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AB Initio Study Of Bond Breaking In Olefins. GVB Computations On Propene ⇔ Methyl + Vinyl And Propene ⇔ H+Propen-2-Yl

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ABSTRACT

The Generalized-Valence-Bond-Perfect-Pairing (GVB-PP) method is used to investigate the structural behaviour, energy, and dipole moment along the reaction coordinates for (1) propene→methyl + vinyl and for(2) propene→H + propen-2-yl. Geometry optimisations are carried out at the GVB(9)/STO-3G level (complete valence shell) for the minimum energy propene structure and for numerous structures up to r(C2-C3) and r(H3-C2) = 10A°(only the elongated C2-C3 and C3-H2 distances are kept fixed, respectively). Both dissociation curves are smooth, without a maximum, and yield predicted dissociation energies for reaction(1) and (2) of 499.1 and 543.6 kJ.mol^{-1}, respectively. (The latter value is about 10 kJ.mol^{-1} lower than those predicted for the primary α(C-H) bond ruptures in propene, using the same method and basis set) GVB(7)/6-31G//GVB(9)/STO-3G computations lower the predicted dissociation energies for reactions(1) and (2) to 392.6 kJ.mol^{-1} and 435.7 kJ.mol^{-1}, respectively. CCSD/cc-pVDZ calculations yield intermediate dissociation energies of 427.6 and 460.5 kJ.mol^{-1} for reactions(1) and (2), respectively. Linear behaviour is observed at long bond distances when the reduced energy concept, $E_R = (E_r - E8)/D_e$, is applied to the reaction coordinates.

KEYWORDS

AB initio;
GVB;
Propene;
Propen-2yl;
Methyl;
Vinyl.

INTRODUCTION

Propene (I) is a very important intermediate in many chemical and industrial process[1]. It is probably formed by corona discharges in Titan's troposphere [2-4] where it can be photolysed[3] and radiolysed[4].

Figure 1 depicts the unimolecular processes involving cleavage of one formal single bond in I. In this paper the coordinates for the reactions

$I \Leftrightarrow CH_3$ + vinyl (II) (1)
$I \Leftrightarrow H$ + propen-2-yl (III) (2)

are investigated using the Generalized-Valence-Bond-Perfect-Pairing(GVB-PP)[5] method.

In previous work we have used the GVB-PP method to follow the reaction coordinates for C-H bond breaking in ethylene[6] and for the rupture of the primary α (C-H) bonds in I[7] to yield trans-or cis-propen-1-yl (IV or V)[7], which are predicted to proceed with no activation energy.

The mechanisms of the thermal[8-15] and photochemical reactions[16-23, 28-35] of are not fully elucidated. Important reasons for this are (i) the large number of products, even at low pyrolysis temperatures[15], and(ii) the reactivity of the initial photochemical products, especially at high photon energies[16-17].

Thermal reactions

At low temperatures and moderate to high pressures, the major initiation step in the pyrolysis of I is the bimolecular disproportionation reaction yielding isopropyl and allyl (VI) radicals[13].

$2\,I \rightarrow$ isopropyl + VI (3)

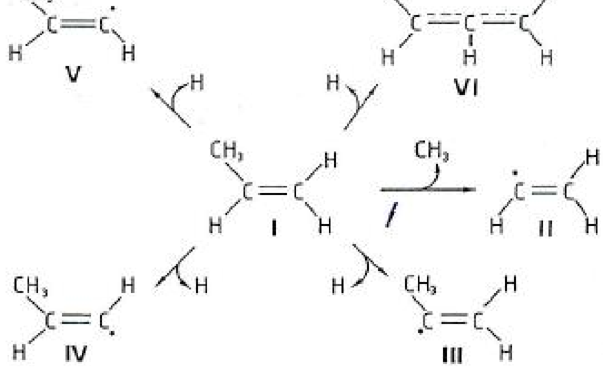

Figure 1 : Unimolecular dissociation processes in propene (I) involving the rupture of only one formal single bond.

