Theoretical Transition Structures for Hydride Transfer to Methyleniminium Ion from Methylamine and Dihydropyridine. On the Nonlinearity of Hydride Transfers

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We recently reported the transition structures of several simple hydride transfers from methoxide to formaldehyde.[1] We have now located the transition structures for the hydride transfers from methylamine and 1,4-dihydropyridine to the methyleniminium cation, as models for the hydride transfers involved in the NAD(P)H-NAD(P)$^+$ couple.[2,3] The basis set and correlation energy dependence of these calculations have been investigated with the simpler methylamine-methyleniminium cation reaction. In each case, a syn transition structure is favored with a bent C-H-C angle (150-160°). This may be understood on the basis of differing orbital interactions between the organic fragments in these transition structures, as described later in this paper.

Syn and anti stationary points, **1** and **2**, for hydride transfer from methylamine to methyleniminium cation were initially located with the 3-21G basis set using Pople's GAUSSIAN 82.[4] The C_{2v} and C_{2h} structures, **1** and **2**, were optimized at 3-21G, 6-31G*, 6-31+G, and MP2/6-31G* levels. As shown in Tables I and II, the geometries do not change very much (±0.01 Å, ±3°) by using different basis sets or upon including electron correlation corrections at the MP2 level. The C_{2v} structures have bent CHC angles ranging from 150° to 161°. As shown in the energetic summary in Table III, the C_{2v} structure is always lower in energy than the C_{2h} structure. This preference is 2.4-2.9 kcal/mol at the RHF level with different basis sets but is increased significantly to 5.7 kcal/mol when electron correlation energy corrections are included. Fortuitously, the MP2/6-31G* geometries are very similar to the 3-21G geometries. The negative activation energies found at the MP2 level reflect the fact that there is an ion-molecule complex, **5**, which is more stable than the reactants. Conversion of this complex to **1** or **2** still requires activation energy. In contrast to a previous report,[5] the C_{2h} structure has two imaginary harmonic vibrational frequencies; a species with lower symmetry must be the true anti transition structure.

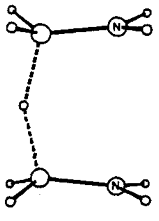
Table I. Geometries of the C_{2v} Transition Structures, **1**, at Different Computational Levels

basis set	r_{CN}, Å	r_{C-H}, Å	∠NCH, deg	∠C-H-C, deg
3-21G	1.345	1.322	109.6	154.7
6-31G*	1.335	1.335	109.7	156.8
6-31+G	1.345	1.322	109.3	160.7
MP2/6-31G*	1.349	1.325	106.8	149.6

Table II. Geometries of the C_{2h} Stationary Point, **2**, at Different Computational Levels

basis set	r_{CN}, Å	r_{C-H}, Å	∠NCH, deg	∠C-H-C, deg
3-21G	1.347	1.317	111.7	180
6-31G*	1.337	1.334	112.5	180[a]
6-31+G	1.348	1.313	111.7	180[a]
MP2/6-31G*	1.347	1.313	113.7	180

[a] C_{2h} symmetry not enforced.



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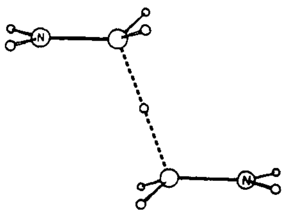

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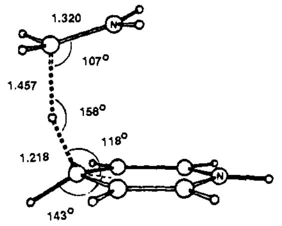

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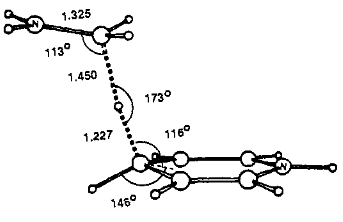

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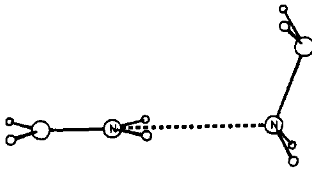

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For the dihydropyridine-methyleniminium cation reaction, the forming C-H bond was chosen as the reaction coordinate[6] and optimizations were performed assuming C_s symmetry. Structures **3** and **4** are the resulting energy maxima. Location of the transition structure with second-derivative techniques and calculations of vibrational frequencies have not been accomplished to date.

