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Ab initio prediction of the structure and energetics of the complexes of 1-nitro-1-(4-nitrophenyl)ethane and TBD and MTBD bases

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Abstract

The ab initio optimized (MP2/cc-pVDZ and PBE0/cc-pVDZ) structures of the complexes of 1-nitro-1-(4-nitrophenyl)ethane with 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) formed along the way of proton abstraction are presented. The structures of the transition states and the products are discussed. The relative energies in the gas phase for each individual entity along the proton abstraction with TBD and MTBD are predicted to be: hydrogen bonded complex (-15.7 and -14.2 kcal mol^{-1}), ion-pair (-7.5 and -5.1 kcal mol^{-1}), relaxed ion-pair (-12.7 and -11.3 kcal mol^{-1}), and free ions ($+88.1$ and $+86.9$ kcal mol^{-1}), respectively. Inclusion of the polar-solvent (acetonitrile) effects changes substantially the appropriate energy levels for the hydrogen bonded complex (-8.3 and -9.6 kcal mol^{-1}), ion-pair (-9.5 and -8.0 kcal mol^{-1}), relaxed ion-pair (-11.4 and -11.2 kcal mol^{-1}) and free ions ($+5.8$ and $+10$ kcal mol^{-1}) for TBD and MTBD, respectively. The energy changes along the C–H internuclear distance computed by the PBE0 method for the TBD and MTBD bases show the maximum energy for the transition-state complex at 1.4 Å (9.9 kcal mol^{-1}) and 1.5 Å (11.9 kcal mol^{-1}) in vacuum, and at 1.3 Å (6.8 kcal mol^{-1}) and 1.4 Å (8.9 kcal mol^{-1}) in acetonitrile. The MP2 method at the PBE0 optimized geometries gives higher transition-state energies values at 1.45 Å (14.2 kcal mol^{-1}) and at 1.5 Å (14.4 kcal mol^{-1}) in vacuum, and at 1.35 Å (10.3 kcal mol^{-1}) and at 1.4 Å (10.5 kcal mol^{-1}) in acetonitrile, relative to the energy of the hydrogen-bonded complex at 1.1 Å (0 kcal mol^{-1}). The width of the barriers is larger by at least ~ 1 Å for MTBD than that for the TBD base. The shape of the energy profiles indicates exo-endoergic course of reaction in MeCN and vacuum, respectively. On virtue of these values, the mechanism of proton abstraction from 1-nitro-1-(4-nitrophenyl)alkanes with the TBD and MTBD bases in aprotic solvents is approached.
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1. Introduction

The proton transfer reactions between C-acids of various structures and strong amine bases in solution have been extensively studied for decades [1–4]. In our previous papers, we put a special emphasis on the influence of steric hindrance brought by reacting C-acids and strong organic bases on the rate of proton abstraction in aprotic solvents [5–9]. We found that the proton transfer reaction from nitroalkanes differing by the bulk of R substituents and also by the types of electron withdrawing group, but having very similar acidity in acetonitrile, showed significant differences in the kinetic rate constants. The product of the proton transfer reaction with

7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) in acetonitrile has been found to dissociate into free ions, whereas that of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) is composed of a comparable amount of ions and ion-pairs. This issued from the electronic spectra for the nitronate anions of $\alpha_{max} = 514$ nm characteristic for the reaction of MTBD with 1-(4-nitrophenyl)-1-nitroethane (**1**), whereas the spectrum of the TBD product was a sum of two spectra for the free nitronate anions and ion-pairs, $\alpha_{max} = 460$ nm, which is close to that of $\alpha_{max} = 450$ nm found in THF, where the dissociation of the ion-pair product is negligible [7]. In general, the same pattern of the products has been observed for other 1-nitro-1-(4-nitrophenyl)alkanes [1,5]. Thus, the equilibrium between the nitronate anions and hydrogen bonded ion pairs for the reaction of the TBD base is illustrated by Scheme 1.

We found that the rate constants k_{2H} for the reactions of 1-nitro-1-(4-nitrophenyl)alkanes and the TBD base decrease by one order of magnitude along with growing bulk of the alkyl substituent R in the C-acid (for R=Me, Et, i-Pr, $k_{2H} = 15200$,

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AH + B ⇌ AHB ⇌ A·H·B ⇌ A⁻,HB⁺ ⇌ A⁻ + HB⁺

Scheme 1. The equilibrium between the nitronate anions and hydrogen bonded ion pairs for the reaction of 1-nitro-1-(4-nitrophenyl)ethane (**1**) and the TBD base in acetonitrile (AH (C-acid **1**), B (TBD base), AHB (hydrogen bonded encounter complex), A···H···B (transition state complex) A⁻, HB⁺ (hydrogen bonded ion pair) A⁻ + BH⁺ (free ions)).

5300, and 1100 $dm^3\,mol^{-1}\,s^{-1}$, respectively). A similar relation was observed for the reaction of more hindered MTBD, but with much smaller rate constants ($k_{2H} = 317$, 86, and 7.6 $dm^3\,mol^{-1}\,s^{-1}$) [5]. On the whole, along with growing bulk of the R substituent, significant reduction of the rate constants is observed, indicating that the steric factors play an important role. This observation is consistent with the results obtained by other authors, who came to the conclusion that the increased crowding in the vicinity of the reaction center causes the steric inhibition to planarity of the carbanion, and most importantly, leads to a different structure of the transition state [10–12].

