

# DEUTERIUM ISOTOPE EFFECTS ON HYDROGEN BONDING<sup>1</sup>

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## ABSTRACT

The interaction of phenol and phenol-*d* with a number of donors of varying basicity has been studied in terms of the equilibrium constants,  $\Delta S^\circ$ ,  $\Delta H^\circ$ ,  $\Delta\nu_{\text{OH}}$ , and  $\Delta\nu_{\text{OD}}$  and various aspects of deuterium isotope effects on hydrogen bonding have been discussed. The deuterium isotope effects are found to vary markedly with the basicity of the donor and the results are discussed in terms of the zero point contributions to the  $K_{\text{H}}/K_{\text{D}}$ .

## INTRODUCTION

While isotope effects on chemical equilibria and kinetics have been reported in a variety of systems in the literature, information on deuterium isotope effects on hydrogen bonding,  $\text{XH}\dots\text{Y}$ , is limited. Bellamy and Rogasch (1) and Dahlgram and Long (2) have reported that deuterium bonds are comparatively weaker than the hydrogen bonds. Josien and co-workers (3) as well as Creswell and Allred (4) have found higher values of the equilibrium constants and the enthalpy and entropy changes for deuterium bonds in alcohols-hexamethylbenzene and fluoroform-tetrahydrofuran systems. Literature data (5) on self-association, however, show lower values of equilibrium constants and enthalpies for deuterium bonds.

In the models for proton transfer reactions, Westheimer (6) and Bigeleisen (7) have considered the importance of the symmetric stretching frequencies of  $\text{X}\dots\text{Y}$  in describing deuterium isotope effects. Recent work of Bader (8) has shown the possible importance of bending modes as well. We have now examined deuterium isotope effects on the thermodynamics ( $K$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$ ) of hydrogen bonding equilibria as well as the frequency shifts of the stretching vibrations for the interaction of phenol with a number of donors,  $\text{Y}$ , of varying basicity. The dependence of isotope effects on the basicity of the donors was expected to throw some light on the importance of various zero point contributions to  $K_{\text{H}}/K_{\text{D}}$ .

## EXPERIMENTAL

All the chemicals, with the exception of tetra-*n*-heptylammonium iodide and tetramethylthiourea, were commercially available and were purified before use. Tetraheptylammonium iodide was kindly provided by Professor P. V. R. Schleyer and tetramethylthiourea by Dr. M. J. Janssen. Deuterated phenol,  $\text{C}_6\text{H}_5\text{OD}$ , was prepared by repeated exchange of phenol with  $\text{D}_2\text{O}$  (supplied by Atomic Energy Establishment, Bombay). The exchange was found to be 80% by measurement of the intensity of the free OH stretching band at different concentrations as well as by quantitative estimation of the  $\text{D}_2\text{O}$  content of the water obtained by the combustion of the sample.

Infrared measurements in the OH and OD stretching regions were obtained with a Carl-Zeiss UR-10 spectrophotometer with LiF optics. The equilibrium constants of hydrogen bond formation were calculated using the expression similar to that of Becker (9) and the uncertainties in  $K$  are within  $\pm 10\%$ . The optical densities of the monomer OH and OD bands in phenol and phenol-*d* solutions (solvent,  $\text{CCl}_4$ ; concentration  $\sim 0.007 M$ ) and in their solution with different donors of known concentration were measured in the overtone region using a Cary-14R spectrophotometer fitted with variable temperature cells (path length 10 cm). From the data on equilibrium constants at three temperatures (in the range 5–45 °C with an uncertainty in temperature of  $\pm 1$  °C) the enthalpy of hydrogen bond formation was calculated. The uncertainty in enthalpy values was  $\pm 0.5 \text{ kcal mole}^{-1}$ . The uncertainty in frequency shifts ( $\Delta\nu_{\text{OH}}$  and  $\Delta\nu_{\text{OD}}$ ) was  $\pm 5 \text{ cm}^{-1}$ .

<sup>1</sup>Taken in part from the Ph.D. thesis of S. Singh to be submitted to the Indian Institute of Technology.

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The experimental procedure and details of the method of evaluation of the equilibrium constants have been discussed in other publications from this laboratory (10).

