The Base Catalysed Dimerisation of 2-Methylpropenol. A MNDO SCF-MO Model Study of the Reaction Mechanism

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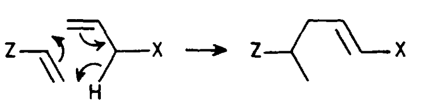
MNDO SCF-MO calculations predict the ene reaction between the alkoxide anion of propenol and ethene to occur by a stepwise mechanism in which initial hydrogen atom transfer is followed by carbon–carbon bond formation; with propenal as the enophile the reaction has a much smaller activation energy and proceeds with initial hydride transfer.

It is now well established that an O^- substituent decreases the homolytic bond dissociation energy of α C–H and C–C bonds relative to the corresponding OH group (the 'oxy-anion' effect).[1] This effect has been used to promote several types of pericyclic process, but appears never to have been applied to the Alder ene reaction (*cf.* reactions 1—3).[2] We report here a MNDO SCF-MO study of these three reactions as models for a concurrent experimental investigation of the ene reaction of 2-methylpropenol.[3]

The MNDO method[4] has previously been shown to predict simple ene reactions to be concerted processes, involving no intermediates, albeit with quite high activation energies.[5] We have found this to be true also for the ene reaction between propenol and ethene (reaction 1, Table 1) but only at the spin restricted single determinantal Hartree–Fock (RHF) level. The cyclic transition state correctly displayed only one negative root in the calculated force constant matrix, but had a very high calculated activation barrier. Since the closed shell RHF approach does not allow the possibility of biradical electronic states, we also optimised the cyclic structure at the spin unrestricted (UHF) level, a technique which is known to lead to *qualitatively* correct behaviour for bond homolysis.[6] Although only a very modest lowering of the energy was obtained (Table 1) the stationary point was now found to have *two* negative force constants and is thus *not* a genuine transition state.[7] It is noteworthy that although the two SCF methods predict quantitatively similar energies for this system, they differ in the predicted qualitative properties of the potential surface.

The second negative force constant corresponds to a distortion towards a stepwise mechanism involving either (a) initial transfer of hydrogen to form the radical pair (**1**, X = OH) or (b) C–C bond formation to give the biradical (**2**, X = OH). Genuine transition states corresponding to both these processes were located on the UHF surface (Table 1). The barrier to the formation of (**2**) is significantly lower than that for (**1**), in agreement with the accepted hypothesis that C–C bond formation preceeds C–H transfer.[2] Although the activation energies for these transition states were both lower than for the previously located cyclic structure, they still represent substantial barriers to the reaction. The transition states corresponding to reaction of (**1**) or (**2**) to give the final ene reaction products were lower in energy and do not correspond to the rate limiting steps.



X = OH, Z = H (1)
X = O^-, Z = H (2)
X = O^-, Z = CHO (3)

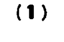
Table 1. MNDO barriers (kcal mol^{-1}) for stationary points on the potential surfaces for the ene reactions (1)—(3) (1 kcal = 4.184 kJ).

		Reaction	
	(1)	(2)	(3)
Cyclic[a]			
RHF	62.3 (1)[b]	47.2 (2)	—
UHF	59.0 (2)	43.5 (2)	—
Acyclic transition state[c]			
RHF	—	25.4 (1)	6.5 (1)
UHF	42.6 (1)	21.9 (1)	6.5 (1)
Acyclic transition state[d]			
UHF	27.6 (1)	27.1 (1)	—

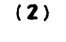
[a] Difference in energy between the stationary point and the reactants. [b] The figure in parentheses is the number of calculated negative roots in the force constant matrix. [c] Corresponding to initial C–H transfer. [d] Corresponding to initial C–C bond formation.

The corresponding alkoxide system (reaction 2) exhibited significantly different behaviour (Table 1). Cyclic stationary points were located at both the RHF and UHF levels, but the calculated force constant matrices had *two* negative eigenvalues in each case. The second such root at the UHF level corresponded to an asymmetric distortion leading to the biradicals (**1**) or (**2**) (X = O^-), whereas the corresponding eigenvector at the closed shell RHF level had a different form, distorting to give only propenal and ethyl anion or the reactants. The calculated energies were 15—16 kcal mol^{-1} lower than for reaction (1), a value typical of the 'oxy-anion' effect.[1] Genuine acyclic transition states corresponding to transfer of hydrogen were located at both the RHF and UHF levels (Table 1). The former, which corresponds to a closed shell reaction, represents hydride (H^-) transfer;[8] the latter represents hydrogen atom transfer to form the radical anion of propenal and ethyl radical (**1**, X =O^-) and exhibits an 'oxy-anion' effect of 20.9 kcal mol^{-1}, making it the lowest energy route. The alternative open shell pathway for reaction (2), involving initial C–C bond formation [*cf.* (**2**, X = O^-)] shows no oxy-anion effect, as expected from the lack of stabilisation of the radical centres in (**2**) (Table 1). Clearly solvation and other structural factors will also determine whether reaction (2) actually proceeds *via* hydrogen atom or hydride ion transfer. The calculated activation barriers, although much lower than those obtained for the cyclic structures, correspond to reactions that would only occur at relatively elevated temperatures.

No differences between the RHF and UHF computational procedures were found for reaction (3), suggesting that in this case a closed shell wavefunction adequately describes the process. No cyclic stationary point could be located, only a genuine *acyclic* transition state corresponding to hydride transfer, now with a low barrier to reaction (Figure 1). This process was predicted to occur with a hydrogen kinetic isotope



(**1**)



(**2**)

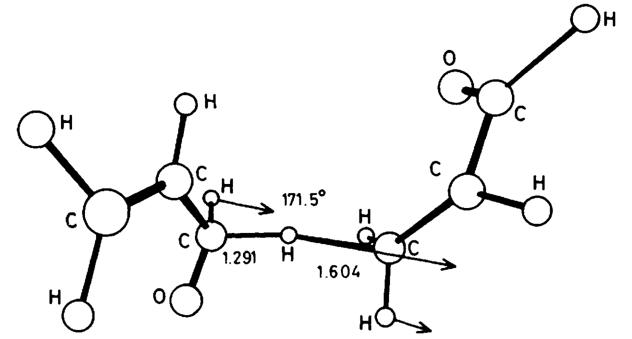


Figure 1. Calculated structure for hydride transfer in reaction (3), the arrows illustrating the form of the normal mode corresponding to the negative force constant.

effect ($k^H/k^D{}_{298}$ = 3.29, $k^H/k^D{}_{373}$ = 2.60) similar to values calculated for other hydride transfer reactions.[8] These calculations are entirely in accord with the experimental results reported in the following communication,[3] in which 2-methylpropenol was treated with potassium hydride. Thus ene reaction products corresponding only to dimerisation of this alcohol were detected, in which the key step was postulated to involve hydride transfer from the corresponding alkoxide to 2-methylpropenal as part of a cyclic redox mechanism. No intermolecular reactions with alternative enophiles such as cyclohexene could be detected, consistent with the much higher barrier we calculate for reaction (2) than for reaction (3).

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