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^{15}N NMR and FTIR studies of 2,4-dinitroanilines and their salts

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Abstract

Twenty-two 2,4-dinitroanilines were synthesised and their pK_a values were determined. The 2,4-dinitroanilines and their protonated forms were studied by ^{15}N NMR spectroscopy. The relations between the ^{15}N NMR chemical shifts and the pK_a values of the 2,4-dinitroanilines and their salts were found to be linear. The deprotonation reaction of *N*-methyl-2,4-dinitroanilines and *N*-methyl-2,4,6-trinitroaniline by MTBD was successful only for the latter and yielded protonated MTBD molecule and the anion in which the electrons are strongly delocalised. The kinetic parameters of the 2,4-dinitroanilines in reactions with hydroxide ions in mixed solvent DMSO:water (95:5, v/v) were determinated and discussed.

Keywords: 2,4-Dinitroanilines; Protonated 2,4-dinitroanilines; pK_a values; ^{15}N NMR; FTIR; σ-Complexes; Kinetic parameters

1. Introduction

The interaction of aromatic nitro compounds with bases can give rise to processes involving: charge transfer, electron transfer, proton transfer and σ-complex formation, as well as to nucleophilic substitution when a displaceable group is present. Activating groups are definitely decisive in the reaction process of formation of a conjugated anion or σ-complexes. The occurrence of one, two or three electron acceptor substituents, at the *ortho*- or *para*-positions, determines the directions of the nucleophilic attack of the base in the aromatic ring.

In solvents amines may be protonated by acids and deprotonated by strong bases, respectively.

$$RNH_2 + H^+ \rightleftharpoons RNH_3^+$$

$$RNH_2 + B \rightleftharpoons BH^+ + RNH^-$$

Nitroanilines have been very interesting compounds because in polar aprotic solvents they react with acids and yield salts. They react also with bases and form several products depending on the structure of the substrate. In the case of 4-nitroaniline and *N*-alkyl-4-nitroaniline interacting with nucleophilic reagent, conjugated base (**1**), nucleophilic substitution product (**2**) or Meinsenheimer complex (**3**) have been identified [1,2 and references given there].

In the reaction between *N*-alkyl-4-nitroaniline and a strong base, two types of products: that of nucleophilic substitution (**4**) or Meinsenheimer complex (**5**) have only been observed to form.

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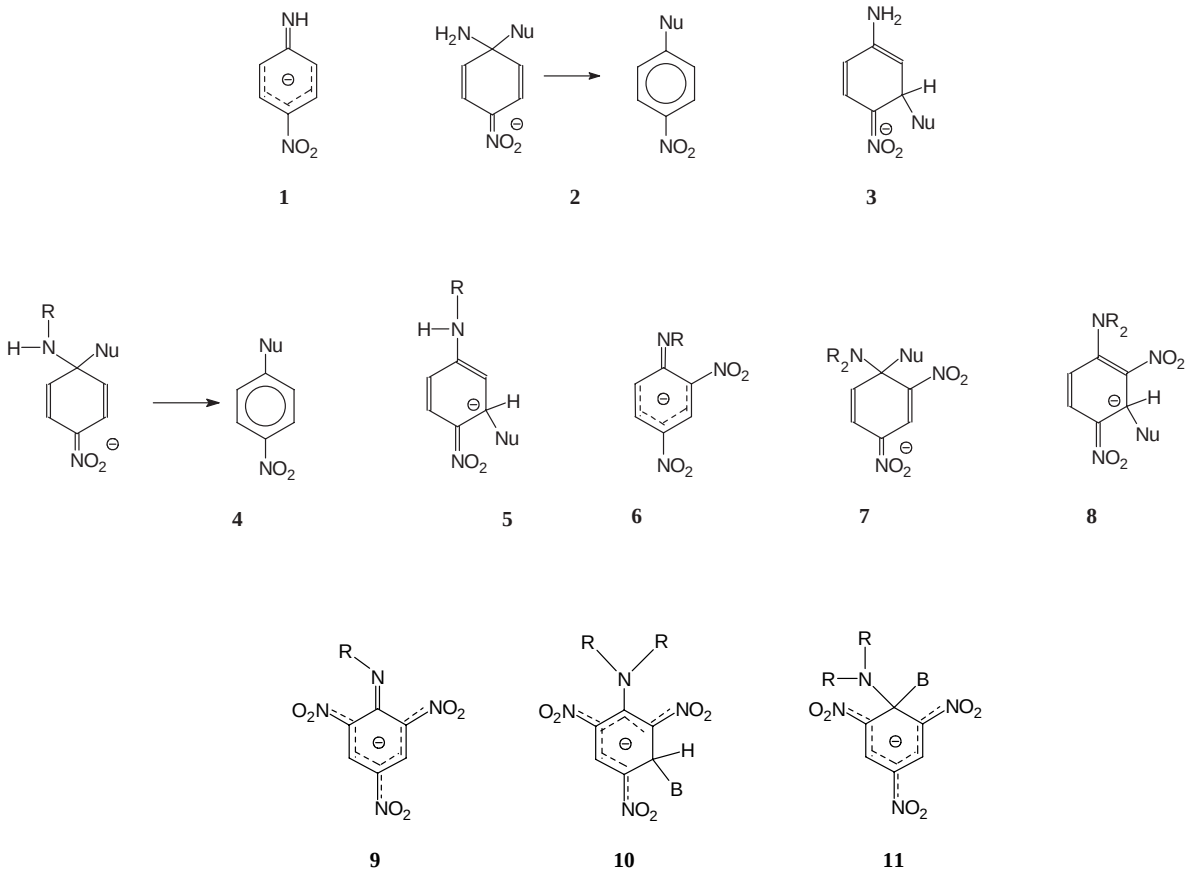


