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Solvent, salt and high pressure effects on the rate and equilibrium constants for the formation of tri-*n*-butylphosphoniumdithiocarboxylate

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Solvent, salt and high pressure effects on the rate and equilibrium constants for the formation of tri-*n*-butylphosphoniumdithiocarboxylate at 298.2 K are reported. This equilibrium is shifted to the phosphobetaine in polar solvents, salt solutions and under high external pressure. The reaction volume changes dramatically on going from less polar diethyl ether ($-69\,\mathrm{cm^3\,mol^{-1}}$) and tetrahydrofurane (THF) ($-66\,\mathrm{cm^3\,mol^{-1}}$), to more polar acetonitrile ($-39\,\mathrm{cm^3\,mol^{-1}}$) and acetone ($-38\,\mathrm{cm^3\,mol^{-1}}$). Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: activation volume; reaction volume; solvent effect; tri-*n*-butylphosphoniumdithiocarboxylate

INTRODUCTION

The formation of red solutions of the complex between colourless trialkylphosphines and carbon disulfide has been known for about 150 years (see reaction (1)).[1]

$$\underset{\mathbf{1}}{\mathrm{Bu_3P}} + \underset{\mathbf{2}}{\mathrm{CS_2}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{3}}{\mathrm{Bu_3P^{+}\text{-}CS_{2^-}}} \qquad K_{\mathrm{eq}} = k_1/k_{-1} \tag{1}$$

For a long time, this reaction was only used as a colour test for the presence of trialkylphosphines.[2,3] It was shown[4–7] that reactions of this kind are reversible and the equilibrium is shifted to the adduct side in polar solvents. This observation is in agreement with the zwitterionic structure of similar phosphobetaines (trialkylphosphoniumdithiocarboxylates), as proven by X-ray analysis,[8] IR spectra and dipole moment measurements.[9,10] The cycloaddition reaction of **3** with maleic anhydride or maleimide takes place in polar solvents, but the chemoselectivity changes sharply in a non-polar medium with the formation of the phosphorus ylide from tributylphosphine.[6,11]

In this work, we have studied the effect of high external pressure on the rate and equilibrium constants of the formation reaction of tributhylphosphoniumdithiocarboxylate, which had earlier been found to be sensitive to solvent polarity and salt (lithium perchlorate) additives.[6,7] We proposed that solvent electrostriction will change the activation ($\Delta V^{\neq}$) and reaction (ΔV) volumes of this reaction significantly in solvents of different polarity (see Eqns (2) and (3)).

$$(\partial \ln k/\partial P)_T = -\frac{(\partial \Delta G^{\neq}/\partial P)_T}{RT} = -\Delta V^{\neq}/RT \tag{2}$$

$$(\partial \ln K/\partial P)_T = -\frac{(\partial \Delta G/\partial P)_T}{RT} = -\Delta V/RT \tag{3}$$

In this way, it becomes possible to locate the position of the transition state on the volume profile for this reaction. Thus, a series of measurements to determine the activation and reaction volumes in solvents of different polarity were carried out over the pressure range 0–150 MPa.

RESULTS AND DISCUSSION

Equilibrium and rate constants of reaction (1) for a series of solvents were determined. In acetone, acetonitrile, tetrahydrofurane (THF) and di-*n*-butyl ether (DBE), stopped-flow measurements for rate and equilibrium constants were carried out. In the rest of the studied solvents the reverse reaction rates (k_{-1}) and equilibrium constants (K_{eq}) were measured directly, whereas k_1 was calculated from $K_{\mathrm{eq}}\cdot k_{-1}$. Values of the rate and equilibrium constants for the series of solvents, and for lithium perchlorate solutions in acetone and diethyl ether are summarized in Table 1.

The change in the forward rate constant (about one order increase on going from non-polar to polar solvents, Table 1) in the studied solvents is much smaller than for the reverse rate constant (about three orders decrease).

