Double Proton Transfer Reactions with Plateau-Like Transition State Regions: Pyrazole−Trifluoroacetic Acid Clusters

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The double proton transfer reactions between carboxylic acids and pyrazole were studied by computational methods up to the coupled-cluster level. Introduction of substituents allowed for a systematic modulation of the reaction profile, resulting in imaginary frequencies of the associated transition states between −1180 and −45 cm^{-1}. In the latter case, a local transition state is replaced by an extremely flat (plateaulike) transition region, which constitutes the transition from a concerted toward a stepwise mechanism. Vertical excitation energies along the reaction path reveal that the feature of a plateau in the ground state is mirrored in the excited states.

Introduction

Double proton transfer reactions (DPTR) belong to the most important reactions in chemistry and biochemistry and have been studied extensively by both experimental and computational approaches.[1−4] Among the most famous examples belonging to this class of reactions are the proton transfer reactions in nucleo base pairs, e.g., adenine−thymine.[5−7] Investigation of proton transfer reactions by means of computational methods usually is a tedious task. In very many cases, theoretical studies on DPTRs need to be augmented by the explicit calculation of quantum effects (e.g., tunneling) as such effects can be large for reactions involving these very light atoms.[8−10] In contrast to most other reactions, this usually puts a further burden on the accurate investigation of DPTRs.

A standard question concerning the nature of a DPTR refers to the existence of a zwitterionic intermediate: is it a concerted or a stepwise mechanism?[11,12] In a series of papers we studied DPTRs, which constitute the transition between these two cases.[13−16] In this borderline situation the reaction profile is characterized by a plateau of almost constant energy along the reaction coordinate. Consequently, these plateau reactions do not show a sharply localized transition state as most other reactions do. Instead, they have a broad transition region, where the system may spend considerable time. As a consequence of the unusual reaction profile, tunneling effects are extremely small for plateau reactions and the reaction dynamics, as studied by the reaction path Hamiltonian,[17,18] differs considerably from those of concerted DPTRs with standard Eckart potentials.[14,15] Environmental effects (solvents, biological environments) may stabilize a zwitterionic intermediate[13] and thus tend to resolve the plateau character of a reaction. However, the introduction of different substituents in close vicinity to the reactive center allows us to antagonize such effects.[15]

It is well-known that photoinduced double proton transfer reactions may proceed significantly faster than those restricted to the electronic ground state. Such electronically excited proton transfer reactions (ESPT) have been studied by many authors.[19−22] The nature of the mechanism may change when switching from the S_0 potential energy surface (PES) to the S_1 surface.[23] Consequently, the question arises what will happen to a plateau in electronically excited states? In many studies proton transfer reactions have been analyzed by Marcus theory,[24−28] which has originally been derived for electron transfer processes. As the two-state model of Marcus is based on electronically excited states along the minimum energy path of the S_0 state (i.e., vertical excitations along the S_0 reaction coordinate), the energy profiles of the excited states do not refer to minimum energy paths on the corresponding PESs and thus to the relaxed reaction profile of the ESPT. However, due to the lifetime on top of the plateau, vertical excitation energies are of particular interest for laser experiments on plateau reactions.

The purpose of this paper is 2-fold: First, all of our previous studies rely on substituted pyrazole−guanidine clusters,[13−16] which allowed for very systematic investigations concerning the change from a concerted toward a stepwise mechanism via very broad plateau systems. In case of the occurrence of zwitterionic intermediates both protons are connected to the guanidine entity; i.e., the pyrazole unit is negatively charged. To rule out that the observed effects are restricted to this particular system only and thus to demonstrate the transferability of our results to other systems, we present here a new system that fulfills all requests in that respect. The skeleton of this system is a pyrazole−trifluoroacetic acid cluster, which differs completely from the previous systems as it shows O···H and N···H hydrogen bridges instead of N···H hydrogen bonds only (see Scheme 1). Moreover, in the transition region the pyrazole is now positively charged. Second, we have computed some low lying electronically excited states along the S_0 reaction coordinate. This allows for a direct comparison with the two-state model of Marcus,[29,30] which works well for concerted reactions with a localized transition state. Moreover, changes in the vertical excitation energies ($S_0 \rightarrow S_1$) between the local minimum and the plateau region of the S_0 reaction path may result in band shifts of corresponding laser experiments. Furthermore, we consider this study of the vertical excitation energies as a first step toward a systematic investigation of excited states for such systems, i.e., the selection of important states, inclusion of geometry relaxation effects, minimum energy paths, etc.

