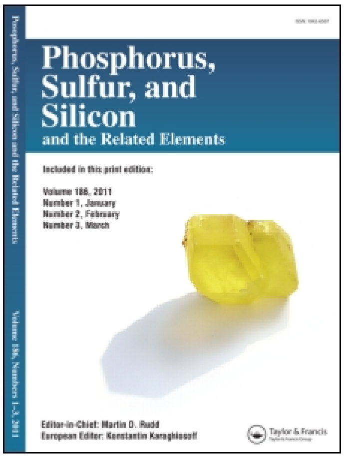

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

H / D ISOTOPIC EFFECT IN HYDROGEN BONDING IN SYSTEMS FORMED BY TERTIARY PHOSPHINES AND ALCOHOLS

Jürgen Mendel[a]; Alfred Kolbe[a]
[a] Sektion Chemie der Martin-Luther-Universität, Halle, DDR

To cite this Article Mendel, Jürgen and Kolbe, Alfred(1983) 'H / D ISOTOPIC EFFECT IN HYDROGEN BONDING IN SYSTEMS FORMED BY TERTIARY PHOSPHINES AND ALCOHOLS', Phosphorus, Sulfur, and Silicon and the Related Elements, 15: 3, 327 — 329

To link to this Article: DOI: 10.1080/03086648308073312

URL: http://dx.doi.org/10.1080/03086648308073312

Phosphorus and Sulfur, 1983, Vol. 15, pp. 327–329
0308-664X/83/1503-0327/$18.50/0

H / D ISOTOPIC EFFECT IN HYDROGEN BONDING IN SYSTEMS FORMED BY TERTIARY PHOSPHINES AND ALCOHOLS

JÜRGEN MENDEL and ALFRED KOLBE

Sektion Chemie der Martin-Luther-Universität, 402 Halle, DDR

(Received November 2nd, 1982; in final form December 27, 1982)

The infrared spectral properties of deuterium bonds have been investigated in systems formed by tertiary aliphatic phosphines and benzyl alcohol-OD and/or isopropanol-OD in toluene as a solvent. The results are to be compared with those obtained in analogous systems using the OH-alcohols. The equilibrium constants of the D bonds are always higher than those of the H bonds, but the association enthalpies are lower.

INTRODUCTION

In continuation of our studies[1] on isotope effects in hydrogen bonding we report here measurements on systems of O-deuteriated alcohols and tertiary phosphines. The experimental conditions employed have been discussed in an earlier paper.[2] In addition to the thermodynamic properties we have here focused on the behaviour of the associate OD band as a very sensitive indicator of association effects.

RESULTS AND DISCUSSION

Table Ia presents the relationships between the equilibrium constants K_H/K_D at 15°C (H or D means the bonding atom), K_D (15°), $-\Delta H$ (H or D bond enthalpy) in kJ/mole, and $-\Delta S$ (association entropy) in J/mole · degree when benzyl alcohol is used as the proton (or deuteron) donor. In the corresponding Table Ib isopropyl alcohol is used in the same role.

The principal conclusions to be deduced from these tables are the following: The quotients K_H/K_D at 15°C are less than unity in all cases. Furthermore the enthalpic effects on association are smaller with one exception using deuteriated alcohols. We have earlier obtained similar findings in systems containing tertiary amines as acceptors.[3] The system phosphabicyclononane-benzyl alcohol is the only exception, which shows a higher enthalpic effect using the deuteriated alcohol. However taking into account the smallness of the difference of the two ΔH values, the observed isotope effect may be assumed to be unity.

From these results it may be tentatively inferred, that the greater the bulkiness of the substituents the larger are the differences in both association enthalpy and equilibrium constant. This may be regarded an indication of the existence of a stereochemical term in the isotope effect, but, particularly in the case of i-Bu$_3$P, such a term cannot play an important role.

TABLE I

Thermodynamic values of the investigated systems
(a) donor: Benzyl alcohol

Acceptor	K_D (15°)	K_H/K_D (15°)	ΔH_{OH}	ΔH_{OD}	ΔS_{OH}	ΔS_{OD}
Et_3P	1.2	0.98	13.1	10.2	44.0	34.3
n-$Prop_3P$	1.5	0.90	9.6	7.2	30.9	21.6
i-$Prop_3P$	4.6	0.59	11.4	8.9	30.9	18.6
n-Bu_3P	2.4	0.87	10.2	7.6	29.2	18.2
i-Bu_3P	1.7	0.82	9.3	8.0	28.3	18.6
sec-Bu_3P	15.2	0.55	14.8	8.9	33.4	8.5
i-$Amyl_3P$	3.2	0.67	12.7	8.5	37.6	22.8
C-hex_3P	9.0	0.61	14.4	10.2	36.0	16.5
EtC-hex_2P	3.9	0.70	11.8	9.3	33.0	21.6
Et_2C-hexP	3.0	0.72	10.6	8.9	30.9	22.0
Et_2PhP	0.8	0.88	7.6	4.7	28.3	17.8
Phosphabicyclo-[3.3.1]-nonane	1.8	0.90	8.5	9.7	27.9	30.9
(b) donor: Isopropyl alcohol						
Et_3P	1.0	0.69	8.5	8.0	32.1	27.5
sec-Bu_3P	6.7	0.45	12.7	11.0	35.5	17.3
i-$Amyl_3P$	2.2	0.58	10.6	8.9	31.3	23.7