However, Hidaka et al.[8] found that including the unimolecular reactions(1) and(4)-(6)

$I \rightarrow H + VI$ (4)
$I \rightarrow CH_4 + C_2H_2$ (5)
$I \rightarrow H_2 + C_3H_4$ (6)

In the mechanism were necessary to explain the pyrolysis results at low concentrations of I and high temperatures. The relative importance of the unimolecular cleavage of the α(C-H) bonds of I in its thermal reactions has not yet been determined experimentally.

Nevertheless, Hidaka et al.[8] proposed the participation of propen-1-yl radicals of undefined geometry (cis or trans) in the shock tube pyrolysis of I.

Photochemistry

Triplet photosensitization

The triplet sensitised photochemistries of I and ethylene are predicted to occur through their hot ground states, after intersystem crossing: the activation energies required for the bond cleavage reactions to occur from the triplet state are too high [18,19]. The cleavage of any of the three vinylic α (C-H) bonds in I requires more energy than the processes(1) and (4), so the latter reactions are more important in the triplet mercury (Hg $6(^3P_1)$; 4.9 eV) photosensitization at low pressures where collisional deactivation plays a minor role[20-23]. Avrahami and Kebarle[22] were the first to show that isomerisation of I to cyclopropane occurs in the Hg $6(^3P_1)$ photo sensitization, presumably via the trimethylene biradical formed by a 1,2 H-atom migration, followed by ring closure and collisional deactivation. Product analysis led them to conclude that the processes (1), (4), and cyclopropane formation occur in the ratio 11:89:0.2 at a total pressure of ca. 10 Torr. Placzek and rabinovitch[23] observed that the cyclopropane yield increased to a maximum of about 1.4 % at 70 Torr pressure, the precursor(s) being deactivated by collisional quenching. This is an important example of photon energy being transformed into potential chemical energy.

Note that the formation of the trimethylene biradical requires a 1,2 H-atom shift and that if it were followed by a second 1,2 H-atom shift in the biradical to yield I, H-atom scrambling in the "unreacted" parent compound should be observed. Thus starting with the 1,3,3,3-I-d_4 isotopomer, one expects the formation of the 2,3,3,3-, 1,1,3,3-, 1,1,2,3-, and 1,2,3,3-I-d_4 isotopomers. However, Hirokami and Sato[21] reported that the ratio of the cis- to trans-1,3,3,3-I-d_4 isomers after prolonged photosensitization with Hg 6($^3P_1$), Cd ($^3P_1$), or benzene was unity. No other isotopomers were reported.

Furthermore they searched specially for 2,3,3,3-I-d_4 and found no evidence for its formation. This is even more remarkable when one considers the facile H-atom scrambling observed in the triplet photosensitizations of ethylene-d_2 by mercury[24, 25], cadmium[26], and organic compounds[27]. Similarly, Sakurai et al.[28] carried out a systematic study of the Hg 6($^3P_1$) photosensitization of cis-I-1-d_1 and found that the yield of I-2-d_1 falls to zero for pressures$\geq$29 Torr. The presence of small amounts of I-3-d_1 was explained by the recombination of H-atoms with the allyl radical.

These results underline the remarkable effect of the CH_3 moiety on the processes following energy transfer to I. Note also that trans-cyclopropane-d_2 isomerises to I-d_2[29]. A possible explanation, put forward by Bernardi et al.[30] is that "It is conceivable that the structural isomerisation proceeds by a path not involving trimethylene, and hence may not be pertinent to the 1,2-shift transition state". Clearly more experimental work is needed on this problem.

