Solvent Effects on the Reaction of Triethylphosphine with Carbon Disulphide

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Thermodynamic and kinetic parameters have been measured for the reaction of triethylphosphine with carbon disulphide in several non-aqueous solvents. The observed free energy, entropy, and enthalpy values are discussed in terms of solvation of the reactants, products, and transition state, using regression on solvent parameters.

In recent years Koppel and Palm,[1] Grunwald,[2] Reichardt,[3] and several others have treated solvent effects semiempirically either through linear regression or factor analysis,[4] and used functions of two or more solvent parameters. The factor analysis leads to better correlations than other simpler methods of statistical evaluation of the data, but the interpretation of the relationships obtained is unclear.

In spite of considerable effort in the area, including theoretical,[5] solvent effects on reaction rates still remain not only unpredictable but also difficult to understand.

Our aim is to study solvent effects on the activation parameters for the reaction of CS_2 with Et_3P. Addition compounds of the type $R_3P{\cdot}CS_2$, formed from trialkylphosphines and carbon disulphide, were formulated by Jensen[6] as trialkylphosphoniodithioformates, $R_3\overset{+}{P}\text{-}CS_2^{\ -}$. The ethyl compound was not soluble enough in carbon disulphide to allow a measurement of its dipole moment, but this must be large since the closely related propyl compound shows a dipole moment of 8.0 D.[6]

In the formation of the adduct one could expect a noticeable solvent effect upon equilibrium because of the relatively low dipole moment of triethylphosphine (μ 1.35 D) compared with the addition compound. If the adduct really shows a high polarity it must be accompanied by a greater stabilisation upon solvation.

For the statistical treatment of the data we prefer to use the Koppel–Palm[1] relationship [equation (1)] instead of a two-

$$A = A_0 + yY + pP + eE + bB \qquad (1)$$

parameter equation containing Gutmann's donor (DN) and acceptor (AN) numbers.[7,8] Both parameters *B* and *E* show good correlations with DN and AN respectively, but equation (1) also includes the polarisability (*P*) and polarity (*Y*) of the solvent.

In equation (1), *A* is the property under examination, and *E* and *B* are the electrophilicity and nucleophilicity of the solvent, respectively.

Experimental

Materials.—Triethylphosphine (Strem Chemicals) and carbon disulphide (Merck, analytical reagent) were used as purchased. Tetrahydrofuran, acetonitrile, and dimethyl sulphoxide (DMSO) were spectroscopic grade. Methyl acetate was a chromatographic reagent. All chemicals were deoxygenated under argon prior to use. The other solvents were reagent grade, purified using standard procedures, and deoxygenated prior to use.

Triethylphosphine and carbon disulphide stock solutions in all solvents were prepared under argon and used immediately.

Kinetic Measurements.—Reaction solutions (2.5 ml) of carbon disulphide ($1.66 \times 10^{\ 2}$M) in the appropriate solvent were introduced into 1 cm cells and placed in the thermostatted cell holder of a Pye–Unicam SP1800 spectrophotometer. After thermal equilibration a stock solution (10—30 μl) of triethylphosphine in the same solvent was injected into the reaction solution. The reaction was followed by monitoring the increase of absorbance with time at 364 nm. The initial concentration of triethylphosphine was $(1.1—3.3) \times 10^{\ 5}$M in all runs. To ensure that CS_2 neither escaped nor was oxidised, tightly stoppered Teflon cells (Hellma 110 QS) were used throughout. All the reactions were followed for more than 10 half-lives and no noticeable changes in absorbance were observed afterwards.

Pseudo-first-order rate constants were observed (k_{obs}) in all cases. These rate constants were determined by the Guggenheim method, the plots remaining linear for at least three half-lives. Plots giving correlation coefficients worse than 0.9990 were discarded.

The apparent equilibrium constants (K') were evaluated from the A_∞ value for each kinetic run and from the absorbance value obtained by adding enough carbon disulphide to displace the equilibrium completely towards the product. CS_2 addition caused a linear increase in the A_∞ values due to the absorbance of CS_2 at 364 nm. The intercept of this straight line should be the absorbance if all the triethylphosphine formed an adduct.

The forward (k_1') and back ($k_{\ 1}$) pseudo-first-order rate constant were evaluated from the k_{obs} ($k_{obs} = k_1' + k_{\ 1}$) and K' values ($K' = k_1'/k_{\ 1}$). The second-order rate (k_1) and the true equilibrium constant (K) were obtained by dividing the k_1' and K' values by the CS_2 concentration at equilibrium.

The values of k_1, $k_{\ 1}$, and K are shown in Table 1 for the different solvents at various temperatures.

