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EQUILIBRIUM OF THE ADDUCT FROM TRIBUTYLPHOSPHINE AND PHENYL ISOTHIOCYANATE AND ^{31}P-NMR CHEMICAL SHIFTS OF THE ADDUCTS FROM TRIBUTYLPHOSPHINE AND ISOTHIOCYANATES

Kin-ya AKIBA, Toshio YONEYAMA, and Naoki INAMOTO
Department of Chemistry, Faculty of Science,
The University of Tokyo, Hongo, Tokyo 113

Equilibrium constants of the adduct (3c) from tributylphosphine (4) and phenyl isothiocyanate (5c) were measured in some solvents and ^{31}P-NMR chemical shifts of the adducts (3) from (4) and isothiocyanates (RNCS) (5) were measured in DMF and correlated linearly with the σ_p values of the R groups.

The adducts of triethylphosphine (1) with carbon disulfide (2) and phenyl isothiocyanate have been known since the last century.[1] After some discussion,[2] the structure of the adduct of (1) with (2) in solid state was finally determined by X-ray crystallography, which showed the presence of P-C σ-bond.[3] On the other hand, the nature of the adducts in solution still remains obscure.[4]

This paper describes the quantitative aspect of the equilibrium between the adducts (3) of tributylphosphine (4) with isothiocyanates (5) and the starting components in solution.

The equilibrium between the adduct (3c) of (4) with phenyl isothiocyanate (5c) and the components was measured in some solvents and the result is shown in Table 1. The equilibrium constants were calculated from the increase in absorbance of a new band due to the formation of the adduct according to Drago's method.[5] A typical example of UV absorption of the system is shown in Fig. 1.

Equilibrium constant becomes larger according to the increase in the polarity of the solvents as expected from the polar nature of the adduct (3c). There is also blue shift of absorption maximun, in which the case of acetone is exceptional, probably due to some specific interaction of the solvent with (3c).

In the case of p-toluenesulfonyl isothiocyanate (5g) and (4), the equilibrium in acetonitrile was shown to be shifted almost completely to the adduct (3g) even in dilute solution as used for UV measurement. From molar extinction coefficient obtained in the presence of excess (4), equilibrium constant was calculated to be $(2.4 \pm 0.5) \times 10^4$ (24 °C).

Equilibrium constant of the adduct (3f) from benzoyl isothiocyanate (5f) and (4) was also measured to be $(3.4 \pm 1.0) \times 10^4$ in acetonitrile (24 °C). In this case, accuracy of measurement was not good, probably due to rather rapid reaction of the adduct (3f) with excess (4).[6]

It is obvious that electron-withdrawing groups shift the equilibrium strongly to the adduct.

Table 1 Equilibrium between the adduct (3c) and tributylphosphine (4) and phenyl isothiocyanate (5c) in some solvents (24 °C)

$$n\text{-}Bu_3P \;(4) + Ph\text{-}N{=}C{=}S \;(5c) \underset{}{\overset{K}{\rightleftharpoons}} Ph\text{-}N{=}C(S^-)\text{-}P^+(n\text{-}Bu)_3 \;(3c)$$

Solvent	Equilibrium constant (K)	ϵ (at 340 nm)	λmax (nm)	Dielectric constant
CH_3CN	840 ± 43	6500	331	37.5
CH_3COCH_3	323 ± 6	5600	337	20.7
CH_2Cl_2	277 ± 20	6400	334	8.9
$(C_2H_5)_2O$	3.7—6.7	—	340	4.3
$n\text{-}C_6H_{14}$	1.5—3.5	—	340	1.9