Direct photolysis

The direct photolysis of I has been studied at $\lambda = 123.6$nm (i.e. at 10. eV, thus above the ionisation energy, 9.73 eV[31])[16,32,33], $\lambda = 147.0$nm[16,32,34], $\lambda = 163.3$nm[17], and $\lambda = 184.9$nm[35,36]. In contrast to the triplet photosensitization(at lower energies) there is evidence for the direct formation of molecular hydrogen and methane at all wave lengths used in the ptotolyses[19]. Nevertheless there is an important difference in the two primary processes: whereas the relative primary yield of molecular hydrogen remains approximately constant with increasing photon energy, that of primary methane formation increases from about 0.02 at $\lambda = 184.9$nm to$\geq$0.34 at both $\lambda = 147.0$ nm and $\lambda = 123.6$ nm where it is estimated to exceed that of methyl radical formation (see TABLE 2 in Ref.19).

In the photolyses at $\lambda = 184.9$nm, processes (1) and (4) are reported to be the most important, occurring in the ratio 0.57:1.0[35]. The cleavage of an α(C-H) bond requires more energy than cleavage of the β (C-H) or α(C-H) bonds, thus it is not surprising that the relative primary yields of the latter reactions are much lower. Their yields are difficult to assess, depending on final product analysis. Thus determination of their yields can be influenced negatively by secondary photolysis of products and/or by structural rearrangement of the radicals before, or during, recombination and deactivation[19, 36]. This may be the reason that, although rupture of the central α(C-H) bond might be statistically expected to be 1:2 compared to that of the terminal α(C-H) bonds, product analysis predicts the ratio to be much higher, 4:1[36].

To our knowledge, the importance of the 1,3-H atom shift corresponding to the reaction $\Leftrightarrow$ no-reaction sequence $H\text{-}CH_2CH{=}CH_2 \Leftrightarrow CH_2{=}CHCH_2\text{-}H$(the products of which would be indistinguishable from those from two consecutive 1,2-H atom shifts in the same direction) has not been determined experimentally[21,28]. However, ab initio computations on the relative energy of the transition state (barrier) for this isomerisation indicate that it may be in competition with process(4) in the vibrationally excited ground state [37,38].

In our previous work it was shown that relatively inexpensive GVB computations could yield reasonable potential energy curves and total dissociation energies that are within 20 % of the best experimental values [6]. The data obtained can be used for theoretical modelling of the photochemical and thermal reactions of I.

Method

The GVB-PP computations were performed with the Monstergauss ab initio program package (MG) [39] using the standard STO-3G[40] and 6-31G[41] basis sets. The optimally conditioned(OC) variable-metric gradient minimization technique [42] was used for the MG geometry optimisations. The molecular orbitals generated by a complete SCF(single configuration) geometry optimisation of I were used to identify the valence-virtual orbital pairs for use in the GVB-PP computations. The computations designated by GVB(N) indicate that N correlated valence-virtual

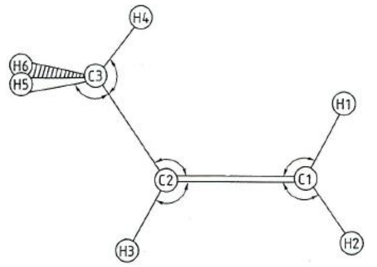

Figure 2 : The atom numbering is used throughout the text.

pairs were used. Thus GVB(9)/STO-3G (referred to as GVB9 in the remainder of the text) included all nine valence orbitals in the correlated valence-virtual pairs. Complete geometry optimisation of I shows that the minimum energy structure has C_s symmetry. Along the reaction coordinates only the C2-C3 or H3-C2 internuclear distances, correspon ding to the bond being broken, where kept rigorously fixed (figures 2-6).

The consistency of the GVB9 optimisations on I at long H3-C2 and C3-C2 internuclear distances (and thus at intermediate distances) was checked by carrying out ROHF-GVB(x)/STO-3G optimisations of CH_3 (x=2), II, (x=5), and III (x=8). The results are referred to as GVB2,GVB5 and GVB8 in the remainder of the text.