The values of the reaction enthalpy of the phosphobetaine **3** formation were determined in four solvents (Table 2). The choice of the solvents was caused by the necessity that the degree of conversion should exceed 98–99%. In less polar solvents it is difficult to achieve this experimentally.

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Table 1. Rate and equilibrium constants for the tri-*n*-butylphosphine – carbon disulfide adduct formation reaction ($T = 298$ K)

Solvent	$[LiClO_4]$ (M)	k_1 ($M^{-1}\,s^{-1}$)	k_{-1} (s^{-1})	K_{eq} (M^{-1})
Benzene		0.343 ± 0.08	$(4.9 \pm 0.3).10^{-2}$	7.0 ± 1.3
Toluene		0.41 ± 0.16	$(9.0 \pm 0.2).10^{-2}$	4.6 ± 1.6
Diethyl ether		0.11 ± 0.03	$(2.22 \pm 0.05).10^{-1}$	0.48 ± 0.15
	0.198	0.127 ± 0.04	$(1.14 \pm 0.10).10^{-1}$	1.11 ± 0.2
	0.495	0.15 ± 0.03	$(7.49 \pm 0.08).10^{-2}$	2.0 ± 0.4
	0.979	0.17 ± 0.02	$(2.83 \pm 0.02).10^{-2}$	5.9 ± 0.6
	1.907	0.46 ± 0.06	$(1.87 \pm 0.13).10^{-2}$	24.6 ± 1.4
	2.797	1.24 ± 0.10	$(1.11 \pm 0.06).10^{-2}$	112 ± 4
	3.626	—	—	247 ± 21
Di-*n*-butyl ether		0.25 ± 0.03[c]	$(5.62 \pm 0.05).10^{-1}$[c]	0.44 ± 0.08[c]
THF		0.70 ± 0.04[c]	$(2.58 \pm 0.27).10^{-2}$[c]	27 ± 4[c]
1,4-dioxane		—	—	37 ± 8
CH_2Cl_2[a]		0.145 ± 0.04	$(3.02 \pm 0.18).10^{-3}$	48 ± 10
Chloroform[a]		—	—	102 ± 2
$CH_2Cl—CH_2Cl$		0.112 ± 0.01	$(3.45 \pm 0.16).10^{-3}$	32.4 ± 1.3[b]
Methanol		0.314 ± 0.10	$(2.14 \pm 0.23).10^{-3}$	147 ± 33
Ethanol[b]		0.53 ± 0.05	$(5.04 \pm 0.15).10^{-3}$	105 ± 6
2-propanol[b]		0.615 ± 0.03	$(1.06 \pm 0.01).10^{-2}$	58 ± 2
Nitrobenzene		—	—	593 ± 1
Acetone		1.23 ± 0.2 [1.21 ± 0.07[c]]	$(2.03 \pm 0.17).10^{-3}$	605 ± 30
	0.511	1.65 ± 0.4	$(1.35 \pm 0.07).10^{-3}$	1220 ± 220
	1.001	2.15 ± 0.2	$(1.18 \pm 0.02).10^{-3}$	1820 ± 140
	1.458	1.98 ± 0.5	$(8.1 \pm 0.7).10^{-4}$	2440 ± 440
	1.886	—	$(5.1 \pm 0.9).10^{-4}$	>4000
Acetonitrile		[1.36 ± 0.01] 1.44 ± 0.17[c]	$(4.35 \pm 0.05).10^{-4}$	3125 ± 320
N,*N*-DMFA		2.23 ± 0.2	$(5.71 \pm 0.13).10^{-4}$	3905 ± 290
DMSO[d]		2.9 ± 0.5	$(3.24 \pm 0.09).10^{-4}$	8930 ± 1240
N,*N*-DMAA		2.0 ± 0.6	$(1.03 \pm 0.11).10^{-3}$	1940 ± 340
Nitromethane[b]		1.61 ± 0.4	$(3.71 \pm 0.10).10^{-4}$	4340 ± 1000

[a] A side reaction (tri-*n*-butylphosphine halogenation) is possible, the measurements were performed during 2 relaxation times. The products of the side reactions were detected in the NMR spectra of the adduct solution after a few hours.