Inspection of the behaviour of the deuteriated systems does not reveal a clear relationship between the $\Delta\nu$ values of the OD band and the thermodynamic parameters. In the case of the benzyl alcohol systems, in which all values have been obtained with phosphines of exclusive, aliphatic substitution, all the shifts encompass values between 156 cm^{-1} (*n*-$Prop_3P$) and 188 cm^{-1} (C-hex_3P). In terms of the Badger–Bauer rule,[4] the differences in ΔH are much higher than can be expected on the basis of such small differences of the shifts. This also may be an indication of the steric factors mentioned above.

The temperature dependence of $\Delta\nu_{OD}$ appears to be about the same as that of the $\Delta\nu_{OH}$ for the undeuteriated benzyl alcohol. It should be mentioned that, in spite of the lower $\Delta\nu_{OD}$ (compared with $\Delta\nu_{OH}$), the same order of magnitude of the values of $\Delta\Delta\nu_{OD(T_1, T_2)}$ is indicative of the lower strength of the deuterium bond, as we have pointed out previously.[5] Table IIa summarizes the relationships between $\Delta\nu_{OH}/\nu_{OH} \cdot 100$ and $\Delta\nu_{OD}/\nu_{OD} \cdot 100$ for benzyl alcohol. Analogous values using isopropyl alcohol as donor are listed in Table IIb. Moreover, it is to be noted that in the case of the latter alcohol a linear relationship between ΔH and $\Delta\nu_{OD}$ does not exist.

The optical densities of the association bands in the case of O-deuteriated alcohols have also received some consideration. The extinction coefficients of these bands are about three times lower in the case of the deuteriated alcohols than in the normal alcohols. Concurrently, in the temperature range under investigation the extinction coefficients of the association bands of the deuterium bonded systems show remarkably smaller increases of intensity with decreasing temperature than those of the proton bonded systems.

In summary, it is difficult to discuss the origins of the isotope effects in H-bonding to phosphorus since all the acceptors used are substituted by three alkyl

TABLE II

Shifts of the associate OD (or OH) band
(a) donor: Benzyl alcohol

Acceptor	$\Delta\nu_{OD}$ cm^{-1}	$\Delta\nu_{OD}/\nu_{OD} \cdot 100$	$\Delta\nu_{OH}/\nu_{OH} \cdot 100$
Et_3P	165	6.23	7.25
n-$Prop_3P$	156	5.89	7.14
i-$Prop_3P$	174	6.57	7.19
n-Bu_3P	158	5.96	6.61
i-Bu_3P	160	6.04	7.39
sec-Bu_3P	172	6.49	7.25
i-$Amyl_3P$	161	6.08	6.72
C-hex_3P	188	7.10	8.11
EtC-hex_2P	168	6.34	7.33
Et_2C-hexP	170	6.42	7.13
(b) donor: Isopropyl alcohol			
Et_3P	132	4.97	
sec-Bu_3P	145	5.46	6.01
i-$Amyl_3P$	141	5.31	5.82

groups and the differences in their basicities are rather small. They amount only to about 10 percent in pK_a units. Following theoretical considerations, differences between H bonds and D bonds should be deduced from the differences in zero point energy. We cannot estimate, however, whether in such complicated systems containing a solvent like toluene, zero point calculations would be capable of deducing the effects measured. From a more intuitive point of view, these effects may be due to the higher polarity and strength of the OH bond and to the greater length of the OD bonds of the alcohols, which is responsible for the higher equilibrium constants for deuterium bonding, possibly arising from differences in steric accessibility to the phosphorus center.

ACKNOWLEDGMENT

We are very indebted to Dr. J. Shorter and to Prof. H. Kwart for making suggestions for the preparation of this manuscript and to Prof. K. Issleib for his interest in this work.

REFERENCES

1. A. Kolbe, *Tetrahedron Lett.*, 1049 (1969).
2. J. Mendel and A. Kolbe, *Phosphorus and Sulfur*, **3**, 21 (1977).
3. J. Mendel, A. Mögel and A. Kolbe, in preparation for *Adv. Mol. Rel. Int. Proc.*
4. R. M. Badger and S. H. Bauer *J. Chem. Phys.*, **5**, 839 (1937).
5. J. Mendel, A. Mögel and A. Kolbe, *Adv. Mol. Rel. Int. Proc.*, **11**, 9 (1977).