Single computations, with the extended 6-31G basis set and including seven correlated pairs were performed at the STO-3G optimised geometries for steps (1) and (2) (Figures 4 and 6). These GVB(7)/6-31G//GVB(9)/STO-3G computations are designated by GVB7 throughout the remainder of the text. The number of correlated pairs had be reduced because of memory limitations in the program.

The dissociation energies for steps(1)and(2) were also determined from CCSD(coupled-cluster with single and double substitutions[43]) calculations with Dunning's cc-pVDZ(correlation-consistent polarised valence double-zeta) basis set[44,45]) using the Gaussian 03 program package (G03)[46]. The results will be referred to as CCSD in the remainder of the

TABLE 1 : Experimental geometry of propene (I) and optimised geometries of I, the vinyl radical (II), the propen-2-yl radical (III), and for structures with r(C2-C3) or r(H3-C2) = 1.8, 3.0, and 10.0 A°, respectively. The dipole moments (μ(D)) and energy differences (ΔE(kJ/mol), see footnote are also given.

Paramater	Expt. [47]	CCSD	GVB9	I ⇔ CH_3 + II			I ⇔ H + III			II	III
					GVB9			GVB9			
R(C1 = C2)	1.336 ± 0.004	0.3468	1.3484	1.3455	1.3378	1.3373	1.3439	1.3383	1.3381	1.3184	1.3303
r(C2-C3)	1.501±0.004	1.5103	1.5427	1.8	3.0	10.0	1.5363	1.5305	1.5303	–	1.4898
r(H1-C1)	1.091 ±0.003	1.0980	1.1001	1.0998	1.1001	1.1002	1.1003	1.1002	1.1001	1.0981	1.1047
r(H2-C1)	1.081 ±0.003	1.0962	1.0999	1.1003	1.1005	1.1005	1.0989	1.0996	1.0996	1.1035	1.0972
r(H3-C2)	1.090 ±0.003	1.1004	1.1032	1.1024	1.1000	1.0996	1.8	3.0	10.0	1.0947	–
r(H4-C3)	1.085 ± 0.004	1.1042	1.1064	1.1056	1.1006	1.0999	1.1073	1.1073	1.1074	–	1.1099
r(H(5,6)-C3)	1.088 ± 0.014	1.1063	1.0956	1.0939	1.0889	1.0883	1.0955	1.0958	1.0959	–	1.1046
∠C1=C2C3	124.3 ± 0.3	124.7	124.4	122.4	119.1	119.2	129.4	133.1	133.3	–	137.5
∠H1C1=C2	120.5 ± 0.3	121.4	122.0	122.2	121.8	121.7	121.3	122.2	122.2	121.3	121.0
∠H2C1=C2	121.5 ± 0.3	121.5	121.8	121.7	122.1	122.2	122.4	121.7	121.7	121.9	122.1
∠H3C2=C1	119.0 ± 0.3	118.9	119.9	123.2	130.7	131.2	117.5	116.5	116.5	135.8	–
∠H4C3C2	111.2 ± 0.3	111.2	110.8	108.4	101.8	101.1	110.2	110.4	110.5	–	110.3
∠H(5,6) C3C2	109.2[a]	110.9	110.6	108.5	101.7	100.9	110.8	110.8	110.8	–	111.0
H(5,6) C3C2C1	± 120.5[a]	± 120.6	± 120.5	–	–	–	±120.2	±120.3	±120.3	–	± 20.0
μ(D)	0.364 ± 0.0003[57]	0.368	0.168	0.166	0.132	0.137	0.425	0.448	0.442	0.588	0.748
ΔE (kJ/mol)	–	–	0.0	313.8[b]	480.6[b]	499.1[b]	330.2[b]	538.8[b]	543.6[b]	427.6[b]	460.5[b]

Calculated using the data in Ref. [47].
The difference between the energy of I at its equilibrium geometry (E_{eq}) and the energy at the elongated internuclear distance.
The difference between E_{eq} and the sum of the energies for fragment.

text. The CCSD optimised geometries of II and III are given in TABLE 1.