In the case of 2,4-dinitroaniline and *N*-substituted-2,4-dinitroaniline reacting with a strong base, the formation of conjugated base (**6**) or two possible Meinsenheimer complexes, i.e. 1,1-σ-complex (**7**) or 1,3-σ-complex (**8**), has been observed. For the *N*,*N*-dialkyl-2,4-dinitroaniline-base system only concentration changes between the two σ-complexes (**7**) or (**8**) have been found.

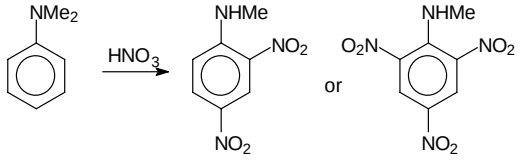
The reaction of 2,4,6-trinitroaniline or *N*-alkyl-2,4,6-trinitroaniline with a strong base yielded a conjugated base (**9**), 1,3-σ-complex (**10**) or 1,1-σ-complex (**11**).

The reaction between *N*,*N*-dialkyl-2,4,6-trinitroaniline and the nucleophilic reagent gave σ-complexes: 1,3-σ-complex (**10**) or 1,1-σ-complex (**11**) have only been identified.

This paper reports syntheses of many new derivatives of 2,4-dinitroanilines and results of determination of their pK_a values. The deprotonation reaction of some of the anilines has been studied by the FT-IR and ^{15}N NMR spectroscopic methods as well as by the kinetic method.

2. Experimental

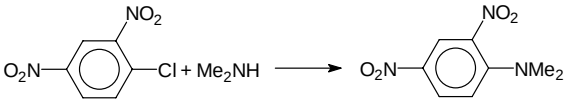
2.1. Synthesis of N-methyl-2,4-dinitroaniline



N,*N*-dimethylaniline (10 g) was nitrated with nitric acid (80 cm^3, $d = 1.3904$ g cm^{-3}) at −30°C for 5 h. 12 g of the mixture of the following products: *N*-methyl-2,4-dinitroaniline (70%), *N*-methyl-2,4,6-trinitroaniline (20%), was obtained after pouring on

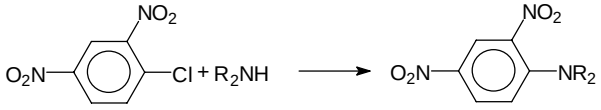
ice. The 2,4-dinitro derivative was purified by fraction crystallisation from ethanol.