Several features are revealed by these calculations. (1) The syn structure, **3**, is 1.4 kcal/mol more stable than the anti structure, **4**. This is in contrast to semiempirical calculations for hydride transfer[7,8] but is consistent with experimental isotope effects and the stereochemistry of hydride transfer in NAD$^+$/NADH models.[3,8-10] (2) The syn structure is significantly bent, with a CHC angle of 158°, while the anti structure is more nearly linear (CHC = 172°). Distorting the syn structure to a linear one (∠CHC = 180°) costs 1.7 kcal/mol of energy. All previous calculations predict that linear hydride transfers are favored.[7,11,12] (3) In both structures, the forming CH bond is considerably longer then the breaking CH bond. (4) The pyridinyl ring is slightly boatlike.[13] The nitrogen is 2-3° out of the plane of the four adjacent carbons. Benner and co-workers proposed that a pseudoaxial hydrogen is transferred;[14] our calculations confirm this.

Why is the syn hydride transfer favored over the anti, and why does the syn prefer a bent transition structure, while the anti is nearly linear? Hydride transfer from methoxide to formaldehyde shows the same trends.[1] The orbitals of the changing bonds in the transition structures are composed of the orbitals of three components. The hydride ion has a filled n orbital, and each C=X

Table III. Negatives of the Total Energies (au) of Optimized Species on the Methylamine-Methyleniminium Cation Surface and Energies of Activation, Δ*E* (kcal/mol)[a]

basis set	CH_3NH_2	$CH_2NH_2^+$	$C_2H_9N_2^+$TS		Δ*E*(C_{2v})	Δ*E*(C_{2h})	ΔΔ*E*
			C_{2v}	C_{2h}			
3-21G	94.68166	93.86284	188.53426	188.52963	6.4	99.3	2.9
6-31G*	95.20983	94.38318	189.56930	189.56540	14.9	17.3	2.4
6-31G**//6-31G*	95.22186	94.39471	189.59363	189.58966	14.4	16.9	2.5
6-31+G	95.17594	94.34846	189.50854	189.50458	10.0	12.5	2.5
MP2/6-31G*	95.50653	94.66759	190.18616	190.17710	−7.6	−1.9	5.7

[a] Uncorrected for ZPE or thermal effects.

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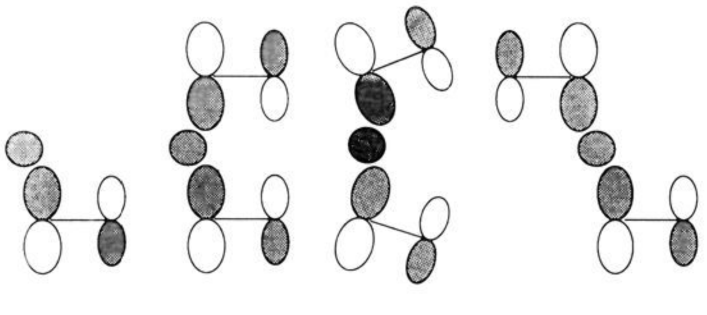
has a π orbital and a π^* orbital. As shown in **6**, the interaction of a hydride HOMO with the LUMO of one electrophilic C=X species occurs with an obtuse angle of attack, to maximize the overlap of these orbitals and to minimize interaction of the hydride HOMO with the C=X HOMO.[15] The corresponding orbital interaction in the transition structure for hydride transfer is the interaction between the hydride HOMO and the bonding combination of π^* orbitals of both C=X groups, shown in **7**. This interaction is increased by the overlap between the two π^* orbitals, which occurs principally at carbon. This overlap lowers the energy of the composite LUMO, decreases the energy difference between the hydride HOMO and the composite LUMO, and increases the interaction energy. The π^*–π^* overlap is best in the syn bent structure, **7**, while it is poor in the two linear structures, **8** and **9**. The variation of CHC angle in the anti structure, **9**, does not influence molecular orbital overlaps appreciably. Therefore, nonlinearity is not important in the anti structures, and additional stabilization by π^*–π^* interaction does not occur.



