Dihydrogen Transfer Reactions. An SCF-MO Study of the Relative Energies of the Concerted and Stepwise Pathways

Dimitris K. Agrafiotis and Henry S. Rzepa*

Department of Chemistry, Imperial College, London SW7 2AY, U.K.

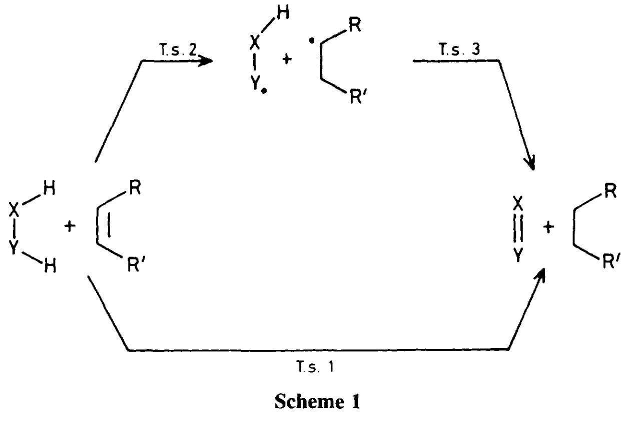
Semi-empirical SCF-MO calculations for a variety of reactions involving dihydrogen transfer to a π bond predict that the energy difference between the concerted pericyclic and the stepwise radical pair pathway is relatively insensitive to structural variation in the π bond, and indicate that the concerted route is favoured more by the AM1 than by the MNDO procedure.

The mechanistic nature of orbital symmetry allowed thermal pericyclic reactions such as the Diels–Alder[1] or the Cope[2] remains the subject of much theoretical discussion.[3] The results of a number of *ab initio* calculations on such systems indicate that a concerted, synchronous mechanism is normally preferred.[1—3] In contrast, Dewar[4] has proposed that synchronous multibond mechanisms are normally prohibited, suggesting instead that the *e.g.* Diels–Alder reactions in general proceed *via* very unsymmetrical transition states, close to biradicals in both structure and energy. Dihydrogen transfers (Scheme 1) represent another class of thermally allowed pericyclic reaction for which both concerted synchronous or stepwise radical pair mechanisms have been suggested.[5,6] Their advantage for theoretical investigation is the minimum requirement of four non-hydrogen atoms, as opposed to six for modelling Diels–Alder or Cope reactions, and the conformational simplicity of any radical pair intermediate. We report here the results of a systematic study of dihydrogen transfer reactions at the semi-empirical MNDO and AM1 levels[†] which show the effect of structural variation in both the dihydrogen donor and acceptor on the barriers to reaction, and particularly on the balance between the concerted and the two stage pathways.

The first set of entries in Table 1 correspond to π bond reductions by diimide, a reaction that is thought to be concerted (t.s. 1, Scheme 1).[5] The predicted MNDO and AM1 structures for t.s. 1 indicate that the dihydrogen transfer is essentially synchronous, but the AM1 barriers were found to be substantially lower than the corresponding MNDO values (Table 1).[7] The AM1 method gives a barrier for t.s. 1 (entry 1) in close agreement to previous *ab initio* results (26.7 kcal mol^{-1}//4–31G; 1 kcal = 4.184 kJ),[8] with the open shell path *via* t.s. 2 being virtually identical in energy in this case. In contrast, the MNDO method clearly indicates the stepwise route to be lower by 11 kcal mol^{-1} (entry 1). There is also a striking difference between the two methods regarding the disproportionation of the intermediate radical pair, whose joint energy is predicted to be either 6.3 (MNDO) or 8.2 (AM1) kcal mol^{-1} above the reactants at the UHF level.[9] Whereas hydrogen abstraction to form the products has virtually no barrier at the AM1 level (t.s. 3), it is quite significant at the MNDO level (entry 1). This discrepancy is unlikely in this case to be due to the UHF approximation as the variationally exact open shell RHF energies for the radical pair[10] are only 1.9 (MNDO) or 2.0 kcal mol^{-1} (AM1) above the UHF result. Both methods predict a significant reverse barrier (37.3/MNDO, 24.6/AM1) for disproportionation of the radical pair back to reactants.

