Dynamics study of the reaction OH⁻ + C₂H₂ → C₂H⁻ + H₂O with crossed beams and DFT calculations

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Abstract

The proton transfer reaction between OH⁻ and C₂H₂, the sole reactive process observed over the collision energy range from 0.37 to 1.40 eV, has been studied using the crossed beam technique and DFT calculations. The center of mass flux distributions of the product C₂H⁻ ions at three different energies are highly asymmetric, characteristic of a direct process occurring on a timescale much less than a rotational period of any transient intermediate. The maxima in the flux distributions correspond to product velocities and directions close to those of the precursor acetylene reactants. The reaction quantitatively transforms the entire exothermicity into internal excitation of the products, consistent with an energy release motif in which the proton is transferred early, in a configuration in which the forming bond is extended. This picture is supported by DFT calculations showing that the first electrostatically bound intermediate on the reaction pathway is the product-like C₂H⁻•H₂O species. Most of the incremental translational energy in the two higher collision energy experiments appears in product translational energy, and provides an example of induced repulsive energy release characteristic of the heavy + light-heavy mass combination.

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I. Introduction

As part of the continuing series of investigations from this laboratory on the reactions of oxygen-containing ions with hydrocarbons,\textsuperscript{1,2} we have studied the reaction of the hydroxide anion with acetylene. Hydroxide is often a contaminant ion in the production of O\textsuperscript{−}, an important reagent in chemical ionization mass spectrometry.\textsuperscript{3} It plays an important role in solution chemistry and gas phase chemistry, and is a stronger base than the atomic oxygen anion. The present work reports the first crossed beam study of the OH\textsuperscript{−} + C\textsubscript{2}H\textsubscript{2} reaction. The proton transfer channel was observed in our experiments:

\[
\text{OH}^{-} + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}^{-} + \text{H}_2\text{O} \quad \Delta H = -50 \text{ kJ/mol} \quad (-0.52 \text{ eV}) \quad (1)
\]

The reaction was studied previously by Bohme \textit{et al.}, who employed the flowing afterglow method at room temperature to determine the rate coefficient and the equilibrium constant.\textsuperscript{4} These workers found that the observed rate of proton transfer was approximately 50\% larger than the predictions of the Langevin and Average Quadrupole Orientation (AQO) theories.\textsuperscript{5} Raksit and Bohme reported the influence of hydration on the reactivity of the hydroxide anion in the gas phase with measurements of the rates and ion products of several reactions.\textsuperscript{6} The results indicate that the rate of proton transfer to OH\textsuperscript{−} is extremely sensitive to the degree of hydration. Carsky, Zahradnik and co-workers performed \textit{ab initio} calculations for the equilibrium constant of the title reaction and compared it with experimental results.\textsuperscript{7,8} Dolgounitcheva and co-workers studied the structures and energies of the reaction intermediates with \textit{ab initio} calculations at the SCF/MP2 level of theory.\textsuperscript{9} The present study provides both new experimental and
theoretical insight into the proton transfer reaction (1) that refines and extends knowledge of the reaction dynamics at the level of the potential energy surface.