RESULTS AND DISCUSSION

I⇔CH_3 + II.

The experimental r_s (substitution) structure of I, determined from the microwave spectra of seven isotopomers[47], is given in TABLE 1 for comparison with the GVB9 optimised geometrical parameters obtained for the minimum energy structure of I and at fixed values of r(C2-C3) = 1.8, 3.0 and 10.0 A°. Note that, as expected, the GVB9 optimised bond lengths of the minimum energy structure are all longer than those obtained from a complete HF/STO-3G geometry optimisation of I[7]. The geometry of the CH_3 moiety, the length of the formal double C1 = C2 bond, the H3-C2 = C1 and the C1 = C2-C3 bond angles undergo the largest variations as C3 is drawn away from the minimum energy position (r(C2-C3) = 1.5427 A°). The optimised C-H bonds in the methyl moiety are unequal, corresponding to a C_s symmetry as has been observed experimentally for I[48,49]. However the methyl moiety maintains C_s symmetry even at r(C2-C3) = 10.0 A°. This is an artefact of the calculations and has little effect on the dissociating energy(< 0.2 kJ mol^{-1}).

There are only minor differences between the corresponding geometrical parameters obtained by the GVB9 optimisation of I at r(C2-C3) = 10.0A° for and the GVB2(CH_3) and GVB5(II) optimisations. Nevertheless, unlike the results for the removal of primary H-atom from ethylene[6] or from I[7], the sum of the energies of the two radical is about 2 kJ.mol^{-1} (0.4 %) higher than that of the "molecule" at long r(C2-C3). This is probably a problem arising because the minimal basis set has only seven MO's for the methyl radical.

Curves depicting the variation of the optimised geometrical parameters as a function of r(C2-C3) are shown in figure 3. As r(C2-C3) is increased up to about 2.7A°, the apparent C1 = C2-C3 angle decreases smoothly. Then the value of the angle becomes erratic up to r(C2-C3)≅3.5A°, after which its value remains equal to that given as input for optimisation. The minimum energy motion of the CH_3 moiety is predicted to be such that C3 and H4 remain in the plane defined by II. The C2 = C1 bond is predicted to be approximately 0.01 A° shorter in II than in I. A similar decrease was predicted for the formal double bond on going from ethylene to II[6,49] and on going from I to IV or V[7].

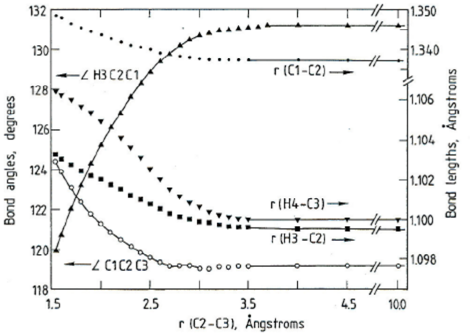

Figure 3. The GVB9 optimised values of r(C1–C2)(•), r(H4–C3)(▾), r(H3–C2) (■), ∠H3C2C1(▴)and∠ C1C2C3(°) as a function of the C2–C3 internuclear distance in I. For r(C2–C3)≥3.2 A° , ∠C1C2C3 remains essentially equal to the input value

The upper curve in figure 4 shows the relative GVB9 energy as a function of r(C2-C3). The curve rises smoothly to a plateau corresponding to a predicted dissociation energy(D_e) of 499.1 kJ mol^{-1}. This is ≈55kJ mol^{-1} less than that predicted for the removal of a primary H atom (from C1) in I, at the same theoretical level[7].These data also predicted that there is no activation energy for recombination of CH_3 with II.

