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Communication

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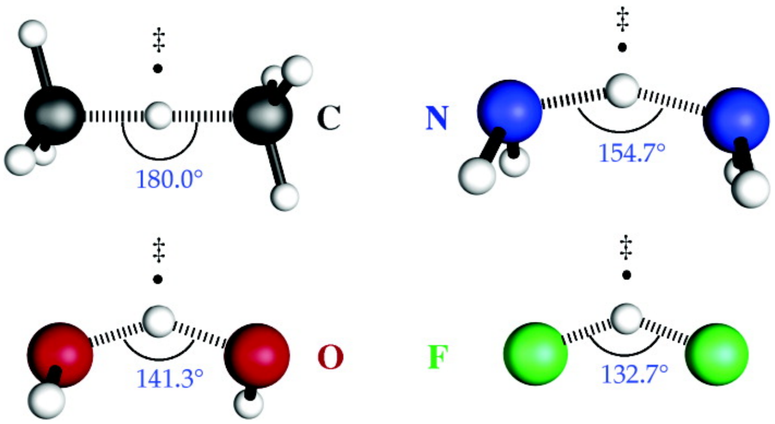

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Factors Controlling the Barriers to Degenerate Hydrogen Atom Transfers

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Hydrogen-atom transfer (HAT) reactions, because of their apparent simplicity, occupy positions of special significance in the effort to understand the factors that control chemical reactivity. They are also of practical importance in a wide variety of domains.[1] It is, therefore, not surprising that much effort has been devoted to developing theoretical models that can describe such reactions in a comprehensive and yet comprehensible fashion.[2] As a contribution to this effort, one of us has demonstrated that the rates of a wide variety of HAT reactions can be correlated by a simple Marcus-type expression,[2d] which uses as part of its input the rate constants of the self-exchange reactions (eq 1).

$$X^{\bullet} + H{-}X \rightarrow X{-}H + {}^{\bullet}X \tag{1}$$

In the present communication, we seek to understand the factors that control the barriers to these degenerate processes. That there is an interesting question to be addressed is revealed by the computational data in Table 1.[3]

Table 1. Computed Bond-Dissociation Enthalpies (BDE) for X−H, and Activation Enthalpies ($\Delta H^{\ddagger}$) and Potential Energy Barriers ($\Delta E^{\ddagger}$) for the Reaction in eq 1 (all values are in kcal/mol)

			Self-Exchange Barriers				
	X−H BDE		MPW1K[c]		CBS−QB3[c]		UCCSD(T)[c]
X	exp.[a]	CBS[b,c]	$\Delta H^{\ddagger}$	$\Delta E^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta E^{\ddagger}$	$\Delta E^{\ddagger}$
CH_3	105.0	105.3	15.2	16.8	15.8	17.4	18.1
NH_2	107.6	107.6	9.7	11.0	9.4	10.6	11.4
OH	118.8	119.1	6.5	8.6	7.7	9.4	8.9
F	136.3	137.1	11.9	16.0	14.0	17.9	17.8
OOH	87.8	87.8	9.9	12.5	8.5	10.9	12.9
ONH_2		77.6	10.9	12.9	8.1	10.2	14.5

[a] Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36*, 255−263. [b] CBS−QB3. The CBS−APNO BDE for $H_2NO{-}H$ is 77.4 kcal/mol. [c] The MPW1K calculations used the 6-31+G(d,p) basis set, while the UCCSD(T) calculations used cc-pVTZ. See Supporting Information for computational details and references.

Although the X−H bond dissociation enthalpies (BDEs) of the element hydrides follow the expected periodic trend, the self-exchange barriers do not. The first three rows of Table 1 seem to show dependence of the barrier height on position in the periodic table, but the trend disappears when $F^{\bullet} + H{-}F$ is included.

As shown in Table 2, the existing quantitative models for HAT reactions do not reproduce these data very well, nor do they agree about the factors that determine the relative sizes of the reaction barriers. Roberts[2b] and Shaik[2e] suggest that the X−H BDE is an important factor, whereas Zavitsas states that it is not.[2c] Zavitsas[2c] ascribes a significant role to X···X triplet repulsion in the configuration X$\uparrow$H$\downarrow$X$\uparrow$, whereas Roberts[2b] and Shaik[2e] find it to be, at best, a minor contributor.

