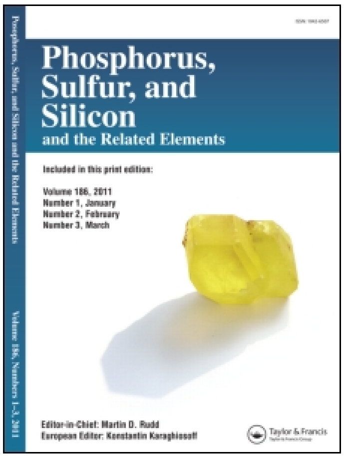

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Zbigniew Brylewicz[a]; Remigiusz Rudnicki[a]
[a] Department of Basic Chemistry, Warsaw University of Technology, Warsaw, Poland

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INVESTIGATION OF THE SOLUBILITY OF COMMERCIAL TETRAPHOSPHORUS DECASULFIDE

ZBIGNIEW BRYLEWICZ and REMIGIUSZ RUDNICKI
Department of Basic Chemistry, Warsaw University of Technology,
ul.Noakowskiego 3, 00-664 Warsaw, Poland

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The solubility of commercial tetraphosphorus decasulfide in 1,1,2,2-tetrachloroethane, chlorobenzene, bromobenzene, *o*-chlorotoluene, *m*-chlorotoluene, *o*-bromotoluene, α-bromonaphthalene, *o*-xylene, *m*-xylene, decaline and carbon disulfide were determined using a dynamic (synthetic) method.

Key words: Tetraphosphorus decasulfide; solubility; organic solvents.

INTRODUCTION

Tetraphosphorus decasulfide (P_4S_{10}) is a substance which can easily react with many organic compounds and thus it is widely applied for introducing sulfur into their structure. There exists practically one method for manufacture of P_4S_{10}, which consists in melting together sulfur with phosphorus (or phosphorus sulfide) in a stoichiometric proportion.[1]

The results of Demarcq's investigations[2] show that at temperatures above the sulfide melting, necessary to synthesize P_4S_{10} the reaction of the synthesis is accompanied by thermal decomposition which leads to formation of P_4S_9 and sulfur. The data published show that it is practically impossible to obtain pure tetraphosphorus decasulfide in that way. It is a common practice to purify the melt or a commercial P_4S_{10} by extraction or recrystallization, both involving CS_2 as a solvent. The solubility of P_4S_{10} in carbon disulfide is low, however (0.22 g in 100 g CS_2 at 298 K)[3] and a process of obtaining P_4S_{10} in laboratory scale is long-lasting.

The aim of this work was to find a solvent that might substitute carbon disulfide in separations of P_4S_{10} from the melts of phosphorus with sulfur or from commercial products.

Preliminary analysis of literature data has shown two groups of compounds that might be used as solvents in extraction of P_4S_{10}. Those were: (1) aromatic hydrocarbons and (2) halogen derivatives of aromatic and aliphatic hydrocarbons.

Tetraphosphorus decasulfide is capable of reacting with aromatic hydrocarbons, but this reaction is slow and noticeable at high temperatures.[4] P_4S_{10} reacts also with alkyl halides. These reactions are catalysed by Lewis acids.[5]

The solubility of tetraphosphorus decasulfide has been investigated by Bourdauducq and Demarcq[6] (carbon disulfide), Barral *et al.*[7] (α-chloronaphthalene, 1,4-dibromobenzene) and Bebikh and Ponizovtsev[8] (chlorobenzene, bromobenzene and iodobenzene).

Recently Demarcq[9] has also observed a dissociation of tetraphosphorus decasulfide to P_4S_9 and small amounts of phosphorus polysulfides in 1-chloronaphthalene and carbon disulfide solutions.

RESULTS AND DISCUSSION

Preliminary investigations of solubilities of pure and commercial tetraphosphorus decasulfide have shown that repeated heating of the same solution in carefully sealed glass container results in decrease of dissolving temperature of the sulfide (see Figure 1). This phenomenon was smaller, however, for the commercial P_4S_{10} while in the case of pure products it is much appreciable.

