previously studied compounds. This is especially so for phosphoryl compounds containing the phosphorus atom as part of a ring. Enthalpy values are plotted as function of $\Delta\nu_{OH}$ in

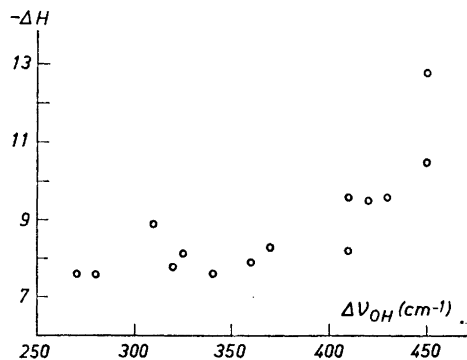


Fig. 2. Plot of ΔH of hydrogen bond complexes as function of $\Delta\nu_{OH}$ (from Table 1).

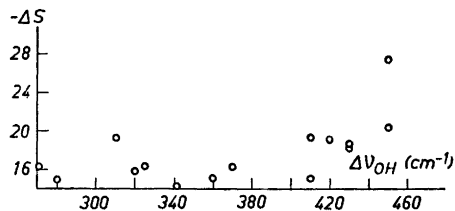


Fig. 3. Plot of ΔS of hydrogen bond complexes as function of $\Delta\nu_{OH}$ (from Table 1).

Table 1. Physical data for phosphoryl compounds and their dimeric hydrogen bond complexes with phenol in carbon tetrachloride.

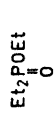

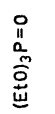
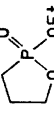
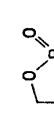
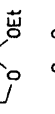
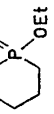
| Compound | b.p./mm Hg | n_D^{20} | $\nu_{P=O}$ cm ⁻¹ | $\Delta\nu_{P=O}$ | $\Delta\nu_{OH}$ | $-\Delta H$ kcal/mole | $-\Delta S$ e.u. | K_{ass} 25°C | $\log K_{ass}$ 25°C |
|--|------------|------------|---------------------------------|-------------------|------------------|--------------------------|---------------------|-------------------|------------------------|
| 1.  | 89/10 | 1.4321 | 1210 | 14 | 410 | 8.2 | 15.2 | 512.9 | 2.710 |
| 2.  | 35/0.5 | 1.4163 | 1231 1253 | 16 | 360 | 7.9 | 15.1 | 325.1 | 2.512 |
| 3.  | 106/16 | 1.4065 | 1267 1281 | 34 | 325 | 8.1 | 16.5 | 217.8 | 2.338 |
| 4.  | 128/10 | 1.4498 | 1247 1280 | 33 | 320 | 7.8 | 15.9 | 168.7 | 2.227 |
| 5.  | 100/0.5 | 1.4305 | 1301 | 20 | 270 | 7.6 | 16.3 | 95.7 | 1.981 |
| 6.  | 130/10 | 1.4585 | 1259 | 14 | 341 | 7.6 | 14.2 | 306.9 | 2.487 |
| 7.  | 120/0.7 | 1.4397 | 1308 | 18 | 280 | 7.6 | 15.0 | 180.7 | 2.257 |

Table 1. Continued.