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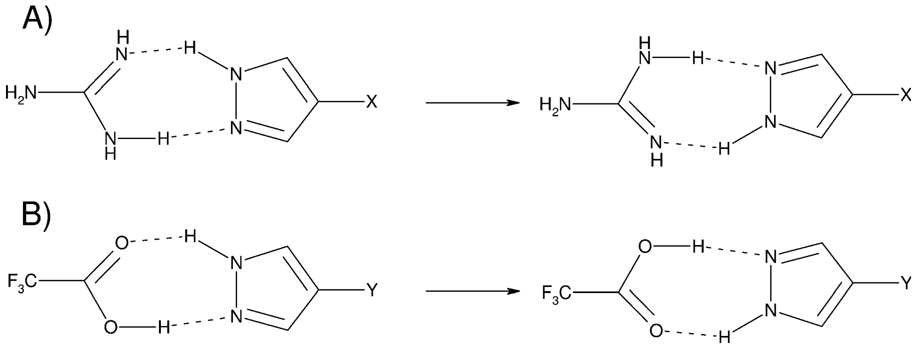
SCHEME 1: Double Proton Transfer Reactions of Substitued Pyrazoles with (A) Guanidine and (B) Trifluoroacetic Acid



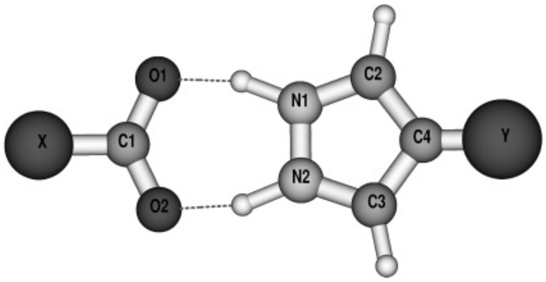
Computational Details

In analogy to our previous studies, all geometries were determined at the MP2/[aug]-cc-pVDZ level.[31] The augmented diffuse functions, i.e., [aug], are enclosed in brackets because they have been added to the four heavy atoms and the two hydrogens involved in the N···H and O···H hydrogen bonds of the clusters only. Likewise, frequency calculations were performed at the same level of theory. Relative energies were determined at the CCSD(T)/[aug]-cc-pVDZ level[32] or the MP2/[aug]-cc-pVDZ level,[33] respectively. Excitation energies were obtained from RI-CC2 response theory, exploiting the resolution-of-identity approximation[34] in combination with a basis set of triple-ζ quality, i.e., TZVPP. All quantum chemical calculations have been performed with a development version of the MOLPRO[35] suite of ab initio programs and the GAMESS-US,[36] TURBOMOLE[37] and GAUSSIAN98[38] program packages. The intrinsic reaction coordinates (IRC) have been traced by the Gonzalez−Schlegel algorithm[39,40] using a reduced stepwidth of 0.05 amu$^{1/2}$·bohr and very tight convergence thresholds in all numerical procedures. These conditions were necessary to yield reliable descriptions of the IRCs in the regions of the plateaus. If not otherwise noted, the reaction coordinates used in this study refer to mass-weighted coordinates.

