Hydrogen isotope fractionation between methanol and diphenylphosphine or dimethylphosphine in the gas phase and in aprotic solvents

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Abstract: D/H fractionation factors between MeOH and Ph_2PH in dilute solutions of tetrachloroethylene, benzene, tetrahydrofuran, pyridine, and acetonitrile and T/H fractionation factors between MeOH and Me_2PH vapors were measured. The experimental results agree very well with values calculated from the statistical theory of isotope effects formulated by Bigeleisen and Mayer. There are correlations between observed fractionation factors and solvent polarity, and the interaction energy of methanol with the given solvent. Another correlation has been found between enthalpy of the exchange reactions and the interaction energy between methanol and the given solvent.

Key words: isotope effects, fractionation factor, diphenylphosphine, methanol.

Résumé : On a mesuré les facteurs de fractionnement D/H entre le MeOH et le PH_2PH, dans des solutions diluées de tétrachloroéthylène, de benzène, de tétrahydrofurane, de pyridine et d'acétonitrile, ainsi que les facteurs de fractionnement T/H entre les vapeurs de MeOH et de Me_2PH. Les résultats expérimentaux sont en bon accord avec les valeurs calculées sur la base de la théorie statistique des effets isotopiques formulée par Bigeleisen et Mayer. Il existe des corrélations entre les facteurs de fractionnement observés et les polarités des solvants ainsi que l'énergie d'interaction du méthanol avec un solvant donné. On a aussi observé une corrélation entre l'enthalpie des réactions d'échange et l'énergie d'interaction entre le méthanol et le solvant donné.

Mots clés : effets isotopiques, facteur de fractionnement, diphénylphosphine, méthanol.

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Introduction

A knowledge of tritium/protium or deuterium/protium fractionation factors in H-exchanging systems is an important aid to understanding the mechanism of chemical and biochemical reactions, and the effects of molecular structure and intermolecular interactions (1–4). A great deal of interest has been devoted to the determination of the D/H fractionation between compounds with exchangeable H-atoms and protic solvents (3, 4). Hydrogen isotope partitioning between chemical species dissolved in aprotic solvents has been less thoroughly studied (4). A cardinal rule in the theory of isotope effects is that isotope substitution does not change the force field (5). On the other hand it is clear that change of aprotic solvents will modify the force field and lead to differences in the zero-point energy (ZPE) of H-isotope exchanging molecules. It is interesting to ask just which physicochemical properties of aprotic solvents determine isotope fractionation.

Phosphines interact very weakly with their environment (6) and this simplifies further discussion. For the present study we chose the alcohol–phosphine system and have studied H/D fractionation between diphenylphosphine (DPP) and methanol (MA) in benzene, tetrachloroethylene, tetrahydrofuran, pyridine, and acetonitrile. Due to the very low vapor pressure of DPP, gas phase exchange reactions with methanol could not be carried out. Instead, the exchange of tritium between dimethylphosphine (DMP) and MA vapors has been studied. The high sensitivity of the radiometric determination of tritium makes such measurements possible even at low vapor pressure. This system forms a convenient reference as well.

Experimental

Hydrogen exchange reaction in the gas phase can be conveniently carried out by using tritium together with appropriate radiometric detection techniques (7). DMP was prepared by a two-step protonation–methylation reaction starting from phosphine (8). Tritium-labelled DMP was synthesized by exchange of Me_2PH with KOH* in $H_2O(T)$ (9).[4] DMP* and MA were dried and degassed. The exchange experiments were

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[4] The asterisk denotes tritium labelling.

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carried out in the same manner as for CH_3OH and H_2S vapors (7). In all experiments the ratio of the partial vapor pressure of DMP to MA was kept equal to 1.5. The total pressure was always smaller than the saturated vapor pressure of any of the components at the given temperature. The radioactivity of DMP was measured in the internal GM gas counter (7) with a standard deviation of ±1.5%.