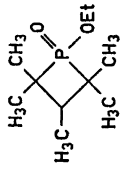


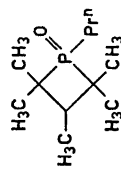
| | | | | | | | | | | |
|-----|---|------------------------|--------|------|----|-----|------|------|-------|-------|
| 8. |  | 70/0.5 | 1.4575 | 1214 | 14 | 370 | 8.3 | 16.4 | 331.1 | 2.520 |
| 9. | $\text{Ph}_3\text{P}=\text{O}$ | m.p. 160.5–161.0 | | 1205 | 25 | 410 | 9.6 | 19.4 | 626.6 | 2.797 |
| 10. | $\text{Ph}_2(\text{CH}_3)\text{P}=\text{O}$ | 113.0–114.0 | | 1205 | 25 | 420 | 9.5 | 19.2 | 682.3 | 2.834 |
| 11. | $\text{Ph}(\text{CH}_3)_2\text{P}=\text{O}$ | 119 | | 1204 | 18 | 430 | 9.6 | 18.7 | 909.9 | 2.959 |
| 12. | $\text{Bu}_3\text{P}=\text{O}$ | 157/10 b.p. | | 1175 | 24 | 430 | 9.6 | 18.5 | 1000 | 3.000 |
| 13. |  | 134.5 | | 1181 | 20 | 450 | 10.5 | 20.5 | 1758 | 3.245 |
| 14. |  | very hygroscopic solid | | 1185 | 19 | 450 | 12.8 | 27.7 | 2148 | 3.332 |
| 15. |  | 150 | | 1225 | 13 | 310 | 8.9 | 19.4 | 191.0 | 2.281 |

Fig. 2. It is obvious that a linear dependence between ΔH and $\Delta\nu_{\text{OH}}$ does not exist for the series of compounds studied. A similar picture is also obtained when ΔS is plotted as function of $\Delta\nu_{\text{OH}}$ (Fig. 3). The mutual compensation effect between ΔH and ΔS is clearly seen when the two functions are plotted against each other (Fig. 4).

Drago *et al.*¹⁰ have claimed that a linear dependence between the enthalpy and the wave number shift of the phenolic hydroxyl of different phenol-base complexes does exist. In a recent publication a theoretical justification for this relationship is attempted.¹¹ With reference to the present study of phosphoryl compounds, we feel inclined to question the validity of this Badger-Bauer¹² relationship. Since in the present case, the complexes between phenol and acceptors with a common acceptor group (P=O) cannot be fitted to a linear enthalpy wave number shift relationship, it seems unlikely that acceptors with different acceptor groups should behave otherwise.

With regard to the enthalpy values, the phosphoryl compounds studied can be classified as follows:

1. Phosphoryl compounds which beside the P=O group contain one, two, or three oxygen atoms linked to phosphorus (phosphinates, phosphonates, and phosphates) have enthalpy values in the region: -8.3 to -7.6 kcal.

2. Open chain phosphine oxides have ΔH values around -9.5 kcal.

3. Cyclic phosphine oxides show strong individual variations of the enthalpy values, from -8.9 kcal for the four-membered cyclic phosphine oxide to the exceptionally high value, -12.8 kcal, for the five-membered phospholane oxide.

The increase of ΔH of approximately 1.5 kcal from phosphinates to phosphine oxides is expected from the stronger polarity of the phosphoryl group in phosphine oxides.

The great individual variation of ΔH among the cyclic phosphine oxides is interesting. With regard to the four-membered phosphine oxide, its rather high P=O frequency, 1225 cm^{-1} , as well as the small hydroxyl shift upon hydrogen bonding with phenol, 310 cm^{-1} , points to steric hindrance of the hydrogen bond formation. The four methyl groups in α -positions in the ring with respect to phosphorus, makes the molecule almost spherical and may give rise to considerable shielding of the P=O group.

The exceptionally high ΔH value for the dimer between phospholane oxide and phenol (-12.8 kcal) points to an extraordinary strong hydrogen bond. But the entropy value is also low, -27.7 e.u., indicating a very restricted

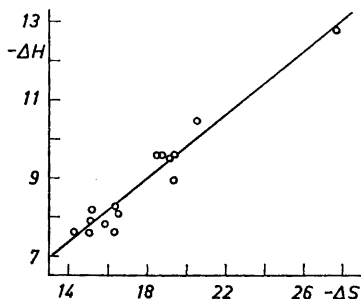
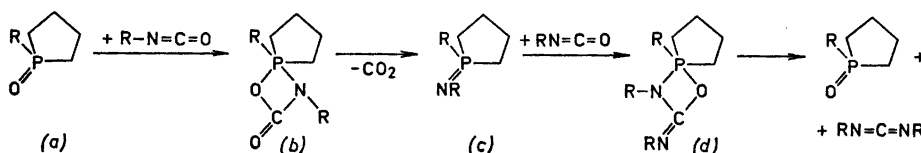