Results and Discussion

Ground State Properties. In a first step we studied the magnitude of the imaginary frequency describing the double proton transfer reaction of some pyrazole−acetic acid clusters. This quantity has been used for identifying plateau reactions.[13,15] Substituents were introduced in the 4-position of pyrazole and at the carbon atoms of the methyl-group of the acetic acid entity. Table 1 shows a short selection of systems and the corresponding imaginary frequencies that range from −1180 to −45 cm^{-1}. While low imaginary frequencies characterize a plateau, those obtained for the acetic acid clusters (without the fluoro substituents) indicate a highly concerted double proton transfer and thus an Eckart potential. In the following we will only focus on the three plateau reactions of the trifluoroacetic acid clusters **1**−**3**. Activation energies and the most important geometrical parameters for systems **1**−**3** are provided in Tables 2 and 3, respectively. A more comprehensive selection of geometrical parameters for the transition states is provided as Supporting Information. In contrast to the pyrazole−guanidine systems presented in our recent studies,[13−15] the formal transition states in the center of the plateaus of the systems **1**−**3** show a zwitterionic character with a positive charge at the pyrazole entity and a negative charge at the substituated acetic acid entity. The electron donating CH_3 group in system **2** and the NH_2 group in system **3** stabilize the transition states and thus lower the barrier height with regard to system **1**. The difference d = $r(O_2H_2)$ − $r(N_1H_1)$ between the bond lengths of the two hydrogen bonds within the reactants of reactions **1**−**3** and thus the difference of the bond strenghts increases slightly from reaction **1** to **3**. Therefore, the plateau reactions **2** and **3** show a somewhat more stepwise character than reaction **1**. The result of this effect is a flatter and broader plateau, a lower energy barrier and a lower imaginary frequency within systems **2** and **3**. These effects were discussed in detail elsewhere.[15]

TABLE 1: Imaginary Frequencies (cm^{-1}) of the Transition States for a Series of Double Proton Transfer Reactions



system	X	Y	$\nu_i^{\ddagger}$
	CH_3	CN	−1180
	CH_3	NH_2	−722
1	CF_3	H	−105
2	CF_3	CH_3	−60
3	CF_3	NH_2	−45

TABLE 2: ZPVE-Corrected Energy Barriers ΔE_A in kJ/mol Calculated at the MP2/[aug]-cc-pVDZ and CCSD(T)/[aug]-cc-pVDZ Levels, Respectively

system	ΔE_A(MP2)	ΔE_A(CCSD(T))	ΔZPVE
1	9.8	13.3	−7.7
2	9.0	12.5	−6.7
3	7.8	11.9	−6.6

TABLE 3: Most Important Geometrical Parameters in Å of the Reactants and Transition States of Reactions 1−3, Obtained at the MP2/[aug]-cc-pVDZ Level of Theory

system	$r(O_1H_1)$	$r(N_1H_1)$	$r(O_2H_2)$	$r(N_2H_2)$
reactant **1**	1.030	1.613	1.921	1.025
reactant **2**	1.032	1.601	1.926	1.025
reactant **3**	1.034	1.593	1.926	1.025
TS **1**	1.466	1.107	1.466	1.107
TS **2**	1.475	1.103	1.475	1.103
TS **3**	1.480	1.101	1.480	1.101

As MP2 is known to underestimate the barrier heights of proton transfer reactions, the potential along the reaction coordinate (i.e., the minimum energy path) has been recomputed by CCSD(T) and RI-CC2 energy single point calculations. The corresponding plots are shown for system **1** in Figure 1. All methods nicely reproduce the structural feature of a plateau instead of a localized transition state but differ in the overall