2.2. Synthesis of N,N-dimethyl-2,4-dinitroaniline



2,4-Dinitrochlorobenzene (5 g) and 5 g of potassium hydroxide were added to 70 cm^3 of 40% water solution of dimethylaniline (in the Teflon vessel, placed in calorimetric bomb). The bomb was heated for 12 h at 130°C. After cooling the mixture was dissolved in water to obtain ca. 250 cm^3 mixture and then the solvent was evaporated under reduced pressure. To the residue dissolved in 100 cm^3 of water, 20 g of K_2CO_3 was added and the obtained mixture was evaporated. The product was extracted three times with 50 cm^3 of acetone, the organic phase was dried with anhydrous Na_2SO_4 and the solvent was evaporated. The dark red oil was washed with 25 cm^3 of 10% solution of potassium hydroxide, next with 25% hydrochloric acid and finally with water. The crude product was dissolved in 200 cm^3 of diethyl ether, dried with anhydrous Na_2SO_4, filtrated and the solvent was evaporated. The residue was chromatographed on a silica gel column with ether–acetone 4:1 (v/v). The obtained product was recrystallised from methanol. About 0.8 g of the final product was obtained.

2.3. Synthesis of 2,4-dinitroanilines (the monoamine derivatives)

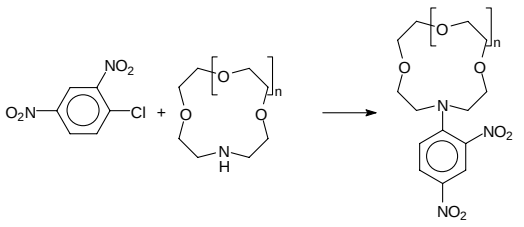


R_2NH = Et_2NH, $PrNH_2$, Bz_2NH, $BzNH_2$, $DcNH_2$, 2-MeO-$PhNH_2$, $C_6H_{11}NH_2$, 2-$NphNH_2$, PhNH
pyrrolidine, piperidine, morpholine

To the mixture of 0.015 mol of amine and 5 g of anhydrous sodium carbonate in 50 cm^3 anhydrous acetone, 0.01 mol of 2,4-dinitrochlorobenzene was added and the total was refluxed for 5 h. The reaction mixture was poured on ice and the following procedure was made, depending on the agglomeration state of crude crystal products.

(a) In the case of precipitate formation, the product was filtered and washed with 100 cm^3 hot water. After drying on air the product was crystallised from methanol or methanol–acetone 1:1 (v/v) mixture.
(b) When the raw product was an oily substance, the water was decanted and the residue was set in ethyl acetate and dried with anhydrous Na_2SO_4 and filtered off. The solvent was evaporated and the residue was chromatographed on the silica-gel column with diethyl ether—acetone 2:5 (v/v) mixture. A crystalline, homogenous phase was crystallised from acetone. In the case of the reaction with decylamine the product was eluted from the column with ether–hexane 2:1 mixture and crystallised from ether.

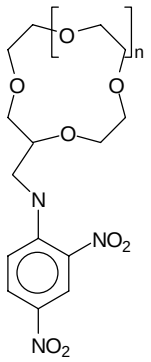
2.4. Synthesis of the products by using azacoronands (Scheme 1)



n=1 1N12C4; n=2 1N15C5; n=3 1N18C6

Scheme 1.

The mixture of 0.006 mol of macrocyclic amine and the 0.01 mol of tetrabutylamine acetate was



n = 1 $NCH_2$12C4

n = 2 $NCH_2$15C5

n = 3 $NCH_2$18C6

Scheme 2.

added to the solution of 0.008 mol of 2,4-dinitrochlorobenzene in 50 cm^3 of anhydrous diethyl ether. The mixture was refluxed for 24 h, cooled and the amine salt was washed three times with water. The diethyl ether phase was dried with anhydrous Na_2SO_4, filtered off and then the solvent was evaporated. The crude product was chromatographed on SiO_2 column with diethyl ether–hexane 10:1 (v/v). The product (about 95% yield), chromatographically and spectroscopically pure, was not crystallised.

2,4-Dinitrophenylazo-15C5 was also obtained by nitration of phenylazo-15C5 (5 g) using nitric acid (100 cm^3, $d = 1.3904$ g cm^{-3}) at −50°C for 30 min. After pouring on ice and neutralisation using 30% KOH water solution, the obtained product was crystallised from ethanol (yield 90%).