II. Experimental

The experimental apparatus has been described previously, so only a brief review is given here. Reactant ions are produced in an electron impact ion source containing a gaseous mixture of 5% NH₃ (99.99%) in N₂O (99.6%). OH⁻ ions are produced by the ion-molecule reaction of O⁻, formed by dissociative ionization of N₂O, with NH₃. The exothermicity of the reaction of O⁻ with NH₃ is -11 kJ/mol, insuring that the reactant OH⁻ ions are produced in the ground vibrational state. The measured pressure in the initial focusing stage vacuum chamber is approximately 5 × 10⁻⁵ Torr, leading to an estimated pressure of 10⁻² Torr in the ionization region. The ions are accelerated to 300 V, and are then mass-selected with a 60° magnetic sector. After deceleration to the desired beam energy and focusing by a series of ion optics, the beam has an energy distribution with a FWHM of 0.22 - 0.26 eV, corresponding to 40% of the laboratory energy at the lowest collision energy, and only 12% at the highest energy. Experiments were performed at three energies over a relative collision energy range of 0.37 to 1.40 eV. The acetylene gas (98%) is first passed through a cold trap to remove the acetone impurity. The beam is formed by supersonic expansion of the pure gas through a 0.07 mm nozzle and a 1.0 mm skimmer. Following collimation in a differentially-pumped vacuum chamber, the neutral beam enters the main collision chamber, where it intersects the ion beam at 90°. A tuning fork chopper modulates the neutral beam at 30 Hz, allowing the separation of background from the true reactive
scattering signal. An electrostatic energy analyzer with resolution of 0.07 eV is used to measure the kinetic energy distributions of the reactant and product ions. The energy analyzer is calibrated before and after each experiment using the resonant charge transfer reaction between NO$^-$ and NO to provide a thermal energy marker for the energy analyzer. The product ions are mass-analyzed by a quadrupole mass spectrometer and detected by a dual microchannel plate ion detector.

Two independent measurements are performed in each experiment. The kinetic energy distributions of the scattered product ions are measured at 19-23 fixed laboratory angles based on the signal level. The kinetic energy distributions are then normalized by measuring angular distributions of product ions in the laboratory coordinate system by summing up the signal over all energies. The angular distributions are corrected for beam drifting and detection efficiency by returning to a reference angle periodically and assuming that the drift of the signal is linear in time.

III. **Data analysis**

Data analysis begins with the transformation of the measured kinetic energy and angular distributions of products to center of mass (c.m.) coordinates. The reactant beams in the experiments have velocity and angular spreads, resulting in distributions of collision energies and intersection angles. The laboratory flux at a particular scattering angle and velocity is expressed as an integral of the c.m. cross section over the beam velocity distributions $f_i(v_i)$, summed over final quantum states $\{n\}$ according to equation (2):
This equation for the laboratory flux can be recast as a summation given by equation (3) that can be inverted to the c.m. cross section from the laboratory flux distributions by iterative deconvolution\textsuperscript{11}

\[
I_{\text{lab}}(v, \Theta) = \sum_{i=1}^{N} f_i \frac{v_i^2}{u_i} I_{\text{c.m.}}(u, \theta_i)
\]  

In this expression, \(v\) and \(u_i\) are the velocities in the laboratory and c.m. coordinates, respectively; the factors \(f_i\) represent the weights of Newton diagram \(i\) based on the reagent beam distributions. Five points are used to represent the energy distributions of each of the two reagent beams, and five points represent the intersection angle distribution; thus, in equation (3), \(N\) is 125. The extracted \(I_{\text{c.m.}}(u, \theta)\) when transformed back to the lab frame with complete averaging over the beam velocity distributions and detector resolution reproduce the laboratory data within 7 to 9%.

The barycentric angular distribution \(g(\theta)\) of the products can be calculated by integrating the derived \(I_{\text{c.m.}}(u, \theta)\) over product translational energy\textsuperscript{12}. The function \(g(\theta)\) represents the relative intensities of products scattered into c.m. scattering angle \(\theta\) averaged over product kinetic energy, evaluated by integration over c.m. speed \(u\), as follows:

\[
g(\theta) = \int_{0}^{\infty} I_{\text{c.m.}}(u, \theta) du
\]  

Similarly, the angle-averaged relative translational energy distributions of products, \(P(E_T')\), are calculated by integrating the c.m. intensities over the appropriate angular range as indicated by equation (5):
\[ P(E_{\gamma}) = \int_{0}^{\pi} u^{-1} I_{c.m.}(u, \theta) \sin \theta d\theta \]

The full flux distributions in velocity space as well as the kinetic energy and angular distributions derived from them provide important physical insight into the nature of reactive collisions.

