On the usefulness of quantum chemical bond order as a local reaction path indicator: The case study of a model carbonyl addition reaction[†]

D. K. Maity, D. Majumdar* and S. P. Bhattacharyya*

Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India
*Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India

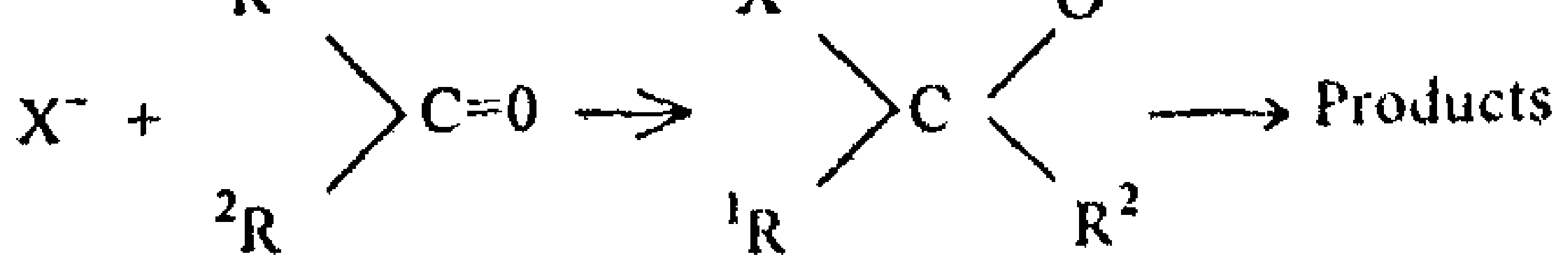
The idea of using quantum chemical bond order (BO) as a local reaction path indicator proposed earlier with reference to ABC ↔ BCA type of isomerization processes is explored further with reference to model carbonyl addition reactions, e.g. $H_2CO + H\text{–}Cl \rightarrow H_2CCl\text{–}OH$ and $H_2COH^+ + H\text{–}Cl \rightarrow ClCH_2OH + H^+$. In each case the reaction is viewed as a superposition of elementary chemical events, some representing bond making and some bond breaking processes, respectively. Altogether four bonds are involved in the model. The active bond order profile in each case is marked by a sharp inflexion signalling the onset of a critical process, viz. bond breaking or bond making. An extended bond energy bond order description of the addition of HCl to the >C=O moiety is suggested and tested numerically. The semilocal description is seen to model the approximate reaction path well and predict the active portion of the transition state structure fairly successfully. The local RP modelling is also seen to predict changeover in the mechanism of the reaction when conditions are altered by protonating the carbonyl group. The origin of the observed BO inflexions is sought to be correlated with Fermi correlation.

CHEMICAL reactions involve breaking and making of bonds. These processes take place gradually along a certain path, the so-called reaction path (RP). The usual indicator of this path is energy and the abstraction of RP in theory is a curving, parabolic potential energy channel stretching from the reactants to the product valley on the potential energy surface (PES). The top of the path defines the so-called saddle point, the activation barrier and the structure of the associated transition state. Energy is, however, a global parameter of the entire system while intuitive visualization of a chemical reaction in terms of breaking and making of specific bonds relies on a more 'local' description. An essential ingredient of this picture is the assumption that the bonds being broken or formed are the 'active' or 'important' bonds while the other bonds are more or less 'spectator like' or 'passive' and do not play any decisive role in shaping at least the gross or dominant features of the RP.

In the recent years a number of reports dealing with the existence of inflexion points in reactive valence or bond order (BO) profiles have appeared[1-5]. It has also been conjectured that such an inflexion point in BO profile may even coincide with or be close to the saddle point on the reaction path[4, 5]. The present communication explores the utility of these concepts further with the specific case of a prototypical carbonyl addition reaction which can be described in terms of a four-bond process. It is also shown that by isolating the active bonds and making use of the appropriate bond order conservation conditions, an extended bond energy bond order (EBEBO) description of the active portion of the transition state geometry can be arrived at and the minimum energy reaction path (MERP) constructed. Although the discussion that follows concerns a reaction in particular, the observations are quite general or further generalizable. It enhances the scope of applicability of the local description to much more[6] complex systems.

Carbonyl addition reaction

Addition of nucleophiles to carbonyl centres is a very fundamental process in organochemical and biochemical reactions. Common examples include hydrolysis of esters and amides, aldol condensation and numerous reactions of organometallic reagents and ylides[7-9]. Analysis of experimental results on these reactions has led to the following $B_{AC}2$ mechanism for these processes[10];



[†] Based on a lecture delivered by SPB in the 1993 mid-year meeting of the Indian Academy of Sciences, Bangalore

Results of gas phase experiments have shown that esters undergo competitive proton transfer, eliminations and S_N2 reactions in favour of $B_{AC}2$ processes[11]. This $B_{AC}2$ mechanism has also been found to be operative for the gas phase additions to acyl halides[12]. Analysis of the kinetic results has led to the conclusion that the reactions in the gas phase feature a double-well potential surface with the tetrahedral species as a transition state and ion–dipole complexes as minima. Using crystallographic data for various nucleophilic groups interacting with different carbonyl centres, Burgi and Dunitz[13] were able to propose likely pathways for the approach of the nucleophile. Using SCF-LCAO-MO calculations[14] on the model addition reaction of hydride ion to formaldehyde, the same authors found no energy maxima in the potential energy profile. In a recent *ab initio* study on the addition of hydroxide ion to formaldehyde, Madura and Jorgensen[15], using a basis set containing diffuse functions, found a small local maxima in the energy profile of the reaction. Bayly and Grein[16] further confirmed that the reaction profiles for these addition reactions might be described adequately by adding diffuse functions to the basis set.

With this background in view, our purpose in the present communication has been to explore the possibility of (a) describing a simple carbonyl addition reaction quantitatively in terms of a rather *local* concept like variation of bond order, (b) constructing an *extended* bond energy bond order (semilocal) description of a process involving four active bonds, (c) using the local picture for predicting changeover in reaction mechanism, if any, when reaction conditions are altered, and (d) checking the validity of a *regional* or *local* hardness extremization principle proposed recently. The specific definition of bond order we choose to employ is due to Mayer[17]. The advantage of this quantity lies in its relative insensitivity to changes in the size of the basis set employed[18]. Irrespective of whether one is working in an *ab initio* or a semiempirical framework, the computed bond order index, which is a bond multiplicity index, turns out to be close to 1 for a single bond, 2 for a double bond, and so on. However, the minor method or basis dependence can be tackled by using renormalized BOs (see later). We have employed the standard AM1 method of Dewar and Thiel[19] with the hope of extending the present study, if useful, to reactions of different types involving much larger systems.

