

Kinetic Studies on the Reaction of Triethyl- and Diethylphenyl-phosphine with Carbon Disulphide in Nitrile Solutions

Trinidad Campino, José G. Santos, and Fernando Ibáñez

Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 6177, Santiago-Chile

The kinetics of the reactions of carbon disulphide with triethylphosphine and diethylphenylphosphine are studied in solutions of acetonitrile, propionitrile, isobutyronitrile, benzonitrile, benzyl cyanide, and some of their mixtures. The reaction shows reversible pseudo-first-order kinetics.

Activation and equilibrium parameters are discussed in terms of solvent properties.

We recently carried out an investigation¹ into solvent effects in the reaction of triethylphosphine with carbon disulphide. That study showed that the Koppel-Palm relationship² fits the kinetic and thermodynamic parameters for this reaction. We are interested in the title reactions because in the above work¹ a great variety of solvents (polar, apolar, protic, aprotic) was used, and specific interactions cannot be ruled out, and also because the behaviour of arylphosphines, which are less polar than alkylphosphines, could be a useful aid to the understanding of the influence of structural changes on the reaction.

In this work we selected several nitriles and some mixtures of them, because of the observation that in acetonitrile only the forward reaction was observed for Et₃P and we expected to succeed in the measurement of the back reaction when the medium is changed.

Experimental

Materials.—Triethylphosphine (Strem Chemicals) was redistilled before use. Diethylphenylphosphine (Strem Chemicals) and carbon disulphide (Merck, analytical reagent) were used as purchased. Acetonitrile (Merck, analytical reagent), propionitrile (Aldrich, I.R. and G.C.), isobutyronitrile (Aldrich, 99%), and benzonitrile (Fluka, purum) were dried for one week on calcium chloride (J. T. Baker) and then refluxed for 2–3 h on phosphorus pentaoxide (Merck, 98% min) and distilled on a 1 m column under nitrogen at atmospheric pressure. Benzyl cyanide (Aldrich) was distilled at reduced pressure (b.p. 99.5 °C, 17 mmHg).

Phosphine and carbon disulphide stock solutions in the various solvents were prepared under nitrogen and used immediately.

Kinetic Measurements.—1-cm Quartz cells (Hellma 110 QS), containing a solution of carbon disulphide at a concentration of 0.0166–0.048M in the appropriate solvent, were placed in the thermostatted cell holder of a Pye-Unicam SP 1800 or a Perkin-Elmer Lambda-3 spectrophotometer. After thermal equilibration a stock solution (10–30 μl) of phosphine in the same solvent was injected into the reaction solution. The reaction was followed by monitoring the increase in absorbance over time at 364 nm.

The rate constants for the forward and back reactions, k_1 and k_{-1} respectively, and the equilibrium constant, K , were obtained as previously.¹ These values are shown in Tables 1 and 2 for the reaction of CS₂ with Et₃P and PhEt₂P, respectively, in different solvents at various temperatures. The thermodynamic parameters for these reactions are shown in Tables 3 and 4.

Data Treatment.—The Interactive Data Analysis program in its operation mode BACK in a digital computer DEC-10 was used for the statistical interpretation of the data. The

correlations obtained through stepwise regression analysis met the 0.15 significance level, which we imposed on the calculations using the Koppel-Palm relationship² [equation (1)].

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

For the calculation of the parameter $Y = (\epsilon - 1)/(2\epsilon + 1)$ in the solvent mixtures we assumed that the relative permittivity is additive according to the relationship $\epsilon = X_1\epsilon_1 + X_2\epsilon_2$, where X_i is the molar fraction of component i .

The parameter $P = \frac{n_D^2 - 1}{n_D^2 + 2}$ was determined by measuring the refractivity at 20 °C. For the parametrisation of E and B we assumed that the mixtures behave ideally, *i.e.* that there is no preferential solvation and that, statistically, the molecules of each solvent contribute their interactions proportionally to their molar fractions. For some nitriles, whose E and B parameters are not reported in the literature, we estimated their values from E vs. $E_T(30)$ and B vs. Donor Number plots for a set of solvents. Table 5 summarises the statistics obtained for the different regression equations.