IV. Results

The proton transfer reaction \( \text{OH}^- + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}^- + \text{H}_2\text{O} \) was studied at relative energies of 0.37, 0.91, 1.40 eV. The flux distributions in c.m. coordinates for the \( \text{C}_2\text{H}^- \) products were obtained by iterative deconvolution as described previously. Figures 1-3 show the flux distributions for the \( \text{C}_2\text{H}^- \) products at these collision energies. In the c.m. coordinate system, the directions of the \( \text{OH}^- \) ion beam and \( \text{C}_2\text{H}_2 \) neutral beam are 0° and 180° respectively.

The experimental results shown in the flux maps indicate that the proton transfer flux distributions are sharply asymmetric; the majority of the \( \text{C}_2\text{H}^- \) products are scattered in the same direction as the precursor \( \text{C}_2\text{H}_2 \) beam, with product velocities similar to the reagent neutral beam velocities. These forward-scattered products indicate that the proton transfer reaction mechanism is direct, proceeding on a time scale much shorter than a rotational period of the transient association complex of the approaching reactants. This impulsive behavior is typical of dynamics of exothermic proton transfer reactions.

The angular distributions and relative translational energy distributions of the products of the proton transfer reaction at all three energies are shown in Figure 4. The widths of the angular distributions show a slight narrowing with increasing collision
energy, consistent with decreased interaction times and thus smaller deflections. Figure 4(b) shows the relative translational energy distributions of the products at different collision energies. As the collision energy increases, the relative translational energy distributions of the products shift towards higher energies; although the distribution widths increase in magnitude, as a fraction of the total energy, the widths actually decrease, decreasing from 72% of the available energy at the lowest collision energy to 47% at the highest.

The energy partitioning results are summarized in Table I. The total energy is the sum of collision energy and reaction exothermicity. The supersonic expansion produces internally cold neutral reactants and the reactant ions, produced by a specific ion-molecule reaction, are in their ground vibrational state. The average values of the product relative energy $E_T'$ for the three distributions shown in Figure 4 (b) are shown in Table I. From conservation of energy, we determine that the fraction of the total energy appearing in product translation increases from 42% to 64% as the collision energy spans the full range studied here. The average internal energy of the reaction products is 0.52 eV (50 kJ/mole) at the lowest collision energy, identical to the reaction exothermicity. With increasing collision energy, the average product internal excitation increases by about one-third to 0.69 eV (67 kJ/mole) at the highest collision energy. The increase in product kinetic energy resulting from increased collision energy, in conjunction with a concomitant narrowing of the product kinetic energy distributions, shows that increased translational energy is selectively focused into product translation. We will discuss the role of the kinematics associated with the heavy + light-heavy mass combination in causing this selectivity in sections to follow.
V. Computational studies

We performed density functional theory (DFT) calculations with the Gaussian 98 program package\textsuperscript{13} in order to elucidate structures of important reactive intermediates and the transition states connecting them. The geometries of all the relevant species were fully optimized at the B3LYP/6-311+G* level, and complex vibrational frequencies were then extracted in the harmonic approximation. Single point energy calculations were performed at the same level based on the geometries and zero-point vibrational energies. Figure 5 shows the reaction coordinate diagram with structures and energies of the key intermediates and energies of the associated transition states. A complete tabulation of the results of all calculations with sketches of the intermediates and transition states is summarized in EPAPS.\textsuperscript{14}

The DFT calculations show that the approaching reactants generate two different initial intermediates, depending on the details of the approach geometry. The first intermediate, denoted 1, corresponds to approach of the oxygen end of OH\textsuperscript{−} toward one of the hydrogen atoms in acetylene, forming a hydrogen-bonded complex of nominal structure C\textsubscript{2}H\textsuperscript{−}⋅⋅⋅OH\textsubscript{2}. This complex serves as direct precursor for the proton transfer product, decaying by simple bond cleavage without a barrier in excess of the reaction endothermicity. No minimum with an acetylene-hydroxide structure was found. This electrostatically bound species indicates that proton transfer occurs at long range while the reactants are approaching.