On the other hand, we have found that solubilities of pure and commercial sulfides differ significantly from each other (at 293 K—commercial, 0.46 g/100 g; pure 0.20 g/100 g of CS_2).

The results of solubilities measurements are shown in Table I. The temperatures given in the table are the means of at least three measurements, and the difference between the individual results was not more than 0.2 K.

The data presented show that the solubility of tetraphosphorus decasulfide in all the solvents tested is low. The best solvent for the decasulfide among the substances tested was α-bromonaphthalene. This solvent permits to obtain at higher temperatures, relatively concentrated solutions of P_4S_{10} (5.0 g/100 g of solvent at 407 K, max. solubility of P_4S_{10} in carbon disulfide 0.88 g/100 g of solvent at 319 K). Comparison of corresponding chloro- and bromo-derivatives enables one to state,

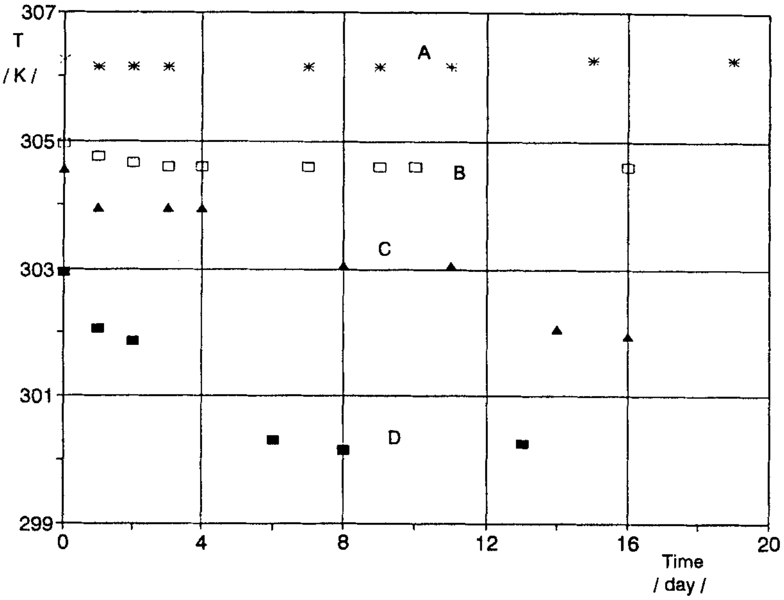

FIGURE 1 The changes of solubilities of pure (A—*, B—□) and commercial (C—▲, D—■) tetraphosphorus decasulfide.

that substitution of bromine to chlorine in the given compound increases the solubility of P_4S_{10} (ex. chlorobenzene-bromobenzene; *o*-chlorotoluene-*o*-bromotoluene; α-chloronaphthalene (Barral *et al.*[7]) -α-bromonaphthalene).

However, the use of α-bromonaphthalene and some other solvents tested for purification of commercial tetraphosphorus decasulfide seems to be limited. In experiments with several solvents we have noticed the above mentioned phenomenon of decreasing of dissolving temperature of the sulfide. This was not observed as only above a certain temperature specific for the given solvent (for example, for α-bromonaphthalene that temperature was about 430 K). Our results seems to confirm Demarcq's[9] observations about the dissociation of the tetraphosphorus decasulfide in solution. We did not define our reaction products because the infrared absorption and ^{31}P NMR studies of the solutions, in which the above-described

TABLE I

Solubility data of commercial tetraphosphorus decasulfide in some organic solvents