### RESULTS AND DISCUSSION

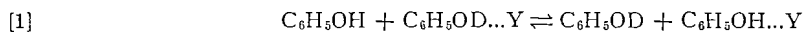
Thermodynamic data on the interaction of phenol and phenol-*d* with donors have been summarized in Table I along with the frequency shifts of the OH and OD stretching vibration bands,  $\Delta\nu_{\text{OH}}$  and  $\Delta\nu_{\text{OD}}$ . It can be seen that the enthalpy of formation of 1:1 complexes is always greater in the case of hydrogen bonding than in deuterium bonding. This may be due to the longer O...Y distance in the deuterated species. The overlap in the hydrogen bond is expected to be greater than in the deuterium bond (11) and crystals containing deuterium bonds often show expansion of the unit cell (12, 13). Rightly enough, it has been pointed out that the barrier height in the double minimum potential (14) for the transfer of deuterium would be higher than for proton transfer due to the lower zero point energy of the O—D bond (15, 16).

The ratio of the equilibrium constants,  $K_{\text{H}}/K_{\text{D}}$ , is found to vary from donor to donor (Table I) and there appears to be no rule that the ratio be greater than unity. The results of this study show that the varied values of  $K_{\text{H}}/K_{\text{D}}$  in the literature probably are all valid and that  $K_{\text{H}}/K_{\text{D}}$  is a function of the basicity of the donor. The entropy change  $\Delta S^0$  is, however, always greater for the deuterium bonds than for the hydrogen bonds. The variation in equilibrium constants has to be interpreted in terms of the contributions from both the  $\Delta H^0$  and  $\Delta S^0$  since  $\Delta F^0 = -RT \ln K = \Delta H^0 - T\Delta S^0$ .

The frequency shift,  $\Delta\nu_{\text{OH}}$ , is always greater than  $\Delta\nu_{\text{OD}}$ . While this is in line with the earlier observation that  $\Delta H^0_{\text{OH}\dots\text{Y}}$  is greater than  $\Delta H^0_{\text{OD}\dots\text{Y}}$ , the  $\Delta\nu_{\text{OH}}$  and  $\Delta\nu_{\text{OD}}$  do not show any simple linear relation with the  $\Delta H^0$  values. This is not unexpected since the linearity between  $\Delta\nu_{\text{OH}}$  and  $\Delta H^0$  holds good only in a limited range of  $\Delta H^0$  (or  $R_{\text{O}\dots\text{Y}}$ ) for the interaction of the same acceptor (proton donor) with donors of comparable basicity (ionization potential) (10). It should also be pointed out that  $\Delta\nu_{\text{OH}}$  or  $\Delta\nu_{\text{OD}}$  is determined by the barrier height in the double minimum potential and is not strictly related to the  $\Delta H^0$ . It is quite conceivable to have a situation where the barrier height (or  $\Delta\nu$ ) varies with little or no variation in  $R_{\text{X}\dots\text{Y}}$  (or  $\Delta H^0$ ) (10).

Since the theories of Westheimer, Bigeleisen, and Bader on isotope effects refer to rate processes, they cannot be applied to the equilibrium data reported in this study. The isotope exchange equilibrium constant can, however, be estimated fairly accurately by employing the expression from statistical thermodynamics in terms of partition functions.

By neglecting all the factors in the partition functions other than the zero point energy contributions, one can write the expression for  $K_{\text{H}}/K_{\text{D}}$  for the equilibrium exchange reaction,



$$[2] \quad K_{\text{H}}/K_{\text{D}} = \exp -(\sum \Delta\nu_{\text{XHY}} + \sum \Delta\nu_{\text{XH}})/2kT,$$

where  $\Delta\nu = \nu_{\text{H}} - \nu_{\text{D}}$  and the subscript XHY and XH refer to the hydrogen-bonded species and the free X—H monomer respectively. The sum in each case is over all the vibrations affected by isotopic substitution. In the case of the free monomer, these vibrations are the  $\nu_{\text{OH}}$ ,  $\delta_{\text{OH}}$ , and  $\gamma_{\text{OH}}$ , and in the bonded species, the  $\nu_{\text{OH}}$  is reduced appreciably from the monomer value. On hydrogen bonding  $\delta_{\text{OH}}$  increases a little while  $\gamma_{\text{OH}}$  increases markedly. By using  $\Delta'$  to denote the difference  $\nu_{\text{H}} - \nu_{\text{D}}$  and  $\Delta$  to denote the frequency change on hydrogen bonding, eq. [2] can be rewritten as

$$[3] \quad 2kT \ln (K_{\text{H}}/K_{\text{D}}) = -\Delta\Delta'\nu_{\text{OH}} - \Delta\Delta'\delta_{\text{OH}} - \Delta\Delta'\gamma_{\text{OH}}$$

TABLE I  
Thermodynamic data\* on the hydrogen and deuterium bond formation with different donors