Table 2. Barriers (in kcal/mol) for the Reaction in eq 1 Calculated from the Models of Zavitsas and Chatgilialoglu (ref 2c), Roberts and Steel (ref 2b), and Shaik et al. (ref 2e)

X	Zavitsas E^{*}	Roberts E_a	Shaik $E^{\ddagger}$
CH_3	14.5	13.4	17.5
NH_2	4.3	10.6	17.9
OH	5.3	12.9	19.8
F	−0.6	15.7	22.7
OOH	∼ −10	6.5−7.5	14.6
ONH_2	∼ −5	5.1−6.1	12.9

In the present calculations, we seek to reconcile these disparate views. We do so by assembling the X−H−X transition structure (TS) in five steps.[4] First, X−H is distorted so that the ancillary atoms attached to X adopt the TS geometry.[5] Second, the bond to the transferring hydrogen is broken. Third, the acceptor $X^{\bullet}$ is distorted so that its ligands adopt the TS geometry. Fourth, the two distorted $X^{\bullet}$ are brought into their TS relationship, with triplet coupling. Finally, the H atom that was dissociated in step 2 is added back with singlet coupling to each $X^{\bullet}$ and with a geometry that completes the TS. The UCCSD(T)/cc-pVTZ potential energy changes associated with each of these steps are shown in Table 3.

Table 3. UCCSD(T) Energy Changes (kcal/mol) Associated with Assembling the X−H−X TS from X−H + $X^{\bullet}$ by (step 1) Distorting X in X−H to Its TS Geometry, (step 2) Breaking the X−H Bond, (step 3) Distorting $X^{\bullet}$ to Its TS Geometry, (step 4) Bringing the Triplet-Coupled $X^{\bullet}$ Radicals to Their TS Geometry, and (step 5) Adding the Hydrogen Atom, with Singlet Coupling to Both $X^{\bullet}$ Radicals to Form the TS

X	step 1	step 2	step 3	step 4	step 5	total
CH_3	1.29	113.36	3.38	10.62	−110.58	18.1
NH_2	0.11	112.75	0.06	10.21	−111.77	11.4
OH	0.08	122.09	0.01	3.81	−117.13	8.9
F	0.00	136.91	0.00	3.67	−122.83	17.8
OOH	2.10	90.63	1.05	5.65	−86.47	12.9
ONH_2	5.84	81.32	2.96	13.36	−89.00	14.5

The potential energy for bond dissociation of X−H (differing from the BDE by zero-point and thermal corrections) would be given by the energy changes for step 1 + step 2 − step 3. The energy for step 4 can be identified with Zavitsas' triplet repulsion.[2c] The calculations find that it is a significant factor, and that it decreases with increasing electronegativity of the heavy atom, as Zavitsas has proposed. However, the formula that Zavitsas uses for estimating triplet repulsion[2c] seems not to do a very good job; it gives values of 19.3, 12.2, 13.4, and 8.7 kcal/mol, respectively, for the C−F series, differing by 2−9 kcal/mol from the UCCSD(T)/cc-pVTZ triplet repulsion energies in Table 3.

A crucial factor, which has not been explicitly discussed in any of the three previous models, is the energy associated with step 5, that is, the symmetrical addition of a H atom to the triplet-coupled $X^{\bullet}$ fragments at their TS geometries. This quantity varies across

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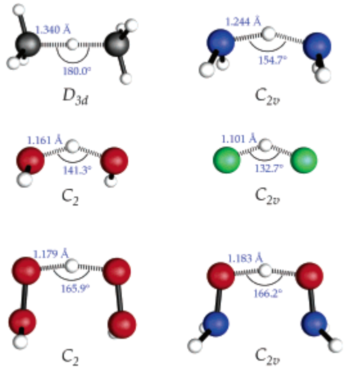

Figure 1. UCCSD(T)/cc-pVTZ optimized geometries for the degenerate HAT reactions considered in this paper.

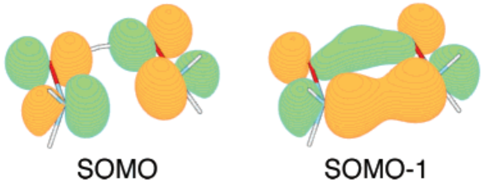

Figure 2. The singly occupied molecular orbital (SOMO) and the one next lower in energy (SOMO-1) from an ROHF/cc-pVTZ calculation on $H_2NO-H-ONH_2$ at the UCCSD(T)/cc-pVTZ optimized geometry.

the periodic table in a way that is qualitatively similar to the trend in bond dissociation energies in step 2, but, of course, with the opposite sign. Thus, the energy change for step 5 tends to cancel out much of the bond-energy dependence, and in our analysis, this is the principal reason that the overall barrier heights have a poor correlation with X−H bond energies.