I⇔H + III

The GVB9 geometry optimisation results at fixed values of r(H3-C2) = 1.8, 3.0, and 10.0A° are presented in TABLE 1. The two CC bond lengths and especially the C1 = C2-C3 bond angle undergo the largest variations as the H3-C2 bond is elongated from its optimized equilibrium position(r(H3-C2) =

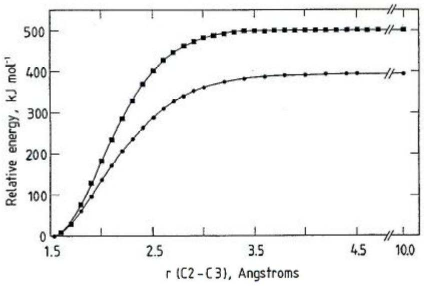

Figure 4: The GVB9 (■) and GVB7 relative energies (•) as a function of the C2-C3 internuclear distance in I.

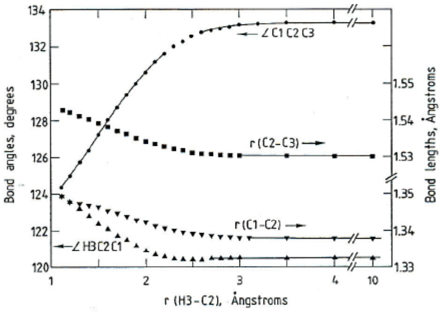

Figure 5 : The GVB9 optimised values of r(C1-C2) (▼), r(C2-C3) (■),∠C1C2C3 (•) and H3C2C1 (▲) as a function of the H3-C2 internuclear distance in I. For r(H3-C2) greater than 2.8 A°, ∠ H3C2C1 remains essentially equal to the input value.

1.1032 A°, TABLE 1; figure 5). The other geometric parameters remain almost constant. Note that as r(H3-C2) is increased, H3 is predicted to remain in the C1=C2-C3 plane and to move in to the space above the formal double bond. This is probably a common feature for C-H bond cleavage in olefins: similar behaviour was observed for the H-atom leaving ethylene[6] and for the primary H atoms breaking away from I[7]. The increase in the C1=C2-C3 bond angle from 124.4 to 133.3° corresponds to the CH_3 group moving towards the space which will be occupied by the unpaired electron in the radical. Similar behaviour is observed for H atom remaining on the radical centre in II, IV and V.

The consistency of the GVB9 results at long H3-C2 internuclear distances was tested by carrying out an ROHF-GVB(8)/STO-3G geometry optimisation of III. Only minor differences are observed between the corresponding geometrical parameters of III and elongated structure of I. The sum of the STO-3G energy of an isolated H-atom and the ROHF-GVB(8)/STO-3G energy of III. is equal to the GVB9 energy of I at r(H3-C2) = 10 A°. Also the computed dipole moments for the radical and the complex are the same.

The predicted GVB9 value of D_e(C2-H3) for I was expected to be near, but slightly lower, than D_e(C1-H1) (555.8 kJ mol^{-1}[7])D_e(C1-H2)(554.8 kJ mol^{-1}[7]) and also for dissociation of ethylene to H + II (549.3 kJ mol^{-1}[6]) obtained at the same theoretical level. Indeed, as the H3-C2 bond is elongated, the energy of the complex, relative to that for I, rises smoothly to a plateau at 543.6 kJ mol^{-1} (Figure 6). Thus there is no predicted activation energy for the reverse step, capture of an H-atom by III. This appears to be a general feature for the GVB-PP potential energy curves for these reactions, even if the correlated pairs include only the most important part of the valence shell[6].

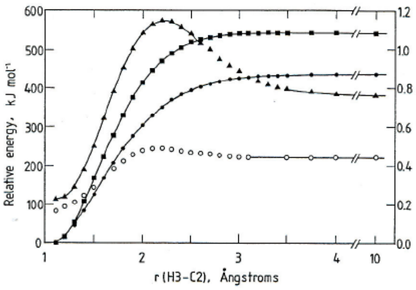

Figure 6 : The GVB9 relative energies (■) and dipole moments (°) and the GVB7 relative energies (•) and dipole moments (▲) as a function of the H3C2 internuclear distance in I.