The second kind of intermediate is characterized by attack of the oxygen end of OH\textsuperscript{−} on a carbon atom and is accompanied by $sp \rightarrow sp^2$ rehybridization on the carbon. Four different isomers result from this approach geometry, according to the relative
stereochemistry of the hydrogen atoms. The lowest energy isomer, shown in Figure 5, lies 96 kJ/mol below the reactants. The hydrogen atoms bound to the carbons are in a cis configuration and the hydrogen atoms bound to the incipient C-O bond are in the trans geometry. Isomerization among all four isomeric forms of complex 2 can occur via internal rotations about either the C-O bond, with activation energies less than 5 kJ/mol, or about the C-C bond, with activation energies between 60 and 80 kJ/mol. The higher activation energies for rotation about the C-C bond in these complexes are consistent with partial double bond character, as are the C-C bond lengths, 1.32 to 1.33 Å. Structural data for all isomers of complex 2 are tabulated in EPAPS.

In complex 2, the hydrogen atom bound to the carbon in the C-O bond may migrate to the second carbon atom, creating complex 3 with two hydrogen atoms bound to the same carbon. Complex 3 has two rotamers of comparable energy, approximately 95 kJ/mol below the reactants. However, the barriers for isomerization from 2 to 3 are more than 110 kJ/mol above the reactants. The high barriers thus suggest that the pathway from complex 2 to 3 does not play an important role in the reaction dynamics.

The most stable intermediate obtained from DFT calculations is the vinyloxy anion, structure 4, which lies 284 kJ/mol below the reactants. Formation of vinyloxy anion from complex 2 occurs by a 1,3-hydrogen atom migration from oxygen to the distal carbon atom over a barrier of ~80 kJ/mol. Vinyloxy anion may lose a hydrogen atom to produce $\text{C}_2\text{H}_2\text{O}^-$, the most stable isomer of which is the ketene anion. However, this decomposition is endothermic by 54 kJ/mol relative to the reactants, and is expected to be a minor channel. The vinyloxy anion may also undergo a 1,2-hydrogen atom migration over a barrier of 270 kJ/mol to form the acetyl anion 5, with all three hydrogen atoms
bound to the same carbon. Acetyl anion may decay to CO + CH₃⁻ products through C-C bond cleavage. The electron affinity of the acetyl radical is 0.516 eV,¹⁵ which makes the CH₃CO + e⁻ products 42 kJ/mol lower than CO + CH₃⁻ products. Thus if complex 5 is formed, one would expect associative detachment to occur. We are unable to detect the electrons from associative detachment; however, the large rate for proton transfer well in excess of the predictions of the Langevin and AQO orbiting complex models suggests that all other channels are insignificant. In particular, reactive processes initiated by the formation of complex 2 are of negligible importance. The chemical reaction products are therefore dominated by the role played by complex 1, in which proton transfer occurs at long distances prior to the formation of the electrostatic complex C₂H⁻…OH₂. Figure 5 shows the relative energies of complexes 1 through 5; all intermediates are in good agreement with those reported by Dolgounitcheva et al.⁹

