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Spectrophotometric Studies of the Reaction of 2,2′,4,4′-Tetranitrodiphenylmethane with Bases in Various Solvents

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A methylene group between two electron-withdrawing moieties is active and is easily subjected to the elimination of a proton from the methylene group, thus yielding a carbanion. For several compounds of this category, the pK_a values have been determined by optical and electrometric measurements.[1-3] For example, 4,4′-dinitrodiphenylmethane has a fairly small pK_a value, 15.8.[2,3] Thus, 2,2′,4,4′-tetranitrodiphenylmethane (abbreviated hereafter to TND) can be expected to be a stronger carbon acid than 4,4′-dinitrodiphenylmethane, in view of the larger number of the nitro groups in TND. At present, however, few reports concerning the carbanion formation of TND have been published.

In this paper, the reaction of TND with such bases as NaOH and triethylamine (TEA) is investigated by means of optical measurements. Especially, solvent effects on the reaction are studied.

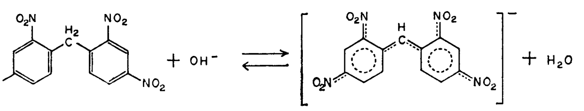
Experimental

Materials. The TND was prepared according to the method of Schöpff[4] and was recrystallized twice from acetic acid and several times from a benzene–ethanol mixed solvent; mp 171°C (lit,[4] 172°C). The solvents used here were purified by the standard procedure for each solvent. The TEA was distilled twice just before its use.

Measurements of Absorption Spectra. The ultraviolet and visible absorption spectra were measured with a Shimadzu Spectrophotometer QV-50, using 1-cm quartz cells. The temperature of the cell compartment was kept constant by circulating water from a constant-temperature bath.

Results and Discussion

When NaOH was added to solutions of TND in mixed solvents of organic solvent–water (4:1 in volume), the solutions immediately showed a blue color. The absorption spectra in a mixed solvent of methanol–water are shown in Fig. 1. If the basic solution is neutralized, the original spectrum (Curve I in Fig. 1) can be reproduced. The spectral change can safely be attributed to the carbanion formation of TND. The following equilibrium is considered to be established;



Some carbanions are known to cause disproportionation or electron transfer to the neutral species, thus giving radical anions.[5] In the case of TND, however no signal was observed in the ESR spectrum of the basic solution, so it was not necessary to consider any radicals of TND.

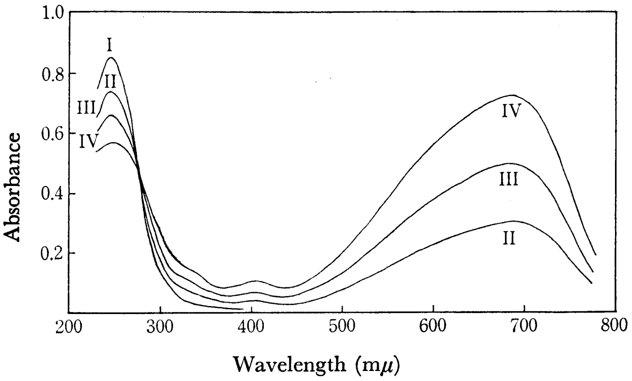


Fig. 1. The absorption spectra of the TND–NaOH system in a methanol–water (4:1) mixed solvent; [TND]=2.74×10^{-5}M.
I; pH=5.8, II; 12.1, III; 12.6, IV; 13.0.

The equilibrium constant for the base-catalyzed reaction was determined by applying the Benesi-Hildebrand equation,[6] while the value of pK_a was obtained by the use of the following equation;

$$\mathrm{p}K_a = \mathrm{pH} - \log \frac{\dfrac{D}{\varepsilon}}{[\mathrm{AH}]_0 - \dfrac{D}{\varepsilon}}$$

where $[\mathrm{AH}]_0$ is the initial concentration of TND and where D and ε are, respectively, the absorbance and the molar extinction coefficient of the carbanion band

TABLE 1. THE EQUILIBRIUM CONSTANT, pK_a AND THE CARBANION BAND FOR THE TND–NaOH SYSTEM IN MIXED SOLVENTS OF ORGANIC SOLVENT–WATER (4:1) AT 25°C

Solvent	Dielectric constant[a]	K ($l\cdot\mathrm{mol}^{-1}$)	pK_a	$\lambda_{\max}$ (mμ)	ε
Methanol+H_2O	32.6	34	12.6	685	33300
Dioxane+H_2O	2.21	1.96×10^4	9.69	715	47000
Acetone+H_2O	20.5	4.90×10^4	9.37	700	46700
Dimethyl sulfoxide+H_2O	48.9	6.80×10^4	9.08	695	38500

a) The values are of the organic solvents.