Although the scatter in the experimental data for the C-H dissociation in ethylene is important, as exemplified by the literature values of D_0(CH2CH-H)=459.0±3.3kJ mol^{-1}[50] and 488.3±5.0kJmol^{-1}[50] kJ mol^{-1}[51], it is obvious that the D_e predicted above are too high. Using various GVB and CI methods, Wu and Carter [49] obtained theoretical D_e(CH_2CH-H) ranging from 436.0 to 490.3 kJ mol^{-1}, thus covering the range of experimental of values. They used much higher levels of theory than the GVB ones used in this work and computing enough points along the reaction coordinate would be expensive in computational time. It is suggested that as a first approximation the GVB9 curves for I could be simply by a factor of 460/555=0.83 to obtain realistic reaction coordinates. Alternatively, considering that the highest value obtained by Wu and Carter[49] was obtained at the highest level of theory, a scaling factor of 490/555=0.88 may be more appropriate.

GVB7 calculations

The GVB7 relative energies versus r(C2-C3) and r(H3-C2) are represented in figures 4 and 6 for comparison with the GVB9 results. Whereas the form of the curves for the relative energies are similar to those from the GVB9 optimisations, the predicted D_e are lowered about 100 kJ mol^{-1} to 392.6 and 435.7 kJ mol^{-1} for steps(1)and(2), respectively. A similar lowering of the predicted D_e(C1-H1) and D_e(C1-H2) was observed on going from the GVB9 to the GVB7 theoretical levels[7].

Reduced energy curves for I

Computed potential energy curves obtained using various molecular orbital generating methodologies and different basis sets can be compared by using a reduced energy (E_R) expression, $E_R=1-E(r)/D_e$, where E(r) is the computed relative energy at the interatomic distance r, D_e is the total computed dissociation energy, and E(r) = 0 at r_e, the equilibrium bond distance[7,52]. Plots of the reduced energy E_R and ln E_R versus r(C2-C3) and r(H3-C2) for the series of GVB9 optimisations and GVB7 computations on I are shown in figure 7. As the internuclear distance in increased, the plot of ln E_R versus r becomes linear. This also occurs when one employs the Morse equation, $E_R = 2\exp(-B(r - r_e)) - \exp(-2B(r - r_e))$. The slope, d(ln E_R)/dr, approaches the value of–B at long distances. Note that $B = (k/2D_e)^{1/2}$, where k is the force constant. The resulting linearity can be used as a criterion of whether the computational results are valid. It should be noted that various molecular dynamic modelling schemes have assumed exponential linearities in the long bond distance region (e.g. see refs.[53,54]). Such linearity is expected for simple two electron bond ruptures because various integral forms that are involved in calculating the interaction energies at longer distances contain exponential terms[55]. Linearity of the ln E_R versus r(C-H) plots was observed for C-H bond cleavage in methane[52], in ethylene[6], and for the primary C1-H1 and C1-H2 bonds in I[7]. Nevertheless, in both the large MCSCF treated OO rupture in HOOH and the H-O rupture in the HOO radical, non-linear ln E_R behaviour was observed in the region where one finds linearity in other systems[6, 52].

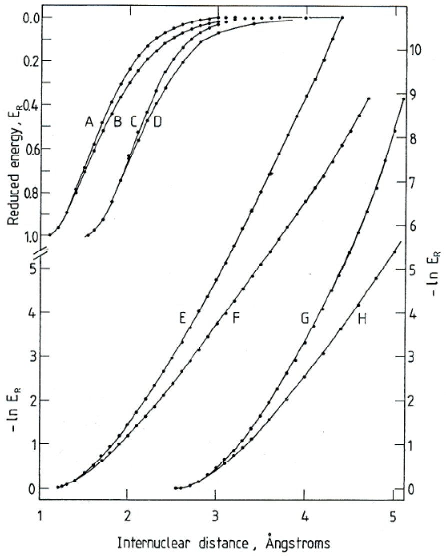

Figure 7 : Plots of E_R (upper curves) and of -lnE_R (lower curves) as a fuction of the internuclear distances along the reaction coordinates for I ⇔ H + III (A,B,E,F) and I H + II (C,D,G,H). Curves A, C, E, G: GVB9; Curves B,D,F,H: GVB7. Plots G and H have been displaced by 1 ? to the right.