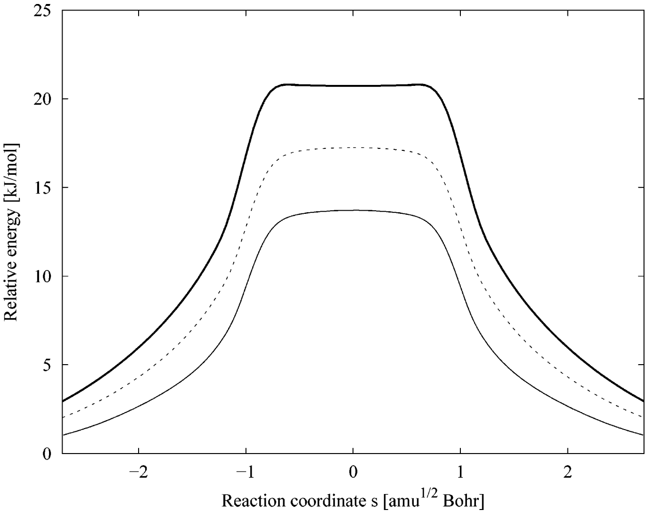


Figure 1. Reaction profiles (without ZPVE correction) of system **1** computed at different theoretical levels (CCSD(T), bold line; MP2, dashed lines; RI-CC2, solid line).

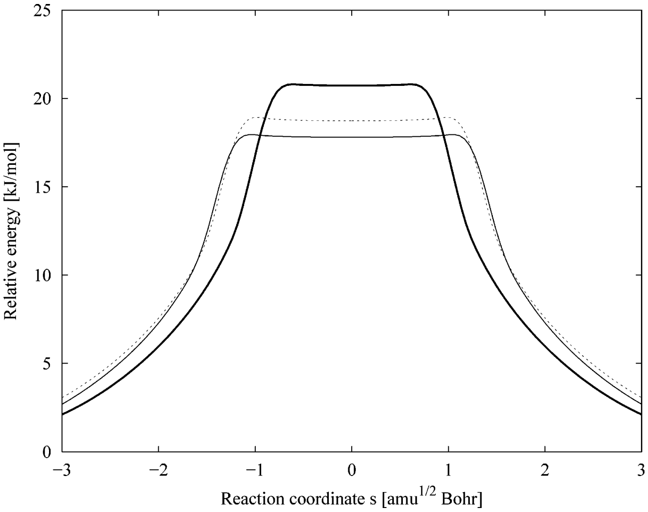


Figure 2. Ground state energy profiles, CCSD(T)/[aug]-cc-pVDZ without ZPVE correction, of the double proton transfer reaction of systems **1** to **3** (**1**, bold line; **2**, dashed line; **3**, solid line).

barrier height. The CCSD(T) calculations must be considered the most reliable ones, although geometry relaxation effects due to an improved description of electron correlation effects have not been accounted for explicitly. However, we consider this effect to be very small. With respect to the CCSD(T) values, MP2 and RI-CC2 underestimate the barrier considerably. All methods predict a plateau width of about 2 amu$^{1/2}$•bohr. However, the formal transition state at $s = 0.0$ amu$^{1/2}$•bohr at the MP2 and RI-CC2 levels switches to a very shallow local minimum at the CCSD(T) level. As the depth of this minimum is about 0.1 kJ/mol only, it is without any physical significance. Corrections for quantum effects, e.g., ZPVE corrections, may again reverse this effect as discussed in detail in ref 15. As reactants and products are identical for each reaction, the potentials depicted in Figure 1 are symmetrical.

The CCSD(T) reaction profiles for systems **1**−**3** are shown in Figure 2. All systems clearly constitute plateau reactions characterized by transition regions or structureless transition states, respectively. Therefore, a novel skeleton cluster (i.e., trifluoroacetic acid−pyrazole) has been found, which must be characterized as a plateau system. An analysis of these reactions based on the reaction path Hamiltonian[17,18] closely resembles the results recently obtained for pyrazol−guanidine clusters. For this very reason we do not repeat presenting these results but refer to the original literature (cf. ref 14). Consequently, plateaus and the associated effects in the curvature of the reaction path, the reaction dynamics, etc. are not a specific feature of the pyrazole−guanidine system but must be considered general effects at the transition from a concerted to a stepwise mechanism.

