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AN AB INITIO STUDY OF SUBSTITUENT EFFECTS ON 1,2-SHIFTS IN RADICALS

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Abstract. Ab initio calculations are presented which show that an electron withdrawing group (protonated formyl) facilitates 1,2-hydrogen shifts to a radical site while an ethynyl substituent promotes dissociation rather than rearrangement. The protonated formyl substituent causes this by rendering the HOMO of the transition state (TS) to be more diffuse and hence less antibonding. The sum of the Mulliken charges on the atoms in the 3-membered ring in the $C_3H_6O^{+\cdot}$ TS is shown to be intermediate between that sum for the TS for a 1,2-hydrogen-shift in the ethyl radical and that for the stable hydrogen-bridged ethyl cation, suggesting that electron withdrawal does facilitate 1,2-H-shifts at radical centers.

In 1961 Zimmerman and Zweig attributed the much greater reluctance of alkyl groups to undergo 1,2-shifts in radicals and carbanions than in carbonium ions to the occupancy of an antibonding orbital in the transition states for the first two, but not the third process. Calculations they employed predicted that a beta phenyl substituent would provide more resonance stabilization to the transition state than to the benzylic product in all three types of reactions. The basic argument was extended to hydrogen shifts in 1963 by Walling,[2] who likened the MO's of the TS to the MO's of the cyclopropenyl system, accomodating only two electrons in bonding MO's. Such 1,2-shifts do not occur in ordinary radicals at 260 K,[3] and they compete poorly with dissociation in highly energized radicals.[4]

In contrast to free radicals, reactions such as

$$CH_3CH_2C^{\cdot}HC(=OH^+)CH_3 \rightleftharpoons CH_3C^{\cdot}HCH_2(=OH^+)CH_3$$

occur readily in radical cations in the gas phase.[5,6] The greater ease of 1,2-shifts in radical cations compared to neutral radicals has been attributed to carbonium ion character in the transition state.[5] However this interpretation has been disputed by Weiske and Schwarz[7] on the grounds that the Mulliken charges are negative on the radical site carbons in $C_2H_5C^{\cdot}(CH_3)C(OH)_2^{+}$ and $CH_3C^{\cdot}HCH(CH_3)C(OH)_2^{+\cdot}$, species that nonetheless interconvert by 1,2-H-shifts. Weiske and Schwarz[7] claimed that the charge is without influence, and therefore that this 1,2-H-shift "is the first proven case for the operation of a unimolecular, uncatalyzed, 1,2-hydrogen migration to a radical centre".

We undertook a computational study of the reaction

$$CH_3C^{\cdot}HCH{=}OH^+ \ (\underline{1}) \rightleftharpoons {}^{\cdot}CH_2CH_2CH{=}OH^+ \ (\underline{2})$$

to clarify the nature of the transition state for 1,2-shifts in radical cations. Our 6-31G calculations using GAUSSIAN 86[8] (and more sophisticated treatments by others)[9] indicate that, although the TS for the 1,2-shift in the ethyl radical is bound with respect to H atom loss, it is higher in energy than the latter process. This situation persists at the 6-31G level in 1, an ethyl radical bearing a protonated formyl substituent. However, the TS energy is significantly lower in $C_3H_6O^{+\cdot}$ than in the ethyl radical, (Table 1). In the 3-butynyl radical no transition state for a 4,3-hydrogen shift was found, as the second derivative matrix showed two negative eigenvalues corresponding to the shift and to expulsion of the hydrogen atom.