Most H/D exchange experiments employed an NMR technique. MeOD (product of Isotope Distribution Center, 99.75% of D), Ph_2PH (Aldrich product), and solvents were carefully dried and degassed. The samples were sealed in NMR tubes. Concentrations of the solutions, in which D-exchange between DPP and MA was studied, was about 1 mol/dm^3. All operations were carried out in a glove box in a dry nitrogen atmosphere. The ^1H spectra were recorded by a JEOL Co FX 90Q spectrometer equipped with a temperature probe. The PH (doublet at 5.08 ppm, $^1J_{PH} = 216$ Hz) (10) and OH signals were observed separately. All NMR conditions for quantitative determination of the I^{PH}/I^{OH} ratio were fulfilled[10] ("I" is an integrated intensity of the signal). The reproducibility of the I^{PH}/I^{OH} was better than 1%. Temperature was determined to better than ±0.5°C.

The tritium fractionation factor for the gas phase reaction:

$$[1] \quad MeOH(v) + Me_2PH^*(v) = MeOH^*(v) + Me_2PH(v)$$

is calculated from the equation:

$$[2] \quad \alpha^T_{MA/DMP}(v) = A^{MA}_{\infty}/A^{DMP}_{\infty}$$

where A_{∞} denotes specific tritium radioactivity at isotope equilibrium. Because only A^{DMP}_0 and A^{DMP}_{∞} were measured, A^{MA}_{∞} was determined from the isotope balance relation (7).

The deuterium fractionation factors for the reaction:

$$[3] \quad MeOD(s) + Ph_2PH(s) = MeOH(s) + Ph_2PD(s)$$

are defined as

$$[4] \quad \alpha^D_{MA/DPP}(s) = (m_D/m_H)/(n_D/n_H)$$

where m and n are the numbers of moles of MA and DPP, respectively; subscripts H and D refer to H and D isotopomers at isotope equilibrium. For the exchange process studied we can define the following material and isotope balance relations: (I) $m = m_H + m_D$, (II) $n = n_H + n_D$, (III) $m_H = n_D$, and (IV) $I^{OH}/m_H = I^{PH}/n_H$. Relation (III) is valid in the present case because the exchange reactions are carried out with fully deuterated methanol (CH_3OD). Starting from eq. [4] and using the above relations, in a few successive steps m_D, m_H, n_D, and n_H can be eliminated. At first, n_D is eliminated by using relation (III), then the use of (IV) eliminates m_H, and in the next step using (I) we eliminate m_D. Finally, defining $n_H = nI^{PH}n/(I^{OH} + I^{PH})$ from (II), (III), and (IV), we obtain eq. [5] expressed in the experimentally measured values only:

$$[5] \quad \alpha^D_{MA/DPP}(s) = \left(\frac{I_{PH}}{I_{OH}}\right)\left(\frac{m\,I_{PH}}{n\,I_{OH}} + \frac{m-n}{n}\right)$$

m and n are as defined above and $I^{PH(OH)}$ denotes the integrated intensities of the PH(OH) hydrogen signals. The standard deviation of α^D was ±1%.

Calculations

It is interesting to compare the experimental fractionation factor with the theoretical value expressed in terms of the reduced partition function ratio (RPFR), $(s/s')f$ (5):

$$[6] \quad \alpha^D = (s/s')f_{MA}/(s/s')f_{DPP}$$

RPFR is given by the equation:

$$[7] \quad (s/s')f = \prod \frac{u_i}{u_i'}\,\frac{1-\exp(-u_i')}{1-\exp(-u_i)}\exp\frac{u_i'-u_i}{2}$$

where $u_i = hc\omega_i/kT$, and ω_i are the normal mode vibrational frequencies; the prime refers to the light isotopic molecule.

The calculation of the fractionation factor for the exchange between methanol and DPP in solution encounters certain difficulties. To begin with, the vibrational spectra of liquid MA are complex due to strong hydrogen bonding, and spectral data for methanol in the solvents of interest are incomplete. To our best knowledge there are no vibrational data for DPP. On the other hand, gas phase vibrational data for both methanol and DMP are available. The gas phase spectra of MeOH/MeOD reported by Serralah, Mayer, and Gunthard (11) have been used for the calculation of $(s/s')f_{MeOH}(v)$ (7). The gas phase spectra of Me_2PH were studied by Durig and Saunders (12) and those of Me_2PD by Clark and Drake (13). However, the assignments proposed by both sets of authors are doubtful. A better assignment, confirmed by a subsequent force field calculation, was given by McKean and McQuillan (14). Their data were used in our calculation of $(s/s')f_{DMP}(v)$.

