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Equilibrium Data, Visible Absorption Spectra and ^{1}H NMR Studies for 1,8-Diazabicyclo [5,4,0]undec-7-ene (DBU) and Sodium Alkoxide Addition to 1-X-2,4,6-Trinitrobenzenes

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Introduction

For many years anionic δ complexes, formed as stable or transient species from covalent addition of nucleophiles to a substitued or unsubstituted ring carbon atom of electron-deficient aromatic and heteroaromatic substrates, have been extensively investigated [1, 2].

Reactions of 2,4,6-trinitrotoluene with different bases lead to formation of Meisenheimer complexes or to products of reactions of proton transfer from the methyl group. These reactions can be consecutive or competitive, and the structure of the base used is the deciding factor which of them is favoured [3 – 6].

Kinetics and mechanism of the reaction of 1-alkyl-2,4,6-trinitrobenzene with 1,1,3,3-tetramethylguanidine in N,N-dimethylformamide were reported by Biswas et al. [7]. For the 2,4,6-trinitrocumene only δ complex formation, for 2,4,6-trinitroethylbenzene and 2,4,6-trinitrotoluene [5] both δ complex formation and proton transfer from the α-carbon atom of the alkyl group were observed.

In the present paper, reactions of 1-alkyl-2,4,6-trinitrobenzene with 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) in aprotic solvents and with sodium alkoxide in alcohols are examined and discussed. The obtained data are compared with the results for 2,4,6-trinitrotoluene and other derivatives of trinitrobenzene.

Experimental

2,4,6-Trinitroethylbenzene and 2,4,6-trinitrotoluene were prepared by the procedure of Gay-Lussac and Ficheroulle [8].

2,4,6-Trinitroethylbenzene; n.m.r. (TMS, $^2H_6$-DMSO) 8.97 (s, 2H), 2.85 (q, 2H), 1.25 (t, 3H); 2,4,6-trinitrotoluene; n.m.r. (TMS, $^2H_6$-DMSO) 9.00 (s, 2H), 3.29 (s, 3H).

2,4,6-Trinitrocumene was prepared by the procedure of Fittig [9], n.m.r. (TMS, $^2H_6$-DMSO) 8.96 (s,2H), 3.20 (s,1H), 1.30 (q,6H).

1,3,5-Trinitrobenzene (Baker Chem. Co.) and 1-bromo-2,4,6-trinitrobenzene (Aldrich) commercial compounds were used.

1,3,5-Trinitrobenzene n.m.r. (TMS, $^2H_6$-DMSO) 9.16 (s); 1-bromo-2,4,6-trinitrobenzene n.m.r. (TMS, $^2H_6$-DMSO) 8.61 (s).

1,8-Diazabicyclo[5,4,0]undec-7-ene (DBU) – Aldrich – was dried with potassium hydroxide and fractionally distilled under reduced pressure.

The solvents were purified by standard methods using fractional distillation under oxygen-free dry nitrogen. The alkoxide (ROM) bases were obtained by dissolving sodium in appropriate absolute alcohols.

Optical density measurements were made on a Specord M-40 spectrophotometer at 20 ± 0.5 °C. The equilibrium constant for the reaction was determined by Hildebrand-Benesi method [10] using $5*10^{-5}$M concentrations of the trinitro-compounds and varying concentrations of DBN ($5*10^{-2} - 1*10^{-3}$M).

^{1}H n.m.r. measurements were made with a Tesla instrument using tetramethylsilane as internal reference. [$^2H_6$] Dimethyl sulphoxide and [^{2}H] chloroform were used as solvents with substrate concentrations of 0.1 M. Anionic species were generated from the substrates by addition of DBU or by the addition of sodium alkoxide to solutions containing the substrate in a molar ratio of 1:1.

Results and Discussion

Addition of primary or secondary amines to trinitrobenzene derivatives initially yields a zwitterion which loses an alkylammonium proton to give the anionic δ complex.

Tertiary amines do not react with trinitrobenzene. With 1-alkyl-2,4,6-trinitrobenzene these amines give conjugated ions only; the δ complex is not observed [1, 2].

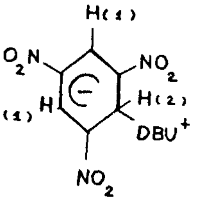
The reactions of amidines with electron-deficient aromatic rings yield different types of products depend on the structure of the parent amidine and solvent [1, 2]. For α-substituted N,N-dimethylacetamidines where the α-substituent is alkyl or hydrogen, only the zwitterionic carbon-bonded complexes are obtained in polar solvents. In contrast, when the α substituent is aryl, only the bridged complexes wich are formed from (1, 1) nitrogen bonded complexes can be isolated. In this work the cyclic amidine –

1,8-diazabicyclo[5,4,0]undec-7- ene (DBU) is used as a very strong proton acceptor ($pK_a = 23.9$ in acetonitrile) and a weak C-nucleophile.