Method

The potential energy surface (PES) for the gas phase reactions studied in this paper has been computed by the standard AM1 Fletcher–Powell technique. For each point on the PES complete optimization of all geometrical parameters has been carried out. Bond orders have been calculated for each pair of atoms for all the relevant points on the RP. The generalized bond order (B_{XY}) between a pair of atoms (X and Y) is given by[17]

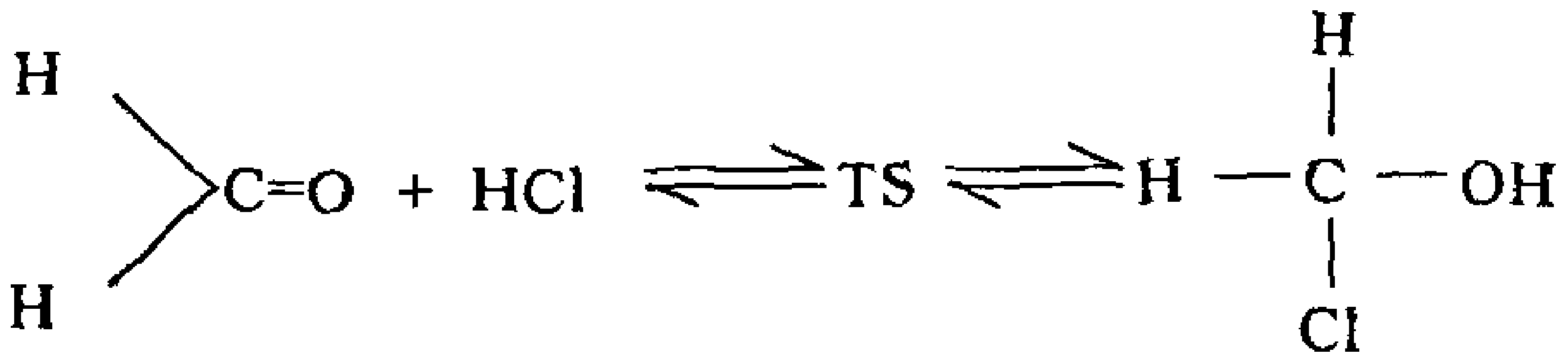
$$B_{XY} = \sum_{\mu\in X}\sum_{\nu\in Y}(\bar{D}S)_{\mu\nu}(\bar{D}S)_{\nu\mu} + \sum_{\mu\in X}\sum_{\nu\in Y}(D^sS)_{\mu\nu}(D^sS)_{\nu\mu}, \tag{1}$$

where the one-electron density matrix (ρ) in AO basis has been partitioned into $\bar{D}$ and D^s. $\bar{D}$ is the part of the one-electron density due to the core or the doubly occupied orbitals and D^s represents that due to singly occupied orbitals. At the AM1 or MNDO level of approximation, $S = 1$ and for closed shell systems $D^s = 0$, leading to corresponding simplifications in the expression for B_{XY} which now becomes identical with Wiberg's bond order[20].

Results and discussion

Addition of HCl to H_2CO in the gas phase: a local versus global description

The gas phase reaction between formaldehyde and hydrogen chloride may be schematically represented as follows:



$$\mathrm{H_2C{=}O} + \mathrm{HCl} \rightleftharpoons \mathrm{TS} \rightleftharpoons \mathrm{H{-}C(H)(Cl){-}OH}$$

We have explored two different pathways (schemes A and B in Figure 1) for the reaction, each passing through a separate transition state [TS(A)/TS(B)]. In scheme A, the HCl molecule has been assumed to approach the carbonyl group laterally, leading to a four-centered transition state [TS(A)] as in Figure 1. In scheme B, the HCl molecule is assumed to approach the nucleophilic centre in a plane perpendicular to the plane containing the >C=O group, leading to a transition state [TS(B)] as in Figure 1. In both the cases the reaction coordinate (RC) involves a predominant participation of the effective C..Cl and O..H distances. However, scheme B turns out to be inappropriate as it fails to lead to any well-defined TS or to product. In scheme A, on the other hand, we find that the reaction proceeds through a well-defined TS characterized by the structure [TS(A)] shown in Figure 1. This TS has been located by varying the >C..Cl and O..H distances (r_1 and r_2) in a preset grid while all other geometrical parameters for each pair of values of r_1 and r_2 have been fully optimized by the Fletcher–Powell technique.

The energy profile along the reaction path is depicted in Figure 2 *a*. The location of the TS corresponds to a value of the path coordinate (PC) = 0.76. At this point on the RP, $r_1 (= r_{\mathrm{C..Cl}}) = 2.19$ Å, $r_2 (= r_{\mathrm{O..H}}) = 1.34$ Å, $r_{\mathrm{C..O}} = 1.30$ Å and $r_{\mathrm{H..Cl}} = 1.63$ Å

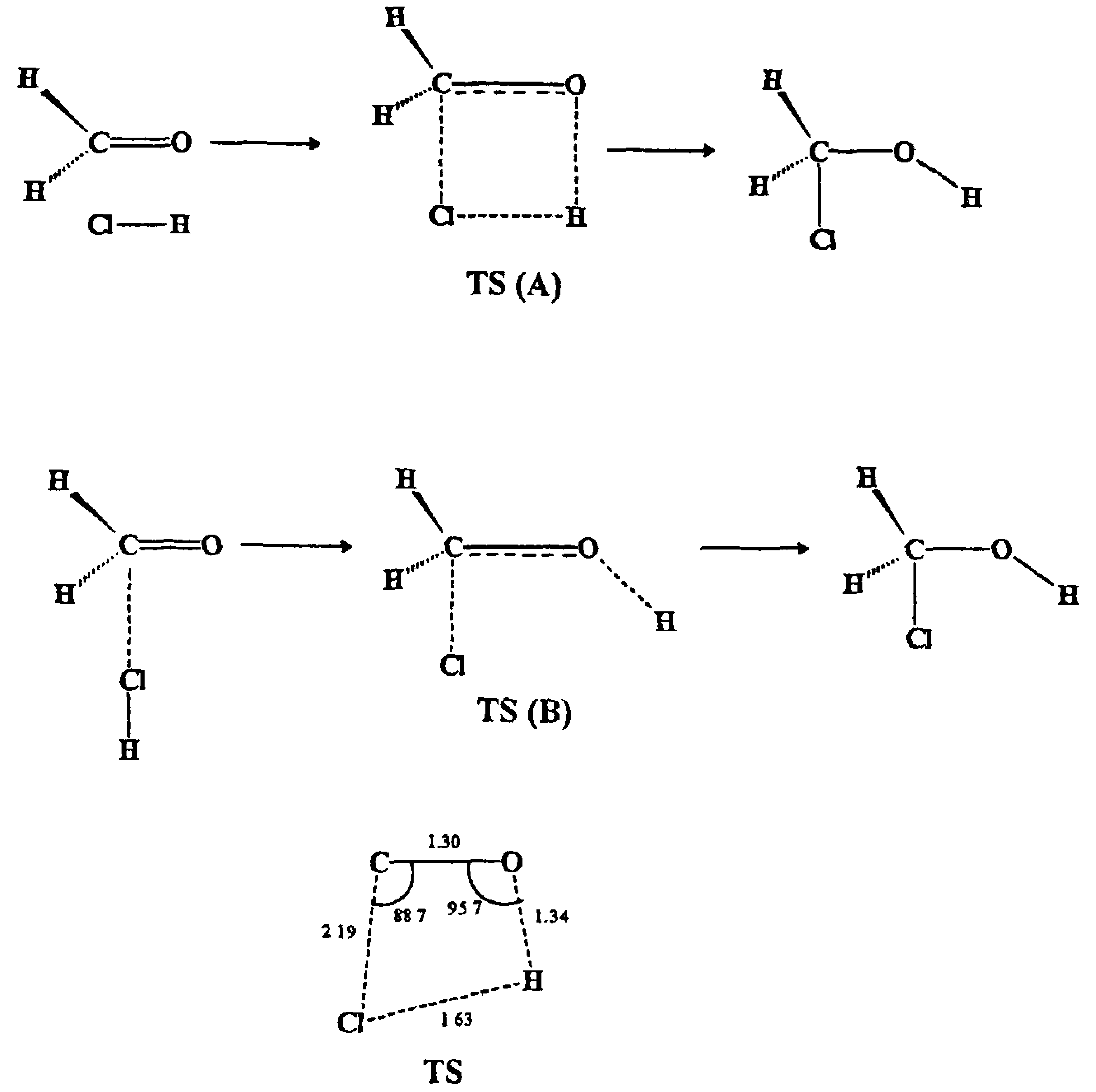


Figure 1. Reaction schemes (A and B) for the addition of HCl to H_2CO and optimized transition state geometry [TS(A)] for the lateral approach of HCl to the formaldehyde molecule.