Results and discussion

The experimental fractionation factors of deuterium and tritium over the temperature range of 283–330 K are collected in Table 1. Calculated values are also presented in Table 1. The experimental points deviate by 1–1.5% from the calculated ones. The fractionation factor, $\alpha_{MA/DPP}$, was used as the reference point for discussion of isotope fractionation in solution. It is equal to the ratio of $\alpha_{MA/DMP}(v)/\alpha_{DPP/DMP}(v)$ in which experimental values of $\alpha_{MA/DMP}(v)$ and the estimated D/H fractionation factor between DPP and DMP, $\alpha_{DPP/DMP} = 0.98$, at 250–330 K have been used. In addition, for greater completeness, the fractionation factors between liquid MA and DPP determined earlier (9) have also been included.

For all systems studied the fractionation factors are much larger than unity, which means that deuterium(tritium) accumulates in the hydroxyl group of methanol regardless of its solvation character. There is relatively little change between gas phase and solution values. The temperature dependence of the fractionation factors between methanol and diphenylphosphine in gas and in solution is shown in Fig. 1. The fractionation factors decrease regularly on going from gas to acetonitrile. In every case the temperature dependence can be described by a simple linear relation,

Table 1. Experimental fractionation factors of deuterium in exchange reaction between diphenylphosphine and methanol in various solvents.

	Fractionation factor α for MA/DPP system								
T/K	v^*	v^{**}	v^{***}	l/l	TCE	Benzene	THF	Pyr	ACN
250.0	2.42	—	—	2.28	2.48	—	2.35	2.30_5	2.24
273.0	—	—	—	2.16_5	—	—	—	—	—
283.0	2.22	2.23 (3.15)	2.28	—	2.25	2.20_5	2.16	2.12_5	2.07
298.0	2.16	2.16_5(3.03)	2.21_5	2.03	2.18_5	2.14	2.10	2.07	2.01_5
303.0	—	—	—	2.00	—	—	—	—	—
312.0	2.09	2.08_5(2.90)	2.14	—	2.11_5	2.07_5	2.04	2.01	1.96
329.0	2.04	2.03 (2.80)	2.08	—	2.05	2.02_5	1.99	1.96_5	1.92

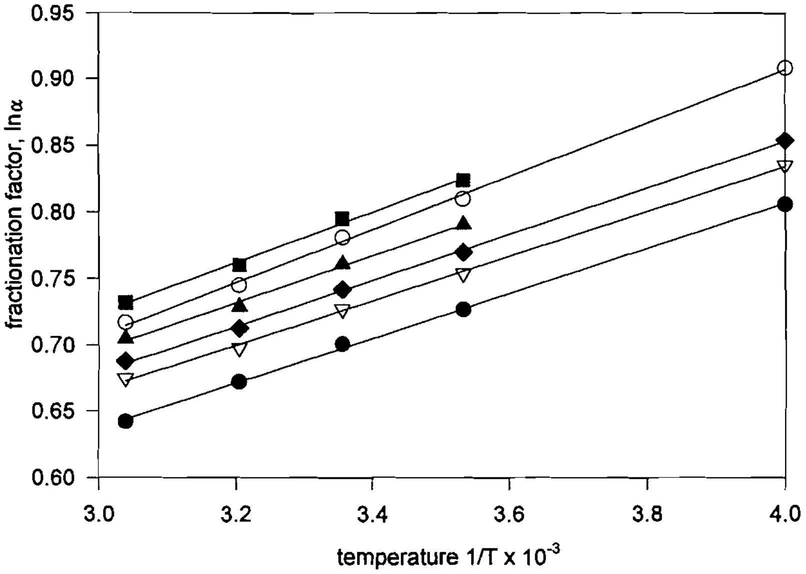
v^*: calculated values for MA/DMP system using eqs. [6] and [7].

v^{**}: recalculated from the experimental gas phase tritium fractionation factor for the MA/DMP system (in parentheses) using the Swain–Bigeleisen relation (refs. 29, 30) with the exponent 1.42.

v^{***}: gas phase deuterium fractionation factor for the MA/DPP system calculated from tritium fractionation factor.

l/l: deuterium fractionation factor in pure liquid MA/DPP system (ref. 9).

