Kinetic and equilibrium study of the deprotonation of 4-nitrophenyl[bis(ethylsulphonyl)]methane by organic bases in acetonitrile in the presence of common cation BH\(^+\) and tetrabutylammonium perchlorate

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Abstract: The results of kinetic and equilibrium experiments with the set of reaction of proton abstraction from 4-nitrophenyl[bis(ethylsulphonyl)]methane in acetonitrile are reported. Two strong organic bases are used: 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD).

The rates of proton transfer reaction have been measured by T-jump method in the presence of perchlorate of the appropriate base as a common cation BH\(^+\) and supporting electrolyte - tetrabutylammonium perchlorate (TBAP) in the temperature range between 20–40 °C are:

- \(k_H = 1.32 \times 10^7 \pm 2.00 \times 10^7 \) and \(2.82 \times 10^7 \pm 4.84 \times 10^7 \) dm\(^3\)mol\(^{-1}\)s\(^{-1}\) for MTBD and TBD respectively.

The enthalpies of activation are:

- \(\Delta H^\#_{MTBD} = 13.5\) kJmol\(^{-1}\) for MTBD
- \(\Delta H^\#_{TBD} = 18.1\) kJmol\(^{-1}\) for TBD

The entropies of activation are negative:

- \(\Delta S^\#_{MTBD} = -62.3\) Jmol\(^{-1}\)K\(^{-1}\) for MTBD
- \(\Delta S^\#_{TBD} = -40.3\) Jmol\(^{-1}\)K\(^{-1}\) for TBD

The change of the absorbance of the anion of 4-nitrophenyl[bis(ethylsulphonyl)]methane at the temperature 25 °C in the presence of common cation BH\(^+\) gives the equilibrium constants \(K = 705\) and \(906\) M\(^{-1}\) for MTBD and TBD respectively.

Kinetic and equilibrium results are discussed. The possible mechanism of proton transfer reaction between 4-nitrophenyl[bis(ethylsulphonyl)]methane and cyclic organic bases: MTBD and TBD in acetonitrile is proposed.

Keywords: proton transfer, carbon acid, T-jump method, TBD and MTBD bases, kinetics

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1 Introduction

The complex mechanism of the proton transfer reaction and the variety of carbon acids with respect to their strength, type of electron withdrawing group and steric hindrance in the reaction center give the opportunity to evaluate the factors influencing rate constants and the mechanism of reaction [1-4]. Two groups of Brønsted aci ds are commonly distinguished. The first group is so called “normal acids”, where the proton is bound to strongly electronegative atoms such as oxygen. In such a case the negative charge after the proton abstraction remains on this electronegative atom with not much reorganization of atomic orbital. This is true for oxymes and in some extent for carboxylic acids or phenols. These acids exhibit fast proton dissociation, not possible to measure by stopped flow method. The second ones are carbon acids where the proton is bound to carbon atom showing small intrinsic dissociation rate constants [5]. The rate of proton abstraction vs. equilibrium appears to be smaller than for other carbon acid families. The substituent effect within the series of arylnitroalkanes is greater on the rate of deprotonation $k_f$ than on the equilibrium acidities $K_a$, giving Brønsted’s $\alpha = d \log k_f / d \log K_a \approx 1.5$ [6, 7]. The reason given for the factor retarding proton transfer from C-acids is an extensive nuclear reorganization and charge relocation upon proton loss [8]. Caldin [9] and Ritchie [10] suggested that the reorganization of solvent molecules from reactant state to transition state is a costly process for carbon acids in protic solvents. Both phenomena are known as the nitroalkane anomaly – solvent dependent [11-13]. On the other hand the abnormal Brønsted slopes observed for nitroalkanes [12, 14] are interpreted by Agmon [15] as a variation in the Marcus’ work terms, which is caused by a variation in the hydrogen bond strengths with the free energy for proton transfer, rather than as anomaly in the proton-transfer itself.

The carbon acids with sulfonyl electron withdrawing groups seem to show the acid-base properties more alike “normal acids” than nitro or cyano-members of C-acids family [16, 17]. The kinetics of the proton transfer reactions of sulfonyl activated carbon acids is of some interest due to the structure of the carbanion. An $sp^2$ hybridized carbanion would involve delocalization of the negative charge away from carbon atom with considerable structural rearrangement, and significant decrease in intrinsic rate constants compared with “normal” carbon acids activated by nitro group [16]. The 4-nitrophenyl[bis(ethylsulphonyl)]methane and cyclic strong bases in acetonitrile make the system of reaction suitable for T-jump measurements [18]. The preliminary kinetic experiments provided some assumptions to reaction mechanism, however; in this case the constant ionic strength was not controlled [18].