[b] Data taken from Ref. [6].

[c] Data obtained from stopped flow measurements; the other k_1 values were calculated from $K_{eq} \cdot k_{-1}$.

[d] No products of the possible side reaction (tri-*n*-butylphosphine oxidation) were detected in NMR spectra at 298 K.

To gain further insight into the role of the medium in the studied reversible reaction, it was appropriate to study the effect of salt solution, lithium perchlorate (LP) in diethyl ether (LPDE) and acetone, on the rate and equilibrium constants of this reaction. Lithium perchlorate solutions can be considered as highly polar media.[12–15] A summary of its remarkable effects was collected in several reviews.[15,16]

It was proposed that the effect of lithium perchlorate solution in diethyl ether (LPDE) was caused by electrostatic stabilization of the charged static or dynamic states.[12–14] Other authors[15,16] considered the rate acceleration in LP solutions as a result of the Lewis acidity of LP. The opposite effects of LP in diethyl ether (DE) on the rate constants of the forward and back reactions and the sharp increase in the equilibrium constant (Fig. 1) are in better agreement with the charge stabilization of phosphobetaine (**3**). A similar but smaller effect was observed for LP in acetone solution (Table 1).

The low charge separation in the transition state of the studied reaction follows from the larger solvent polarity effect (Table 1)

Table 2. Thermodynamic parameters for tri-*n*-butylphosphoniumdithiocarboxylate formation ($T = 298$ K)

Solvent	ΔH ($kJ\,mol^{-1}$)	ΔS ($J\,mol^{-1}\,K^{-1}$)	ΔG ($kJ\,mol^{-1}$)	K_{eq} (M^{-1})
Ethanol	-26.5 ± 1.0	-50.3 ± 4	-11.5	105 ± 6
N,*N*-DMFA	-47.1 ± 1.3	-89.3 ± 10	-20.5	3905 ± 290
Acetone	-51.2 ± 1.1	-118.5 ± 8	-15.9	605 ± 30
Acetonitrile	-54.3 ± 0.8	-115.4 ± 13	-19.9	3125 ± 320

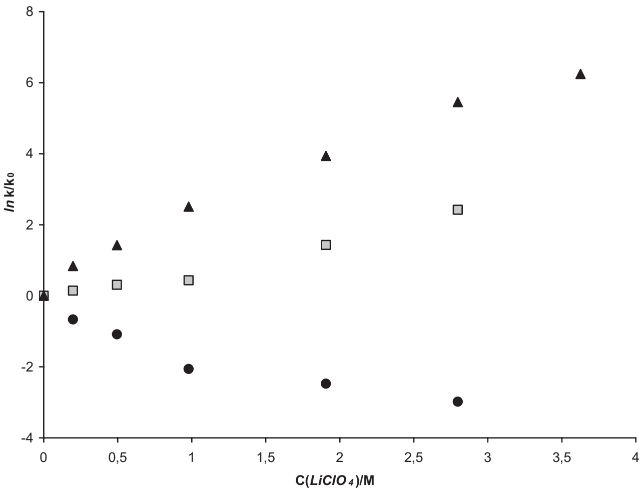

Figure 1. Effect of $LiClO_4$ concentration in diethyl ether on the forward (▢), reverse (●) reaction rate constants, and equilibrium (▲) constant of tri-*n*-butylphosphoniumdithiocarboxylate formation

on the value of k_{-1} compared with k_1. The effect of high external pressure on the equilibrium and rate constants of phosphobetaine formation (1) was studied in some solvents. Since the equilibrium constant of reaction (1) sharply depends on the solvent polarity (Table 1), different methods had to be employed to determine the reaction volumes. Partial molar volume (PMV) measurements are appropriate to determine the reaction volume in acetone and acetonitrile (Table 3).