Results and Discussion

The reactions of Et₃P and PhEt₂P with CS₂ in AN, PN, iBN, BN, and BC and in some of their mixtures behaved as a pseudo-first-order reversible reaction system, according to equation (2).



For the reaction of Et₃P with CS₂ in acetonitrile, and in its mixtures with other nitriles, only the forward reaction can be observed because the equilibrium is completely displaced towards adduct formation. The similarity of the ΔG^\ddagger values for the forward reactions of Et₃P and PhEt₂P is worth noting (Tables 3 and 4). This can be explained in terms of the principle of least nuclear motion,³ because of the considerable change in the S–C–S angle from 180° in CS₂ to a smaller value, which is 128° in the solid state.⁴ Besides, the C–S bond length is 1.68 Å in the solid state, longer than a double bond (1.55 Å) but shorter than a single bond (1.81 Å).⁴ In other words, for the forward reaction, ΔG^\ddagger is due mainly to changes in the molecular parameters in the CS₂ moiety. If we consider ΔG^\ddagger to consist of the additive contribution of an intrinsic parameter, ΔG_{in}^\ddagger , and an environmental one, ΔG_{env}^\ddagger , due to solvent reorganisation,⁵ we must conclude that this last term is less significant.

The ΔG_{in}^\ddagger values are approximately 8 kJ mol⁻¹ lower for the reaction of PhEt₂P than those for the reaction of Et₃P. We failed to observe the reaction of CS₂ with Ph₂EtP and Ph₃P. Introduction of a second or a third phenyl moiety at the phosphorus atom leads to a further lowering of ΔG^\ddagger for the

Table 1. Values of k_1 , k_{-1} , and K for the reaction of CS_2 with triethylphosphine in different solvent mixtures at various temperatures

Solvent ^a	T/K	$10^3 k_1 / \text{l mol}^{-1} \text{s}^{-1}$	$10^3 k_{-1} / \text{s}^{-1}$	$K / \text{l mol}^{-1}$
AN	282.8	7.1		
	287.7	8.4		
	298.1	15.2		
	303.3	18.8		
	308.4	24.5		
	312.1	28.1		
PN	283.5	1.32	0.53	247
	289.0	2.10	0.76	277
	292.6	3.05	1.17	260
	296.8	5.20	1.92	270
	299.2	6.19	2.33	268
	303.4	9.45	4.07	232
iBN	278.3	5.22	1.15	454
	283.1	6.20	1.79	346
	288.6	8.63	3.48	249
	293.7	12.2	6.03	203
	298.1	14.9	8.17	183
BN	277.9	2.36	1.10	205
	283.2	3.08	1.90	163
	289.1	3.97	3.29	121
	293.6	4.94	4.73	104
	300.7	6.01	9.79	61
BC	285.9	8.4	—	—
	289.5	9.7	1.01	957
	295.3	12.6	1.50	834
	298.7	15.8	2.96	534
	303.5	18.2	4.47	406
	308.6	25.5	7.61	344
AN-PN 1:1 v/v	267.7	3.2		
	280.6	4.4		
	283.8	5.1		
	287.0	6.0		
	290.2	7.4		
	293.2	9.0		
	295.1	10.1		
	298.2	11.5		
AN-PN 1:3 v/v	276.9	3.2		
	280.2	4.0		
	283.5	5.1		
	286.9	6.2		
	289.9	7.8		
	292.8	9.3		
	295.3	11.1		
	298.2	12.8		
AN-BN 1:1 v/v	276.5	3.5		
	278.6	3.9		
	280.8	4.3		
	284.4	5.7		
	286.5	6.3		
	292.1	9.5		
	294.7	11.5		
	296.7	12.1		

^a AN = acetonitrile; PN = propionitrile; iBN = isobutyronitrile; BN = benzonitrile; BC = benzyl cyanide

Table 2. Values of k_1 , k_{-1} , and K for the reaction of CS_2 with diethylphenylphosphine in different solvent mixtures at various temperatures