Reactions with DBU in aprotic solvents

The 1,3,5-trinitrobenzene reaction

The reaction 1,3,5-trinitrobenzene with DBU in DMSO leads to a δ-complex (**1**) $\lambda_{max} = 440$ and 495 nm.



(1)

The ¹H n.m.r. spectrum of the product (**1**) shows two singlets: (TMS, ²H₆-DMSO) 6.15 (s, 2H$_{(2)}$), 8.29 (s, H$_{(1)}$).

In chloroform the product (**1**) gives $\lambda_{max} = 435$ and 480 nm; ¹H n.m.r. (TMS, ²HCCl₃) 6.23 (s, 2H$_{(2)}$), 8.58 (s, H$_{(1)}$).

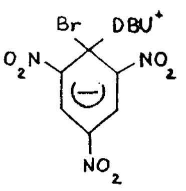
The equilibrium constants and the molar extinction coefficient for these reaction systems are K^{20}_{eq} = 400 ∓ 100 dm³·mol⁻¹, ε = (2.2 ∓ 0.2)*10⁴·cm⁻¹·M⁻¹ in DMSO; K^{20}_{eq} = 270 ∓ 90 dm³·mol⁻¹, ε = (2.2 ∓ 0.1)* 10⁴·cm⁻¹·M⁻¹ in acetonitrile; and K^{20}_{eq} = 80 ∓ 20 dm³mol⁻¹, ε = (2.1 ∓ 0.1)*10⁴·cm⁻¹·M⁻¹ in chlorofom.

Kinetic and equilibrium studies are reported by Crampton et al. [11] for the reaction of 1,3,5-trinitrobenzene with amines (n-butylamine, benzylamine, isopropylamine and piperidine) in dimethyl sulphoxide. These reactions lead to the formation of anionic δ-complex via zwitterionic ($Ar^-NHR_2^+$) intermediates, and it is shown that proton transfer may be kinetically significant.

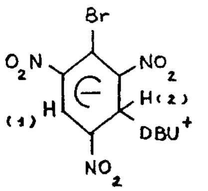
The 1-bromo-2,4,6-trinitrobenzene reaction

The coloured product of the reaction of 1-bromo-2,4,6-trinitrobenzene with DBU in DMSO appears to be (1,1) the δ-complex (**2**), $\lambda_{max} = 380$ nm; ¹H n.m.r. (TMS, ²H₆-DMSO) 8.59 (s).

As a result of the reaction of 1-bromo-2,4,6-trinitrobenzene with DBU in CHCl₃ (1, 3) the δ-complex (**3**) is formed, λ_{max} = 420 and 514 nm; ¹H n.m.r. (TMS, ²HCCl₃) 8.69 (s, 2H$_{(2)}$), 9.25 (s, H$_{(1)}$).



(2)



(3)

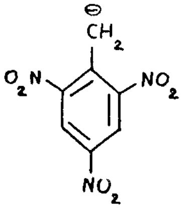
The fast formation of the (1, 3) complex which was observed in acetonitrile, chloroform and DMSO was followed by slow conversion to the (1,1) adduct in DMSO only.

The equilibrium constant and the molar extinction coefficient for the formation of (1,1) adduct in DMSO are K^{20}_{eq} = 1400 ∓ 10 dm³·mol⁻¹, and ε = 9100 ∓ 100 cm⁻¹ M⁻¹ (λ = 380).

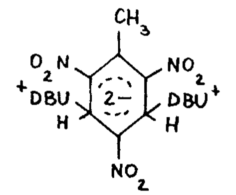
The equilibrium constant and the molar extinction coefficient for the formation of (1, 3) adduct in acetonitrile are K^{20}_{eq} = 1100 ∓ 100 dm³·mol⁻¹, ε = 15900 ∓ 100 cm⁻¹ M⁻¹ (λ = 510); and in chloroform: K^{20}_{eq} = 850 ∓ 90 dm³mol⁻¹, ε = 14800 ∓ 200 cm⁻¹·M⁻¹ (λ = 514).

The 2,4,6-trinitrotoluene reaction

The reaction of 2,4,6-trinitrotoluene with DBU in DMSO proceeds via proton transfer from the methyl group giving the anion (**4**), λ_{max} = 380, 520 and 640 nm; ¹H n.m.r. (TMS, ²H₆-DMSO) 5.73 (s, CH₃), 8.25 (s, Ar). Changing of solvents from DMSO to CHCl₃ leads to a new product: dianion (**5**), λ_{max} = 440 and 500 nm; ¹H n.m.r. (TMS, ²HCCl₃), 2.67 (s, CH₃), 6.10 (s, Ar).