The value of the reaction volume in acetonitrile was independently confirmed by UV-spectrophotometric measurements of the effect of pressure on the equilibrium constant, see Eqn (3). For such measurements it is necessary to determine the molar absorption change of **3** due to the change in solvent properties induced by high pressure. In the solvents of low polarity (diethyl ether and THF) the reaction volumes were determined by high pressure ^{31}P NMR measurements of integral absorption of ^{31}P in **1** and **3** at equilibrium (Table 3).

The results of PMV measurements on the reactants **1** and **2**, and the adduct **3**, along with the reaction volumes determined in the studied solvents, are presented in the Table 3.

The pressure effects on the equilibrium constants of reaction (1), observed in acetonitrile by UV-spectroscopy and in ether by NMR-spectroscopy measurements, are presented in the Fig. 2.

The corresponding dependencies are given by Eqn (4) in acetonitrile and Eqn (5) in ether solutions (pressure scale in MPa). The initial concentration of tri-*n*-butylphosphoniumdithiocarboxylate [$C_0(Bu_3PCS_2)$] is shown for each experiment.

$$\begin{aligned}\ln K_p/K_0 &= (-7.71 \pm 19.89) \times 10^{-3} + (1.57 \pm 0.01) \times 10^{-2} p \\ &\quad - (3.21 \pm 0.97) \times 10^{-5} p^2 \\ R &= 0.997 \\ \Delta V &= -39 \pm 2\,\mathrm{cm^3\,mol^{-1}}\ \text{in acetonitrile}\ [C_0(Bu_3PCS_2) \\ &\quad = 6.74 \times 10^{-4}\,\mathrm{M}]\end{aligned} \tag{4}$$

$$\begin{aligned}\ln K_p/K_0 &= (0.0564 \pm 0.0514) + (2.83 \pm 0.16) \times 10^{-2} p \\ &\quad - (6.04 \pm 1.02) \times 10^{-5} p^2 \\ R &= 0.998 \\ \Delta V &= -70 \pm 4\,\mathrm{cm^3\,mol^{-1}}\ \text{in diethyl ether}\ [C_0(Bu_3PCS_2) = 0.215\,\mathrm{M}]\end{aligned} \tag{5}$$

For a repeated measurement in diethyl ether at 298 K with an initial concentration of phosphobetain of 0.150 M, a similar curve was obtained with $R = 0.999$ and a reaction volume of $-68 \pm 4\,\mathrm{cm^3\,mol^{-1}}$. The average value equals $-69\,\mathrm{cm^3\,mol^{-1}}$. In THF-$D_8$ at 303.2 K, the dependence of $\ln K_p$ on pressure gave $\Delta V = -66 \pm 2\,\mathrm{cm^3\,mol^{-1}}$ with $R = 0.995$ [$C_0(Bu_3PCS_2) = 0.142$ M].

There are certain experimental restrictions for quantitative measurements of the concentration of P-containing compounds using ^{31}P NMR, and they have been discussed in the literature.[17–21] The selected conditions were a compromise between the requirements of the high pressure NMR experiment and the quantitative ^{31}P NMR measurements,[17–20] which states that a flip angle of 30° is optimal and the delay time (between rf pulses) must be at least three times larger than the largest T_1 (phosphorus atom spin lattice relaxation time). T_1 was determined with the inversion-recovery method for the concentrations used in the high pressure experiments. In diethyl ether, T_1 for **1** was 13.2 ± 0.6 s and 8.7 ± 0.3 s for **3** in a solution with an initial adduct concentration of 0.217 M. In THF, T_1 equals 12.7 ± 0.4 s for **1** and 9.7 ± 0.2 s for **3** in a solution with an initial adduct concentration of 0.145 M. The solutions for the relaxation time (T_1) measurements were prepared in the same way as for the high pressure experiments. These values are not considered here as reference data, but they were used as criteria for the correctness of the quantitative ^{31}P NMR measurements. In our experiments T_1 was always less than the delay time, the flip angle was 30° as recommended,[17–20] and the use of two different concentrations of phosphobetaine in DE gave similar values for the reaction volume. A separate experiment in which the delay time was varied from 20 to 50 s with a flip angle of 30° was