Donors	$I_i$ eV†	Phenol-d						Phenol					
		$K_D$		$-\Delta H^0$	$\Delta S^0$	$\Delta\nu_{OD}$	$K_H$	$K_H$		$-\Delta H^0$	$-\Delta S^0$	$\Delta\nu_{OH}$	$K_H/K_D$
		25 °C	40 °C					25 °C	40 °C				
1. $(n-C_7H_{15})_4N^+I^-$	6.0±1‡	89	78.4	1.5	4.0	225	382	239	5.9	8.0	380	4.3	
2. $(C_2H_5)_3N$	7.5	32	23.7	2.7	-2.0	180	58	27.6	9.2	22.0	450	1.8	
3. $(C_6H_5)_3P$	8.02	5.6	5	1.1	0.0	230	6	5.4	1.3	0.8	360	1.1	
4. $[(CH_3)_2N]_2C=S$	8.12	16.5	15	1.1	2.0	220	14	10.5	3.1	5.0	310	0.8	
5. $C_6H_5OH(D)\S$	8.5	3.2	2.8	1.6	-3.0	80	0.74	0.5	5.1	18	120	0.2	
6. $(CH_3)_2C=O$	9.69	27	25	0.8	3.7	150	14	8.7	4.5	10	210	0.5	
7. $C_5H_5N$	9.85	33	30	1.1	3.3	310	41	20	9.0	23	475	1.2	
8. $CH_3CN$	12.39	7.2	6.8	0.6	2.0	100	5	38	2.3	8	160	0.7	

\*Solvent is  $CCl_4$ ;  $K$  in l mole<sup>-1</sup>;  $\Delta H^0$  in kcal mole<sup>-1</sup>;  $\Delta S^0$  in e.u. at 25 °C;  $\Delta\nu_{OD}$  and  $\Delta\nu_{OH}$  in cm<sup>-1</sup>.

†Values of ionization potentials were taken from refs. 17-20.

‡The value of ionization potential of tetraethylammonium iodide was estimated to be  $6 \pm 1$  eV from the electronic spectrum of alkali iodide (21). The ionization potential of free I<sup>-</sup> is, however, equal to minus the electron affinity of free iodine atom (3.2 eV).

§Data for dimerization.

In eq. [3]

$$\Delta\Delta'\nu_{\text{OH}} = [\nu_{\text{OH}(\text{XHY})} - \nu_{\text{OD}(\text{XDY})}] - [\nu_{\text{OH}(\text{XH})} - \nu_{\text{OD}(\text{XD})}]$$

and  $\Delta\Delta'\nu_{\text{OH}}$  is negative since  $\nu_{\text{OH}}$  decreases on hydrogen bonding. The terms  $\Delta\Delta'\delta_{\text{OH}}$  and  $\Delta\Delta'\gamma_{\text{OH}}$  are both positive since  $\delta_{\text{OH}}$  and  $\gamma_{\text{OH}}$  increase on hydrogen bonding. Further, when  $K_{\text{H}}/K_{\text{D}} > 1$  the proton is more tightly bound in the monomer, and when  $K_{\text{H}}/K_{\text{D}} < 1$  it is more tightly bound in the complex. The deuterium is always concentrated in the species which has the largest zero point energy difference. Since only data on  $\nu_{\text{OH}}$  have been obtained in the present study, it is not possible to discuss all the major zero point contributions; but the observed isotope effects can be understood in terms of the known isotope effects on the three vibrations discussed earlier.

If the isotope effects in terms of  $K_{\text{H}}/K_{\text{D}}$ ,  $\Delta H^0_{\text{OH}\dots\text{Y}}/\Delta H^0_{\text{OD}\dots\text{Y}}$  or  $\Delta\nu_{\text{OH}}/\Delta\nu_{\text{OD}}$ , are plotted against the ionization potentials of the donors (as measures of basicities), the plots show minima around 8.5 eV. It is difficult to rationalize the observation of these minima. The minima are likely to be fallacious since ionization potentials are probably not good measures of base strengths. On the other hand one may be justified in using  $\Delta\nu_{\text{OH}}$  or  $\Delta H^0_{\text{OH}\dots\text{Y}}$  as the measure of base strengths of the donors (10a).

