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PHYSICAL CHEMISTRY

Electron Donor-Acceptor Phenomena. VI.*) Hexamethylphosphotriamide and Trinitrosubstituted Benzenes

by

Krystyna POBŁOCKA, Tadeusz URBAŃSKI, Witold WACŁAWEK

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Summary. Complexation constant and enthalpy data have been determined for charge transfer complexes of hexamethylphosphotriamide with trinitrobenzene and trinitrotoluene in 1,2-dichloroethane solutions from −15.5 to +22.0°C.

Hexamethylphosphotriamide (HMPT), one of the best aprotic solvents, was found to be suitable for investigation of the CT-complexes [1–3]. However, in spectrophotometric studies on molecular complex formation of pyrimidine and purine bases with D-mannitol hexanitrate (MHN) in HMPT [2], it appeared that this solvent is an electron donor. It seems to cause an appearance of bands at 450 nm and 310, 390 nm for MHN–HMPT and MHN–pyrimidine, purine base systems, respectively. Adenine does not produce a new band. In the cases when pyrimidine and purine bases were studied with erythritol tetranitrate in HMPT [2], the new bands have not been observed. Similar studies have been carried out with the high-resolution NMR technique [3] for the HMPT–erythritol tetranitrate in chloroform-D_6 and no changes in proton signal resonance positions were observed for both HMPT and erythritol tetranitrate. This seems to be in agreement with the conclusions [2] that the CT-complexes are not formed in this system. On the other hand, it was shown by dipole moments, calorimetric and NMR measurements that HMPT forms complexes with chlorides of transition metals [4]. It seemed of interest to study complexing ability of HMPT with 1,3,5-trinitrobenzene (TNB) and 2,4,6-trinitrotoluene (TNT) because both electron acceptors form molecular complexes with a great number of compounds which were thoroughly studied by various physical methods.

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*) Part V: Bull. Ac. Pol.: Chim., **22**, 1 (1974).

Experimental

Materials. TNT and TNB were purified by recrystallization from ethyl alcohol until m.ps. 80.5 and 130°C, respectively, were reached.

HMPT and 1,2-dichloroethane were redistilled just before the preparation of the solutions.

Determinations. To determine the composition of molecular complexes formed the Job method of continuous variation was applied using NMR [5] and UV-VIS spectrophotometric [6] measurements. 1,2-Dichloroethane was used as a solvent for all the studied systems. The solutions were prepared by mixing x cm^3 of 0.1 mole/kg of HMPT solution with $(5-x)$ cm^3 of 0.1 mole/kg of TNT or TNB solution, both in 1,2-dichloroethane (where x varied from 0 to 5 cm^3). NMR spectra were measured on a BS 487 C spectrometer—Tesla Brno (Czechoslovakia). Proton signal positions in the spectra of TNT or TNB electron acceptors, were determined with an internal 1,2-dichloroethane resonance signal. In the UV-VIS spectrophotometric measurements for HMPT–TNT and HMPT–TNB systems the changes in the 510 and 315 nm absorption band intensities were followed. The complexation constants were evaluated for both NMR and UV-VIS spectra data with the Benesi–Hildebrand equation [7]. Concentration of the donor HMPT was changed within 0.05–2.0 mole/kg of the solution (for both NMR and UV-VIS measurements), while that of the acceptor (TNT or TNB) was kept constant at 0.01 mole/kg of the solution (in the NMR determination) and $1.5 \cdot 10^{-3}$ mole/kg of the solution (in the UV-VIS measurement). All the solutions were made by weight.

Results and discussion

The Job plots are shown in Figs. 1–4. In all the Figures *a* and *b* refer to stock solutions of the 0.1 and 0.05 mole/kg concentrations, respectively. The data in Figs. 1 and 2 were derived from the NMR measurement, whereas those in Figs. 3 and 4—from the UV-VIS measurements. It may be seen that all the curves exhibit a maximum at $x_D = 0.5$, i.e. it indicates the molar ratio of the HMPT–TNB (TNT) complex of 1:1. The results for the complexation constant K values (for both methods) are summarized in the Table. The stability data determined by both methods are very similar. Moreover, one can see that the HMPT–TNB complex is more stable than that of HMPT–TNT, which is in agreement with the electron acceptor

TABLE

Complexation constants K (determined from NMR and spectrophotometric measurements) and enthalpy ΔH (from NMR measurement)

Complex	K [kg/mole] NMR	K [kg/mole] optical	ΔH [kcal/mole] NMR
HMPT–TNB	0.19	0.20	−0.9
HMPT–TNT	0.13	0.13	−0.8