Table 3. Partial molar volumes of tri-*n*-butylphosphine, carbon disulfide, and tri-*n*-butylphosphoniumdithiocarboxylate, and volume of the reaction (1) calculated from the difference between the PMV of the reactants and products (A), and from the dependence of ln *K* on *p* (B)

	$\overline{V}$ ($\mathrm{cm^3\,mol^{-1}}$)			ΔV_{r-n} ($\mathrm{cm^3\,mol^{-1}}$)	
Solvent	Bu_3P	CS_2	Bu_3P^+-CS_2^-	A	B
Acetonitrile	248.8 ± 1.0	65.9 ± 0.2	274.9 ± 2.0	-39.8 ± 2.5	-39 ± 2
Acetone	248.3 ± 0.3	65.3 ± 0.4	275.9 ± 0.5	-37.7 ± 1.2	—
Diethyl ether	—	—	—	—	-69 ± 4
THF-D_8	—	—	—	—	-66 ± 2

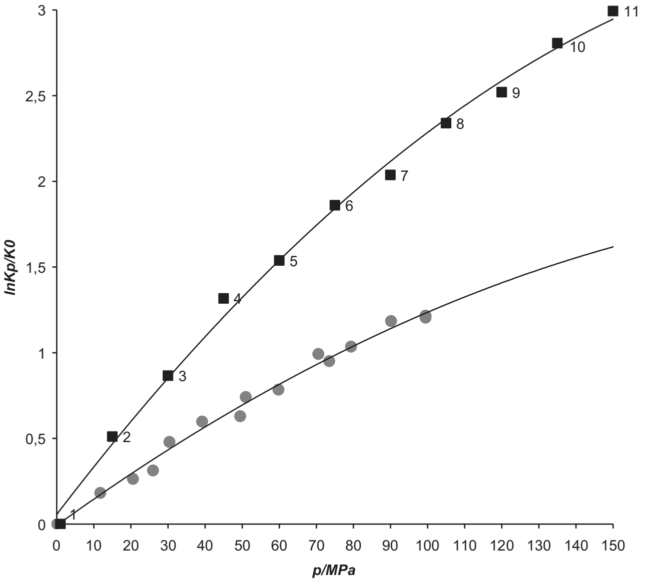

Figure 2. The pressure dependence of the equilibrium constant of tri-*n*-butylphosphoniumdithiocarboxylate formation reaction. ■ – in diethyl ether (^{31}P NMR, 298 K, $C_0(Bu_3PCS_2) = 0.215$ M); ● – in acetonitrile. (UV–Vis spectrometry, 298 K, $C_0(Bu_3PCS_2) = 6.74 \times 10^{-4}$ M)

performed in DE solution, and the relation of the integrals remained constant within 1%. Half of the experimental points in the pressure dependence recorded at 30 MPa intervals, were obtained on increasing the pressure (Fig. 2, square points for higher concentration dependence, odd point numbers), and the other half (even point numbers) were obtained on decreasing the pressure. All experimental points gave a good fit.

The effect of high pressure on the relaxation time of phosphorus has not been completely studied by now. However, it was shown in a separate experiment that under the conditions of the present study (pressure up to 150 MPa), the ratio of the integrals of the two independent compounds not reacting with each other (triphenylphosphine and triphenylphosphineoxide), did not change at elevated pressure.