Table 1. Relative Energies of Radicals and Transition States

Structure	UHF 6-31G//6-31G Relative Energy (kJ/mole)[a]	6-31g**//6-31G Relative Energy	MP3 UHF6-31G//6-31G Relative Energy
$C_2H_5{}^\cdot$	0	0	0
T.S. for 1,2 shift	250.6	233.8	225.8
$C_2H_4 + H^{\cdot}$[b]	173.4	179.7	145.3
$CH_3C^{\cdot}HCH{=}OH^+$ ($\underline{1}$)	0	0	0
$^{\cdot}CH_2CH_2CH{=}OH^+$ ($\underline{2}$)[c]	83.2	75.9	95.1
T.S. for $\underline{1}$ $\underline{2}$	199.3	188.6	182.8
$CH_2{=}CHCH{=}OH^+ + H^{\cdot}$	196.5	204.6	193.9
$CH_3C^{\cdot}HC$ CH (3)	0		
$^{\cdot}CH_2CH_2C{\equiv}CH$	71.2		
$CH_2{=}CHC{\equiv}CH + H^{\cdot}$	221.0		

a Total energy (AU): C_2H_5 -78.568729; (1) -191.576470; (3) -154.237619 b Experimental value[15] 153.1 c Experimental value[13] = 96 kJ mol^{-1} with HOCH trans

The HOMO for a 1,2-shift in the ethyl radical resembles the π^* orbital of C_2H_4, as pointed out by Harding.[9] The HOMO of the $C_3H_6O^{+\cdot}$ TS is similar, except that the π^* orbital is now distributed over all three carbons and the oxygen. Although these atoms do not lie in a plane, and all the atomic orbitals have nonzero coefficients, the HOMO in the $C_3H_6O^{+\cdot}$ TS nevertheless resembles the lowest vacant MO of protonated acrolein. The coefficient of correlation between the coefficients of these MO's is 0.93. In the cyclopropenyl analogy mutual overlap of three atomic orbitals in C_3 symmetry produces two degenerate antibonding molecular orbitals. Present studies illustrate that the nature of a substituent can control which of the two becomes the HOMO. In contrast to the preceding transition states, the HOMO of TS candidate structures in the $C_4H_5^{\cdot}$ system is centered on the migrating H atom. However $<S^2>$ given by these trial structures is typically >1.0, indicating that UHF theory deals poorly with the $C_4H_5^{\cdot}$ TS in the 6-31G basis set.

A P orbital on the shifting hydrogen is of the correct symmetry to bond to the carbons in the HOMO of the $C_2H_5^{\cdot}$ and $C_3H_6O^{+\cdot}$ transition states. The 6-31G** has such orbitals on hydrogen; use of this basis lowers the activation energy for the rearrangements substantially. At this level the $C_3H_6O^{+\cdot}$ rearrangement becomes more favorable than dissociation, in accord with experimental results.[6f,13]

Comparison of the barrier calculated for such rearrangements at different levels of computation shows that correlation effects are important in determining the transition state energy.[9,14] Third order Moller-Plesset perturbation theory confirms that the TS between 1 and 2 should lie below the dissociation limit, while the TS in the $C_2H_5^{\cdot}$ case is still higher than the dissociation products (Table 1).

The Mulliken charges for the three atoms involved in the TS for 1,2-H-shift total -0.72 in the $C_2H_5^{\cdot}$ system and -0.39 in the corresponding $C_3H_6O^{+\cdot}$ TS. In $C_2H_5^+$ the hydrogen-bridged configuration is the global energy minimum;[10,11] the sum of the Mulliken charges on the atoms in the 3-membered ring in this species is -0.33.[12] In light of the TS for $1 \rightarrow 2$ being intermediate between the radical and the ion in its charge distribution, the reduced activation energies for 1,2-shifts in cation radicals compared to neutral radicals may be considered to stem either from a less strongly antibonding HOMO or from partial carbonium ion character of the TS, contrary to some conclusions.[7] This adds to our understanding of the contrasts between the reactivities of ions and free radicals.

Methods

Calculations were run on a VAX 8250 computer, except those employing the 6-31G** basis set were done on a Cray XMP.

Optimization to stable structures were conducted with the Berny routine using the default force constants and standard cutoffs. It was found that 1 was more stable with the HOCH dihedral angle cis rather than trans; 2 and the TS between 1 and 2 were presumed to behave similarly and the values in the table all refer to the cis orientation. Optimizations were conducted for several different starting conformations for 2 and the flexible $C_4H_5^{\cdot}$ isomer and the energies in the table are believed to refer to global minima.

Additional details of the methods are available from the authors.

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