The slopes d(ln E_R)/dr(C2-C3) (which are related to the effective Morse constant B discussed above), are -3.63 and -2.57A°$^{-1}$ at r = 3A° for the GVB9 and GVB7 curves, respectively. At r(H3-C2) = 3 A°, the values of d(ln E_R)/dr are -3.73 and-2.76 A°$^{-1}$ for the GVB9 and GVB7 curves, respectively. Although these values are all larger than normal Morse B constants (1.8-1.9 A°$^{-1}$)[53], they are in the same range as those found for other STO-3G calculations[6,7,52].

CCSD/cc-pVDZ results

The CCSD calculations yield D_e = 427.6 and 460.5 kJ mol^{-1}, for steps (1) and (2), respectively. These D_e lie between those obtained from the GVB9 and GVB7 calculations. Using the same method and basis set Wilson et al.[56] obtained dissociation energies for N_2 and HF that are lower than experiment. Increasing the basis set size increased the predicted dissociation energies for both molecules. This could indicate that the dissociation energies for steps (1) and (2) are somewhat higher than the present CCSD results.

Dipole moments

In Ref.[6] it was concluded that, for GVB and MCSF computations on C-H bond cleavage(or the reverse reaction), the dipole moment behaviour could be used as a criterion to predict whether the computations are valid and also to predict the distance at which effective interaction between dissimilar(or polar) species begins or ends[6]. The same conclusion can be made from the present results for r(H3-C2)(Figure 5).

With increasing r(H3–C2) the computed GVB(9) and GVB(7) dipole moments both rise a maximum at r(H3-C2)≅2.2 A° before falling to constant values for r(H3-C2)≤3.5A°, of 0.44 and 0.76 D, respectively

(Figure 5). The computed GVB(9) dipole moments for the equilibrium structure of I is 0.168D compared to an experimental value of 0.366 D[57]. If one can simply adjust the computed value to the experimental one, the dipole moment of III should be$\cong$0.96 D, higher than the predicted values of 0.53 and 0.81 D for IV and V, respectively[7]. Using the same reasoning for the GVB(7) values, one obtains 1.65, 1.09, and 1.41 D for III, IV, and V, respectively. These values are considerably higher than those predicted from the GVB9 results and the true values probably lie between them.

CONCLUSIONS

One of the main results of the present work is that the behaviour of the potential energy surfaces for the secondary H3-C2 and C2-C3 bond ruptures in I are similar to those for the hydrogen bond ruptures in ethylene, methane, water, HF and primary α(C-H) bond ruptures in I. The behaviour of the E_R curves is very similar to that found for ethylene, where it was found to be independent of geometry optimisation. This behaviour will allow for a simple modelling of the dynamics of animalcular decomposition via primary α(C-H) and α(C-C) bond dissociation in olefins. These channels are identical to those for H-atom or radical capture by the corresponding radicals.

Cleavage of the secondary α(C-H) bond in I is predicted to require about 2 to 3 % less energy than cleavage of the primary α(C-H) bonds. Also, as expected, reaction (1) is predicted to require about 11% less energy than cleavage of the primary α(C-H) bonds.

Although the energy is still increasing, the remaining structural parameters become essentially independent of the r(C-H) distance between 2.75 and 3.0A°. It is interesting to note that, as in the case of ethylene, the departing H-atom is predicted to move towards the space above the formal C-C double bond, probably reflecting the attraction of the π-electrons.

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