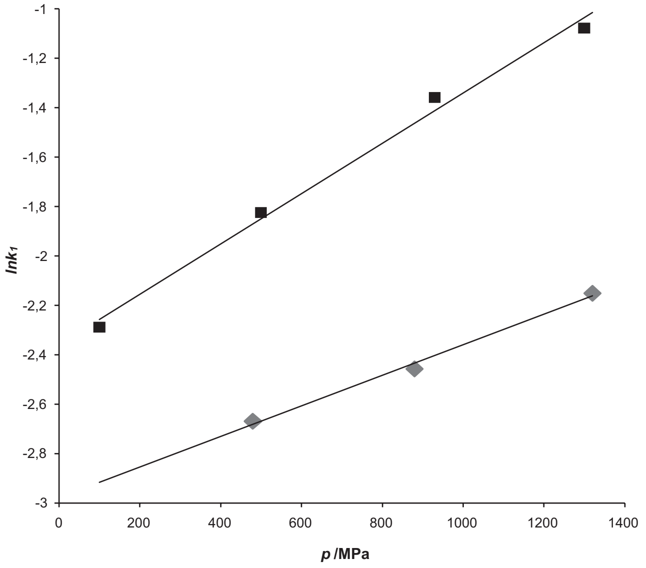

Figure 3. The dependence of the forward reaction of tri-*n*-butylphosphoniumdithiocarboxylate formation rate constant on the pressure. ■ – di-*n*-butyl ether; ◆ – tetrahydrofurane, 298 K

The reaction volume determined in acetonitrile by two different methods (PMV measurements and high pressure UV-spectroscopy) is in a good agreement within the accuracy of the measurements. The reaction volume in acetone ($-38\,\text{cm}^3\,\text{mol}^{-1}$) is close to that found for acetonitrile ($-39\,\text{cm}^3\,\text{mol}^{-1}$) and exceeds the data in less polar solvents, *viz*. DE ($-69\,\text{cm}^3\,\text{mol}^{-1}$) and THF ($-66\,\text{cm}^3\,\text{mol}^{-1}$).

Activation and reaction volumes are usually considered as a sum of two contributions: changes in the intrinsic structure and in the solvation shell.[22–24]

$$\Delta V = \Delta V_{\text{struct}} + \Delta V_{\text{solv}} \tag{6}$$

Calculations of van der Waals volumes of the reactants **1** and **2** and adduct **3** according to the Bondi method[25] resulted in the values of $31\,\text{cm}^3\,\text{mol}^{-1}$ for CS_2, $120.3\,\text{cm}^3\,\text{mol}^{-1}$ for Bu_3P and $146.9\,\text{cm}^3\,\text{mol}^{-1}$ for phosphobetaine **3**. Thus, the difference in van der Waals volumes of the product and reactant molecules is only $-4.4\,\text{cm}^3\,\text{mol}^{-1}$. The difference between this value and the reaction volumes found in acetone/acetonitrile pair, and DE/THF pair, can clearly be ascribed to the reorganization and electrostriction of the solvation shell (ΔV_{solv}).

An attempt to determine the activation volume for the forward reaction was performed in di-*n*-butyl ether and THF using a high pressure stopped-flow method. For these solvents the activation volumes were determined by use of Eqn (2). An attempt to determine the activation volume for the forward reaction was performed in di-*n*-butyl ether and THF using a high pressure stopped-flow method (Fig. 3). From these data, the activation volume equals $-24 \pm 3\,\text{cm}^3\,\text{mol}^{-1}$ in di-*n*-butyl ether and $-15 \pm 3\,\text{cm}^3\,\text{mol}^{-1}$ in THF. From the very small solvent effect on the values of the rate constants (k_1 in di-*n*-butyl ($0.09\,\text{L}\,\text{M}^{-1}\,\text{s}^{-1}$) and diethyl ether ($0.11\,\text{L}\,\text{M}^{-1}\,\text{s}^{-1}$)), we can assume approximately the same volume parameters in these ethers. As a result, the activation volume for the reverse reaction can be estimated as $+51 \pm 5\,\text{cm}^3\,\text{mol}^{-1}$ in THF and $+45 \pm 8\,\text{cm}^3\,\text{mol}^{-1}$ in ether. Thus activation volume data demonstrate that the transition state volume is closer to the volume of the reactants than to the volume of the products.