In our previous paper [19] we have studied the structure of the complex formed between 4-nitrophenyl[bis(ethylsulphonyl)]methane and TBD using X-ray and spectroscopic methods. Crystal data for the 1:1 complex indicates that a pair of relatively weak NH-O bonds links the anion of C-acid with TBD cation. The rings of TBD are slightly distorted to opposite sides of TBD plane. The 4-nitrophenyl[bis(ethylsulfonyl)]methane is rotated by about 35°, relative to the phenyl ring. However, the ethylsulfonyl groups are
approximately coplanar. Generally, the H-bonded ionic pairs in the crystal structure are arranged antiparallel [19]. Spectroscopic results obtained for the 1:1 complex in KBr pellets and solved in chloroform are in excellent agreement with the crystal description of the complex structure [19]. The position of the band of \(\nu(\text{NH}^+)\) vibrations also indicates that both N-H protons of protonated TBD molecule are involved in hydrogen bonds. Moreover, the spectra show delocalization of negative charge after deprotonation of carbon acid. However, the FT-IR spectrum of the 1:1 complex in acetonitrile indicates that the \(\nu_{as}(\text{NO}_2)\) and \(\nu_s(\text{NO}_2)\) vibrations are no longer observed as results of interaction of the nitro group of carbon acid with N-H protons of TBD base by hydrogen bonds [19]. Therefore, the final anionic product of the proton transfer reaction between 4-nitrophenyl[bis(ethylsulfonyl)]methane and TBD in acetonitrile has different structure than in chloroform and the solid state [19]. The crystal structure of the complex of TBD catalyst and nitroalkane [20] also confirmed the interaction of the nitro groups with NH protons, giving cyclic form of the complex with dihedral angle between the guanidine plane N-C-N and the nitronate plane O-N-O.

In this paper the results of kinetic and equilibrium experiments are reported. It seems to be worthy to study the different reactivity of TBD \(\text{pK}_a = 26.0\) [21] and MTBD \(\text{pK}_a = 25.4\) [21] with 4-nitrophenyl[bis(ethylsulfonyl)]methane in acetonitrile in the buffer containing base perchlorate as common cation \(\text{BH}^+\). The results are compared with those obtained for carbon acids [4, 18, 22, 23]. The possible structure of the activated complex, formed in the reaction of 4-nitrophenyl[bis(ethylsulfonyl)]methane with TBD and MTBD in acetonitrile is also proposed.

![Scheme 1 Tittle carbon acid and organic bases used in the experiments.](image)

2 Experimental

Acetonitrile, the spectroscopic grade solvent from Scharlau, was stored over CaH₂, distilled over P₄O₁₀ and finally, fractionally distilled over CaH₂. The middle fraction (81.5–82 °C) was collected and stored under nitrogen free from moisture and CO₂.

4-nitrophenyl[bis(ethylsulphonyl)]methane was synthesized according to modified method described by Cronyn [24]. \(^1\text{H} \text{NMR (Gemini 300 VT Varian)}, \text{MS spectroscopy (AMD 604/402)}\) and m.p. = 199–202 °C confirmed the purity of the C-acid. The melting point, MS and \(^1\text{H} \text{NMR spectra were in accordance with the literature [16].}\)

The 0.025 M stock solution of 4-nitrophenyl[bis(ethylsulphonyl)]methane in dioxane was originally prepared and then the calculated volume of this solution was transferred to the reaction vessel.
to acetonitrile to make a $1.25 \times 10^{-5}$ M substrate solution. This manner of preparation of working solution results from the poor solubility of 4-nitrophenyl[bis(ethylsulphonyl)]methane in acetonitrile.

Bases: 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), and 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), from Aldrich were used without any further purification. The purity of the samples of bases as tested by NMR spectroscopy and titration [25] was satisfactory.

The stock solutions of C-acid and bases were freshly prepared before experiments and handled with precautions to protect them from atmospheric carbon dioxide and moisture.