(see Figure 1). Since the reaction scheme involves breaking of the H–Cl and p(C–O) bonds, respectively, and formation of a C . . Cl and an O..H bond, we designate them as 'active bonds'. A local model of the reaction should, therefore, be able to describe the process mainly in terms of quantities related to these four bonds only.

Figures 2 *b* and *c* display variations in H–Cl and O–H bond orders, respectively, as they change along RP, while Figure 3 *a* exhibits variations in the p bond order of the C–O bond as a function of the path coordinate. Variation in C–Cl bond order along the RP is also shown in the same figure (Figure 3 *b*). It is clearly seen that each of the H–Cl, C–Cl, C–O and O–H BO profiles reveals the occurrence of a definite and rather sharp point of inflexion. The C–Cl separation at the corresponding BO inflexion point is 2.19 Å, the H–Cl length is 1.63 Å , the C–O length is 1.30 Å and the O–H separation is 1.34 Å. If we compare these lengths with the bond length in the TS obtained by energy optimization route (i.e. by adopting a scheme of global RP analysis), we find that H–Cl, C–Cl, C–O and O–H bond lengths at the corresponding inflexion points match rather nicely with the corresponding bond lengths already found for the TS structure located on the given energy hypersurface.

It may be noted that the reaction in scheme A involves participation of four atoms (C, O, Cl and H). It would be of interest, therefore, to examine whether the total bonding capacity of the 'active atoms' is conserved along the MEP. We have, therefore, plotted the sum of the computed bond orders of the p(C–O), C–Cl, O–H and H–Cl bond (Figure 3 *c*) of the four relevant atoms along the RP. It is interesting to note that the so-called principle of bond order conservation (PBOC) advocated by Lendvay[2] appears to remain only approximately valid in this particular reaction in regions appreciably away from the critical region surrounding the saddle point. Around the saddle point, the active BO sum is not conserved. On the other hand, it passes through a minimum.

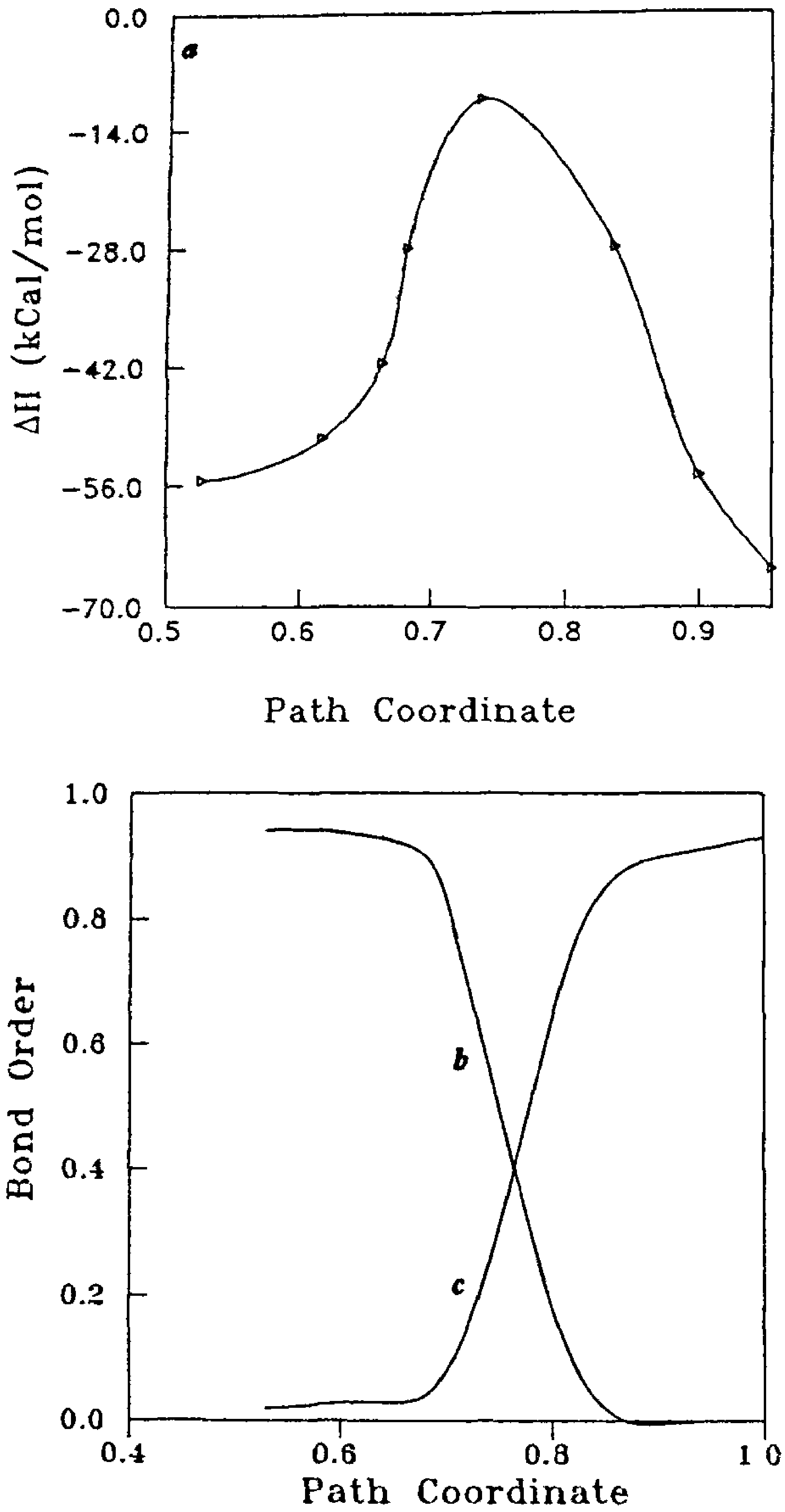


Figure 2. *a*, Energy profile in gas phase for formaldehyde +HCl reaction (scheme A): *b*, HCl bond order profile; *c*, O..H bond order profile along the RP.