CONCLUSIONS

The equilibrium and rate constants, and reaction volumes for the formation of tri-*n*-butylphosphoniumdithiocarboxylate are very sensitive to the solvent polarity and LP concentration. The effect of high external pressure on the equilibrium of this reaction results in extremely negative reaction volumes, which change sharply on going from acetone and acetonitrile to the less polar THF and diethyl ether. The experimental data demonstrate that the solvation contributions to the overall reaction volume substantially exceed the structural contributions. Solvent, added salt and high pressure effects allow us to conclude that the transition state is closer to the reactants than to the zwitterionic product.

EXPERIMENTAL

Materials

Preparation of tri-n-butylphosphoniodithiocarboxylate (**3**). Tri-*n*-butylphosphine (Aldrich) (0.01 mol) was added to a cooled (0–5 °C) solution of carbon disulfide (0.01 mol) in dry petroleum ether (b.p. 40–60 °C, 50 ml). After short stirring, red crystals precipitated. The bulb with adduct was left in the freezer (*ca.* −15 °C) overnight and then filtered off and washed with petroleum ether to give **3** as dark red needles, m.p. = 65–66 °C (lit.[2] 65.5 °C). Solvents were purified by known methods,[26] dried over 4 Å molecular sieves for 20–30 h and were stored under molecular sieves (4 Å) under argon. The solvents were bubbled with argon, and all the flasks, cuvettes and syringes were filled with argon before preparing the solutions.

Measurements

Kinetic measurements of the reverse reaction rate and equilibrium measurements at ambient pressure were performed in a 1 cm quartz cell with a fine fitting stopper, that was placed in a thermostated (±0.1 K) cell compartment of a SF-46 spectrophotometer. The reverse reaction rate (k_{-1}) was determined by monitoring the absorption of $(5–20) \times 10^{-5}$ M solutions of tri-*n*-butylphosphoniumdithiocarboxylate at 370–380 nm. The accuracy of determination of the rate constants for the reverse reaction was ±5% for a degree of conversion up to 90%.

The equilibrium constant, $K_{eq} = [Bu_3PCS_2]/[Bu_3P][CS_2]$, was calculated from the initial (D_0) and equilibrium (D_∞) optical densities of the solutions with an initial concentration of tri-*n*-butylphosphoniumdithiocarboxylate of $(1–50) \times 10^{-3}$ M after keeping the reaction mixture in the cells for not less than 6 relaxation times. The D_0 values were determined by extrapolation of the kinetic curve to the initial moment after introducing the reactants. The rate constant of the forward reaction was calculated from the equation $k_1 = k_{-1} \cdot K_{eq}$. The forward reaction rates for (1) were measured independently using the stopped-flow method in acetone, acetonitrile, DBE and THF. Di-*n*-butyl ether was used instead of diethyl ether because of experimental convenience of the higher viscosity. The results of the stopped-flow measurements for k_1 are in reasonable accordance with the calculated k_1 values (Table 1).

Stopped-flow UV kinetic measurements were performed using a Dionex D110 instrument under pseudo-first order conditions. In acetone, $C(Bu_3P) = 0.001–0.0015$ M, $C(CS_2) = 0.02–0.08$ M; in acetonitrile and THF, $C(Bu_3P) = 0.01–0.1$ M, $C(CS_2) = 0.0004–0.0009$ M; in DBE $C(Bu_3P) = 0.07–0.27$ M, $C(CS_2) = 0.0004–0.0009$ M.