Solvent	T/K	$10^3 k_1 / \text{l mol}^{-1} \text{s}^{-1}$	$10^3 k_{-1} / \text{s}^{-1}$	$K / \text{l mol}^{-1}$
AN	278.4	1.75	5.85	29.9
	283.5	2.80	13.0	21.5
	288.8	4.16	28.5	14.6
	293.8	5.64	57.3	9.8
	297.9	8.69	103.0	8.4
PN	273.5	0.87	9.2	9.4
	276.1	1.42	13.9	10.2
	276.3	1.29	12.3	10.5
	278.4	1.82	19.2	9.5
	280.3	2.17	23.7	9.2
	280.7	2.42	27.4	8.9
	283.6	3.56	38.3	9.3
	289.5	5.88	69.8	8.4
iBN	270.5	0.90	11.4	7.9
	272.1	1.07	13.9	7.7
	274.1	1.37	17.2	8.0
	278.3	2.07	28.0	7.3
BN	270.2	1.01	10.5	9.6
	271.7	1.18	13.1	9.0
	273.2	1.28	15.4	8.3
	275.1	1.41	19.8	7.1
	276.0	1.37	20.5	6.7
	277.7	1.72	28.1	6.1
	279.3	1.93	34.1	5.7
	280.7	2.08	41.2	5.1
BC	270.6	0.667	4.48	14.9
	272.9	0.836	5.95	14.1
	275.2	0.929	6.84	13.6
	279.9	1.52	13.5	11.3
	283.0	2.27	20.7	11.0
BN-PN 1:1 v/v	271.0	0.98	7.7	12.6
	272.9	1.17	10.2	11.5
	274.4	1.29	12.6	10.2
	275.4	1.26	12.3	10.2
	275.7	1.60	15.4	10.3
	277.2	1.47	15.1	9.8
	278.3	1.73	19.6	8.8
	281.2	2.46	29.6	8.3
	282.1	2.45	30.7	8.0
	282.8	2.49	31.0	8.0
BN-PN 1:3 v/v	270.5	0.94	7.0	13.4
	270.6	0.82	7.5	11.0
	272.3	0.97	9.2	10.5
	273.9	0.99	10.8	9.2
	275.6	1.23	11.8	10.4
	275.7	1.25	13.3	9.4
	278.1	1.15	17.8	6.5
	279.8	1.43	24.3	5.9
AN-BN 1:1 v/v	282.6	1.60	25.8	6.2
	283.0	1.49	29.5	5.0
	272.2	0.89	4.2	21.2
	274.4	1.21	7.0	17.2
	277.8	1.43	10.7	13.3
	280.0	1.95	15.7	12.4
	282.2	2.22	20.4	10.9
	285.2	3.16	30.6	10.3
AN-BN 1:3 v/v	288.2	3.89	47.5	8.1
	269.9	0.90	5.9	15.3
	274.6	1.29	10.0	12.5
	276.6	1.39	12.0	11.5
	278.8	1.79	18.0	10.0
	281.2	2.07	22.9	9.0
	284.3	2.81	37.0	7.6

Table 3^{a,b}. Thermodynamic parameters for the forward and back reactions of triethylphosphine with carbon disulphide in various solvent mixtures at 298 K

	ΔH_1^\ddagger	ΔS_1^\ddagger	ΔG_1^\ddagger	ΔH_{-1}^\ddagger	ΔS_{-1}^\ddagger	ΔG_{-1}^\ddagger	ΔH°	ΔS°	ΔG°
AN	33.0 ± 0.8	-130 ± 10	71.9						
PN	69.8 ± 2.5	-15 ± 26	74.4	71.5 ± 4.6	-56 ± 48	88.2	-3.8 ± 7.1	33 ± 74	-13.8
iBN	35.5 ± 2.5	-122 ± 23	71.9	68.1 ± 2.9	-55 ± 29	84.9	-32.6 ± 5.4	-66 ± 52	-13.0
BN	27.6 ± 2.1	-157 ± 19	71.9	63.1 ± 1.7	-74 ± 16	84.9	-35.5 ± 3.8	-84 ± 35	-10.9
BC	33.0 ± 1.7	-131 ± 18	71.9	78.6 ± 6.7	-30 ± 67	87.8	-44.7 ± 8.4	-96 ± 86	-15.9
AN/PN 1:1	38.5 ± 1.3	-115 ± 11	72.7						
AN/PN 1:3	42.6 ± 0.4	-100 ± 5	72.3						
AN/BN 1:1	41.0 ± 1.3	-105 ± 13	72.3						

^a ΔH and ΔG values in kJ mol⁻¹; ΔS values in J K⁻¹ mol⁻¹; ^b The errors in ΔH and ΔS are the standard errors.