2.5. Synthesis of N-methyl-crown-2,4-dinitroanilines (see Scheme 2)

The structure of *N*-methyl-crown-2,4-dinitroanilines is shown in Scheme 2. *N*-methyl-crown-2,4-dinitroanilines were prepared from (10 mmol) 2-aminomethyl-crown ethers (2-aminomethyl-12-crown-4, 2-aminomethyl-15-crown-5, 2-aminomethyl-18-crown-6; commercial products of Aldrich): dissolved in 1 cm^3 of dry acetone (oxygen free) including (12 mmol) 2,4-dinitrophenyl chloride as starting materials. The reaction mixture was heated under reflux for 2 h. The solvent was evaporated under reduced pressure. The crude product (*N*-methyl-crown-2,4-dinitroanilines) was chromatographed on IRA-410 column with water:methanol 1:1 (v/v).

The analytical data and ^{1}H NMR spectra of *N*-aminomethyl-crown-2,4-dinitroanilines are following:

N-methyl-12C4-2,4-dinitroaniline (Scheme 2, $n = 1$, $NHCH_2$12C4); oil; ^{1}H NMR [$(CD_3)_2C=O$, TMS], 3.7–3.9 ppm, m, 15H; 7.3 ppm, d, 1H; 8.6 ppm, dd, 1H; 9.1 ppm, d, 1H; 9.0 ppm, s, N–H. *N*-methyl-15C5-2,4-dinitroaniline (Scheme 2, $n = 2$, $NHCH_2$15C5); oil; ^{1}H NMR ($(CD_3)_2C=O$, TMS), 3.7–3.9 ppm, m, 19H; 7.3 ppm, d, 1H; 8.6 ppm, dd, 1H; 9.1 ppm, d, 1H; 9.0 ppm, s, N–H. *N*-methyl-18C6-2,4-dinitroaniline (Scheme 2, $n = 3$, $NHCH_2$18C6); oil; ^{1}H NMR (acetone-d_6, TMS), 3.7–3.9 ppm, m, 21H; 7.3 ppm, d, 1H; 8.6 ppm, dd, 1H; 9.05 ppm, d, 1H; 8.98 ppm, s, N–H.

2.6. pK_a measurements

The pK_a measurement was made following the procedure given in Ref. [3].

2.7. Kinetic measurements

The kinetic runs were carried out with a stopped-flow spectrophotometer (Applied Photophysics) with the cellblock thermostated to +/−0.1°C. The kinetic runs are completed under pseudo-first-order conditions with the base concentration in large excess. The observed rate constants (k_{obs} and k'_{obs}) were calculated from the traces of absorbance vs. time. For the fast step of σ-complex formation, the rate constants for forward (k) and backward (k_-) reactions are defined by the equilibrium (1), while for the slow step (k_{slow}) rate constants are given by Eq. (2).

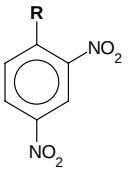
$$k_{obs} = k[OH^-] + k_- \quad (1)$$

$$k'_{obs} = k_{slow}[OH^-]/1 + K[OH^-] \quad (2)$$

where K is the equilibrium constant of the fast step.

2.8. ^{15}N NMR measurements

^{15}N NMR spectra of the aniline were recorded in CD_3CN and those of the salts in H_2SO_4, respectively, the operating frequency 30.682 MHz; $a_t = 3.0$ s; $d_1 = 2.0$ s; $T = 293.0$ K and CH_3NO_2 as the internal standard. The proton decoupling procedure was used.



R= NH_2, NHMe, NHEt, NHnPr, NHnBu, NHnDec,  , NHPh, NHBz, $NHCH_2$12C4,$NHCH_2$15C5, $NHCH_2$18C6, NEt_2,  ,  , 1N12C4, 1N15C5, 1N18C6

Scheme 3.

2.9. FTIR measurements

7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) was purchased from Fluka. The mixtures of anilines with MTBD were prepared by addition of pure MTBD to the acetonitrile solutions of the anilines at the concentration ratio 1:1. The concentrations of all the samples were 0.1 mol dm^{-3}.

The solvent was stored over 3 Å molecular sieves. All preparations and transfers of solutions were carried out in a carefully dried glove box under nitrogen atmosphere.