Tetrachloroethane		Chlorobenzene		Bromobenzene	
T	x	T	x	T	x
(K)	$(\cdot 10^5)$	(K)	$(\cdot 10^5)$	(K)	$(\cdot 10^5)$
307.50	7.51	309.10	9.72	300.60	14.13
307.95	7.69	325.60	17.99	311.05	21.57
322.70	13.90	335.20	28.56	341.00	59.77
330.35	18.70	337.35	32.13	351.55	85.77
334.60	23.00	345.35	42.26	359.30	101.00
344.55	30.40	345.50	41.29	370.80	133.33
355.00	40.20	357.60	56.62	374.55	146.20

o-Chlorotoluene		m-Chlorotoluene		o-Bromotoluene	
T	x	T	x	T	x
(K)	$(\cdot 10^5)$	(K)	$(\cdot 10^5)$	(K)	$(\cdot 10^5)$
306.55	25.15	311.15	21.60	323.55	75.49
308.65	25.41	329.95	37.68	329.05	84.21
316.45	30.21	342.55	53.66	331.35	95.31
323.15	40.37	358.75	87.58	335.45	114.33
346.35	68.59	369.85	124.20	341.35	127.10
355.65	92.19			430.85	150.40
363.85	114.90			444.55	203.70

TABLE I (*continued*)

α-Bromonaphthalene		o-Xylene		m-Xylene	
T (K)	x $(\cdot 10^5)$	T (K)	x $(\cdot 10^5)$	T (K)	x $(\cdot 10^5)$
348.15	525.2	306.70	49.78	309.90	30.99
361.75	708.6	324.95	76.53	318.95	44.83
372.15	972.0	327.65	79.41	322.35	53.84
387.55	1405.0	335.85	94.22	326.45	58.80
407.05	2273.0	338.65	103.50	333.25	68.42
425.15	3507.0	346.65	124.30	333.45	74.67
		351.65	139.10	338.95	87.73

Decaline		Carbon Disulfide	
T (K)	x $(\cdot 10^5)$	T (K)	x $(\cdot 10^5)$
318.30	5.49	289.65	71.11
328.70	8.35	289.85	73.88
340.35	14.36	294.30	81.99
355.60	24.73	301.85	99.90
365.95	35.60	302.70	103.00
380.00	55.75	305.35	109.70
388.80	74.01	305.85	109.20
394.90	89.18		

x—is mole fraction of the solute.

phenomenon was observed, did not permit for univocal explanation of its origin. Further investigations of the phenomenon will be described in a next paper.

EXPERIMENTAL

Solubilities were determined using a dynamic (synthetic) method. Mixtures of solute and solvent prepared by weighing pure components to within 5×10^{-7} kg were placed in a carefully sealed Pyrex glass cell. The cell was placed in a glass thermostat and the mixtures had been preheated 5–10°C above the equilibrium temperature and next has been quickly cooled to obtain very small crystals. Then the mixture has been heated very slowly (less than 2 Kh^{-1} near the equilibrium temperature) with continuous stirring inside a Pyrex glass cell. The temperatures of crystal disappearance, detected visually, were measured with calibrated thermometer (subdivided in 0.1 K) totally immersed in the thermostatting liquid. The accuracy of temperature measurement was ±0.05 K. The measurement was repeated three times for each sample.

The material used in the study was a commercial Montedison product containing 28.1% by weight of phosphorus. A presence of 35% by weight of P_4S_9 was found by the IR absorption method.[2,10] The solvents tested were dried over anhydrous magnesium sulfate and distilled through 50 cm Vigreux column (diameter—24 mm). The solvents were manufactured: by Polskie Odczynniki Chemiczne POCH Gliwice, Poland (Bromobenzene, *o*-Bromotoluene, α-Bromonaphthalene, 1,1,2,2-Tetrachloroethane and Decaline); by International Enzymes Ltd. Windsor, Berkshire UK (Chlorobenzene); by Reachim Vio Sojuzchimexport (*o*-Chlorotoluene, *m*-Chlorotoluene, *o*-Xylene and *m*-Xylene) and by Merck Darmstadt, Germany (Carbon Disulfide).

Pure P_4S_{10} was obtained by multistage extraction with the use of CS_2 by the method described in Reference 11.

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