Table 4^{a,b}. Thermodynamic parameters for the forward and back reactions of diethylphenylphosphine with carbon disulphide in various solvent mixtures at 298 K

	ΔH_1^\ddagger	ΔS_1^\ddagger	ΔG_1^\ddagger	ΔH_{-1}^\ddagger	ΔS_{-1}^\ddagger	ΔG_{-1}^\ddagger	ΔH°	ΔS°	ΔG°
AN	51.8 ± 2.5	-72 ± 25	73.5	98.6 ± 0.4	67 ± 5	78.6	-46.4 ± 2.9	-139 ± 30	-5.0
PN	75.7 ± 3.8	14 ± 39	71.9	82.8 ± 3.8	20 ± 40	76.9	-7.1 ± 7.5	-6 ± 79	-5.0
iBN	64.4 ± 1.7	-26 ± 19	71.9	70.2 ± 1.3	-21 ± 13	76.5	-5.9 ± 2.9	-5 ± 32	-4.6
BN	39.7 ± 2.9	-116 ± 32	74.4	78.6 ± 2.5	9 ± 25	75.7	-38.9 ± 5.4	-125 ± 57	-1.7
BC	58.9 ± 4.6	-48 ± 48	73.5	76.1 ± 5.0	-8 ± 51	78.6	-16.7 ± 9.6	-39 ± 99	-5.0
PN/BN 1:1	50.6 ± 3.8	-77 ± 40	73.5	74.8 ± 3.8	-8 ± 41	77.3	-24.2 ± 7.5	-69 ± 81	-3.8
PN/BN 1:3	26.3 ± 3.3	-166 ± 35	71.9	69.0 ± 3.3	-30 ± 35	77.7	-42.6 ± 6.7	-136 ± 71	-1.7
AN/BN 1:1	56.8 ± 2.5	-54 ± 28	73.2	93.2 ± 2.9	53 ± 29	77.3	-35.9 ± 5.4	-107 ± 56	-4.2
AN/BN 1:3	47.2 ± 2.5	-89 ± 28	74.0	78.6 ± 4.2	5 ± 43	77.3	-30.9 ± 6.7	-92 ± 71	-3.8

^a ΔH and ΔG values in kJ mol⁻¹; ΔS values in J K⁻¹ mol⁻¹; ^b The errors in ΔH and ΔS are the standard errors.

Table 5. Statistical data from the regressions

Equation	<i>n</i> ^a	<i>F</i> ^b	<i>R</i> ^c	Free term s.t.d. error	<i>Y</i> s.t.d. error	<i>E</i> s.t.d. error	<i>B</i> s.t.d. error
3	6	11.09	0.9204	12	24.41		0.015
4	6	13.75	0.9344	139	274		0.17
5	6	14.74	0.9384	485	956		0.59
6	6	7.02	0.7642	2.0			0.019
7	6	17.85	0.8839	17.6			0.17
8	6	17.43	0.8815	64			0.628
9	9	13.47	0.8112	4.9		1.7	
10	9	10.62	0.7764	17.4		6.1	

^a *n* = Number of solvents. ^b Statistical *F*. ^c *R* = Correlation coefficient.

back reaction. This can be related to the decreasing basicity of the phosphine (*pK_a* values in water: Et₃P 8.69, PhEt₂P 6.25, and Ph₃P 2.73).⁶ The less basic Ph₃P is probably unable to polarise charges on the CS₂ molecule and the stabilisation of the adduct by solvent interactions is only small. A very conspicuous feature of the reaction of Et₃P with CS₂, which confirms this point, is that the reaction in CS₂ is almost completely displaced to the left-hand side in spite of the very great excess of substrate. This is due to the low polarity of CS₂ which destabilises the adduct relative to Et₃P.