The thermodynamic parameters for the reaction in the solvents studied are shown in Table 2.

Data Treatment.—The Statistical Analysis System program was used for the statistical interpretation of the data. All the correlations obtained through stepwise regression analysis met the 0.15 significance level, which we imposed on the calculations using equation (1). The solvent polarity *Y* was calculated from $Y = (\varepsilon - 1)/(2\varepsilon + 1)$. Table 3 summarises the statistics obtained for the different regression equations.

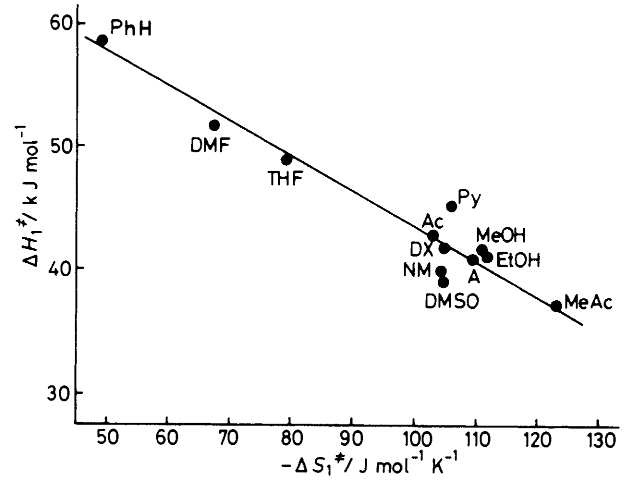
Results and Discussion

Because of the ability of MeOH and EtOH to accept an electronic charge by means of hydrogen-bond formation we decided to exclude these solvents in the statistical data treatment. In fact, inclusion of these solvents in the analysis strongly distorts the correlations obtained and makes the interpretation of the solvent effects impossible.

Free Energy.—In spite of the fact that the rates at *ca.* 25 °C vary by a factor of *ca.* 13 between DMSO and pyridine, in the

Table 1. Values of k_1, k_{-1}, and K for the different solvents at various temperatures

Solvent	T/ °C	k_1/l mol^{-1} s^{-1}	10^3k_{-1}/ s^{-1}	$10^{-2}K$/ l mol^{-1}
Benzene	14.9	0.295	12.1	0.244
	15.2	0.298	12.5	0.239
	20.1	0.455	26.8	0.170
	20.1	0.464	27.3	0.170
	25.0	0.692	53.7	0.129
	25.0	0.696	53.6	0.130
Tetrahydrofuran	3.2	0.154	0.687	2.23
	3.2	0.135	0.709	1.92
	10.3	0.233	2.147	1.09
	10.3	0.206	1.896	1.08
	16.0	0.374	5.09	0.73
Acetonitrile	2.6	0.270		
	2.6	0.257		
	8.6	0.366		
	14.0	0.566		
	20.9	0.813		
	25.8	1.163		
	30.9	1.446		
Acetone	11.9	0.440	0.33	13.2
	11.9	0.425	0.31	13.7
	17.5	0.642	0.83	7.75
	22.6	0.863	1.56	5.54
	29.7	1.321	4.12	3.21
p-Dioxane	11.2	0.417	1.80	2.31
	16.8	0.547	4.63	1.18
	22.4	0.770	9.26	0.831
	27.2	1.170	21.41	0.488
	32.1	1.430	36.90	0.386
Pyridine	5.1	0.063	0.177	3.54
	13.8	0.115	0.488	2.36
	24.8	0.248	2.750	0.904
	36.4	0.498	14.27	0.364
	36.4	0.498	13.83	0.360
Nitromethane	5.1	0.758		
	10.1	0.982		
	15.0	1.316		
	20.1	1.937		
Dimethyl sulphoxide	20.7	2.630		
	20.7	2.535		
	24.3	3.237		
	24.3	3.118		
	29.6	4.338		
	34.0	5.998		
Dimethylformamide	4.2	0.358		
	15.0	0.787		
	19.5	1.199		
	25.3	1.885		
Methyl acetate	3.5	0.206	0.262	7.89
	9.3	0.340	0.763	4.46
	15.2	0.444	1.713	2.56
	15.2	0.407	1.535	2.65
	21.9	0.625	4.940	1.25
	26.7	0.828	9.419	0.88
Ethanol	3.9	0.147	0.268	5.50
	9.6	0.221	0.572	3.86
	16.2	0.323	1.315	2.45
	21.4	0.442	2.813	1.57
	26.0	0.601	5.838	1.03
	30.9	0.801	10.07	0.80
Methanol	10.0	0.223	0.118	19.0
	19.5	0.418	0.649	6.45
	24.4	0.557	1.185	4.70
	29.3	0.734	2.486	2.96
	35.1	1.024	5.863	1.75



Plot of $\Delta H_1^{\ddagger}$ *versus* $\Delta S_1^{\ddagger}$ for the reaction of triethylphosphine with carbon disulphide

stepwise regression analysis no variable met the requirement of the 0.15 significance level for entry into the model. On the other hand, although a plot of $\Delta H_1^{\ddagger}$ *versus* $\Delta S_1^{\ddagger}$ shows some correlation (Figure), suggesting isokinetic behaviour, Exner's[9] criteria are not satisfied, and we must therefore reject this proposition.