The calculations reveal another feature of degenerate HAT reactions that seems to have received relatively little attention — the TS geometries change dramatically with the identity of X. As shown in Figure 1, the X−H−X angle is predicted to decrease across the series X = C, N, O, and F, but also to depend on the groups attached to X, as indicated by the very different angles for HO−H−OH and HOO−H−OOH. Furthermore, the lowest energy TSs do not seem to be the ones that would minimize steric repulsions between the X groups. This is perhaps most strikingly illustrated by the $H_2NO-H-ONH_2$ TS whose geometry would appear to maximize lone-pair repulsion between the nitrogens.[6] In line with that view is the very large repulsion between triplet-coupled $H_2NO^\bullet$ radicals held in this geometry (Table 3).

One might, therefore, ask why the system adopts such a structure. The answer to that question provides insight into the X−H−X angle variation, as well. Figure 2 shows the singly occupied molecular orbital (SOMO) and the highest doubly occupied MO (SOMO-1) from a simple ROHF calculation on $H_2NO-H-ONH_2$. The in-plane orbitals on both oxygen and nitrogen have out-of-phase interactions in the SOMO but in-phase overlaps in SOMO-1. Since the former is singly occupied but the latter doubly occupied, the overlap of erstwhile lone-pair orbitals is net stabilizing in $H_2NO-H-ONH_2$, even though it is repulsive in the triplet radical pair, in which the SOMO-1 contains only one electron. A similar effect occurs in the HOO−H−OOH TS. For the $H_2N-H-NH_2$, HO−H−OH, and F−H−F transition states, there exists an in-plane orbital on each X atom that can overlap in a qualitatively similar way. Moving to the right in the periodic table localizes SOMO-1 more on the X atoms in X−H−X because of their increasing electronegativity. The increasing localization of the SOMO-1 orbital on X enhances the benefit of direct X•••X overlap and, consequently, reduces the X−H−X angle.

When the H atom affinities of the transition states are corrected for differences in X•••X triplet repulsion (accomplished by adding the energy values for step 4 to those for step 5 in Table 3), the resulting numbers turn out to be a consistent −90 ± 3% of those in step 2 for all six of the reactions that we have studied. In other words, only about 10% of the intrinsic bond strength of the reactant can be viewed as making a contribution to the barrier height. This is a small enough number that other factors such as ligand distortion energies and triplet repulsion can outweigh it.

Although the barriers to some X−H + X self-exchange reactions exhibit an apparent dependence on X−H bond strength,[2e,h] the present calculations show that this is not a general relationship and reveal why. They also predict that, as the electronegativity of X increases, the X−H−X HAT transition structure becomes more bent. The effect is consequently particularly pronounced for the F−H−F transition state. The prediction could be tested by looking for a vibrational progression in the photoelectron spectrum of the linear bifluoride ion, $F-H-F^-$.[7]

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Supporting Information Available: Details of calculations, including Cartesian coordinates of stationary points and literature citations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(3) Experimental activation energies are known for the $H_3C^\bullet + H-CH_3$ and $HO^\bullet + H-OH$ reactions. However, comparison with experiment apparently requires large tunneling corrections. See Supporting Information for references.

(4) The procedure used here is quite similar in philosophy to that developed by Guthrie: Guthrie, J. P. *ChemPhysChem* **2003**, *4*, 809−816.

(5) There is not a uniquely defined way to do this. We distorted X−H to its TS geometry by a pure stretching of the X−H bond.

(6) There is a C_s-symmetry TS close in energy to the C_{2v} one. It has one nitrogen acting as a hydrogen bond donor to the other. MPW1K calculations place it 0.97 kcal/mol below the C_{2v} TS ($\Delta H°$), whereas CBS−QB3 puts it 1.29 kcal/mol above. The low symmetry makes geometry optimization at the UCCSD(T) level difficult. In any event, we judge the existence of this alternative TS to be irrelevant to the present discussion since it apparently depends on a hydrogen bond for its relative stability, and so would not be generally competitive.

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