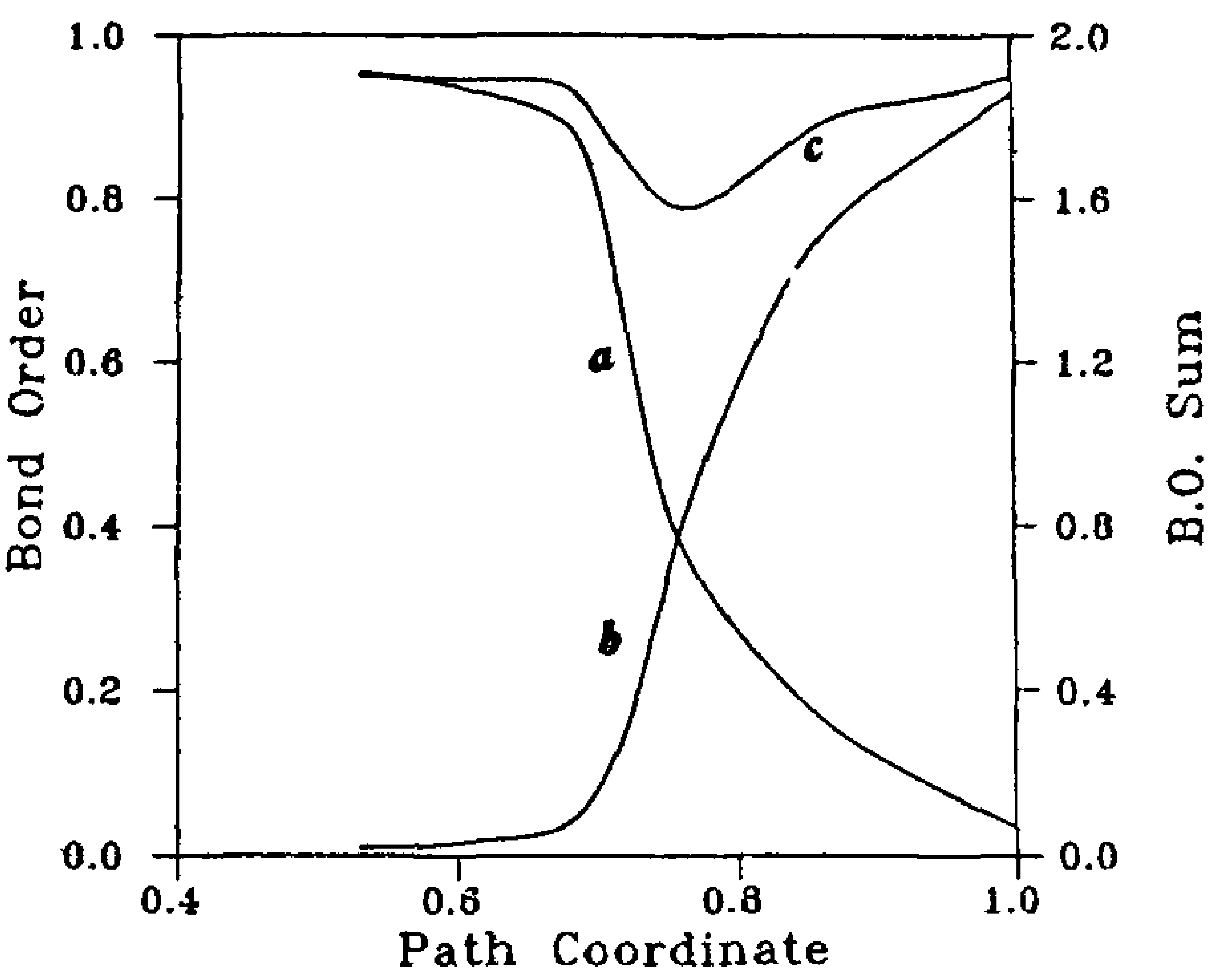


Figure 3. The BO profiles of *a*, the Π (C–O) bond and *b*, the C–Cl bond along the reaction path for the gas phase addition of HCl to H_2CO *c*, The extent of validity of the active BO sum conservation is shown for the carbonyl addition reaction.

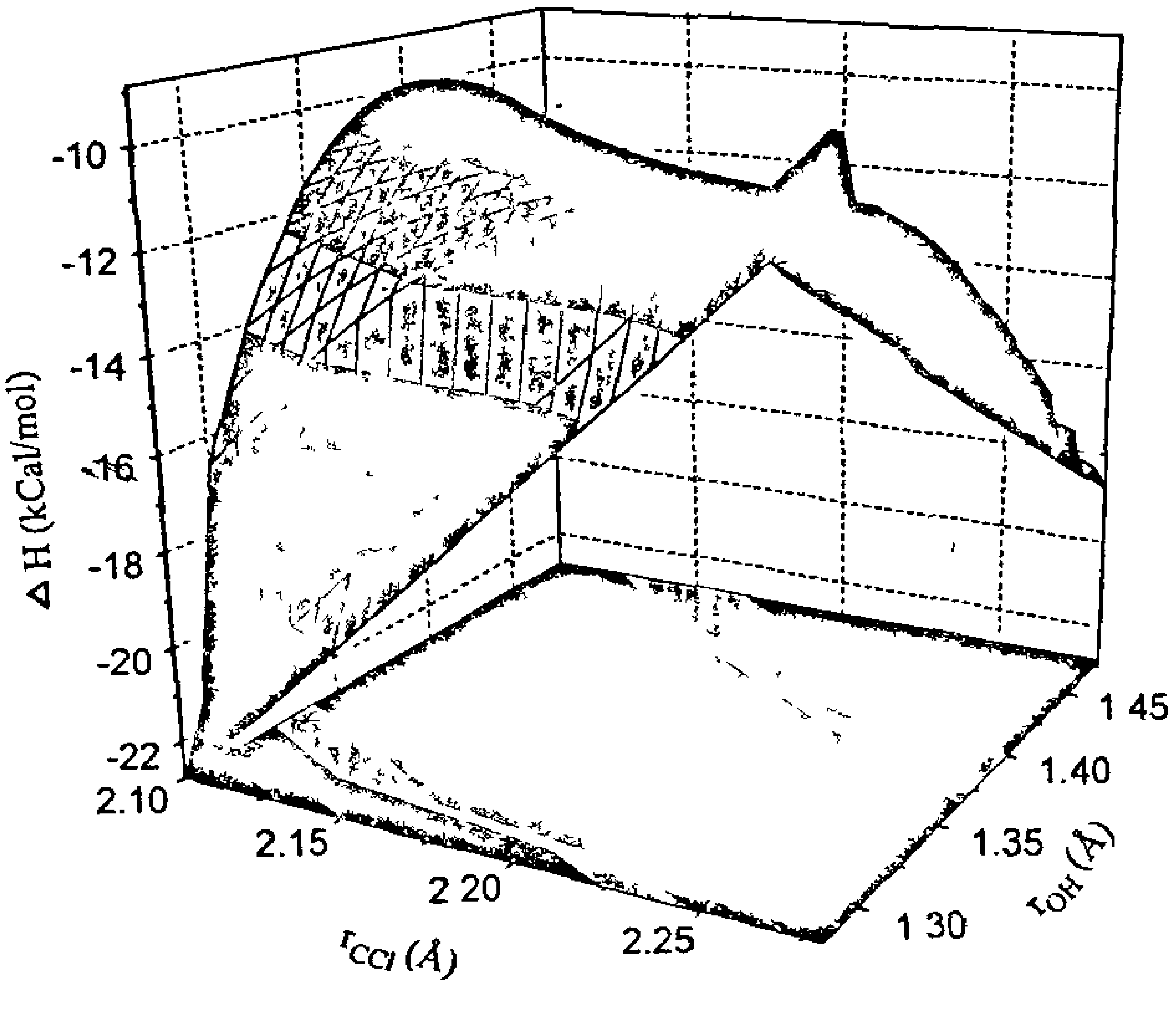


Figure 4. Energy contour as a function of O. H and C. Cl bond lengths for the formaldehyde +HCl reaction in the gas phase and the three-dimensional plot of the interaction energy The transition state (×) on the reaction path (marked by the dotted line).

It has recently been shown that this behaviour of the active BO sum could amount to a local or regional softness or hardness extremization principle[21]. The saddle point, and the inflexion points in the BO profiles of the reaction under consideration occur almost at the same value of the path coordinate, viz PC = 0.76. The BO profiles of Figure 2 and 3, therefore, tend to suggest that the H–Cl, π(C–O), C–Cl and O–H bonds are each associated with a critical process occurring in the course of the reaction. They are then the active bonds. It would be worthwhile, therefore, to map the corresponding energy changes on the plane defined by the bond lengths of a pair of the active bonds, say C–Cl and O–H bonds. We have studied the reactive PES in three dimensions (two of these are the C–Cl (r_1) and O–H (r_2) bond lengths) and mapped its contour on the (r_1, r_2) plane. The energy map in two dimensions and the plot in three dimensions are displayed in Figure 4. The 'reaction path' has been marked on the contour map by a dotted line and the