1,5,7-triazabicyclo[4.4.0]dec-5-ene perchlorate was prepared by mixing stoichiometric amounts of TBD base and HClO$_4$ (71%) in ethanol. Water and ethanol were then removed under reduced pressure. The white residue was dissolved in ethanol and the solvent was evaporated again. This procedure was repeated until the solvent was removed completely and the weight of perchlorate corresponded to the calculated amount of the salt was achieved.

7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene perchlorate was prepared in a procedure analogous to TBD perchlorate.

Tetrabutylammonium perchlorate, commercial product from Fluka, was used without purification.

The spectra of neutral and ionized forms of 4-nitrophenyl[bis(ethylsulphonyl)]methane in acetonitrile (Fig. 1) and the equilibrium of the reaction between C-acid and studied bases were taken using a Hewlett Packard Diode-Array Spectrometer (HP 8452A) fitted with a thermostated cell holder to keep the temperature constant within $\pm 0.1$ °C.

![Fig. 1](image-url) 

**Fig. 1** Electronic spectra of 4-nitrophenyl[bis(ethylsulphonyl)]methane (a, $\lambda_{max} = 278$ nm) and its anion (b, $\lambda_{max} = 446$ nm) in acetonitrile.

The proton abstraction from 4-nitrophenyl[bis(ethylsulphonyl)]methane with TBD and MTBD in acetonitrile is fast and the equilibrium temperature dependent. The deprotonation of 4-nitrophenyl[bis(ethylsulphonyl)]methane with these bases in MeCN has been measured by means of the “temperature-jump” relaxation technique, using the Hi-Tech Scientific IS-2 apparatus [5, 18, 26]. The observation cell with 3 mm light path,
made of quartz and carefully thermostated was connected with capacitor via two stain-
less electrodes. The discharge of a capacitor of 13 kV, heated the 100 µL volume of
solution giving the temperature rise in acetonitrile $\Delta T = 19.3 \, ^\circ C \left(\Delta T = C \cdot V^2 / 2 \cdot Q_s \cdot m_s \, [^\circ C]\right)$; where $C$ = capacitance [F], $V$ = voltage across capacitor [V], $Q_s = 2.23$ specific heat of acetonitrile [$J \cdot g^{-1} \cdot deg^{-1}$], $m_s =$ mass of solvent [g], heating time $< 5 \mu s$.

Syringes were used to fill up the measuring cell and to drain used solution. The constant
temperature of the cell within $\pm 0.1 \, ^\circ C$ was achieved with an external liquid circulating
bath (Haake DC 10-K 10). Spectral changes after the temperature jump were recorded
and analyzed by computer. Up to ten runs were taken to have an average value of the
rate constant.

The perchlorates of the appropriate base were chosen as a source of common cation
BH$^+$, because their solutions are transparent over a broad spectral range and they are
presumed to be well dissociated even at high concentration used in the kinetic experiments
and in the presence of tetrabutylammonium perchlorate as a supporting electrolyte.

3 Results and discussion

4-nitrophenyl[bis(ethylsulfonyl)]methane is relatively strong carbon acid with pK$_a$ value
found by Sorensen in water pK$_a = 10.08$ [16] and by Jarczewski at al. in acetonitrile pK$_a = 22.9$ [27]. Electronic spectra (Fig.1) indicate that the product of reaction of this carbon
acid with TBD and MTBD is largely dissociated into free carbanion which has an intense
visible absorption at $\lambda_{max} = 446 \, nm$. Similar large dissociation has already been found
for other reaction of carbon acids with strong organic bases where the dissociation into
free ions reached at least 87 %, in acetonitrile [28]. For these reactions the equilibrium
constants are large (Table 1), provided the concentration of the base is reasonably high.
However, the ion association effect is not observed neither at large concentration of the
base nor the large concentration of the common cation BH$^+$, as formerly found for other
system of reactions between 1-nitro-1-(4-nitrophenyl)alkanes and strong guanidine bases
in acetonitrile [29].

The lack of the shift of the $\lambda_{max} = 446 \, nm$ characteristic for free anion toward the
shorter wavelength along with increasing concentration of the base and also with BH$^+$
cation indicates that there is no association process to ion pairs in acetonitrile (Fig. 2
and 3). Together with increasing concentration of the BH$^+$ cation there is a significant
equilibrium decrease (Fig. 3). Thus the postulated product of reaction with TBD and
MTBD bases in acetonitrile seems to be fairly well dissociated into free ions. The proof
of the formation of the product as free ions in acetonitrile is limited to TBD base since
this base produced a mixture of ions and ion pairs in case of reaction with 1-nitro-1-(4-
nitrophenyl)alkanes, while the product of reaction with MTBD in acetonitrile appeared
to be entirely dissociated [4].