TABLE 4: $\pi\pi^*$ Excitation Energies (nm) for Pyrazole in Dependence on the Computational Level

method[a]	$\Delta E_{\pi\pi^*}$
CIS	169.1
CISD	189.2
TDDFT	193.9
CASSCF	232.7
CASPT2	219.7
RI-CC2[b]	210.8
MRCI[c]	220.9

[a] All calculations refer to a aug-cc-pVTZ basis set. [b] Based on a TZVPP basis set. [c] Taken from ref 44, based on a TZVP basis set.

In comparison to the pyrazole−guanidine cluster investigated in our previous studies the new system has fewer acidic protons and is thus significantly better suited for experiments. Self-aggregation is much more controlled as hydrogen bridges involve just one acidic proton of the pyrazole entity and one of the trifluoroacetic acid. However, it is well-known that pyrazole has a strong tendency of building trimers or even tetramers.[4,41,42] Consequently, one could thus imagine that plateau reactions may arise in clusters of two pyrazole molecules and one trifluoroacetic acid molecule. However, this is not subject of this study here. To prove that the pyrazole−trifluoroacetic acid system is a favorable complex in comparison to the pyrazole and trifluoroacetic acid dimers, we have computed the BSSE corrected interaction energies at the CCSD(T)/[aug]-cc-pVDZ level.[43] While the pyrazole−trifluoroacetic acid complex is stabilized by −97.6 kJ/mol, the pyrazole and trifluoroacetic acid dimers are stabilized by −81.8 and −82.7 kJ/mol only. Considering entropic effects, the stabilization of the pyrazole−trifluoroacetic acid complex should be even enhanced. As the pyrazole dimer has been observed in experimental studies,[4,41,42] the pyrazole−trifluoroacetic acid complex should hence be seen as well.

Excited States. As shown in Figure 1, RI-CC2 yields energy barriers being too small in comparison to the most reliable CCSD(T) values. On the other hand, the shape of the profile is nicely reproduced. Therefore, the question arises if RI-CC2 is a suitable method for calculating the first excited states along the reaction coordinate of the systems considered here. For this very reason we have performed a systematic study for the first $\pi\pi^*$ transition of pyrazole. Results are shown in Table 4. The most accurate value of 220.9 nm based on MRCI/TZVP calculations has been provided by Palmer et al.[44] While CIS, CISD and TDDFT calculations based on the B3LYP hybrid functional lead to a considerable underestimation of the excitation energy, multireference calculations (CASSCF(6,6) and CASPT2(6,6)) perform significantly better. However, to rule out changes in the active space for the structures along the reaction coordinate, a one-determinantal approach is the preferred choice. RI-CC2 actually provides the best value of all one-determinantal approaches, which is even closer to the MRCI value than the CASSCF(6,6) result. Therefore, RI-CC2 appears to be a very reasonable compromise between accuracy, CPU time and consistency and has thus been used for the studies presented below.