The DFT calculations allow us to evaluate vibrational frequencies for bound complexes and transition states, which serve as input into rate constant calculations using RRKM statistical theory.¹⁶-¹⁹ By examining the relative rate constants for direct dissociation in comparison with isomerization, we provide further evidence against the participation of complexes other than C₂H⁻…OH₂, complex 1. Complex 1 dissociates to the product over a barrier of 72 kJ/mol. We approximated the transition state frequencies by calculating the structure of complex 1 with the cleaving (O)H-C bond extended to 2.5 Å. This leads to an imaginary frequency corresponding to the stretching vibration of the H-C bond. As discussed by Li and Baer,²⁰ some adjustments for these estimated transition-state frequencies are necessary. In this study, the lowest five frequencies are scaled by a factor of 0.5. By using these frequencies, the activation entropy of the
dissociation reaction, $\Delta S_{600K}^{\neq}$, is determined to be 18.1 J/(mol·K), a characteristic value of a reaction with a loose transition state. The calculations show that the rate of simple decay of complex 1 to the proton transfer product is approximately $1 \times 10^{13}$ s$^{-1}$. All the rate constants reported here refer to the intermediate experimental energy. This rate corresponds to a lifetime of 100 fs for complex 1, two orders of magnitude shorter than the rotational period of the complex estimated from moments of inertia extracted from the DFT calculations. The result is consistent with the direct dynamics we observed for this process. Although Phase Space Theory calculations, which conserve angular momentum explicitly, would provide a more quantitative rate estimate, the RRKM rates discussed here are adequate to check the consistency of the observation that the reaction is direct. In cases where experimental data do suggest, via angular distributions for example, that broader regions of phase space may be populated, PST calculations would be called for. Such calculations have been provided in recent work from our laboratory on the O$^-$ + C$_2$H$_2$ reaction, where formation of the ketenyl anion, HCO$, does appear over a broad angular range.

As noted previously, the high barrier between complexes 2 and 3 suppresses reaction through this pathway. We also calculated the rate constant for the 2 $\rightarrow$ 4 isomerization process to be $4 \times 10^{11}$ s$^{-1}$. The vinyloxy-acetyl anion (4 $\rightarrow$ 5) isomerization process is even slower with a rate of $2 \times 10^9$ s$^{-1}$. Both transition states, TS$_{24}$ and TS$_{45}$, lie slightly below reactants, consistent with the low isomerization rates. We expect these transition states to be tight. Consequently, nonreactive decomposition of complex 2 can play an important role. We estimated the rate constant for decomposition of complex 2 back to reactants to be in the range $2 - 6 \times 10^{12}$ s$^{-1}$, an order of magnitude faster than any
further isomerization process of complex 2. We conclude that after hydroxide attacks acetylene to form complex 2, nonreactive decay is much more favorable than isomerization. Unfortunately, our experiment does not have the kinematic resolution to distinguish nonreactive decay from elastic scattering. Nevertheless, this kinetic argument provides further support for the claim that complex 1 is the exclusive intermediate that leads to the products of chemical reaction.

VI. Discussion

When the oxygen on OH\textsuperscript{−} approaches an H atom on C\textsubscript{2}H\textsubscript{2}, complex 1 will be formed and proton transfer occurs. The proton transfer process forming C\textsubscript{2}H\textsuperscript{−} exhibits many of the characteristics of direct proton transfer that we have studied recently in this laboratory.\textsuperscript{2,24-26} This proton transfer reaction is another example of a heavy + light-heavy system in which a light particle, H, is transferred between heavier molecular fragments. The potential energy surface for this transfer, expressed in scaled and skewed coordinates,\textsuperscript{27} is characterized by an angle of 18° between the entrance and exit channels, essentially the same as for the O\textsuperscript{−} + C\textsubscript{2}H\textsubscript{2} system. The classic energy disposal motif for this mass combination is “mixed energy release”\textsuperscript{28-31} in which the reactions occur with the cleaving and incipient bonds in an extended configuration. Reactive collisions on such highly skewed surfaces are direct, with a strong propensity to cut the corner separating the entrance and exit valleys. These motions correspond to light atom transfer from configurations extended from equilibrium bond lengths with little momentum transfer to the departing heavy atoms and yield reaction products that are vibrationally excited. The data at the lowest collision energy show that 58% of the available energy is
partitioned in product internal excitation. The quantitative transformation of the entire reaction exothermicity into internal excitation is consistent with an early release of the exothermicity with the nascent bond extended from its equilibrium configuration, which is expected for attractive or mixed energy release.