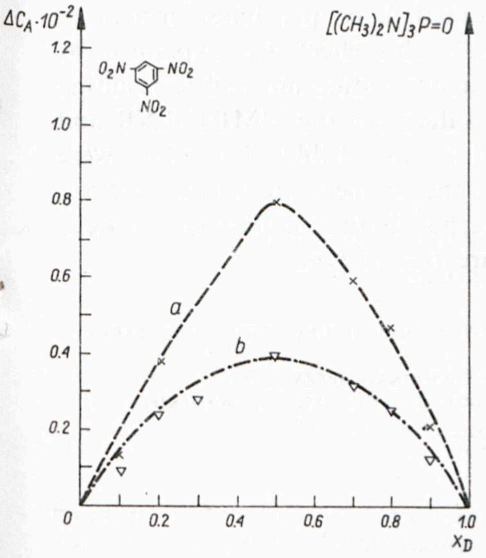

Fig. 1. NMR Job plots for the HMPT–TNB system in 1,2-dichloroethane at room temperature

a—0.10 mole/kg of the solution, *b*—0.05 mole/kg of the solution (in all figures)

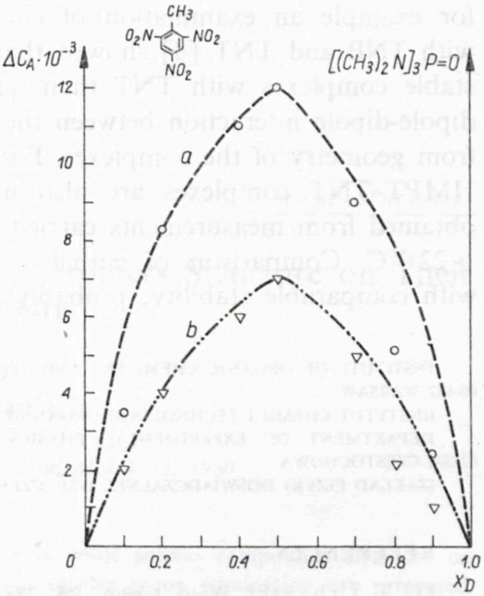

Fig. 2. NMR Job plots for the HMPT–TNT system in 1,2-dichloroethane at room temperature

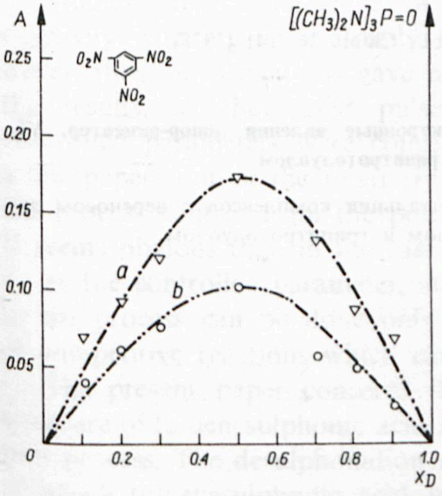

Fig. 3. UV-VIS Job plots for the HMPT–TNB system in 1,2-dichloroethane at 315 nm, at room temperature

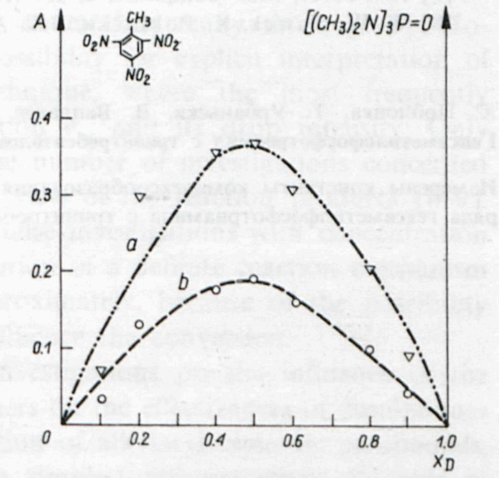

Fig. 4. UV-VIS Job plots for the HMPT–TNT system in 1,2-dichloroethane at 510 nm, at room temperature

abilities of the two nitroaromatic molecules. This is not always the case, for example an examination of charge transfer complexes of azaaromatic with TNB and TNT [8] showed that monomethylated pyridines form more stable complexes with TNT than with TNB. This effect was explained by dipole-dipole interaction between the TNT and pyridine molecules, resulting from geometry of the complexes. Enthalpy values for the HMPT–TNB and HMPT–TNT complexes are also included in the Table. The data were obtained from measurements carried out in the temperature range $-15.5+$ $+22.0$°C. Comparison of enthalpy shows that both complexes are week with comparable stability; probably they are of σ-π type.

INSTITUTE OF ORGANIC CHEMISTRY AND TECHNOLOGY, TECHNICAL UNIVERSITY, KOSZYKOWA 75, 00-662 WARSAW
(INSTYTUT CHEMII I TECHNOLOGII ORGANICZNEJ, POLITECHNIKA WARSZAWSKA)
DEPARTMENT OF EXPERIMENTAL PHYSICS, PEDAGOGICAL UNIVERSITY, ZAWADZKIEGO 13/15, 42-200 CZĘSTOCHOWA
(ZAKŁAD FIZYKI DOŚWIADCZALNEJ, WSP, CZĘSTOCHOWA)

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К. Поблоцка, Т. Урбаньски, В. Вацлавэк, **Электронные явления донор-акцептор. VI. Гексаметилофосфотриамид с тринитробензолом и тринитротолуолом**

Измерены константы комплексообразования и энтальпии комплексов с переносом заряда гексаметилфосфотриамида с тринитробензолом и тринитротолуолом.