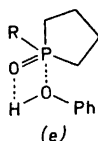
Fig. 4. Plot of ΔH against ΔS for hydrogen bond complexes (from Table 1).

complex. From a chemical point of view, the phospholane oxide is an especially interesting compound since it is known that many phospholane derivatives show exceptionally great reactivity in various reactions.³⁻⁵ With regard to phospholane oxides it is known that such compounds catalyze the transformation of isocyanates to carbodiimides at a rate 10^4 times higher than triphenyl phosphine oxide.⁶ Detailed kinetic as well as ^{18}O -exchange studies support the following reaction steps:



The strong catalytic effect of phospholane oxide as compared with other phosphine oxides should therefore be due to an easy formation of the intermediate or transition state (b) since this step is found to be rate determining. The reason for the easy formation of (b) may be sought in the small C—P—C angle of the phospholane ring (95° of the corresponding phosphonium salt⁷), which therefore might exert little resistance towards formation of the bipyramidal intermediate (b) where the C—P—C angle of the ring has to be 90° . A similar explanation has been given for the high reactivity of substitution reactions in various phospholane derivatives.^{4,5}

With regard to the hydrogen bond between phospholane oxide and phenol, its exceptionally high strength might be explained as caused by contribution from a four-center interaction where in addition to the H-bond, *d*-orbitals of phosphorus might also be involved in bonding with *p*-electrons of the phenolic oxygen atom, (e).



In comparison with a normal H-bond between the hydroxyl group and the phosphoryl oxygen atom, the four-center cyclic complex might thus give rise to an additional interaction energy. But a corresponding decrease of entropy is also expected due to the stronger restriction laid upon a four-center complex as compared with a two-center one.

EXPERIMENTAL

Materials. The solvent, carbon tetrachloride, was thoroughly dried over phosphorus pentoxide. The fraction boiling between 76.0 and 76.5°C was used.

The phenol was purified by sublimation *in vacuo*.

The organophosphorus compounds studied (Table 1) were made according to earlier descriptions.^{1,3,8,9} The liquid compounds were gas chromatographically purified, whereas the solid compounds were recrystallized several times until constant melting point.

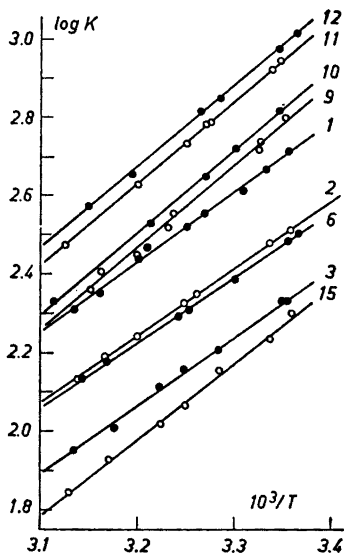


Fig. 5. Examples of the plot $\log K$ versus $1/T$ for dimeric hydrogen bond complexes between phenol and organic phosphoryl compounds in CCl_4 . The numbers in the figure refer to numbers in Table 1.

The phosphine oxides were sublimated *in vacuo*. The extremely hygroscopic phospholane oxide, compound No. 14, had to be handled in drying box.

Measurement. The association constants K were calculated from measurements of the intensity of the free hydroxyl band at 3611 cm^{-1} at 5–10 different temperatures. The concentrations of phenol and of phosphorus compounds in carbon tetrachloride were in the range 10^{-3} and 10^{-5} to 10^{-3} , respectively. In this concentration region self-association of phenol was not observed.¹ Infrared cells of 5 mm path length were used. The temperature was kept constant using a water jacket cell. The precise temperature was measured with a thermocouple connected to the front of the cell. The infrared spectra were recorded on a high resolution infrared spectrophotometer, Unicam SP-100, MK.2. The logarithms of the association constants are plotted as function of $1/T$ in Fig. 5. The estimated error in ΔH is ± 0.2 kcal.

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