Fig. 1. Temperature dependence of the experimental fractionation factor in isotope exchange reaction of diphenylphosphine with methanol in various solvents (■ gas phase; ○ tetrachlorethylene; ▲ benzene; ◆ tetrahydrofuran; ∇ pyridine; ● acetonitrile).



$$[8] \quad \ln \alpha^{\mathrm{D}}_{\mathrm{MA/DPP}} = \frac{A}{T} + B$$

and A and B values are collected in Table 2. Equation [8] enables us to calculate isotope effects on the enthalpy changes for reaction [1] or [3]. Values ranging between 1.4 and 1.7 kJ/mol are reported in Table 2. It is worth noting that $\Delta(\Delta H^0)$ for deuterium exchange between methanol and hydrogen sulphide (2.4 kJ/mol) (7) is remarkably larger than that observed for the present solutions. Such a result could have been anticipated from the ZPE differences. There is a much smaller change in ZPE for the Ph_2PH/Ph_2PD pair than for the HSH/HSD one. Another interesting observation is the relatively small change in $\Delta(\Delta H^0)$ that occurs in the series from vapor through the range of solvents, C_2Cl_4 to pyridine (Fig. 1).

Before entering upon the discussion of these effects, let us first consider the experimental conditions. Usually the mole fractions of MA and DPP in C_6H_6, $(CH_2)_4O$, C_5H_5N, and CH_3CN were in the range of 0.04–0.08 and only in C_2Cl_4 solution were they larger (0.10–0.15). In such dilute solutions DPP exists mainly as monomer. It was shown earlier (6) that DPP interacts as a weak proton donor with various electron donors (for example tri-n-butylphosphine or diethylphosphide) with an energy of about 3 kJ/mol. It is likely in the present case that the interaction of DPP with the solvents used is also weak, and results in small or negligible differences between individual cases. The same refers to the solutions of deuterated DPP.

Table 2. The values of A and B parameters in the $\ln \alpha^{D} = A/T + B$ equation for the MA/DPP system and enthalpy changes $\Delta(\Delta H^0)$ in various solvents.

Solvent	A (K)	B	$\Delta(\Delta H^0)$ (kJ/mol)
Vapor*	199 ± 1	0.103 ± 0.002	1.67 ± 0.01
Vapor**	194 ± 7	0.108 ± 0.008	1.63 ± 0.06
Vapor***	196 ± 9	0.133 ± 0.004	1.64 ± 0.07
C_2Cl_4	199 ± 5	0.108 ± 0.007	1.67 ± 0.04
C_6H_6	177 ± 8	0.164 ± 0.06	1.48 ± 0.06
$(CH_2)_4O$	174 ± 2	0.158 ± 0.008	1.42 ± 0.02
CH_3CN	169 ± 3	0.129 ± 0.01	1.39 ± 0.02
C_5H_5N	163 ± 3	0.163 ± 0.01	1.34 ± 0.02

$(v)^*$, $(v)^{**}$, $(v)^{***}$ have the same meaning as in Table 1.

Fig. 2. The correlation between the fractionation factor and hydrogen bond energy for the given methanol–solvent system (temperature 298 K).

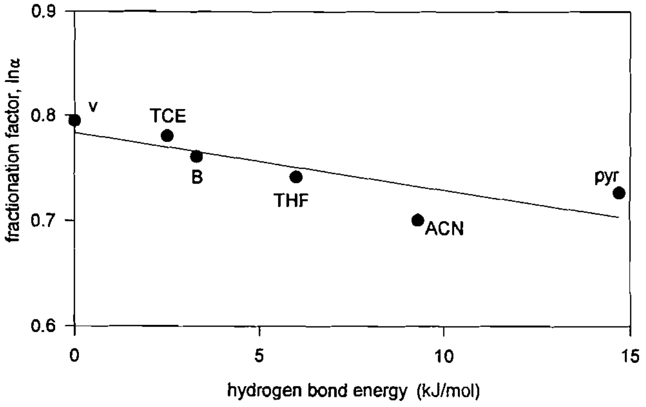
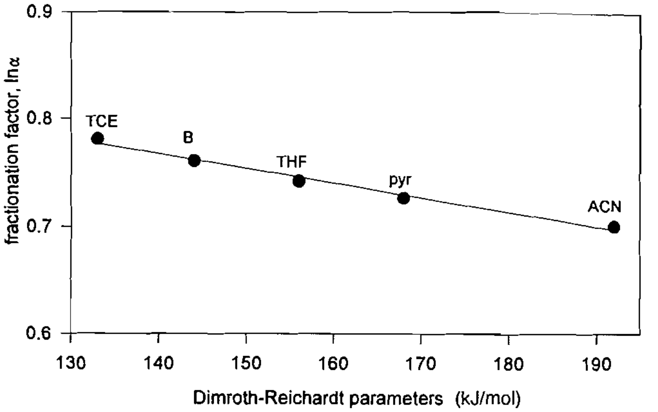


Fig. 3. The correlation between the fractionation factor and Dimroth–Reichardt parameters of the solvent (temperature: 298 K).