6 7 8 9

Complications may occur because the syn structure may be destabilized by charge or dipolar interactions, while the anti structure is stabilized by dipole interactions. Consequently, the general trends uncovered here for this reaction may have to be altered for other charge types.

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Multisubstitution of $Os(CO)_5$ by Ethylene: Isomeric $Os(CO)_2(C_2H_4)_3$ and a Derivative of $Os(CO)(C_2H_4)_4$[1]

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Although the synthesis and isolation of a variety of mono-, bis-, and even tris-olefin derivatives of the iron triad carbonyls have been reported,[2] progress with the simplest olefin, ethylene, has been surprisingly slow. However, recent observations by Wrighton[3] have revealed hitherto unobserved multisubstitution of CO by ethylene with iron and ruthenium carbonyl complexes. In view of this work, we wish to communicate our preliminary results on $Os(CO)_5$–ethylene photochemistry which allowed the isolation and full characterization of most members of the series of ethylene complexes $Os(CO)_{5-x}(C_2H_4)_x$, $x = 1–4$.

Photolysis of $Os(CO)_5$ and ethylene in hydrocarbon solvent gives, in a wavelength-dependent fashion, $Os(CO)_4(C_2H_4)$ (**1**) and $Os(CO)_3(C_2H_4)_2$ (**2**) in excellent and moderate yields, respectively[4] (eq 1).

$$Os(CO)_5 + C_2H_4(\text{purge}) \xrightarrow[\text{butane, }-20\ °C]{h\nu,\ \lambda > 370\text{ nm}} \underset{\mathbf{1}\ (92\%)}{Os(CO)_4(C_2H_4)}$$

$$\mathbf{1} + C_2H_4(\text{purge}) \xrightarrow[\text{pentane, }-20\ °C]{h\nu,\ \lambda > 330\text{ nm}} \underset{\mathbf{2}\ (35\%)}{Os(CO)_3(C_2H_4)_2} \qquad (1)$$

Further photolysis at low temperature, which is especially rapid and efficient in a quartz vessel, results in IR changes which are

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(1) Parts of this report were first presented at the 69th Canadian Chemical Conference, Saskatoon, Saskatchewan, Canada, June 1986: Abstr. IN-DP-16.

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(4) Full characterization of compounds **1** and **2** appears in the supplementary material. Compound **1** has been described before.[5] It is interesting to note that small amounts of $Os_2(CO_8)(\mu\text{-}\eta^1,\eta^1\text{-}C_2H_4)$[6,7] (~8%) are also formed in the first step of eq 1.

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(8) **5**, colorless moderately air stable solid: IR(pentane) ν_{CO} 1939 cm^{-1}; ^1H NMR (CD_2Cl_2, 25 °C) δ 0.88 (d, $J = 8$ Hz, PMe_3), 1.69 (d, $J = 8$ Hz, PMe_3), 0.8 (m, 2 H), 1.2 (m, 2 H), 1.3 (m, 2 H), 1.8 (m, 2 H); ^{13}C NMR (CD_2Cl_2, −20 °C) δ 183.0 (dd, $J = 7, 109$ Hz, CO), 21.6 (d, $J = 31$ Hz, PMe_3), 11.5 (d, $J = 27$ Hz, PMe_3), 10.5 (d, $J = 7.0$ Hz, CH_2CH_2), 3.8 (d, $J = 6$ Hz, CH_2CH_2); ^{31}P NMR (CD_2Cl_2, 25 °C) δ −53.2 (d, $J = 23$ Hz), −54.2 (d, $J = 23$ Hz); yield, 48%.

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