That the highest value of $\Delta G_1^{\ddagger}$ is in pyridine is understandable because of the reactivity of the amine with carbon disulphide. Therefore, one can assume preferential association of the relatively soft Lewis base pyridine with the similar Lewis acid, CS_2. On the other hand, the high $\Delta G_1^{\ddagger}$ values for MeOH and EtOH could be explained through hydrogen-bonding stabilisation for triethylphosphine, whereas this possibility is missing for the transition state.

The stepwise regression analysis for $\Delta G_{-1}^{\ddagger}$ gives relation (2).

$$\Delta G_{-1}^{\ddagger} = 76.77 + 21.5Y \qquad (2)$$

This explains why the more polar solvents (A, NM, DMSO, and DMF) do not allow the measurement of activation parameters for the back reaction under the experimental conditions employed.

The stepwise regression for ΔG° gives no relation with the solvent parameters, although according to the criteria of maximal R^2 improvement, the best one-variable model found was one of Y dependence ($R^2 = 0.426$).

It is perhaps not fortuitous that the above mentioned solvents have also the greatest values of the acceptor numbers[8] (with the exception of MeOH and EtOH, which are capable of accepting electronic charge by means of hydrogen-bond formation). At this stage it seems difficult to decide if polarity or acceptor number is the relevant parameter for the explanation of the ΔG° values. The importance of the dipole moment is in agreement with greater stabilisation of the products through solvation since solvation of the reactants must be discrete and restricted only to triethylphosphine. Among the eight solvents in which the back reaction appears one finds the smallest ΔG° value for acetone in accordance with its highest dipole moment (μ 2.88 D).

Enthalpy.—From the stepwise regression analysis for the activation enthalpy of the forward reaction equations (3) and (4) obtain. The dependence of $\Delta H_1^{\ddagger}$ upon E and B suggests

$$\Delta H_1^{\ddagger} = 50.5 - 1.89E \qquad (3)$$

$$\Delta H_1^{\ddagger} = 61.6 - 2.72E - 0.067B \qquad (4)$$

stabilisation of the transition state due to the solvent as in (I). The theory of absolute rates assumes an equilibrium between

Table 2.[a,b] Thermodynamic parameters for the forward and back reactions of triethylphosphine with carbon disulphide in various solvents at 298 K

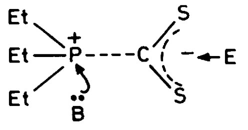
	$\Delta H_1^{\neq}$	$\Delta S_1^{\neq}$	$\Delta G_1^{\neq}$	$\Delta H_{-1}^{\neq}$	$\Delta S_{-1}^{\neq}$	$\Delta G_{-1}^{\neq}$	ΔH°	ΔS°	ΔG°
Benzene (PhH)	58.6	−51.5	74.1	103.3	77.4	80.3	−44.8	−129.3	−6.3
Tetrahydrofuran (THF)	48.9	−78.7	72.4	99.6	59.4	82.0	−51.0	−138.1	−8.8
Acetonitrile (A)	40.6	−109.2	72.8						
Acetone (AC)	42.7	−102.5	73.2	100.4	40.6	88.3	−57.3	−141.8	−15.1
Dioxane (DX)	41.8	−104.6	73.2	102.3	62.8	83.7	−61.9	−172.8	−10.5
Pyridine (Py)	45.2	−105.4	76.6	100.0	41.8	87.5	−54.4	−145.2	−10.9
Nitromethane (NM)	39.7	−104.2	70.7						
Dimethyl sulphoxide (DMSO)	38.9	−104.2	69.9						
Dimethylformamide (DMF)	51.9	−66.9	71.6						
Methyl acetate (MeAC)	37.2	−122.6	73.6	107.5	60.3	85.3	−66.1	−184.1	−11.3
Ethanol (EtOH)	41.0	−111.7	74.5	92.9	22.2	86.2	−51.9	−134.3	−11.7
Methanol (MeOH)	41.4	−110.9	74.5	109.2	66.5	89.5	−67.8	−177.0	−15.1

[a] ΔH and ΔG values in kJ mol^{-1}; ΔS values in J mol^{-1} K^{-1}. [b] The average error in $\Delta H^{\neq}$ was less than 4.5 and 3.0% for the forward and back reactions, respectively, whereas the average error in $\Delta S^{\neq}$ for the corresponding reactions was 20 and 60%.