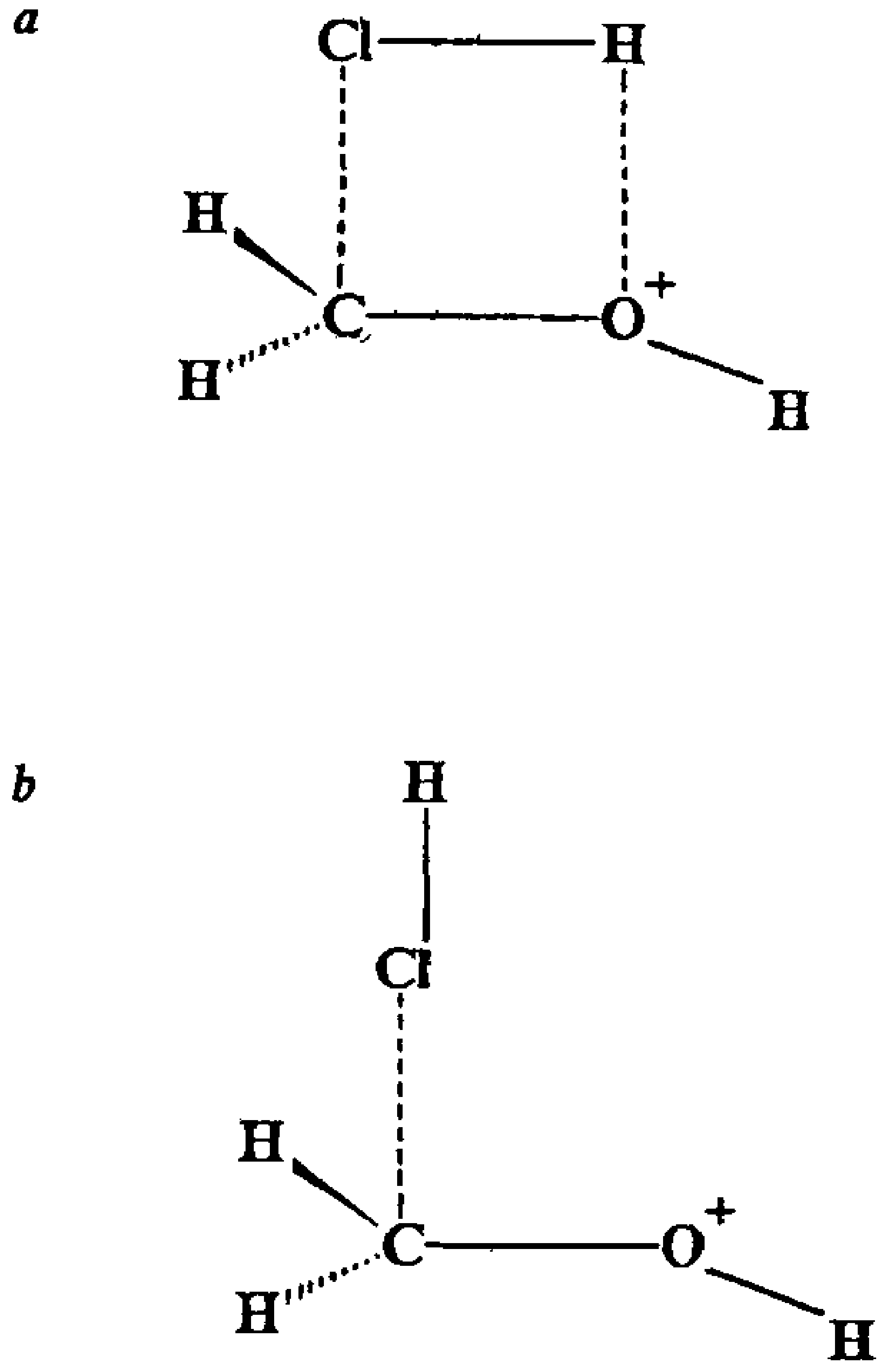


Figure 5. Schematic representation of *a*, lateral and *b*, orthogonal approach of HCl to the protonated formaldehyde.

location of the TS by a cross (x) which corresponds to $r_1 = 2.19$ Å and $r_2 = 1.34$ Å. These values match well with those obtained from the points of inflexion on the BO profiles. The gas phase reaction is exoenergic by a small amount (5.34 kcal/mol) and the activation barrier turns out be ≈ 48.0 kcal/mol.

Gas phase addition of HCl to H_2COH^+: local description of mechanistic changeover

How would protonation of formaldehyde affect the course of addition of HCl to the carbonyl group? One can anticipate a drastic change in the mechanism since the addition of a proton would (i) severely distort the π electron distribution within the carbonyl moiety and (ii) create positive charge density on all atoms in the molecule. As expected, our calculations reveal the inappropriateness of the lateral approach, which fails to initiate the reaction (Figure 5 *a*). Initial search showed that the HCl molecule would prefer to approach the protonated >C=O group in a plane orthogonal to the plane containing the carbonyl group (Figure 5 *a*) with the Cl end pointing towards the carbonyl carbon atom. Figures 6 *a*

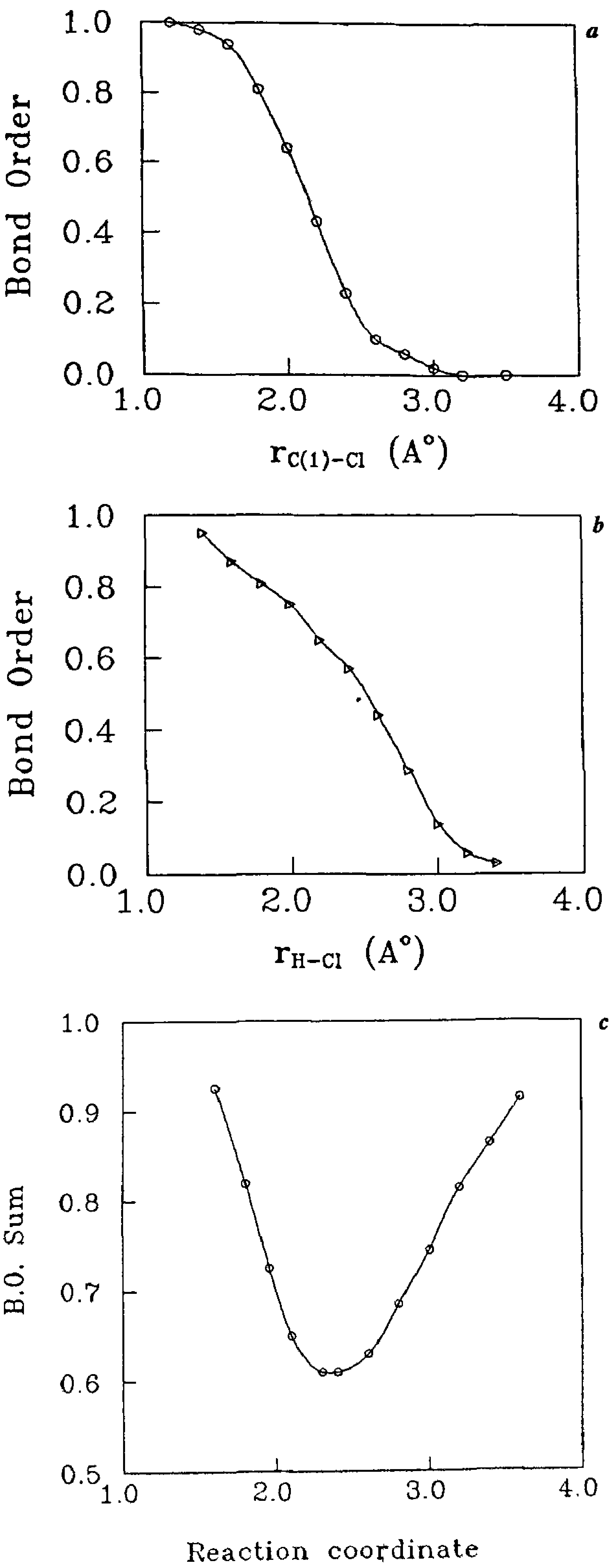


Figure 6. *a*, C–Cl bond order profile as a function of C. Cl bond distance; *b*, H–Cl BO profile as a function of H–Cl distance; *c*, sum of C–Cl and H–Cl BOs along the RP in the $HCl + H_2COH^+$ reaction.