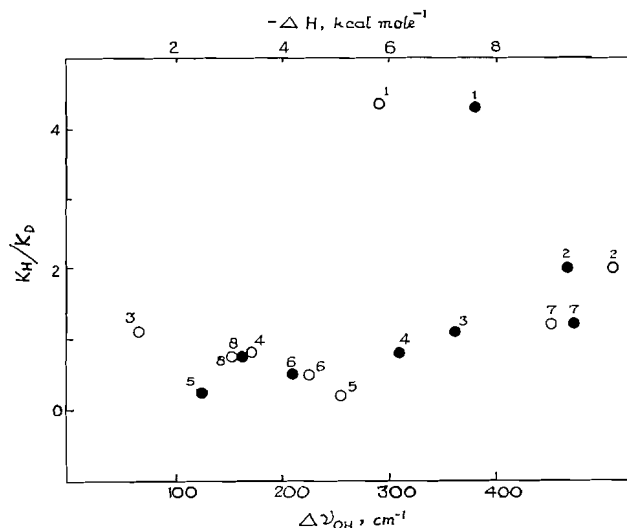


FIG. 1. Correlation of equilibrium isotope effect in hydrogen bonding with base strengths (in terms of  $\Delta\nu_{\text{OH}}$  and enthalpies of formation of hydrogen bonds). O,  $K_{\text{H}}/K_{\text{D}}$  vs.  $\Delta H^0$ ; ●,  $K_{\text{H}}/K_{\text{D}}$  vs.  $\Delta\nu_{\text{OH}}$ .

A plot of  $K_{\text{H}}/K_{\text{D}}$  against  $\Delta\nu_{\text{OH}}$  or  $\Delta H^0_{\text{OH}\dots\text{Y}}$ , Fig. 1, shows that some proportionality exists (with the exception of the charged donor  $(\text{C}_7\text{H}_{15})_4\text{N}^+\text{I}^-$  which falls out of line) between these quantities. This appears to be reasonable; as the hydrogen bond becomes stronger, the  $\nu_{\text{OH}}$  is decreased and the  $\gamma_{\text{OH}}$  is increased. Apparently, for weak bases, the increase in  $\gamma_{\text{OH}}$  is greater than the decrease in  $\nu_{\text{OH}}$  and the converse is true for the stronger bases. The positive slopes of the plots in Fig. 1 indicate that the proton is more tightly bonded in the free acid than in the hydrogen-bonded complex. This is indeed a new and interesting result, which needs to be examined more carefully by theory and further experimentation.

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## REFERENCES

1. L. J. BELLAMY and P. F. ROGASCH. Proc. Roy. Soc. London, Ser. A, **257**, 98 (1960).
2. G. DAHLGRAM and F. A. LONG. J. Am. Chem. Soc. **82**, 1303 (1960).
3. J. P. LERCKMAN, J. LASCOMBE, and M. L. JOSIEN. Proc. Intern. Conf. Mol. Spectry. 4th Bologna, 1959, **2**, 858 (1962).
4. C. J. CRESWELL and A. L. ALLRED. J. Am. Chem. Soc. **84**, 3966 (1962).
5. G. C. PIMENTEL and A. L. McCLELLAN. The hydrogen bond. W. H. Freeman & Co., San Francisco, 1960.
6. F. H. WESTHEIMER. Chem. Rev. **61**, 265 (1961).
7. J. BIGELEISEN. Paper presented at the I.A.E.A. Symposium, Vienna, Austria, 1963. S.M. 50/24.
8. R. F. W. BADER. Can. J. Chem. **42**, 1822 (1964).
9. E. D. BECKER. Spectrochim. Acta, **17**, 436 (1961).
10. (a) S. SINGH, A. S. N. MURTHY, and C. N. R. RAO. Trans. Faraday Soc. **62**, 1056 (1966).  
(b) S. SINGH and C. N. R. RAO. J. Am. Chem. Soc. **88**, 2142 (1966).
11. A. R. UBBELONDE and K. J. GALLAGHER. Acta Cryst. **8**, 11 (1955).
12. R. E. RUNDLE. J. Chem. Phys. **21**, 937 (1953).
13. C. E. NORDMAN and W. N. LIPSCOMB. J. Chem. Phys. **19**, 1422 (1951).
14. E. R. LIPPINCOTT and R. SCHROEDER. J. Phys. Chem. **61**, 921 (1957).
15. C. G. CANNON. Spectrochim. Acta, **10**, 341 (1958).
16. N. D. SOKOLOV. Opt. Spectry. USSR English Transl. **11**, 8 (1961).
17. A. STREITWEISER, JR. In Progress in physical organic chemistry. Vol. I. John Wiley & Sons, Inc., New York, 1964.
18. K. R. BHASKAR, S. N. BHAT, S. SINGH, and C. N. R. RAO. J. Inorg. Nucl. Chem. **28** (1966). In press.
19. K. R. BHASKAR, R. K. GOSAVI, and C. N. R. RAO. Trans. Faraday Soc. **62**, 29 (1966).
20. J. D. MORRISON and J. C. NICHOLSON. J. Chem. Phys. **20**, 1021 (1952).
21. J. FRANK, H. KUHEN, and G. ROLLEFSON. Z. Physik, **43**, 155 (1927).