Table 3. Statistical data from the stepwise regression procedure

Equation	n[a]	F[b]	R^2[c]	Y s.t.d. error (F_{partial})	E s.t.d. error (F_{partial})	B s.t.d. error (F_{partial})	P s.t.d. error (F_{partial})
2	6	4.61	0.535	10.0108 (4.61)			
3	10	5.18	0.393		0.8306 (5.18)		
4	10	5.69	0.619		0.8118 (11.21)	0.033 07 (4.16)	
5	6	18.34	0.821		0.2446 (18.34)		
6	6	5.22	0.566		0.9781 (5.22)		
7	6	15.47	0.911		0.6007 (30.59)	0.0272 (11.72)	
8	6	72.78	0.991		0.27 (105.47)	0.0107 (74.91)	17.808 (17.48)
9	10	3.34	0.294		2.924 (3.34)		
10	10	3.84	0.523		2.97 (7.38)	0.121 (3.36)	
11	6	9.26	0.698	35.977 (9.26)			
12	6	10.29	0.720		2.218 (10.29)		
13	6	30.49	0.953		1.235 (60.89)	0.0559 (14.91)	

[a] n = Number of solvents. [b] Statistical F. [c] R^2 = Squared correlation coefficient.



(I)

reactants and transition state, but there is no doubt that solvent reorganisation takes place during the reaction. This was proposed by Ogg and Polanyi in 1935. Later Bernasconi,[10] Bertran,[11] and several others studied this problem. For $\Delta H_{-1}^{\neq}$ one finds relation (5) with the electrophilic power of the solvent.

$$\Delta H_{-1}^{\neq} = 99.6 + 1.05E \qquad (5)$$

We can understand this relation if we assume that the product is stabilised by interaction between the CS_2 group and the electrophilic function of the solvent.

For ΔH° equations (6)—(8) were obtained. The dependence

$$\Delta H^{\circ} = -50.4 - 2.23E \qquad (6)$$

$$\Delta H^{\circ} = -36.1 - 3.32E - 0.09B \qquad (7)$$

$$\Delta H^{\circ} = -56.6 - 2.77E - 0.09B + 74.4P \qquad (8)$$

of ΔH° on E and B can be explained as in equations (3)—(5). Equation (8) shows a term with the parameter P. This contribution implies greater exothermicity as the solvent polarisability increases.

Entropy.—The negative entropy change for the reaction points to an important reorganisation of the solvent. The least ΔS° change is observed for benzene, which interacts weakly with the adduct dipole. In ethanol, there is less entropy change than in methanol. This fact suggests that the reactants are more strongly solvated, due to hydrogen bonding, as in the case of methanol, so that the reaction involves an increasing degree of order.

For $\Delta S_1^{\neq}$ the stepwise regression gives the equations (9) and (10). The dependence of $\Delta S_1^{\neq}$ on both E and B is a consequence

$$\Delta S_1^{\neq} = -78.19 - 5.34E \qquad (9)$$

$$\Delta S_1^{\neq} = -41.79 - 8.06E - 0.22B \qquad (10)$$

of the solvent acid–base interactions with the transition state, which imposes a greater order to the transition state relative to reactants.

For $\Delta S_{\ 1}^{\neq}$, one finds relation (11) which points to a decrease

$$\Delta S_{\ 1}^{\neq} = 96.45 - 109.5Y \qquad (11)$$

in $\Delta S_{\ 1}^{\neq}$ with increasing solvent polarity. In other words, this suggests a greater polarity of the product relative to the transition state.

For ΔS° we find relations (12) and (13). The negative

$$\Delta S^{\circ} = -134.37 - 7.11E \qquad (12)$$

$$\Delta S^{\circ} = -101.27 - 9.63E - 0.126B \qquad (13)$$

contributions of E and B can be understood, as in the case of $\Delta S_1^{\neq}$, due to acid–base interaction of the solvent with the product.

In conclusion, the study of solvent effects on the reaction of CS_2 with EtP_3 shows a polar transition state. The basicity (B) and acidity (E) of the solvent are the most relevant parameters for the enthalpy and entropy values, except in the case of $\Delta S_{\ 1}^{\neq}$ where the most important parameter is Y, probably because the contributions of E and B to the product and transition state are similar.

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