(4)



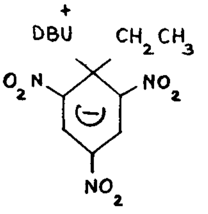
(5)

The equilibrium constant for the formation of conjugated anion (**4**) in polar aprotic solvents is: K^{20}_{eq} = 960 ∓ 20 dm³·mol⁻¹, and the molar extinction coefficient ε = 8500 ∓ 300 cm⁻¹·M⁻¹ (λ = 520) in DMSO, and K^{20}_{eq} = 450 ∓ 30 dm³mol⁻¹, ε = 7800 ∓ 200 cm⁻¹· M⁻¹ (λ = 521) in acetonitrile.

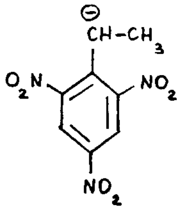
The 2,4,6-trinitroethylbenzene reaction

As a first product of the reaction between DBU and 2,4,6-trinitroethylbenzene (TNEB) in DMSO the (1,1) Meisenheimer complex is formed, λ_{max} = 460 and 530 nm. This complex changes to the product (**7**) with λ_{max} = 380, 523 and 640 nm. These maxima are characteristic for proton transfer reaction products. ¹H n.m.r. (TMS, ²H₆-DMSO) 1.85 (d, CH₃), 6.05 (q, CH⁻) and 8.25 (s, Ar).

(1,1) Meisenheimer complex was also formed in the reaction of TNEB with DBU in CHCl₃; λ_{max} = 435 and 530 nm; ¹H n.m.r. (TMS, ²HCCl₃) 1.38 (t,CH₃), 3.10 (q, CH₂) and 8.41 (s, Ar).



(6)



(7)

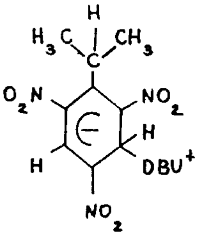
The equilibrium constants and the molar extinction coefficient for the formation of (1, 1) complex are in DMSO: K^{20}_{eq} = 200 ∓ 20 dm³·mol⁻¹, ε = (1.9 ∓ 0.1)*

$10^4 \cdot cm^{-1} \cdot M^{-1}$; in acetonitrile: $K^{20}_{eq} = 150 \mp 10 dm^3 \cdot mol^{-1}$, $\varepsilon = (2.1 \mp 0.1)*10^4 \cdot cm^{-1} \cdot M^{-1}$; in chloroform: $K^{20}_{eq} = 37 \mp 5 \cdot dm^3 \cdot mol^{-1}$, $\varepsilon = (1.9 \mp 0.1)*10^4 \cdot cm^{-1} \cdot M^{-1}$.

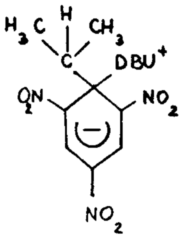
The 2,4,6-trinitrocumene reaction

The first coloured product of the reaction of 2,4,6-trinitrocumene with DBU in DMSO is the (1,3) Meisenheimer complex (**8**); λ_{max} = 470 and 540 nm; which next affords a new product (**9**). The (1,1) Meisenheimer complex; λ_{max} = 530 nm, ^1H n.m.r. (TMS, $^2H_6$-DMSO) 1.30 (q, CH_3), 3.20 (m, CH) and 8.98 (s, Ar).

The (1,1) Meisenheimer complex can be observed in the reaction of 2,4,6-trinitrocumene with DBU in chloroform, too. In this case the absorption maximum occurs at 510 nm; ^1H n.m.r. (TMS, $^2HCCl_3$) 1.47 (q, CH_3), 3.25 (m, CH) and 8.55 (s, Ar).