High pressure stopped-flow kinetic measurements were performed using a stopped-flow apparatus suitable for such experiments, described earlier.[27] Concentrations range: $C(Bu_3P) = 0.06–0.12$ M, $C(CS_2) = 0.001–0.0025$ M in DBE and THF, $\lambda = 395–405$ nm. The k_1 values at each pressure were used as averaged of four experimental repeated measurements.

The effect of pressure on the equilibrium constants was studied by UV-spectroscopy in acetonitrile, $C_0(Bu_3PCS_2) = 6.74 \times 10^{-4}$ M. The UV-spectrophotometric measurements and the instrumentation are described in the literature.[28] $\lambda = 399.7$ nm was used for calibration and measurements of K_{eq} at high pressure. Calibration of the absorption was made in the interval of pressures 1–100 MPa, $C_0(Bu_3PCS_2) = 3.85 \times 10^{-4}$ M, $C_0(Bu_3P) = 0.05$ M. With these initial concentrations, the portion of adduct **3** in solution exceeded 99%. The result of calibration is the following equation:

$$D_p/D_0 = (0.9989 \pm 0.0013) + (5.927 \pm 0.587) \times 10^{-4} p - (1.493 \pm 0.559) \times 10^{-7} p^2 \quad (7)$$
$$R = 0.9936,\ N = 8$$

The calibration results were used for the calculations of equilibrium concentration of tri-*n*-butylphosphoniumdithiocarboxylate under pressure.

The enthalpies of reaction were measured at 298 K in a differential calorimeter, as previously reported.[29] Samples were weighted in a small cylinder made of stainless steel, both polish sides of which were covered by a thin (0.1 mm) Teflon seal. For all solutions three to five measurements of sequentially dissolving of the samples were carried out.

Measurements of the enthalpy of reaction between tributylphosphine and carbon disulfide were performed in acetone, acetonitrile, ethanol and DMFA. The concentrations of the reagents were adjusted in order to have a degree of conversion of more than 99%. Each value of the enthalpy was determined as the average of two to four measurements. The accuracy was within 4%. $C(Bu_3P) = 0.004–0.005$ M, $C(CS_2) = 0.19–0.35$ M.

NMR spin-lattice relaxation time measurements were performed on a Varian Unity 300 spectrometer with H_3PO_4 as standard, operating at a ^{31}P resonance frequency of about 121.44 MHz. High pressure NMR measurements were performed on a Bruker AVANCE DRX400 WB spectrometer, operating at a ^{31}P resonance frequency of about 161 MHz. The high pressure generating system uses commercially available 'Nova SWISS' equipment (pump, valves, tubing and manometer) combined with a home-built separator unit. The design of the high pressure NMR probe head is described elsewhere.[30] The equilibrium constants from the ^{31}P NMR spectra were calculated using the reagent concentrations, obtained from the integrals of singlets at −30 to −32 ppm (Bu_3P) and 13.7–28.5 ppm (Bu_3PCS_2).

$\bar{V}$ were determined at $25 \pm 1 \times 10^{-3}$ °C by means of an Anton Paar digital vibrating-tube densimeter (DMA 602) with an accuracy of $\pm(1–2) \times 10^{-6}$ g cm^{-3}. The high level of temperature control was achieved using a triple cascade of water thermostats (22.0, 24.5 and 25.0 °C) with reduced heater power in the last one (15 W, 20 dm^3 of water).[29] The densimeter was placed in a box with a constant air temperature of 25 ± 0.2 °C. The apparent molar volumes of all studied compounds for each of the solutions were invariable in the range of concentration 0.03–0.3 mol L^{-1}. No change in the densities of solutions was observed during the time of measurement.

PMVs of solutes at infinite dilution were calculated by extrapolation of the apparent molar volumes (φ) obtained by measuring the solvent and solution densities:

$$\varphi_A = 1000(d_o - d)/c_A d_o + M_A/d_o \quad (8)$$

In Eqn (8), M_A denotes the molar mass of solute, d and d_o are the densities of solution and solvent, c_A is the concentration scale in molarity.

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