and *b* present the H–Cl and C–Cl bond order profiles along the reaction path. These BO profiles, the active BO profiles, once again enable us to have a local description of the reaction in terms of elementary chemical events. It is interesting to note that the inflexion point in the BO profile of the H–Cl bond corresponds to an H–Cl distance of 2.75 Å when the C–Cl distance is about 2.25 Å. This C–Cl distance is much too large for any significant extent of C–Cl bond formation to have taken place. The inflexion point on the BO profile of the C–Cl bond itself, however, occurs only at a much shorter C–Cl length ($r_{C-Cl} \approx 2.08$ Å) indicating that the C–Cl bond formation takes place much later. In other words, *the breaking of the* H–Cl *bond does not synchronize with the formation of the* C–Cl *bond.* Obviously, this tends to suggest that the sum of H–Cl and C–Cl BOs is not conserved, a feature that is clearly seen to be true from Figure 6 *c*.

One can contemplate, therefore, that the mechanism of addition of HCl to H_2COH^+ could be fundamentally different from the mechanism established for the addition of HCl to unprotonated H_2CO. If the two asynchronous inflexion points, one rather early and the other late, observed in the H–Cl and C–Cl BO profiles, respectively, can be assumed to be associated with the physical process of bond breaking or making, one would be tempted to think that the addition of HCl to H_2COH^+ must be a two-step process. The H–Cl bond breaks first producing H^+ and Cl^-, the latter then attacking the carbon atom of the >C=O–H^+ group with the formation of chloromethanol. The entire process may be schematically represented as follows:

$$H_2CO + H^+ \rightarrow H_2COH^+,$$
$$HCl \rightarrow H^+ + Cl^-,$$
$$Cl^- + H_2COH^+ \rightarrow ClCH_2OH.$$

The inflexion that occurs in the C–Cl BO profile as Cl^- attacks H_2COH^+ is not very sharp, indicating that the associated energy profile also would be relatively featureless. Figure 7 *a* shows the energy profile for the first step when HCl approaches the carbonyl carbon atom of the protonated formaldehyde in an orthogonal plane. A small hump appears followed by a monotonic decrease in the total energy. The location of the hump corresponds to $r_{C-Cl} \approx 2.20$ Å and $r_{H-Cl} = 2.80$ Å, so that it may be taken to correspond to the breaking of the H–Cl bond, essentially corroborating what has already been revealed clearly by the bond order profiles. Figure 7 *b* represents energy profile for the second step of the reaction, in which chloride anion produced in the first step attacks the carbon atom of the H_2COH^+ moiety and formation of C–Cl bond of the product chloromethanol takes place. This step has been simulated by first determining the minimum-energy ground state geometry of H_2COH^+ and bringing in a chloride ion (Cl^-) from a large distance. The net charge of the combined system has been kept zero and the entire system has been allowed to relax at each C–Cl distance. The energy decreases monotonically as chloromethanol is formed, without encountering any activation barrier. The first step, viz. the breaking up of HCl into H^+ and Cl^- must, therefore, be the rate-determining step in the addition of HCl to H_2COH^+. Relevant kinetic data are, however, unavailable to confirm this scenario experimentally. Similar behaviour has been noted for the addition of H–*X* (*X* = Cl, Br, CN, etc.) to the >C=O moiety, in general. The details will be presented elsewhere.

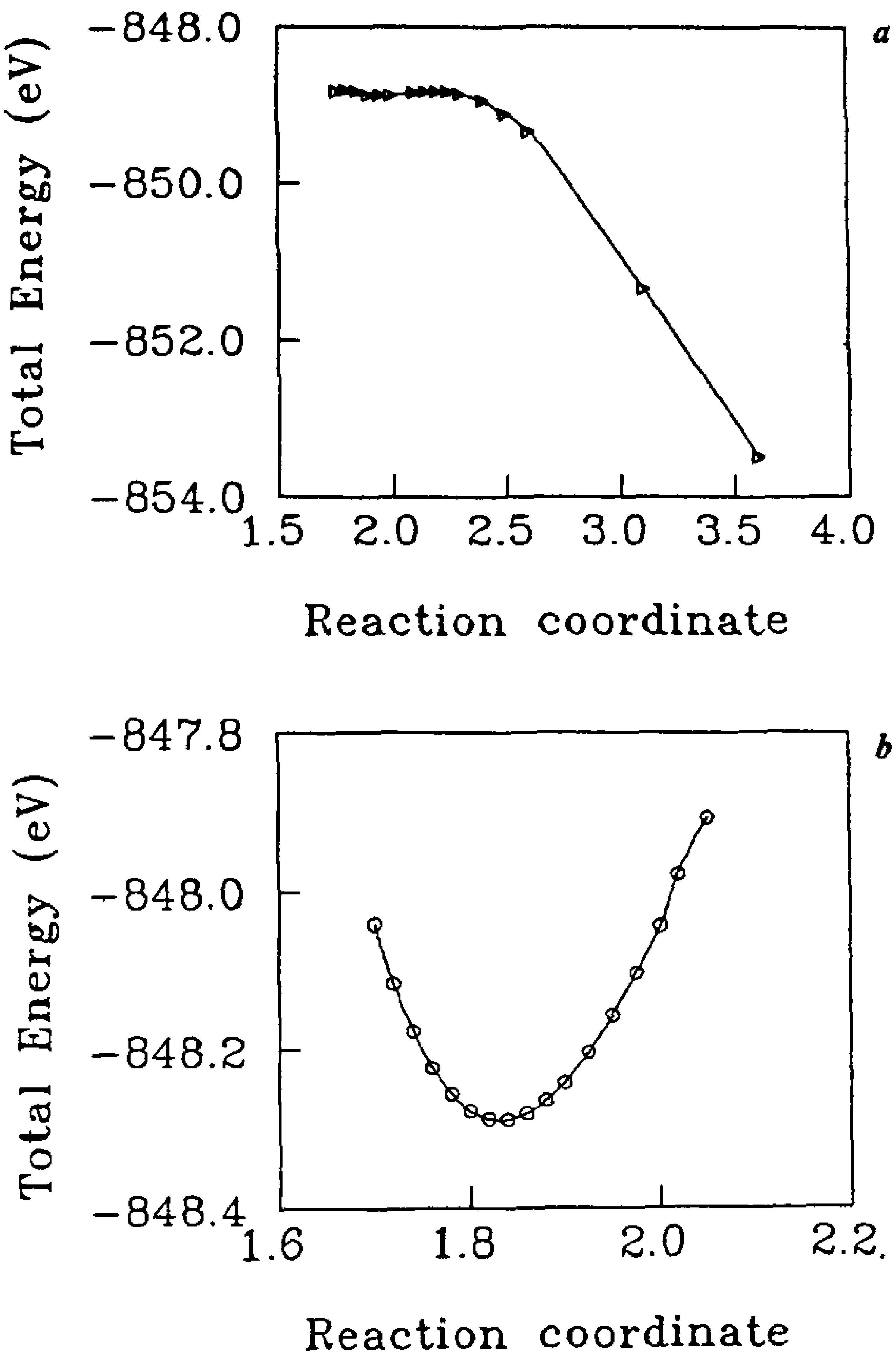


Figure 7. *a*, Energy profile for the orthogonal approach of HCl to the protonated formaldehyde. The RC essentially represents the H–Cl bond length. *b*, Energy profile for the orthogonal approach of Cl^- ion to the carbonyl carbon of protonated formaldehyde The RC essentially represents the C–Cl bond length