A cell with Si windows and a wedge-shaped layer was used to avoid interferences (mean layer thickness 0.176 mm). The mid-IR spectra were taken with a FTIR spectrophotometer IFS 113v from Bruker with a DTGS detector (125 scans, resolution 1 cm^{-1}).

3. Results and discussion

3.1. ^{15}N NMR measurements

The twenty-two studied compounds are summarised in Scheme 3 (studied R-2,4-dinitrobenzenes). The pK_a values of new and known compounds are given together with ^{15}N NMR data in Table 1. The ^{15}N NMR chemical shifts of the bases were observed in the region of the substituted anilines discussed previously [4–8]. For the studied family of new 2,4-dinitroanilines for the first time the linear dependencies between the ^{15}N chemical shifts and the pK_a values were found (Fig. 1). Fig. 1 shows that the ^{15}N atoms of the secondary anilines are strongly deshielded in comparison with those of tertiary anilines. This effect is probably due to the existence of relatively strong intramolecular hydrogen bond between the N–H proton and the nitro group in *ortho*-position. The positions of the ^{15}N NMR signals

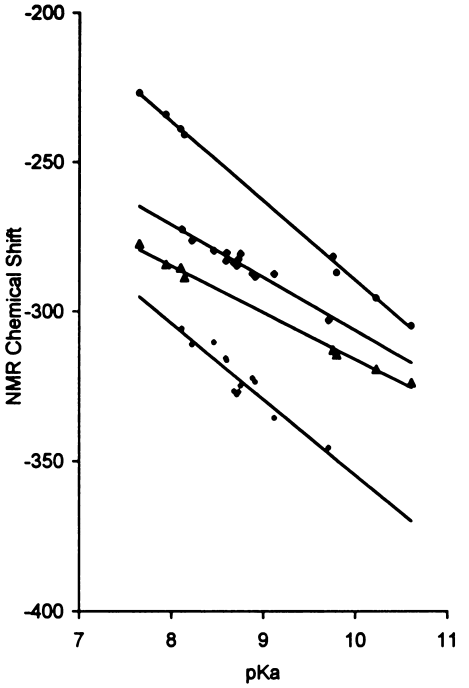


Fig. 1. Correlation between ^{15}N NMR chemical shifts and pK_a values of substituted anilines: (◆) secondary amines; (■) protonated secondary amines; (●) tertiary amines; (▲) protonated tertiary amines.

Table 1
^{15}N NMR chemical shift and pK_a values of R-2,4-dinitrobenzenes and their protonated forms

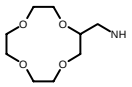
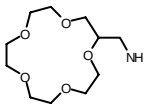
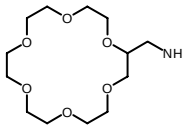
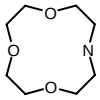
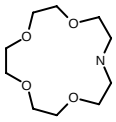
R	pK_a	Free forms	Protonated forms
NHPh	8.22	−276.2	−310.9
NHn–Bu	8.68	−283.8	−326.4
NHBz	9.12	−287.4	−335.5
NH_2	9.71	−302.8	−345.4
NHMe	8.46	−279.6	−310.2
NHn–Pr	8.60	−280.3	−316.1
NHEt	8.59	−283.1	−315.4
NHn–Dec	8.11	−272.4	−305.7
	8.71	−284.7	−327.6
NHn–Hex	8.73	−282.4	−326.8
	8.75	−280.7	−324.6
	8.88	−287.3	−322.1
	8.91	−288.4	−323.4
NEt_2	9.80	−287	−314.3
	10.23	−295.4	−319.1
	10.61	−304.7	−323.7
	8.14	−240.6	−288.7
	8.10	−238.7	−285.4
	7.94	−233.8	−284.3
	7.65	−226.8	−277.4
Me_2N	9.76	−281.5	−312.8

Table 2
Rate constants of the formation of 3σ-complex in the reaction between R-2,4-dinitrobenzenes and NaOH in DMSO:water (95:5%, v/v) at 25°C

R	k $dm^3 mol^{-1} s^{-1}$	$k_- s^{-1}$
NMe_2	4.28 ± 0.17	0.074 ± 0.002
NEt_2	6.54 ± 0.08	0.0067 ± 0.001
	0.048 ± 0.007	0.0007 ± 0.0001
$N(CH_2Ph)_2$	0.041 ± 0.006	0.0005 ± 0.0002
	4.87 ± 0.09	0.083 ± 0.002
	5.78 ± 0.14	0.098 ± 0.003

of protonated anilines are much higher ($\Delta\delta$ ca. 30–40 ppm) then those of other amines (ca. 10 ppm [4–8]). This result demonstrates that the shielding effects of N atoms in the studied compounds are relatively high.