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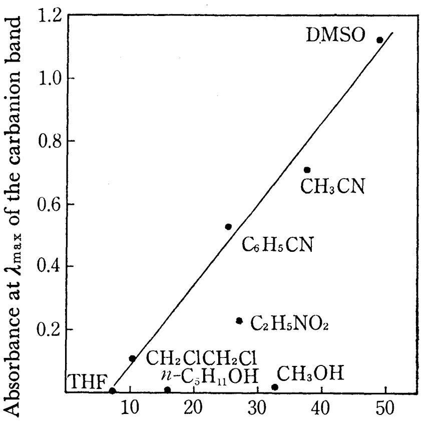

Fig. 2. Relation between the absorbances of the carbanion bands around 700 mμ and dielectric constants of the solvents; [TND]$=2.5\times10^{-5}$M, [TEA]$=0.143$M.

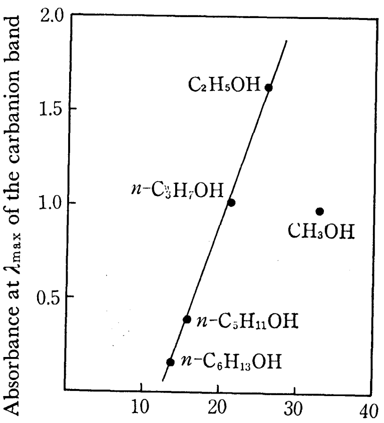

Fig. 3. Relation between the absorbances of the carbanion bands around 700 mμ and dielectric constants of the alcohols; [TND]$=3.5\times10^{-4}$M, [TEA]$=1.19$M.

appearing around 700 mμ. The results are presented in Table 1.

Obviously, TND is a stronger carbon acid than 4,4′-dinitrodiphenylmethane. The results in Table 1 indicate that the polarity of the solvent used significantly influences the carbanion formation. Therefore, we considered a TND–TEA system in various solvents. TND reacts with TEA, showing a spectral change similar to that shown in Fig. 1. However, it was found that the reaction occurred only in solvents with dielectric constants larger than 7.39 (THF). A linear relationship was found to hold between the absorbance of the carbanion band around 700 mμ and the dielectric constant of the solvent used, as is shown in Fig. 2. This seems to indicate that the stabilization of the carbanion, probably by solvation, plays an important role in the reaction. As for the reaction in nitroethane or alcohols, factors other than the polarity of the solvent must be took into account, for their behavior is exceptional. Since these solvents can cause an interaction with TEA, the concentrations of the free TEA molecule decrease in these solvents. Nevertheless, in alcohols also the absorbance is related linearly to the dielectric constant, except in the case of methanol, as is shown in Fig. 3. The lower absorption intensity in methanol may indicate that the interaction of methanol with TEA is stronger than those of the other alcohols.

In the solvents with dielectric constants smaller than 7.39, the absorption spectrum changes only in the ultraviolet region upon the addition of TEA. From the relation between the concentration of TEA and the change in absorbance, it can be said that TND forms a 1 : 1 complex with TEA through hydrogen-bonding between the methylene group of TND and the N atom of TEA.

In 1,2-dichloroethane, the rate of the reaction was much slower than that in a solvent with a higher dielectric constant, in which the carbanion was formed immediately after the addition of TEA. Since the absorbance at 700 mμ increases quadratically with respect to time in the initial stage, an intermediate reaction step may exist between the reactants and the product.[7] At present, the hydrogen-bonded complex is inferred to be the intermediate, because the spectral change in the initial stage is similar to that observed in the less polar solvents.

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