A BEBO description of the TS in the carbonyl addition reactions

One wonders at this point whether some kind of energy-based description of the carbonyl addition reaction is feasible within the local model. In other words, how could we transcribe the local picture in terms of the BO profiles of active bonds into a semilocal energy-based picture? A possible recipe that immediately comes to mind is the BEBO model of Johnston and Parr[22, 23] which has been extensively used fairly successfully in studying atom transfer reactions[23–27] of the type $A + BC \rightarrow AB + C$. These reactions basically involve the active bond and the BEBO theory works well. In the present case, however, the basic model needs to be extended. Considering the four active bonds, viz. H–Cl, C–Cl, π(C–O) and O–H, and the corresponding bond orders, the sum of which is constrained to remain conserved along the reaction path, we have the following BEBO function for monitoring the energy changes during the reaction.

$$V = -D^0_{\mathrm{HCl}} n^p_{\mathrm{HCl}} - D^0_{\mathrm{CCl}} n^q_{\mathrm{CCl}} - D^0_{\pi(\mathrm{CO})} n^r_{\pi(\mathrm{CO})} - D^0_{\mathrm{OH}} n^s_{\mathrm{OH}}.$$

In short-hand notation, we may write (with $D^0_{\mathrm{HCl}} = D^0_1$,

$D^0_{\mathrm{CCl}} = D^0_2$, $D^0_{\pi(\mathrm{CO})} = D^0_3$ and $D^0_{\mathrm{OH}} = D^0_4$),

$$V = -D^0_1 n^p_1 - D^0_2 n^q_2 - D^0_3 n^r_3 - \mathrm{D}^0_4 n^s_4 \qquad (2)$$

where

$$n_1 + n_2 + n_3 + n_4 = 2; \qquad (3)$$

p, q, r and s are, parameters and D^0_{AB}, in general, is the energy of the A–B bond of unit order. Using the active BO sum conservation constraint (3) to eliminate n_4, we have

$$V = -D^0_1 n^p_1 - D^0_2 n^q_2 - D^0_3 n^r_3 - \mathrm{D}^0_4 \{2 - (n_1 + n_2 + n_3)\}^s \quad (4)$$

As the TS, we have

$$\frac{\delta V}{\delta n_1} = \frac{\delta V}{\delta n_2} = \frac{\delta V}{\delta n_3} = 0. \qquad (5)$$

This leads us to a set of three coupled, non-linear equations:

$$\begin{aligned} -p\ D^0_1 n^{p-1}_1 + s\ D^0_4\ \{2 - (n_1 + n_2 + n_3)\}^{s-1} &= 0, \\ -q\ D^0_2 n^{q-1}_2 + s\ D^0_4\ \{2 - (n_1 + n_2 + n_3)\}^{s-1} &= 0, \qquad (6) \\ -r\ D^0_3 n^{r-1}_3 + s\ D^0_4\ \{2 - (n_1 + n_2 + n_3)\}^{s-1} &= 0, \end{aligned}$$

and the BO conservation condition, which demands that

$$n_1 + n_2 + n_3 + n_4 = 2.$$

For $p = q = r = s = 2$, the equations in (6) are linear and can be solved together with $n_4 = 2 - (n_1 + n_2 + n_3)$. For other values of p, q, r, s equations (6) are to be solved iteratively. We have adopted a steepest descent (ascent)

Table 1. Comparison of the active bond lengths in the TS of the gas phase reaction $H_2CO + HCl \rightarrow ClCH_2OH$ computed by the EBEBO model and the AM1 method

Method		r_{HCl} (Å)	r_{CCl} (Å)	r_{OH} (Å)	r_{CO} (Å)
	$p=q=r=s=2$	1.470	1.907	1.120	1 318
EBEBO	$p=q=r=s=3$	1 470	1.930	1 162	1.321
	$p=q=r=s \doteq 4$	1 465	1.935	1 156	1.323
AM1		1 493	2 000	1.211	1.346

type of technique to solve the equations in (6) for $p, q, r, s \neq 2$. However, the TS BOs are found to be only weakly dependent on the p, q, r, s values. Our experience so far indicates that $p = q = r = s = 2$ is a good choice. The BO values obtained by solving equations (6) provide an approximate estimate of the active Bos in the TS. Using Pauling's bond length bond order relationship, $r_{AB} = r^0_{\mathrm{AB}} - c^0_{\mathrm{AB}} \ln n_{AB}$, the active bond lengths in the TS can also be calculated. The active bond lengths in the TS computed by our EBEBO recipe for (i) $p = q = r = s = 2$, (ii) $p = q = r = s = 3$, (iii) $p = q = r = s = 4$ are reported in Table 1 along with their corresponding values obtained from TS BOs predicted by the global energy-based analysis of the RP at the AM1 level of approximation (standard bond energy data have been used). We must mention here that Pauling's relation assumes that r^0_{AB} corresponds to the length of the A–B bond with BO = 1. However, frequently, the MO calculations predict equilibrium BOs of the A–B bonds that are different from 1. In such cases, one can use a renormalized Pauling bond length bond order relation:

$$r_{AB} = r^0_{AB} - c^0_{AB}\ \ln(n_{AB} / n^0_{AB}),$$

where n^0_{AB} is the computed bond order at the equilibrium internuclear separation (r^0_{AB}). The most important point to note is that it is the rate of change of BOs of different active bonds along the RP that dominantly determines where the critical point is going to be located. The absolute values of BOs are thus unimportant, rendering renormalized BOs useful and effective. Attempts have been made to improve the bond length bond order relation further by making c_{AB} dependent on the value of r^0_{AB}. Agmon's proposal[27] to take $c^0_{AB} = b^{AB}_1 r^0_{AB} - b^{AB}_2 r^2_{AB}$ invariably leads to further improvement. But in the present study, we have not used renormalized Pauling's relation or Agmons's improvement on it. When this is done, the agreement between extended BEBO and AM1 results could improve further. The values predicted by the EBEBO model do not fare too badly compared to values obtained from standard energy-based reaction path analysis. The V function of equation (2) can be used to generate energy surface or contour maps either in the BO space or in the internuclear distance space. They are very much like the one described already and are, therefore, not reproduced here.

The origin of BO inflexions

We have already seen that only a few bonds are characterized by inflexions in their BO profiles along a given reaction path. That is, a reaction system appears to discriminate between two sets of BO variables, viz., the active and the inactive ones. The active BO variables are characterized by sharp inflexions along the reaction path. Why does it happen? It is clear that the BO inflexions occur over a rather short range. It will not be too speculative to assume, therefore, that forces responsible for the observed behaviour of the active BO profiles during a reaction must be changing rapidly over a rather short range. A clue to the nature of these forces may be hidden in the statistical interpretation of BO.