3.2. FTIR measurements

The deprotonation reaction between *N*-methyl-2,4-dinitroaniline as well as *N*-methyl-2,4,6-trinitroaniline with MTBD were studied by FTIR spectroscopy. The spectra of both anilines as well as of their 1:1 mixtures with MTBD are given in Fig. 2a and b, respectively.

In the spectrum of the 1:1 mixture of *N*-methyl-2,4-dinitroaniline with MTBD the ν(N–H) vibration of

Table 3
Rate constants of the formation of the phenolate ion in the reaction between R-2,4-dinitrobenzene and NaOH in DMSO:water (95:5%, v/v) at 25°C

R	k $dm^3 mol^{-1} s^{-1}$
NMe_2	0.0028
NEt_2	0.0026
$N(CH_2Ph)_2$	0.0021
	0.0034
	0.0046

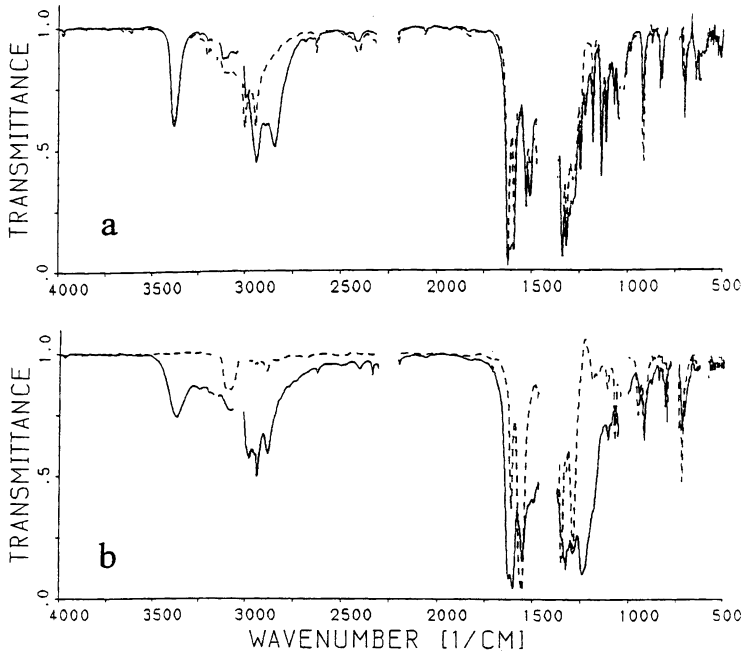
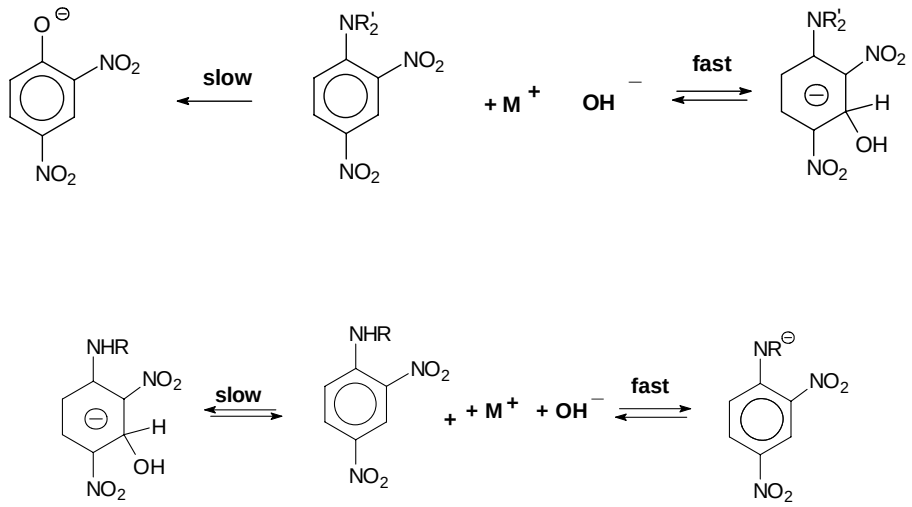