Structural variation in the dihydrogen acceptor results in a wide range of activation energies for the concerted process (Table 1). The most highly strained systems (entries 8 and 9) reveal very low barriers, but interestingly the less stable alkene (entry 9) has the *higher* barrier! This is attributable to the π type HOMO of this alkene being twisted out of plane, in such a manner as to reduce overlap with the σ N–H type LUMO of the diimide and raising the energy of the essentially planar transition state. In this case, the transition state is the least synchronous of all the systems studied, the lengths of the two forming C–H bonds being 1.68 and 1.87 Å (AM1) or 1.60 and 1.69 Å (MNDO). Where the double bond is not twisted at all, but activated by bending (entry 10), the barrier to hydrogenation almost vanishes! Allene has a *higher* predicted barrier than ethene, and the next cumulene is higher still, in apparent contrast to the observation that allene participates more readily in electrocyclic reactions than does an isolated double bond.[11] This may be because the σ type diimide LUMO orbital can only interact with *one* of the two orthogonal π orbitals of the allene. In *e.g.* cycloaddition or electrocyclic reactions, interaction is possible between the π system of the diene and *both* the orthogonal π systems of the allene.

Gain of aromaticity as a result of loss of dihydrogen significantly decreases the barrier to reaction (entries 23, 24, 25, 26) with 9,10-dihydronaphthalene having a barrier similar to diimide,[12] and conversely loss of aromaticity increases the barrier (entry 27). Alkoxide anion substitutents also reduce barriers for α bond cleavage (the 'oxy-anion' effect[13]). Thus



Scheme 1

[†] MNDO and AM1 calculations were carried out using the AMPAC program system,[15] with all putative transition states (t.s.) characterised as such *via* calculation of the force constant matrix.[16] The concerted transition states for path 1 were located at the single determinantal RHF SCF level, whilst t.s. 2 and 3 were investigated at the spin-unrestricted UHF level.[9] This procedure has been shown to lead to qualitatively correct bond homolytic behaviour. The energies of the intermediate radical pairs were calculated *via* the UHF method, and cross-checked against a variationally exact open shell RHF method which results in pure spin states.[10] For simple radicals, the two open shell methods agreed within 2—4 kcal mol^{-1}. For delocalised radicals as cyclohexadienyl or allyl, the RHF open shell method gave combined energies for the radical pairs 10—15 kcal mol^{-1} higher than the UHF procedure.

Table 1. MNDO and AM1 activation energies (in kcal mol^{-1}) for the concerted and stepwise pathways for dihydrogen transfer reactions.

			RHF		UHF			
			1[a]		2[b]		3[c]	
Entry	Reactants		MNDO	AM1	MNDO	AM1	MNDO	AM1
1	Diimide	Ethene	54.7	32.3	43.6	32.8	12.3	0.8
2	,,	Allene	56.2	34.5	[d]48.2	39.3	13.2	1.3
					[e]41.3	31.9	15.4	4.6
3	,,	Buta-1,2,3-triene	58.8	36.6	41.5	29.7	19.5	7.7
4	,,	Cyclopropene	50.1	25.0	45.5	26.4	12.3	0.8
5	,,	Cyclobutene	54.3	27.5	40.3	28.7	13.0	0.5
6	,,	Cyclobutadiene	47.6	20.5	34.8	19.6	15.7	3.9
7	,,	*trans*-Cycloheptene	42.8	17.4	21.9	19.8	16.3	4.8
8	,,	Bicyclo[2.2.1]hept-1-ene,$\Delta^{1,2}$	32.2	7.0	[f]30.2	15.9	7.3	0.0
					[g]18.7	6.1	14.9	3.0
9	,,	Bicyclo[2.2.1]hept-1-ene,$\Delta^{1,7}$	38.9	9.0	[f]30.5	14.2	6.2	0.1
					[g]19.0	6.2	15.2	2.3
10	,,	[o]	21.5	4.6	16.9	8.8	5.9	0.5
11	,,	Ethyne	57.6	36.8	48.1	38.3	7.2	0.2
12	,,	Formaldehyde	66.7	45.5	[h]56.6	49.4	8.6	3.9
					[i]63.9	47.6	15.3	4.4
13	,,	Diazacyclopentene	77.4	64.4	54.3	44.1	20.8	15.2
14	Ethane	Ethene	81.2	52.4	49.7	39.0	24.4	7.4
15	,,	Ethyne	82.2	57.0	54.5	44.6	16.2	3.0
16	,,	Allene	82.3	53.7	[d]50.5	40.3	22.2	5.2
					[e]44.2	33.7	29.9	13.1
17	Ethanol	Ethene	78.1	52.1	44.7	35.0	26.8	10.1
18	Ethane-1,2-diol	,,	76.5	51.2	44.6	34.6	25.3	10.7
19	Ethoxy anion	,,	46.6[n]	21.5[n]	23.1	10.1	6.8	0.0
20	Ethanedioxy dianion	,,	48.0[n]	21.4[n]	9.3	10.4	84.4	61.3
21	Ethanedioxy dianion[p]	,,	66.4[n]	33.7[n]	23.0	12.7	10.2	3.2
22	Ethanedioxy dianion[q]	,,	71.6[n]	44.1[n]	33.0	22.0	17.8	6.6
23	Cyclohexa-1,3-diene	Ethene	71.0	41.0	42.5	30.4	22.4	6.2
24	,,	Allene	72.8	42.7	[d]42.6	30.9	22.4	4.1
					[e]39.7	29.5	27.5	11.0
25	2,3-Dihydronaphthalene	Ethene	68.5	38.1	41.1	27.9	22.6	6.4
26	9,10-Dihydronaphthalene	,,	62.9	32.4	38.0	25.0	19.0	3.7
27	Cyclobutene	,,	96.9	71.6	48.0	39.4	29.8	14.7
28	Hydrogen peroxide	Ethene	104.6	57.5	59.8	42.2	35.9	10.5
29	,,	Allene	104.3	60.2	[d]65.2	42.7	32.2	7.1
					[e]62.0	38.7	47.5	33.1
30	Methanol	Formaldehyde	87.2	52.5	[j]55.2	57.1	15.2	2.4
					[k]66.5	53.8	3.8	5.7
			96.1	62.7	[l]99.9	76.3	21.4	4.4
					[m]62.5	51.0	30.6	6.4