Table 1 presents equilibrium constants and molar absorption coefficients for the re-
action between 4-nitrophenyl[bis(ethylsulfonyl)]methane and TBD and MTBD bases in
acetonitrile in the presence of appropriate base perchlorate. The values were calculated
Fig. 2 Visible spectra of the reaction between 4-nitrophenyl[bis(ethylsulfonyl)]methane (2×10^{-4} M) and TBD (2×10^{-3} M) in acetonitrile and tetrahydrofuran (THF): a – free anions in acetonitrile, b – a mixture of free anions and ion pairs in THF, c – ion pairs in THF.

Fig. 3 Visible spectra of the reaction between 4-nitrophenyl[bis(ethylsulfonyl)]methane (2×10^{-4} M) and TBD (2×10^{-3} M) in acetonitrile with increasing concentration of added TBDHClO_4 (BH^+). Concentrations of added [BH^+] are: 0.0 mol dm^{-3} (a), 8.0×10^{-3} mol dm^{-3} (b), 2.5×10^{-2} mol dm^{-3} (c), 5.0×10^{-2} mol dm^{-3} (d).

from the absorbancies at 25 °C using the Benesi-Hildebrand equation.

| Base | Base concentration M | C-acid concentration M | BH^+ concentration M | λ_{max} nm | K M^{-1} | ε dm^3 mol^{-1} cm^{-1} |
|------|---------------------|------------------------|----------------------|-------------|---------|------------------------|
| TBD  | 0.001 – 0.008       | 1.25×10^{-5}           | 6×10^{-3}            | 446         | 906 ± 70 | 31000 ± 1500           |
|      | 0.001 – 0.004       | 2.5×10^{-5}            | 0.0                  | 446         | 947 ± 134| 35000 ± 4000           |
| MTBD | 0.001 – 0.009       | 2.5×10^{-5}            | 7.5×10^{-3}          | 446         | 705 ± 80 | 33000 ± 4000           |
|      | 0.001 – 0.005       | 2.5×10^{-5}            | 0.0                  | 446         | 698 ± 120| 40000 ± 5000           |

Table 1 Equilibrium constants K and molar absorption coefficient ε at 25 °C for the reaction between 4-nitrophenyl[bis(ethylsulfonyl)]methane and TBD and MTBD bases in acetonitrile and in the presence of the appropriate base perchlorate as common cation BH^+. 
The values of equilibrium constants calculated from equilibrium experiments (Table 1) and determined from kinetic measurements (Table 2) are in a good agreement, showing that the proton transfer reaction is not disturbed by the side reactions [18].

In our previous paper, much faster proton abstraction from 1-nitro-1-(4-nitrophenyl)alkanes was observed for TBD than MTBD base [4]. This observation was unusual taking into account their equal base strength (Scheme 1). The rate ratios for proton transfer between 1-nitro-1-(4-nitrophenyl)alkanes and TBD and MTBD bases were \(k_{TBD}/k_{MTBD} = 118 - 287\) in THF, and \(48 - 150\) in acetonitrile [4] depending on the steric bulk of the alkyl substituent in the vicinity of the reaction center of the C-acid. These large differences in the rate constants were attributed to the structure of the transition state with two hydrogen bonds in the case of TBD and single hydrogen bond for the MTBD base. These different structures result from the interaction between electronegative oxygen atoms of the nitro group of the C-acid and TBD or MTBD base. Taking into account that both bases are of equal strength, the much faster reaction of TBD indicates that the Brønsted relationship does not hold. Such results could indicate the importance of steric factors, or as in this case, prove different reaction mechanism via two distinct structures of the transition state [4, 30, 31].

4-nitrophenyl[bis(ethylsulfonyl)]methane is a type of compound having the properties in between so-called “normal” acids and carbon acids [19] being closer to the latter.

The measured rate constants \(k_{obs}\) and \(k_2\) for the proton transfer reaction between 4-nitrophenyl[bis(ethylsulfonyl)]methane and TBD and MTBD bases in acetonitrile in the presence of common cation BH\(^+\) are given in Table 2.