The chemical bond between a pair of atoms has been traditionally interpreted in terms of a build-up of electron density in the region (the bond region) between the two atoms. Customarily, therefore, the first-order density ρ_1 or quantities related to or obtainable from ρ_1 have been used for describing chemical bonds. A description based on ρ_1 cannot, however, reflect the 'electron pair' character of the most commonly encountered bonds. The second-order density matrix (ρ_2) is a more natural and logical candidate for analysing chemical bonds. The bond order index used by us is due to Mayer[17] and has been shown to be related to the normalization of the diatomic exchange part of the second-order reduced electron density (ρ_2). For a single determinant representable state, ρ_2 is factorizable and the bond order can then be expressed in terms of ρ_1. For such a state it has been shown[28] that

$$B_{AB} = -2\,\{\langle\hat{q}_A\hat{q}_B\rangle - \langle\hat{q}_A\rangle\langle\hat{q}_B\rangle\}, \tag{7}$$

where $\hat{q}_A$ and $\hat{q}_B$ are the LCAO atomic charge density operators for the atoms A and B, respectively, $\hat{q}_A$ and $\hat{q}_B$ are defined by

$$\hat{q}_A = \sum_{\mu\in A} \chi^+_\mu\phi^-_\mu$$
$$\hat{q}_B = \sum_{\nu\in B} \chi^+_\nu\phi^-_\nu \tag{8}$$

where χ^+_μ and ϕ^-_μ are the 'creation' and the corresponding 'true-annihilation' operators corresponding to the spin orbital χ_μ on atom A. χ^+_μ and ϕ^-_ν are defined accordingly for atom B. These operators satisfy the following relation:

$$\{\chi^+_\mu, \phi^-_\nu\} = \delta_{\mu\nu} \tag{9}$$

It can be shown that the right-hand side of equation (7) is related to the density–density correlation function C_{AB}, defined as

$$C_{AB} = \langle(\hat{q}_A - \langle\hat{q}_A\rangle)(\hat{q}_B - \langle\hat{q}_B\rangle)\rangle, \tag{10}$$

which immediately leads to the identification

$$B_{AB} = -2C_{AB} \tag{11}$$

Now, $\hat{q}_A - \langle\hat{q}_A\rangle$ measures the fluctuations of electron density on atom A and $\hat{q}_B - \langle\hat{q}_B\rangle$ the same on atom B. C_{AB} in equation (10), therefore, represents the correlation between the fluctuations of the local electron densities on atoms A and B. The BO between two atoms A and B (B_{AB}) which we are monitoring is, therefore, twice C_{AB} (with sign reversed) and measures the correlation between these localized charge fluctuations. The force responsible for this correlation could be Fermi correlation only, as Coulomb correlation is absent in single determinant description of a state. At this stage a comment on the range of Fermi correlation would be in order. It has been shown by Cooper and Paunder[29] that the range of Fermi correlation appears to be somewhat longer than that of Coulomb correlation, contradicting observations made earlier by Boyd and Coulson[30] and also by Benesch and Smith[31]. However, the definition of Fermi correlation used by Cooper and Paunder is different. But even in the study made by Cooper and Paunder, the maximum and the most rapid change in Fermi correlation occurs over a rather short range and so Fermi correlation would abruptly decrease as a bond is stretched beyond the effective range of correlation as the system moves along a given RP. If two atoms are brought closer by such a motion, new correlations develop between charge fluctuations on the atoms involved and we may note an equally abrupt growth of a particular BO. It may be possible to propose another model to explain the observed behaviour of the active BO profiles based on orbital crossings and Walsh diagrams. But we have preferred to adhere to the explanation based on Fermi correlation in order to be consistent with the statistical interpretation. of BO.

Conclusions

Study of quantum chemical BO profiles may be quite helpful in visualizing the course of a chemical reaction. The BO inflexions provide us with a local view of a reaction involving the breaking and making of a number of bonds. We have been able to demonstrate the viability of an EBEBO description of a reaction involving up to a maximum of four active bonds. This brings quite a large variety of reactions under the ambit of our EBEBO model. They include (i) addition to >C=C<, (ii) ABC ↔ BCA isomerization, (iii) cyclopropyl$^+$ ↔ allyl$^+$rearrangement, (iv) reverse 1,3 dipole addition in tetra-aza cyclopentadienes, (v) intramolecular proton transfer in formamidene, (vi) 1,3 H shift, (vii) Cope rearrangement, etc. Many more reactions are being studied to assess the overall applicability of the local model in studying chemical reactions.

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1. Mayer, I, in *Modelling of Sructure and Properties of Molecules* (ed Maksic, Z B), Ellis Haewood, Chichester, 1987, p. 45
2. Lendvay, G., *J. Phys Chem.* 1989, **93**, 4422–4429.
3. Ponec, R , *Collect Czech. Chem. Commun* , 1987, **52**, 2603–2612.
4. Maity, D K and Bhattacharyya, S. P., *J Am. Chem Soc.*, 1990, **112**, 3223–3225
5. Maity, D K., Das, K K and Bhattacharyya, S P., *Proc. Indian Acad Sci (Chem Sci)*, 1989, **101**, 421–428; Majumdar, D, Maity, D. K. and Bhattacharyya, S. P., *Int J. Quant. Chem.*, 1992, **43**, 567–572, Maity, D. K Majumdar, D. and Bhattacharyya, S P., *J Mol Struct (Theochem)*, 1992, **276**, 315–325.
6. Maity, D K , Majumdar, D and Bhattacharyya, S P., *J. Mol Struct. (Theochem)*, 1995, **332**, 1–20
7. Bender, M. L , *Chem Rev.*, 1960, **60**, 53–113; Jencks, W P., *Catalysis in Chemistry and Enzymology*, McGraw-Hill, New York, 1969
8. Blow, D M, *Acc Chem. Res* , 1976, **9**, 145-152
9. March, J., *Advanced Organic Chemistry*, Wiley, New York, 1985.
10. Jencks, W P , *Acc. Chem. Res* , 1980, **13**, 161–169
11. Faigle, I F G., Isolani, P C and Riveros, J M , *J Am Chem. Soc.*, 1976, **98**, 2049–2052
12. Asubiojo, O. I. and Brauman, J. I , *J. Am Chem. Soc.*, 1979, **101**, 3715–3724
13. Burgi, H. B , and Dunitz, J. D., *Acc. Chem. Res.*, 1983, **16**, 153–161
14. Burgi, H. B . Lehn, J. M. and Wipff, G , *J Am Chem Soc* , 1974, **96**, 1956–1957.
15. Madura, J D and Jorgensen, W. L., *J. Am. Chem Soc* , 1986, **108**, 2517–2527.
16. Bayly, C. I. and Grein, F., *Can. J. Chem.*, 1989, **67**, 176–182
17. Mayer, I., *Theo Chim Acta*, 1985, **67**. 315–322
18. Mayer, I , Revesz, M. And Hargittai, I , *Acta Chim Hung.*, 1983, **114**, 159–172; Mayer, I. and Revesz, M , *Inorg Chim Acta*, 1983, **77**, L205–L206.
19. Dewar, M. J. S. and Thiel, W., *J. Am Chem. Soc.*, 1977, **99**, 4899–4907, 4907–4917.
20. Wiberg, K. B , *Tetrahedron*, 1966, **24**, 1083–1096.
21. Maity, D. K. and Bhattacharyya, S. P., *J Phys. Chem* (submitted 1995)
22. Johnston, H. S and Parr, A. C., *J. Am Chem Soc.*, 1963, **85**, 2544–2551.
23. Johnston, H S., *Gas Phase Reaction Rate Theory*, Ronald Press, New York, 1966
24. Truhlar, D. G., *J Am Chem. Soc.*, 1972, **94**, 7584–7586.
25. Garret, B C. and Truhlar, D. G., *J. Am. Chem Soc.*, 1980, **102**, 2559–2570
26. Garret, B C., Truhlar, D. G and Magnuson, A W., *J Chem Phys* , 1982, **76**, 2321–2331.
27. Agmon, N. and Levin, R. D., *J Chem. Phys.*, 1979, **71**, 3034–3041.
28. De Giambiagi, M. S., Giambiagi, M. and Jorge, F E , *Theo. Chim Acta*, 1985, **64**, 337–341
29. Cooper, I. L. and Paunder, C N. M , *Int. J. Quant. Chem* , 1980, **17**, 759–774.
30. Boyd, R J and Coulson, C. A., *J. Phys. B*, 1974, **7**, 1805–1816
31. Benesch, R and Smith (Jr), V. H , *J Chem Phys* , 1971, **55**, 482–488

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