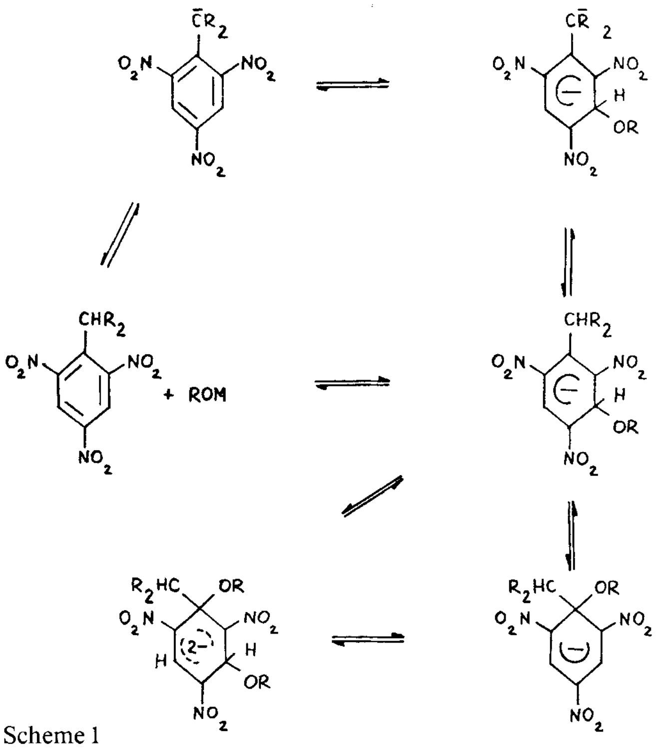


(8)



(9)

The equilibrium constant and the molar extinction coefficient for the formation of (1, 1) complex in DMSO are: $K^{20}_{eq} = 220 \mp 20 dm^3 \cdot mol^{-1}$, $\varepsilon = (1.4 \mp 0.1)*10^4 \cdot cm^{-1} \cdot M^{-1}$; in acetonitrile: $K^{20}_{eq} = 150 \mp 10 dm^3 \cdot mol^{-1}$, $\varepsilon = (1.4 \mp 0.1)*10^4 \cdot cm^{-1} \cdot M^{-1}$; in chloroform: $K^{20}_{eq} = 87 \mp 7 \cdot dm^3 \cdot mol^{-1}$, $\varepsilon = (1.4 \mp 0.1)*10^4 \cdot cm^{-1} \cdot M^{-1}$.



Scheme 1

The reaction with alkoxide bases

The reaction of trinitrobenzene derivatives (2,4,6-trinitroethylbenzene and 2,4,6-trinitrocumene) with alkoxide bases was investigated using three bases: sodium ethoxide, isopropoxide and t-butoxide in the corresponding alcohols.

Using ^1H n.m.r. and UV spectra (Table 1) the structure of products of the reaction 2,4,6-trinitroethylbenzene and 2,4,6-trinitrocumene with alkoxide bases in alcohols was de-

Table 1 The products of the reaction 2,4,6-trinitroethylbenzene and 2,4,6-trinitrocumene [$5*10^{-5}$M] with alkoxide bases in alkohols

Alkoxide bases	Base concentrations [B] = $1*10^{-3}$ M	 [B] = $1*10^{-2}$ M
	2,4,6-trinitroethylbenzene	
EtONa in EtOH	(1,3) δ adduct λ = 440, 513 nm	dianion: (1,3) δ adduct and conjugated anion λ = 344, 507 nm
iso-PrONa in iso-PrOH	(1,3) δ adduct λ = 443, 513 nm	
t-BuONa in t-BuOH	(1,1) and (1,3)dianion λ = 473 nm	(1,1) δ adduct λ = 401 nm
	2,4,6-trinitrocumene	
EtONa in EtOH	(1,3) δ adduct λ = 447, 513 nm	dianion: (1,3) δ adduct and conjugated anion λ = 342, 500 nm
iso-PrONa in iso-PrOH	(1,3) δ adduct λ = 451, 513 nm	
t-BuONa in t-BuOH	(1,1) and (1,3) dianion λ = 446 nm	(1,1) δ adduct λ = 401 nm

termined. ^1H n.m.r. spectra of products with alkoxide bases was analogue to the products of reaction with DBU.
The reaction products for two concentrations of bases $1*10^{-2}$ and $1*10^{-3}$M are given in Table 1. The type of products of the reaction 2,4,6-trinitroethylbenzene and 2,4,6-trinitrocumene with alkoxide bases in alkohols depends on the concentration of the bases used. Scheme 1 shows, on the base of changes of UV spectrum, the sequence of product formation in the reaction of 2,4,6-trinitroethylbenzene and 2,4,6-trinitrocumene with alkoxide bases in alkohols.
In the series of bases from t-BuOM via iso-PrOM to EtOM in the corresponding alkohols the dissociation degree of alkoxide bases increases with the solvent polarity. The concentration of free RO^- ions is a first factor determining the type of the reaction product with trinitrobenzene derivatives. The ions and ion-pairs reactivity is the second important factor. Norriss et al. [3, 4] and Crampton [12] observed the influence of the dissociation degree of alkoxide bases on the structure of the products in different solvents.

The free ions in solvents with high dielectric constants prefer (1,3)-addition and conjugated ion formation as a result of proton transfer while in the solvents with low dielectric constant, when bases exist in associated forms, the (1,3)-adduct is observed, which then transforms into the (1,1)-adduct. This is induced by the strong ion-pair and neighbouring nitrogen group interaction.

According to this it was found that the deprotonation including the side chain depends on the form of the nucleophile in the solution.

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