More detailed insight into the reactive dynamics comes from the experimental data at the higher collision energies. At the intermediate collision energy of 0.91 eV, 74% of the incremental translational energy appears in product translation; at the highest collision energy of 1.40 eV, a significantly increased fraction, 94% of the increment, partitions in product translation. As we have noted earlier, the widths of the product kinetic energy distributions decrease, when expressed as a fraction of the total available energy, further emphasizing the selectivity whereby incremental reactant translation appears in product translation. The concept of "induced repulsive energy release" was introduced to address partitioning of incremental translational energy on heavy + light-heavy potential surfaces. In this picture, reactive trajectories with excess translation penetrate far into the "corner" of the highly skewed potential surface where both the forming and breaking bonds are compressed. The trajectory moves into the exit valley with little motion perpendicular to the reaction coordinate, yielding products with high translational excitation. Depending on the extent to which the collision geometry in the corner is bent, the nascent products will partition some of the incident translation into product rotation. The trajectory therefore explores a new portion of the potential surface relative to reference trajectories at lower energies. The corner cutting trajectories that produce vibrationally excited products at lower collision energies are replaced by trajectories at higher translational energy that are more effective at reaching the
compressed configurations that facilitate translation in the separating products. This proton transfer reaction provides a particularly clear example of induced repulsive energy release.

Like the $\text{O}^- + \text{C}_2\text{H}_2$ system, the product kinetic energy distributions at two higher collision energies, shown in Fig. 4(b), exhibit oscillatory structure with spacings of 0.24-0.30 eV. From DFT calculations, the vibrational frequency of C-C stretching in $\text{C}_2\text{H}^-$ is 1907 cm$^{-1}$ (0.24 eV) and O-H stretching in H$_2$O is 3762 cm$^{-1}$ (0.47 eV). We thus assign these spacings to the C-C and O-H stretching excitations. For visualization of the energy disposal, we have superimposed circles of constant barycentric speed corresponding to excitation of the C-C and O-H stretching modes on the Newton diagrams in Figs. 1-3. The O-H stretching frequency is almost twice of the C-C stretching. Therefore its excitations overlap with the latter with even vibrational quanta numbers and can not be distinguished. In Figs. 1-3, the product distributions are peaked at speeds closely corresponding to products with two quanta of C-C stretching or/and first excited O-H stretching. As the collision energy increased, some of the products are excited to C-C stretching with $v=3$. Rotational excitations in either fragment may account for the shifts in the observed peak positions relative to the calculated positions.

V. Conclusions

The crossed beam technique and DFT calculations are used to study the reaction dynamics between OH$^-$ and $\text{C}_2\text{H}_2$. The only reaction channel observed is proton transfer, which is in agreement with Bohme’s work.$^4$ The c.m. flux distributions of the proton transfer product ions at three energies exhibit sharply asymmetry, with the maxima close
to the velocity and direction of the precursor acetylene beam. The proton transfer reaction shows characteristics of both mixed energy release and induced repulsive energy release typical of the energy dependence of the dynamics associated with the heavy + light-heavy mass combination. The RRKM calculations show that the lifetime of the intermediate complex is 100 fs, two orders of magnitude shorter than the rotational period of the complex. The results indicate that the proton transfer reaction proceeds through a direct channel with large impact parameters.

We hope the study of this simple system will provide a foundation for detailed dynamical calculations to confirm and extend the present conclusions, and for studies on more complex systems.
Table 1. Energy partitioning at different relative energies (in eV) for \( \text{OH}^- + \text{C}_2\text{H}_2 \rightarrow \text{H}_2\text{O} + \text{C}_2\text{H}^- \).