As was expected, the faster reaction in the set takes place for the system of reaction of 4-nitrophenyl[bis(ethylsulfonyl)]methane with stronger TBD base: \(k_{2}^{TBD} = 3.3 \times 10^7\) dm\(^3\) mol\(^{-1}\)s\(^{-1}\) while the reaction driven with MTBD is reduced by two times: \(k_{2}^{MTBD} = 1.5 \times 10^7\) dm\(^3\) mol\(^{-1}\)s\(^{-1}\) (Table 2). In this case Brønsted relationship is obeyed as the ratio of \(k_{TBD}/k_{MTBD} = 2.2\) while the ratio of \(K_{TBD}/K_{MTBD} = 1.4\) and the approximate Brønsted coefficient \(\beta \approx 0.7\) in contrary to the proton transfer reaction carried out between 1-nitro-1-(4-nitrophenyl)alkanes and TBD and MTBD bases [4], [22]. The decrease of the rate constants \(k_2\) observed for MTBD could not be accounted for steric arguments. Therefore, we presume that this small reduction of the rate constants could be attributable to the strength of the bases used, but not different structures of the transition states since we measure the equilibrium between the substrates and the products (Scheme 2). However, in this case different ways of stabilization of the transition state are proposed (Scheme 2) on the basis of the different values of the entropy of activation (Table 3). The large negative \(\Delta S^\ne\) values -40 and -62 J mol\(^{-1}\) K\(^{-1}\) for TBD and MTBD are characteristic for ionogenic mechanism of reaction. The more negative value of \(\Delta S^\ne\) for MTBD reaction indicates the more ordered T.S. with more advanced separation of the negative charge that result in a better solvation by polar solvent.

Then the stabilization by two hydrogen bonds of the transition state of TBD reaction is confirmed by the less negative \(\Delta S^\ne\) values than for MTBD indicating the negative charge diffused in the cyclic structure of the T.S.. This is true regarding the values in
MTBD

| Temperature °C | \( k_{\text{obs}} \times 10^{-5} \) s\(^{-1}\) | \( k_2 \times 10^{-7} \) dm\(^3\)mol\(^{-1}\)s\(^{-1}\) | \( k_{-1} \times 10^{-4} \) s\(^{-1}\) | \( K_{\text{kin}} = k_2 / k_{-1} \) M\(^{-1}\) |
|---------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 20            | 0.67 - 1.07                     | 1.32 ± 0.03                     | 4.08 ± 0.21                     | 324 ± 7                        |
| 25            | 0.71 - 1.16                     | 1.47 ± 0.06                     | 4.23 ± 0.24                     | 348 ± 22                       |
| 30            | 0.80 - 1.31                     | 1.70 ± 0.03                     | 4.61 ± 0.12                     | 369 ± 12                       |
| 35            | 0.84 - 1.38                     | 1.82 ± 0.06                     | 4.66 ± 0.21                     | 392 ± 21                       |
| 40            | 0.89 - 1.49                     | 2.00 ± 0.02                     | 4.86 ± 0.09                     | 412 ± 5                        |

TBD

| Temperature °C | \( k_{\text{obs}} \times 10^{-5} \) s\(^{-1}\) | \( k_2 \times 10^{-7} \) dm\(^3\)mol\(^{-1}\)s\(^{-1}\) | \( k_{-1} \times 10^{-4} \) s\(^{-1}\) | \( K_{\text{kin}} = k_2 / k_{-1} \) M\(^{-1}\) |
|---------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 20            | 1.06 - 1.90                     | 2.82 ± 0.12                     | 4.75 ± 0.44                     | 595 ± 60                       |
| 25            | 1.28 - 2.26                     | 3.29 ± 0.43                     | 5.51 ± 0.16                     | 597 ± 59                       |
| 30            | 1.40 - 2.59                     | 3.84 ± 0.28                     | 6.36 ± 0.10                     | 604 ± 34                       |
| 35            | 1.60 - 2.91                     | 4.32 ± 0.24                     | 7.08 ± 0.89                     | 610 ± 26                       |
| 40            | 1.80 - 3.25                     | 4.84 ± 0.24                     | 7.92 ± 0.86                     | 611 ± 23                       |

\( k_2 = k_{\text{obs}} C_{\text{base}} + k_{-1} \)

Carbon acid concentration: \(1.25 \times 10^{-5}\) M; TBD and MTBD base: 0.002-0.004 M; base perchlorate: \(7.5 \times 10^{-3}\) M; TBAP: 0.2 M.