For MA, on the other hand, the OH group interacts with the π-electrons of C_2Cl_4 and C_6H_6 and interacts via O—H...O and O—H...N hydrogen bonds with $(CH_2)_4O$, C_5H_5N, and CH_3CN. These interaction energies (6, 15–19) and, consequently, the solvation energies differ greatly and this should affect the observed fractionation factor. As can be seen from Fig. 2 there is a correlation between the fractionation factor and hydrogen bonding energy (15, 18, 19). An especially good correlation is found between the fractionation factor and the Reichardt E_T parameters (20) (Fig. 3). It is worth noting that an excellent correlation between fractionation factor and hydrogen bond energy was found earlier for $HX_2 + DX$ (X = F, Cl, Br, I) exchange reactions (21). Analysis of the isotope effect calculated from the vibrational data nicely confirms the suggested one-to-one correspondence between isotope effect and force field. The strongest correlation is with the stretching force constant. Even small changes in hydrogen bonding seriously affect the stretching force constant and this is reflected in the isotope effect. Therefore these results clearly show how the given solvent influences the intermolecular force field between methanol and solvent. The second correlation, which is evident between the fractionation factor and E_T, shows that the isotope effect may be a very sensitive indicator of the electron charge distribution. In general, E_T parameters define the electron acceptor properties of the solvent and therefore this correlation is surprising. We would more likely expect a correlation with Gutman DN parameters (22). In this particular case E_T increases from TCE to pyridine; the isotope effects decrease in the same direction. It means, again, that the interaction between solvent and solute molecules seriously affects the solute force field. However, this time it is not the specific interaction centered on the hydrogen atom (more correctly, the OH bond) but the interaction involving oxygen electrons.

As far as the enthalpies of reaction are concerned, we observe some differences over the range of solvents studied. The changes are small but the tendency is clear: more polar solvents lower the enthalpy change. In general $\Delta(\Delta H)$ values correlate poorly with solvent parameters based on electron charge distribution.

It is worth noting that previously determined fractionation factors for the neat liquid MA/DPP system are consistent with the present results. They are placed between acetonitrile and pyridine, in qualitative agreement with the correlations described above (hydrogen bond energy in liquid methanol is reported as 9.3 kcal/mol (23)). It may be of some interest to compare the fractionation factor for the liquid MA/DPP system with those existing in the literature concerning hydrogen exchanges in OH, NH, SH, and PH groups. Most of these reactions were carried out with water; therefore the present result should be recalculated. This can easily be done since the fractionation factor between liquid methanol and water has been accurately determined ($\alpha_{MA/W} = 1.12$ at 298 K (24)). The simple calculation gives $\alpha_{W/DPP} = 1.81$. Since water is used as the reference substance it would be more appropriate to take the reciprocal of the latter, hence $\alpha_{DPP/W} = 0.55$. This is a very low value when compared with exchanges in OH and NH groups where, in most cases, values close to unity have been reported (25). For systems with very strong hydrogen bonding, fractionation factors much smaller than unity have been found (26). Although a small fractionation factor between H_2S and water in the gas phase ($\alpha_{HS/W} = 0.46$ (27)) has been also reported, its low value comes from the low stretching force constant of the SH bond. On the other hand, $\alpha_{DPP/W}$ can be fairly well compared with the value 0.61 reported for PH_3(gas) + HDO(liquid) exchange (28). It seems, therefore, that the peculiar properties of the PH bond and very weak intermolecular interactions involving this group are responsible for the small value presently reported.

In conclusion, it seems that the most striking feature of the results obtained is the role of the solvent and its effect on the fractionation factor and enthalpy changes. We suggest that it is not the specific interaction between the OH(OD) group of methanol and the solvent but the charge redistribution of each molecule in the solvent shell that determines the force field shifts that result in the final isotope fractionation factor.

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