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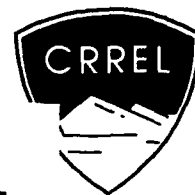
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Daniel C. Leggett

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PREFACE

This report was prepared by Daniel C. Leggett, Research Chemist, of the Geochemical Sciences Branch, Research Division, U. S. Army Cold Regions Research and Engineering Laboratory. Funding for this research was provided by DA Project 4A161102AT24, *Research in Snow, Ice and Frozen Ground*, Task SS, Work Units 031, *Chemical Persistence at Low Temperatures*, and 020, *Chemical Species Transport Phenomena in Frozen Ground*.

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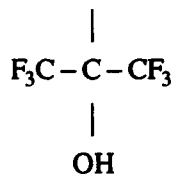
Complex Formation Between Dimethyl Methylphosphonate
and Hexafluoroisopropanol

DANIEL C. LEGGETT

INTRODUCTION

Previous work on the partitioning of dimethyl methylphosphonate (DMMP) between water and organic solvents suggested that the controlling mechanism was H-bond formation between it and the solvent (Leggett 1990). For effective extraction of DMMP from water the solvent had to have H-donor properties, although there was no direct correlation with its pK_a. The structural and electronic similarity between DMMP and some of the chemical agents (sarin, soman) suggested that solvent extraction methods for these compounds could be improved by using a more powerful H-donor solvent such as trifluoroethanol or hexafluoroisopropanol.

Two research groups involved in the development of polymer coatings for vapor phase sorption of phosphorus esters have also identified the importance of H-bonding sites (Barlow et al. 1987, Grate et al. 1988). One of the polymers used was hexafluorocarbinol-substituted polystyrene, which contains the same active moiety as hexafluoro-isopropanol (HFIP), namely

$$F_3C - \overset{\displaystyle |}{\underset{\displaystyle |}{C}} - CF_3$$
$$OH$$

Barlow et al. (1987) reported equilibrium constants for complex formation between DMMP and HFIP based on spectroscopic data in ethylbenzene. I report here complex-formation constants for DMMP and HFIP in several solvents determined by a liquid–liquid partition method. These results are compared with those for similar compounds in the literature.

Experimental

The same protocol was followed as in the earlier work (Leggett 1990) except that the partitioning solvents were doped with a 10-fold molar excess of HFIP:

$$\left\{ \frac{[HFIP]}{[DMMP]} \approx 10 \right\}.$$

Initial trials were plagued by emulsion of the organic phases and only the aqueous phases were analyzed. Since addition of excess sodium chloride gave rapid phase separation without emulsion formation in all cases, all reported measurements were performed in the presence of saturated NaCl. Both phases were analyzed. The data were treated as follows. The aqueous phase concentration of DMMP in the presence of HFIP was assumed to be uncomplexed, and a corresponding estimate of free DMMP in the organic phase was calculated using the partition coefficient obtained earlier (Leggett 1990) on each system. The small correction was then subtracted from the measured organic phase concentration to obtain a corrected value for the complexed DMMP. The ratio of complexed to free DMMP was then taken to give a dimensionless complexation constant. A one-to-one complex was assumed to form according to the usual equation:

$$DMMP + HFIP \Leftrightarrow DMMP - HFIP$$

and the resulting equilibrium is

$$K_{eq} = \frac{[DMMP - HFIP]}{[DMMP][HFIP]}$$

To obtain K_{eq} the dimensionless constants obtained

Table 1. Stability constants for DMMP-HFIP complexes in various solvents.

	K *	K_{eq} †	$\overline{K}_{eq}$ **	$-\Delta G_f^\circ$ ††
Hexane	1250.0	53,400	407,000	7.55
Carbon disulfide	64.7	3,510	58,300	6.41
Carbon tetrachloride	110.0	2,860	29,500	6.01
Benzene	26.4	650	7,350	5.20
Chloroform	2.9	73	910	3.98

$$*K = \frac{[DMMP - HFIP]}{[DMMP]} \text{(dimensionless concentration)}$$

$$†K_{eq} = \frac{[DMMP - HFIP]}{[DMMP][HFIP]} (L / mole)$$

$$**\overline{K}_{eq} = \frac{[DMMP - HFIP]}{[DMMP][HFIP]} \text{(mole fraction)}$$

$$††-\Delta G_f^\circ = RT \ln \overline{K}_{eq} \text{ (cal / mole • K)}$$

above were simply divided by the free HFIP remaining in the organic phase. This was estimated by subtracting the amount complexed from the total added minus the amount remaining in the aqueous phase, the amount complexed being identical to the molar concentration of DMMP complexed. The fraction of HFIP remaining in aqueous solution was estimated from the relative detector responses for the HFIP peak in the two phases. Finally, the K_{eq} in units of L/mole was multiplied by the reciprocal of the solvent molar volume (V_m^{-1}) to obtain the dimensionless mole fraction form, $\overline{K}_{eq}$. The standard free energy of complexation, ΔG_f°, was calculated from the usual relation, $\Delta G_f^\circ = - RT \ln \overline{K}_{eq}$, at the experimental temperature of 294 K.