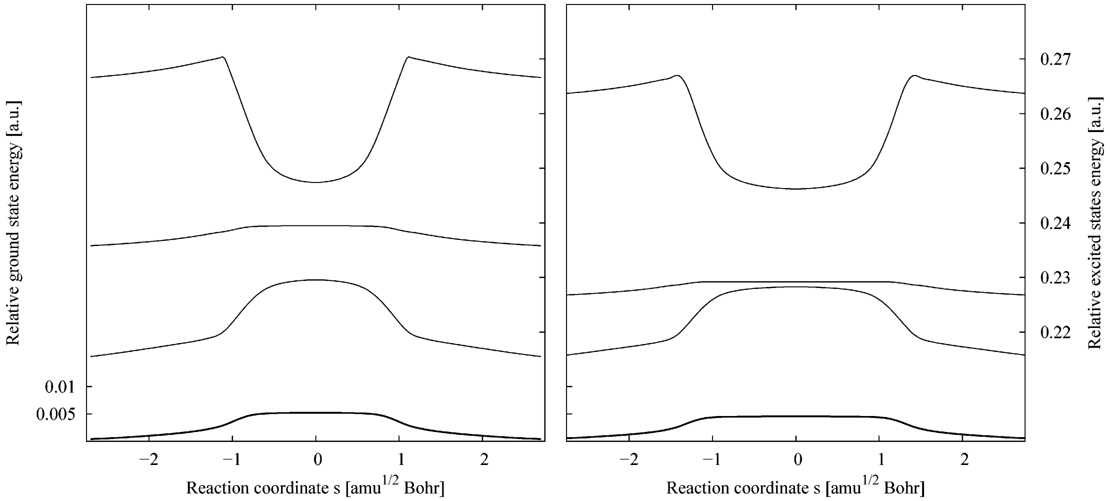


Figure 3. Reaction path of the ground state S_0 (bold line) and energy profiles of the excited states S_1-S_3 for reactions **1** (left) and **2** (right) obtained by vertical excitations from the ground state, using the RI-CC2/TZVPP level of theory.

In the past, Marcus theory has often been used to estimate the barrier height of proton transfer reactions.[20,26,45] This two-state model is based on the assumption of two intersecting harmonic potentials, which lead to an avoided crossing and thus to the picture of a double-cone in the region of the transition state.[29,30] Within this framework, the intersection of the (diabatic) potential curves is given by one-fourth of the vertical excitation energy in the minimum of the reactants. Moreover, in the region of the transition state the shape of the (adiabatic) upper cone of the excited state roughly resembles that of the ground state. This picture gives rise to the speculation if vertical excitations along the ground state reaction path also lead to plateaus in the excited state. The RI-CC2 energy profiles for systems **1** and **2** obtained for the lowest three excited states (and the ground state) are shown in Figure 3. The S_1 state essentially is characterized by a transition from an (in-plane) lone pair of the carboxylic oxygen into a π^* orbital of the trifluoroacetic acid. Due to symmetry, this lone pair is delocalized between both oxygen atoms at the formal transition state but is shifted to the double bonded oxygen in the entrance and exit channels of the reaction. The energy profiles of the S_2 states are extremely flat for both reactions depicted in Figure 3 and the associated oscillator strengths are about one magnitude larger than for the other two transitions, i.e., $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_3$. As this $\pi\pi^*$ transition is localized in the pyrazole entity, it is not directly associated with the double proton transfer, but of course experiences an influence from the π-shift in the pyrazole molecule, which is a consequence of the proton transfer. The most relevant state for the double proton transfer reaction is the S_3 state, because the associated transition is mainly given from the orbital localized between the oxygen and nitrogen atoms in direct vicinity of the hopping proton into a π^* orbital of the trifluoroacetic acid. The donor orbital has strong lone pair character in the region of the plateau but changes toward an σ(OH) orbital as the system leaves the plateau. In all cases the energy profiles for the excited states are extremely flat and thus indeed show a plateau type character. However, the plateaus in the excited states appear not as pronounced as for the ground state. At the edges of the plateau, significant energy changes can be observed in the excited states, which are much larger than for the electronic groundstate. In any case, using a simple two-state Marcus model for plateau reactions must be considered a misapplication and consequently reaction barriers of such reactions should not be estimated this way.

Summary and Conclusions

The double proton transfer reactions of some substituted pyrazole−trifluoroacetic acid clusters were studied by computational methods up to the coupled-cluster level. The energy profiles along the ground state reaction coordinates show a plateau of almost constant energy instead of a localized transition state. Consequently, these systems constitute the borderline case between a concerted and a stepwise mechanism passing through a structureless transition region. The properties of the clusters studied in this paper closely resemble those of the pyrazole−guanidine systems that have been investigated recently. However, as outlined above, these new systems differ considerably (e.g., due to O···H hydrogen bonds) from our previously studied systems. Therefore, results for plateau reaction can be generalized and are not restricted to a particular model system only. Moreover, vertical excitation energies essentially remain constant across the entire plateau region, whereas significant shifts may occur at the edges of the plateau. Nonnegligible lifetimes on top of the plateau give rise to the speculation if these shifts can be seen in corresponding laser experiments.

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Supporting Information Available: Geometrical parameters for TS **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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