**Table 2** Rate constants for the proton transfer reaction between 4-nitrophenyl-[bis(ethylsulfonyl)]methane and TBD and MTBD bases in acetonitrile in the presence of common cation BH\(^+\) and supporting electrolyte TBAP.

Table 3. Similar effect was observed in the previous study of deprotonation reaction of 1-nitro-1-(4-nitrophenyl)alkanes with TBD and MTBD bases [4].

| Base  | \( \Delta H^\# \) kJmol\(^{-1}\) | \( \Delta S^\# \) Jmol\(^{-1}\)K\(^{-1}\) | \( \Delta G^\# \) kJmol\(^{-1}\) |
|-------|--------------------------------|--------------------------------|--------------------------------|
| TBD   | 18.1 ± 0.7                      | -40.3 ± 2.2                    | 30.1 ± 0.9                     |
| MTBD  | 13.5 ± 1.4                      | -62.3 ± 4.8                    | 32.1 ± 2.0                     |

**Table 3** Activation parameters for proton transfer reaction between 4-nitrophenyl[bis(ethylsulfonyl)]methane and TBD and MTBD bases in acetonitrile in the presence of common cation BH\(^+\) and supporting electrolyte TBAP.

There is a significant difference between the enthalpy of activation \(\Delta H^\#\) found for TBD and MTBD reaction (Table 3) indicating a different reaction mechanism. The enthalpy of activation \(\Delta H^\#\) is compensated by the entropy of activation \(\Delta S^\#\) resulting in a larger free enthalpy of activation \(\Delta G^\#\) by 2 kJ mol\(^{-1}\) for MTBD reaction. The compensation effect is characteristic of reactions in which solvation changes are kinetically important [32].

Taking into account the values of the rate constants, activation parameters and that the product of both reactions appeared to be dissociated into free anions the following mechanism of the reactions can be proposed (Scheme 2).

The structures of the transition state, seem to be different for the reaction of TBD and MTBD with two or one N-H–O hydrogen bond formed between sulfonyl oxygen and TBD.
The rearrangement of the structure of the transition state of the reaction of 4-nitrophenyl[bis(ethylsulfonyl)]methane with TBD to nitronium anion (NA) involves a lot of structural changes, via ion-pair (IP), and dissociated ions (I) (Scheme 2). However, this route is possible due to fast dissociation-association process and also in the kinetic range of the TBD base concentration (pseudo-first-order conditions) (Table 2). We presume that the other molecule of the protonated TBD base can strongly interact with the ion-pair or with dissociated carbanion, giving the product (NA) stabilized by interaction of the oxygen atoms of the nitro group with NH protons of the base (Scheme 2). This may produce relatively strong hydrogen bonds, producing the possible nitronium complex or MTBD molecule or between the nitro group of carbon acid and TBD base (Scheme 2).

Scheme 2 The mechanism of the reaction between 4-nitrophenyl[bis(ethylsulfonyl)]methane and organic bases: TBD and MTBD in acetonitrile. Where: (TS) – transition state complex, (IP) – ion-pair, (I) – ions, (NA) – nitronium anion.
already confirmed by FTIR spectroscopy [18].

For steric reasons and the lack of the second NH group, the structures of the transition state and the final product with MTBD base could not be formed alike. However, in our kinetic experiments we observed the equilibrium between ionized products (I) and the substrates in both systems of reactions. So, taking into consideration the fast ion dissociation-association process already assumed, the small, two times reduction of the rate constants for weaker MTBD base is to be comprehended (Table 2). Therefore, the kinetic behavior of methanedisulfone carbon acid is certainly not as different as for nitroalkanes reported before [4], [23]. Then we presume that despite different structures of the transition states assumed, the products of the reaction of 4-nitrophenyl[bis(ethylsulfonyl)]methane with MTBD and TBD, being well dissociated forced similar rate constants observed (Table 2, Scheme 2).

In conclusion, we declare that the mechanism of proton transfer reaction between 4-nitrophenyl[bis(ethylsulfonyl)]methane and TBD base is different compared to MTBD base presenting for TBD and MTBD bases two entirely different structures of the transition state, which have a little influence on the rate constant observed. The carbon acid 4-nitrophenyl[bis(ethylsulfonyl)]methane behaves more alike other nitroalkanes undergoing similar structure changes on the way from its substrate, via transition state to the final product –dissociated ions.

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