RESULTS AND DISCUSSION

Table 1 summarizes the stability constants and standard free energies of formation for DMMP-HFIP complexes obtained in different solvents. The stability is markedly greater in hexane than in the more polar H-bonding solvent, chloroform. Even benzene suppresses the formation constant considerably, evidently by interaction with either DMMP, HFIP, or both. Benzene can act as an electron-pair donor (Lewis base) towards HFIP. Partitioning of HFIP into benzene was greater

than that into the other solvents (Table 2). Benzene may also behave as a Lewis acid (electron-pair acceptor) towards DMMP. However, DMMP was extracted very poorly from water by benzene (Leggett 1990; Table 2), indicating that DMMP-benzene association is of only secondary importance. On the other hand, chloroform interacts with both HFIP and DMMP (Leggett 1990; Table 2). This undoubtedly explains the relatively low K_{eq} for HFIP-DMMP in chloroform. Surprisingly, even carbon tetrachloride and carbon disulfide, two solvents that are ordinarily thought of as inert, suppress the formation constant of DMMP-HFIP. This effect has been noted elsewhere (Higuchi et al. 1969), being attributed to weak H-bonding with Cl and S, but this does not explain why HFIP partitioning is greater into hexane than into CS_2. Perhaps CS_2 and CCl_4 suppress complex formation by interacting as aprotic Lewis acids with the base DMMP. Since spectroscopic investigations are often done in CCl_4, the purity of the observed stability constants in these cases can be questioned.

Barlow et al. (1987) found K_{eq} for HFIP-DMMP in ethyl benzene by spectroscopic measurements to be 21 L/mole at 25°C, lower than any of the values in Table 1. Ethyl benzene should be a stronger base than benzene toward HFIP because of the electron-donating substituent. Thus a value of < 650 L/mole is consistent with the values reported here. The pK_a of HFIP in water is 9.3 (Taft et al. 1969) similar to that of the m-fluoro- and p-iodo-substituted phenols (Higuchi et al. 1969); however, its heat of mixing with DMMP is greater than that of o-chlorophenol, pK 8.48 (Chang et al. 1987). K_{eq} for DMMP-HFIP is higher than that of p-nitrophenol, pK_a 7.15, with tributyl phosphate and sarin (Higuchi et al. 1969), suggesting that the acidity of HFIP in nonaqueous media may be underestimated.

Table 2. Distribution of DMMP and HFIP, and DMMP + 10-fold excess HFIP between salt-saturated water and solvents.

Solvent	$\log P_s^{DMMP}$	$\log P_{s+HFIP}^{DMMP}$	$\log P_s^{HFIP}$ *
Hexane	−2.46	0.64	0.15
Carbon disulfide	−1.48	0.38	−0.03
Carbon tetrachloride	−1.00	1.04	0.49
Benzene	−0.67	0.77	1.22
Chloroform	0.97	1.56	1.02

*Includes both free and complexed HFIP; correction for HFIP complexed by DMMP lowers these values by no more than 0.09 log units.

Table 3. Estimated stability constants of HFIP with phosphonate esters in CCl$_4$ at 21°C.

Acceptor	K$_{eq}$	log K$_{eq}$	Ref.
Dimethyl ethyl phosphonate	1680	3.23 ± 0.10	Taft et al. (1969)
Diethyl chloromethyl phosphonate	2280	3.36 ± 0.10	Taft et al. (1969)
Diethyl methylphosphonate	4130	3.62 ± 0.10	Taft et al. (1969)
Dimethyl methylphosphonate	2860	3.46 ± 0.10	This work

The strength of DMMP as a base is also important in determining the magnitude of K_{eq}. According to Hudson (1965) phosphonates should be stronger bases than phosphates because of the electron-releasing methyl group attached to phosphorus. The octanol–water partition coefficients of DMMP and trimethyl phosphate (TMP) were found to be –1.13 and –0.60, respectively (Leggett 1987), which also suggests greater basicity for DMMP, with water as the proton donor. Empirical correlations (linear free energy relationships) given by Taft et al. (1969) also support this general conclusion. Predicted values for stability constants of HFIP with phosphonates similar to DMMP at 21°C were obtained by linear interpolation of the data of Taft et al. (1969) for log K_{eq} with $T(K)$. These are shown in Table 3. The reported measurement is in good agreement with these predicted values. ΔG°_f of complexation (Table 1) supports the H-bonding mechanism and is similar to the measured heat of complexation in ethyl benzene, 6.4 kcal/mole-K (Barlow et al. 1987), which is probably low due to interaction of HFIP with the solvent.

In concluding, HFIP was found to complex strongly with DMMP, as inferred from solvent extraction data (Leggett 1990). The measured complex-formation constant was greater in hexane than in other solvents, due to competing interactions with HFIP in these solvents. The formation constant is similar in magnitude to a spectroscopically measured heat of complexation (Barlow et al. 1987), which strongly supports an H-bonding mechanism. Small amounts of HFIP were found to markedly increase the extraction of DMMP into nonaqueous solvents; because of mass action, however, most complete extraction will be obtained when pure HFIP is used as the extraction solvent. By analogy with the correlations of Taft et al. (1969) and the data reported by Higuchi et al. (1969), related compounds such as phosphates, phosphites, phosphonofluoridates and other phosphonates all should be well-extracted from water by HFIP.

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A solvent/water partitioning method was used to measure the complex formation between dimethyl methylphosphonate (DMMP) and hexafluoroisopropanol (HFIP). The highest formation constant was obtained when n-hexane was used as the partitioning solvent. Other solvents all interfered to some extent with complex formation, probably by interacting with HFIP. The log formation constant in carbon tetrachloride was 3.46 ± 0.10 at $21°C$, which was similar to literature estimates for other phosphonates. The data support formation of H-bond charge transfer complexes as the mechanism for HFIP interaction with phosphonates and as primarily responsible for HFIP extraction of these compounds from water.

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