In the reaction of Et₃P with CS₂ in various solvents we have found¹ that in the stepwise regression analysis no variable for ΔG_1^\ddagger met the requirement of the 0.15 significance level for entry into the Koppel-Palm model. The behaviour of Et₃P in nitriles is similar and can be explained on the basis of the greater reactivity of the phosphine, which determines a small selectivity with respect to solvation. For the reaction of PhEt₂P with CS₂ we found the relationships shown in equation (3), (4), and (5).

$$\Delta G_1^\ddagger = 111 - 0.071 B - 64.1 Y \quad (3)$$

$$\Delta H_1^\ddagger = -256 + 0.88 B + 466 Y \quad (4)$$

$$\Delta S_1^\ddagger = -1230 + 3.17 B + 1780 Y \quad (5)$$

We exclude the parameters for the reaction in propionitrile and in its mixtures because of significant deviations compared with the other solvents. Possibly this behaviour is due to the London attraction forces between similar ethyl groups.

The variation range for *Y* is very small (0.46 for benzyl cyanide and 0.48 for acetonitrile; *ca.* 4%), whereas the variation range for *B* is more significant (90 for benzonitrile and 116 for isobutyronitrile, *ca.* 22%) and a small effect of the Lewis basicity of the solvent on ΔG_1^\ddagger must be recognized. The more basic solvent is able to compete favourably for the solvation of the transition state.

It seems more appropriate to relate the activation parameters only to the solvent property *B*, because the inclusion of the parameter *Y* implies only a slight improvement of the correlation. The relationships shown in equation (6), (7), and (8) met the imposed 0.15 significance level requirement.

$$\Delta G_1^\ddagger = 78.6 - 0.051 B \quad (6)$$

$$\Delta H_1^\ddagger = -21.4 + 0.73 B \quad (7)$$

$$\Delta S_1^\ddagger = -335 + 2.62 B \quad (8)$$

For the back reaction of PhEt₂P the one-parameter equations for ΔH_{-1}^\ddagger and ΔS_{-1}^\ddagger contain the property E [equations (9) and (10)]. This may be due to interaction of the adduct CS₂ moiety with the acid function of the solvent.

$$\Delta H_{-1}^\ddagger = 63.8 + 6.4 E \quad (9)$$

$$\Delta S_{-1}^\ddagger = -41.8 + 20.0 E \quad (10)$$

In spite of the fact that some correlations have been found for the equilibria thermodynamic parameters, the errors for ΔH° and ΔS° values are too large to allow for an analysis. For Et₃P it is meaningless to analyse the multiparametric equation since there are only four solvents in the set.

We conclude that the solvent effects on these reactions in nitriles and in nitrile mixtures are small, and that specific interactions of the nitrile hydrocarbon chain cannot be ruled out. The additivity and separability of effects which the Koppel-Palm relationship supposes are questionable in this case and probably the energy and symmetry of the acceptor and donor molecular orbitals, LUMO and HOMO respectively, play a role as well.⁷

Acknowledgements

We are grateful to Dr. E. A. Castro for critically reading the manuscript. The financial support given to this work by the Dirección de Investigación de la Pontificia Universidad Católica de Chile (DIUC) is also gratefully acknowledged.

References

- 1 F. Ibáñez and J. G. Santos, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1323.
- 2 I. A. Koppel and V. A. Palm, 'Advances in Linear Free-Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum Press, London, 1972, Ch. 5, pp. 203 ff.
- 3 J. Hine, *Adv. Phys. Org. Chem.*, 1977, **15**, 1.
- 4 T. N. Margulis and D. H. Templeton, *J. Chem. Phys.*, 1962, **36**, 2311.
- 5 H. Kwart and T. H. Lilley, *J. Org. Chem.*, 1978, **43**, 2374.
- 6 W. A. Henderson, Jr., and C. A. Streuli, *J. Am. Chem. Soc.*, 1960, **82**, 5791.
- 7 W. B. Jensen, *Chem. Rev.*, 1978, **78**, 1.

Received 11th September 1985; Paper 5/1561