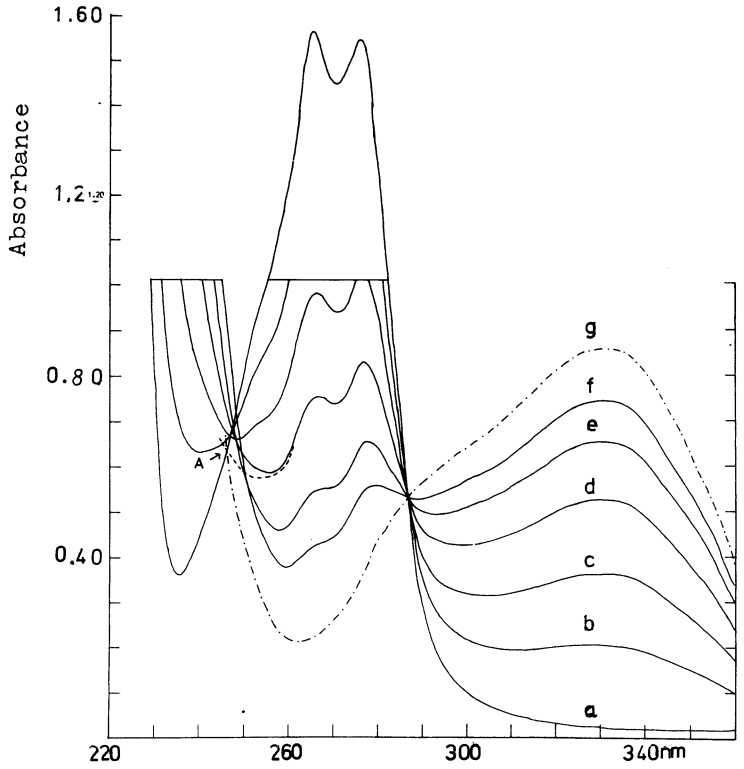

Fig. 1 UV spectra of tributylphosphine (4) and phenyl isothiocyanate (5c) system in acetonitrile

The ratio of (4) to (5c): b=2.9; c=7.3; d=15; e=29; f=57. a is the spectrum of (5c). Concentration of (5c), (1.23×10^{-4} M), was maintained constant throughout the measurement.

—·—·—(g) Calculated spectrum of the adduct (3c) based on the equilibrium constant (K=840): ϵ=6900 (at 331 nm).

A: One of isosbestic points of (3c) and (5c).

----- Calculated spectrum of d where the absorbance of (4) was subtracted by using a calibration curve of (4).

Then, ^{31}P-NMR spectra were measured for the adducts (3) of (4) with (5) in dimethylformamide (DMF) and the results are shown in Table 2. Plots of data in Table 2 against σ_p values of the R group gave a rather good straight line (ρ=-9.08, r=0.990, and s=0.532).

In these measurements, no residual (4) was detected except for methyl isothiocyanate in which the rate of formation of the adduct should be slow. Equilibrium is shifted almost to the adduct (3) in concentrated solutions used for NMR measurements, and this fact is supported by simple calculation of the concentration of three components in equilibrium by using data in Table 1.

When excess (4) was present in DMF [(4):(5c)=2:1], two ^{31}P-NMR peaks were observed which correspond to (4) and (3c), respectively, showing that the rate of equilibration is slow for observation by NMR.

Based on these observations and some reactivity of (3), the structure of the adduct in solution is depicted as a phosphonium betaine (3) with a P-C σ-bond.

Table 2 ^{31}P-NMR chemical shifts of the adduct (3) of tributylphosphine (4) with isothiocyanates (5) in DMF at 34 °C

$$\underset{(4)}{n\text{-}Bu_3P} + \underset{(5)}{R\text{-}N{=}C{=}S} \rightleftharpoons \underset{(3)}{R\text{-}N{=}C(S^-)\text{-}\overset{+}{P}(n\text{-}Bu)_3}$$

	R of (3)	δ(ppm)	σ_p of R group*
a)	CH_3	-18.3	-0.17
b)	$CH_2{=}CHCH_2$	-18.1	
c)	Ph	-20.0	-0.01
d)	α-$C_{10}H_7$	-20.9	
e)	$Ph_2P(S)$	-21.9	0.28[8]
f)	PhCO	-23.1	0.43[9]
g)	p-$CH_3C_6H_4SO_2$	-26.8	0.72**

External standard: 85% H_3PO_4

Concentration of each charged material (4 and 5) was about 0.83 M.

* σ_p values were taken from reference 7), unless otherwise stated.

** For CH_3SO_2 group

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