[a] Barrier for t.s. 1 relative to reactants. All energies in kcal mol^{-1}; 1 kcal = 4.184 kJ. [b] Barrier for t.s. 2. [c] Barrier for t.s. 3, relative to the intermediate radical pair. [d] *Via* vinyl radical. [e] *Via* allyl radical. [f] *Via* the tertiary bicyclic radical. [g] *Via* the secondary bicyclic radical. [h] *Via* hydroxymethyl radical. [i] *Via* methoxy radical. [j] O to O hydrogen atom migration in the first step. [k] C to C hydrogen atom migration in the first step. [l] O to C hydrogen atom migration in the first step. [m] C to O hydrogen atom migration in the first step. [n] The stationary points of these reactions displayed two large negative roots in the calculated force constant matrix. [o] Tetracyclo[4.4.0.0^{2,10}.0^{5,7}]deca-6-ene, *cf.* R. T. Seidner, N. Nakatsuka, and S. Masamune, *Can. J. Chem.*, 1970, **48**, 187. [p] Results for a unipositive hard-sphere with ionic radius 0.7 Å with position optimised with respect to the oxygen atoms. [q] Result for a dispositive hard-sphere with ionic radius 0.7 Å.

the barrier for ethane-1,2-diol (entry 18) is similar to that for ethane itself (entry 14) whereas the symmetrical synchronous pathway is reduced by either 28.5 (MNDO) or 29.8 (AM1) kcal mol^{-1} for the dianion (entry 20). However, these synchronous stationary points are no longer genuine transition states, having two negative roots in the calculated force constant matrix. The stepwise stationary points now represent the only genuine transition states. A similar effect on the concerted pathway was noted previously for oxy-anion mediated ene reactions.[13b] Two other effects are also noteworthy. Modelling counter-ions with point charges attenuates the 'oxy-anion' effect, as expected (entries 21 and 22). Less predictable is that the effect due to a second alkoxide substituent (entries 18 and 20) is much less than that due to the first (entries 17 and 19).