Despite the fact that the strength of both bases is very similar ($pK_a^{TBD} = 25.9$; 24.7 [13,14], $pK_a^{MTBD} = 25.4$; 25 [13,15]) the ratios k_{TBD}/k_{MTBD} varied from 48 to 150 and 118 to 281 depending on the structure of C-acids in acetonitrile and THF, respectively. The much slower reaction for MTBD than the TBD base was accounted for two different structures of hydrogen-bonded complexes of the transition state with one or two hydrogen bonds, respectively [5]. The different mechanism for reaction of the TBD and MTBD base was reflected in the activation parameters. They were characteristic for the ionogenic mechanism of a reaction with large, negative values of the entropy of activation and were similar for both reactions $\Delta S^{\neq} \cong -110\,J\,mol^{-1}$ deg. We found a significant difference between the $\Delta H^{\neq}$ values for the TBD and MTBD reactions with (**1**) being $\Delta H_{TBD}^{\neq} - \Delta H_{MTBD}^{\neq} \cong 8\,kJ\,mol^{-1}$.

The free enthalpy of activation $\Delta G^{\neq} = 6.7$ and 9.3 $kJ\,mol^{-1}$ for TBD and MTBD, respectively, revealed a lack of the compensating effect due to simultaneous increase of the enthalpy of activation $\Delta H^{\neq}$ and the negative entropy of activation $\Delta S^{\neq}$ along with increasing steric hindrance.

In case of the TBD reaction the double hydrogen bonds determined the structure of the transition state (Scheme 2).

Using the semiempirical PM3 method [16,17], we proved that for the assumed TS structure (Scheme 2) for the reactions of 1-nitro-1-(4-nitrophenyl)alkanes with the TBD base, the HCNO dihedral angle decreases along with the bulk of the R substituent in the C-acid [5]. We presumed that the reaction with MTBD proceeds with different structures of the TS complexes (Scheme 2). The PM3 calculations for the C- acid **1** showed that the Me group of the MTBD base is located between NO_2 and $PhNO_2$ and that the HCNO dihedral angle is small. This means that the nitro group is almost coplanar with the proton transfer axis. Generally, the MTBD transition states have larger energies compared to those for the TBD reaction.

We also found that the values of the primary deuterium kinetic isotope effects KIE are greatly influenced by the factors resulting from the structures of the complexes of the transition state. On the whole, we can conclude that for the TBD reactions, a decrease in the HCNO angle caused by the growing bulk of the R substituent in the C-acid results in larger KIE values. Also, the additional stabilization of the TS by a hydrogen bond in case of the TBD reaction operates in the same direction, thus increasing KIE. In conclusion we suggested that the KIE values for the reactions of nitroalkanes with guanidine bases increase when the structure of the transition state is less product-like.

We also found the unusual KIE values for the reaction of the MTBD base, as they decline along with the increasing bulk of the R substituent [5]. This is just opposite to the previously observed effect, because usually the KIE values increase with the steric hindrance. Hence, this effect was attributed to either desolvation of the transition state or a steeper energy barrier [9,12].

The structures of the transition states and the products for the proton transfer reaction between 1-nitro-1-(4-nitrophenyl)-alkanes and the strong cyclic bases TBD and MTBD in acetonitrile were determined in the thorough kinetic studies and then estimated by the PM3 method, thus providing premises for the mechanism of reaction already presented [5]. Further study of this problem seems to be worthwhile.
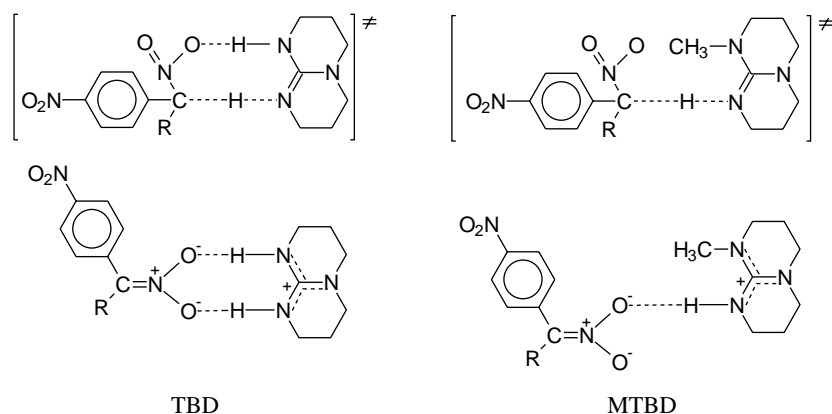
Scheme 2. Predicted structures of the transition state and the product for the reaction of the 1-nitro-1-(4-nitrophenyl)alkanes and the TBD and MTBD bases on virtue of kinetic experiments in acetonitrile solvent. R = CH₃ (**1**).