<table>
<thead>
<tr>
<th></th>
<th>( E_{\text{rel}} )</th>
<th>( E_{\text{total}} )</th>
<th>( \langle E_{T'} \rangle )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactant relative energy</td>
<td>0.37</td>
<td>0.91</td>
<td>1.40</td>
</tr>
<tr>
<td>Total energy, ( E_{\text{total}} )</td>
<td>0.89</td>
<td>1.43</td>
<td>1.92</td>
</tr>
<tr>
<td>Product average relative energy, ( \langle E_{T'} \rangle )</td>
<td>0.37</td>
<td>0.78</td>
<td>1.23</td>
</tr>
<tr>
<td>( \langle E_{T'} \rangle / E_{\text{total}} )</td>
<td>42%</td>
<td>54%</td>
<td>64%</td>
</tr>
<tr>
<td>Product average internal energy</td>
<td>0.52</td>
<td>0.66</td>
<td>0.69</td>
</tr>
</tbody>
</table>
References


14. See EPAPS Document No. XXX for structural parameters, vibrational frequencies, and electronic energies of all intermediates and transition states. This document can be reached via a direct link in the online article's HTML.
reference section or via the EPAPS homepage
(http://www.aip.org/pubservs/epaps.html).


Figure captions

**Figure 1.** Newton diagram and scattered C\(_2\)H\(^-\) product flux contour map at the collision energy of 0.37 eV. The circles correspond to the velocity space loci of products formed with specified quanta numbers in the C-C stretching mode. The velocity space loci of products with O-H stretching excitation overlap with those of C-C stretching with even vibrational quanta numbers.

**Figure 2.** Newton diagram and scattered C\(_2\)H\(^-\) product flux contour map at the collision energy of 0.91 eV. The circles correspond to the velocity space loci of products formed with specified quanta numbers in the C-C stretching mode. The velocity space loci of products with O-H stretching excitation overlap with those of C-C stretching with even vibrational quanta numbers.

**Figure 3.** Newton diagram and scattered C\(_2\)H\(^-\) product flux contour map at the collision energy of 1.40 eV. The circles correspond to the velocity space loci of products formed with specified quanta numbers in the C-C stretching mode. The velocity space loci of products with O-H stretching excitation overlap with those of C-C stretching with even vibrational quanta numbers.

**Figure 4.** (a) Angular distributions; (b) relative translational energy distributions for C\(_2\)H\(^-\) product in c.m. coordinate at all energies.

**Figure 5.** Schematic reaction coordinate for OH\(^-\) + C\(_2\)H\(_2\) reaction.
OH$^-$ + C$_2$H$_2$ → C$_2$H$^-$ + H$_2$O
$E_{\text{rel}} = 0.37$ eV
\[
\text{OH}^- + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}^- + \text{H}_2\text{O} \\
E_{\text{rel}} = 0.91 \text{ eV}
\]
\[ \text{OH}^{-} + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}^{-} + \text{H}_2\text{O} \]
\[ E_{\text{rel}} = 1.40 \text{ eV} \]

Fig.3
Fig. 4

(a) Graph showing the relationship between the c.m. angle (degrees) and the function $g(\theta)$, with curves labeled for $E_{rel}=0.37$ eV, $E_{rel}=0.91$ eV, and $E_{rel}=1.40$ eV.

(b) Graph showing the distribution of $P(E_{T}'$, eV) with different energy values on the x-axis.
Fig. 5

The diagram illustrates the reaction coordinate and relative energy ($\text{kJ/mol}$) for the reaction $\text{OH}^- + \text{C}_2\text{H}_2 \rightarrow \text{H}_2\text{O} + \text{C}_2\text{H}^-$. The reaction pathway is marked by transition states (TS) labeled as TS$_{23}$, TS$_{24}$, and TS$_{45}$.

The energy levels are as follows:

1. Initial state: $\text{OH}^- + \text{C}_2\text{H}_2$ at $0 \text{ kJ/mol}$
2. Intermediate state 1
3. Intermediate state 2
4. Intermediate state 3
5. Final state: $\text{H}_2\text{O} + \text{C}_2\text{H}^-$ at $-300 \text{ kJ/mol}$