Several reactions are known to be initiated by the formation of a radical pair, followed by a radical chain mechanism.[6] Thus the reaction of ethane itself has recently been demonstrated to involve radical intermediates.[6] Both MNDO and AM1 indicate a clear preference for this route. We note also that the disproportionation of ethyl radical is calculated to have a very large barrier by MNDO (entry 14), and a much smaller, although not insignificant value by AM1. Experimentally, this barrier is thought to be very small.[14] Several other entries (nos. 2, 13, 16, 23, 24, 25, 26, 29) also exhibit significant barriers to the radical disproportionation at both the MNDO and AM1 level. In these cases, the intermediate radicals are highly delocalised and we noted that the UHF energies were some 10—15 kcal mol^{-1} lower than the RHF values.[10] Here, the UHF method itself may be responsible for at least part of the calculated barrier,[9] and the energies of t.s. 2 and 3 may represent a *lower* limit to the energy of the open shell route. The thermal uncatalysed reduction of aldehydes by alcohols is also thought to proceed with the involvement of radicals.[6b] For methanol–formaldehyde (entry 30) MNDO indicates a clear preference for the open shell route, whereas AM1 predicts a finely balanced mechanism.

We conclude that semi-empirical methods such as MNDO may have an intrinsic preference for a stepwise mechanism for pericyclic reactions compared with more recent parametrisations such as AM1, and that dihydrogen transfer reactions may provide one means of calibrating semi-empirical against *ab initio* calculations of pericyclic mechanisms.

We thank the University of London for a generous grant of time on the FPS-164 system at Imperial College.

Received, 25th February 1987; Com. 251

References

1 F. Bernardi, A. Bottoni, M. A. Robb, M. J. Field, I. H. Hillier, and M. F. Guest, *J. Chem. Soc., Chem. Commun.*, 1985, 1051 and references therein.

2 D. Feller, E. R. Davidson, and W. T. Borden, *J. Am. Chem. Soc.*, 1984, **106**, 3362. For a recent experimental study on this problem, see J. J. Gajewski and J. L. Jimenez, *ibid.*, 1986, **108**, 468.

3 For two recent summaries, see (a) F. Bernardi, M. Olivucci, J. J. W. McDouall, and M. A. Robb, *J. Am. Chem. Soc.*, 1987, **109**, 544; (b) M. J. S. Dewar, S. Olivella, and J. J. P. Stewart, *ibid.*, 1986, **108**, 5771.

4 M. J. S. Dewar, *J. Am. Chem. Soc.*, 1984, **106**, 209.

5 E. E. van Tamelen, R. S. Dewey, M. F. Lease, and W. H. Pirkle, *J. Am. Chem. Soc.*, 1961, **83**, 4302; S. K. Vidyarthi, C. Willis, R. A. Back, and R. M. McKitrick, *ibid.*, 1974, **96**, 7647.

6 D. Malwitz and J. O. Metzger, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 762; J. Metzger, *ibid.*, 1983, **22**, 889; 1986, **25**, 80.

7 This may be due to the superior treatment of the core–core repulsion terms in AM1 for internuclear distances in the region 1.5—2.5 Å typical of values found in transition states. A similar explanation has been noted previously for hydrogen transfer from oxygen; M. L. McKee, P. B. Shevlin, and H. S. Rzepa, *J. Am. Chem. Soc.*, 1986, **108**, 5793.

8 D. J. Pasto and D. M. Chipman, *J. Am. Chem. Soc.*, 1979, **101**, 2290.

9 M. J. S. Dewar, S. Olivella, and H. S. Rzepa, *Chem. Phys. Lett.*, 1977, **47**, 80.

10 M. J. S. Dewar and S. Olivella, *J. Chem. Soc., Faraday Trans.*, 1979, **75**, 829.

11 J. S. Burnier and W. L. Jorgensen, *J. Org. Chem.*, 1984, **49**, 3001.

12 W. V. E. Doering and J. W. Rosenthal, *J. Am. Chem. Soc.*, 1967, **89**, 4534.

13 M. L. Steigerwald, W. A. Goddard, and D. A. Evans, *J. Am. Chem. Soc.*, 1979, **101**, 1994. For MNDO calculations on this subject, see I. G. El Karim and H. S. Rzepa, *J. Chem. Soc., Chem. Commun.*, 1987, 193.

14 R. W. Fessenden, *J. Phys. Chem.*, 1964, **68**, 1508.

15 M. D. S. Dewar and J. J. P. Stewart, *Quantum Chemistry Program Exchange*, Bloomington, Indiana, Program No. 506.

16 *Cf.* J. N. Murrell and K. J. Laidler, *Trans. Faraday Soc.*, 1968, **64**, 1431; M. J. S. Dewar, G. P. Ford, M. L. McKee, H. S. Rzepa, W. Thiel, and Y. Yamaguchi, *J. Mol. Struct.*, 1978, **43**, 135.