Fig. 2. FTIR spectra of (- - -) anilines and (—) their 1:1 mixtures with MTBD: (a) *N*-methyl-2,4-dinitroaniline; (b) *N*-methyl-2,4,6-trinitroaniline.

the aniline at 3382 cm^{-1} as well as the so-called Bohlmann band [9,10] of the MTBD molecule at 2845 cm^{-1} are unchanged indicating no interactions between these molecules in the acetonitrile solution. A completely different result is observed in the spectrum of 1:1 mixture of *N*-methyl-2,4,6-trinitroaniline and MTBD. In this case the band at 3375 cm^{-1} is assigned to the ν(N–H) + vibration of free protonated MTBD molecule and the broad absorption in the region 3300–2500 cm^{-1} to the



Scheme 4.

Table 4
Rate constants formation of conjugated bases for reaction between R-2,4-dinitrobenzene and NaOH in DMSO:water (95:5%, v/v) at 25°C

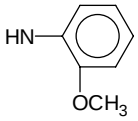
R	k $dm^3 mol^{-1} s^{-1}$	$k_- s^{-1}$
NHMe	Very fast	
NHEt	Very fast	
NHBu	Very fast	
$NH(CH_2Ph)$	23.1 ± 0.3	0.8 ± 0.2
NHPh	350 ± 6	5 ± 2
	0.047 ± 0.003	0.008 ± 0.003
$NHCH_2$12C4	Very fast	
$NHCH_2$15C5	Very fast	
$NHCH_2$18C6	Very fast	

Table 5
Rate constants of the formation of 3σ-complex for reaction of R-2,4-dinitrobenzene with NaOH in DMSO:water (95:5%, v/v) at 25°C

R	k $dm^3 mol^{-1} s^{-1}$
NHMe	8.18 ± 0.20
NHEt	11.41 ± 0.20
$NH(CH_2Ph)$	0.056 ± 0.005
NHPh	Very small

hydrogen bonded MTBD molecule with *N*-methyl-2,4,6-trinitroaniline. This result is further confirmed by the vanishing of the Bohlmann band of MTBD at 2845 as well as by the doublet band appearance at 1602 and 1626 cm^{-1}, which is very characteristic of protonated MTBD molecule [11,12]. The FTIR spectrum of *N*-methyl-2,4,6-trinitroaniline (dashed line) shows very intense bands $\nu_{as}(NO_2)$ at 1553 cm^{-1} and $\nu_s(NO_2)$ at 1346 cm^{-1}. In the spectrum of 1:1 mixture the intensity of these bands decreases significantly. This result indicates that after deprotonation of the N–H group of the aniline molecule the formed anion is delocalised and the nitro groups become more negative NO_2^-, which is indicated by the broad bands at 1325 and 1250 cm^{-1}, previously observed in the spectra of other nitro compounds [13–16].

In conclusion, the results of the FTIR measurements demonstrate that the deprotonation reactions of *N*-methyl-2,4-dinitroaniline can be only investigated using bases stronger than the MTBD base, i.e. alkali metal hydroxides.

3.3. Kinetic measurements

The kinetic data obtained for the reaction between some R-dinitrobenzenes with NaOH are summarised in Tables 2–5.

The reactions between the R-2,4-dinitrobenzenes ($R = NR'_2$) studied with alkali metal hydroxides in a mixed solvent DMSO:water (95:5, v/v) give the σ-adducts at position 3 in the fast reversible step and in the slow step a phenolate ion as the final product. The neutralisation of the reaction mixture allows the isolation of 2,4-dinitrophenol. On the other hand, for $R = NHR'$ in the fast reaction the conjugated base and in the slow reaction the 3σ compound are formed (Scheme 4).

The number of substituents at the N atom determines the reaction direction and first of all characterises the transformation rate (Tables 2–5). The products yielded in the fast processes (i.e. in the case of NR_2 group the 3-σ-adduct and in the case of NHR the conjugated base) are formed as kinetic products, however the final products are controlled thermodynamically.

Acknowledgement

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