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The Thermal Energy Gas-Phase Reaction between \( \text{D}_2\text{CC}^- \) and \( \text{O}_2 \)

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Rate constants and product branching ratios for the reaction between vinylidene anion, \( \text{D}_2\text{CC}^- \), and molecular oxygen have been determined at 90 and 297 K. The overall measured rate constants are \( 3.8 \times 10^{-10} \) and \( 4.5 \times 10^{-10} \) cm\(^3\) s\(^{-1}\), respectively. The present study has found the reaction to be more complicated than originally reported in the literature. The ionic products observed, listed in order of decreasing abundance, are \( \text{O}_2^- \), \( \text{O}^- \), \( \text{CHD}^- \), \( \text{COD}^- \), and \( \text{OD}^- \). In addition, a substantial associative electron detachment product channel was detected. The measured efficiency (27% at 90 K) of the charge-transfer channel, which produces \( \text{O}_2^- + \text{D}_2 \) suggests that this reaction is driven by the exothermic isomerization of vinylidene (\( \text{D}_2\text{CC} \)) to acetylene (\( \text{DCCD} \)) within the complex. This charge-transfer reaction would be endothermic if the neutral product were vinylidene but is exothermic for production of neutral acetylene.

1. Introduction

The reaction between the vinylidene anion, \( \text{H}_2\text{CC}^- \), and molecular oxygen was first reported by Lindinger et al.\(^1\) 15 years ago. They observed the reaction to proceed by charge transfer; i.e., the \( \text{O}_2^+ \) ion product was observed. The rate constant reported was \( 3.0 \times 10^{-10} \) cm\(^3\) s\(^{-1}\) at 300 K. This rate constant increased to slightly greater than \( 5 \times 10^{-10} \) cm\(^3\) s\(^{-1}\) when the relative (i.e., center of mass) kinetic energy of the reactants was increased to 0.3–0.5 eV by means of an electric field in the flow-drift tube. This increase implies that the reaction is slightly endothermic and hence that the electron affinity of vinylidene is slightly greater than that of \( \text{O}_2 \). Subsequently, the electron affinity of vinylidene was determined to be \( 0.490 \pm 0.006 \) eV.\(^2,3\) i.e., slightly greater than the electron affinity of \( \text{O}_2 \) = \( 0.451 \pm 0.007 \) eV.\(^4,5\) Recently the rate constant for the reaction of \( \text{H}_2\text{CC}^- + \text{O}_2 \) was measured by Guo and Grabowski\(^6\) to be \( (3.4 \pm 0.3) \times 10^{-10} \) cm\(^3\) s\(^{-1}\). They found the charge-transfer reaction

\[
\text{H}_2\text{CC}^- + \text{O}_2 \rightarrow \text{O}_2^- + \text{CH}_2
\]

(1)

to be the major channel and found minor channels leading to production of \( \text{HC}_2\text{H}^+ \) and \( \text{CH}_2\text{OH}^- \). The Langenollion collision rate constant, \( k_L = \frac{2 \sqrt{\pi \alpha}}{\mu} \frac{1}{\mu} \), where \( \alpha \) is the polarizability of \( \text{O}_2 \) and \( \mu \) the reduced mass of the reactant pair, is \( 7.4 \times 10^{-16} \) cm\(^3\) s\(^{-1}\), so that the reaction efficiency, \( k/k_L \), is \( 40–60\% \).

The present investigation was motivated by the realization that the present, precise values of the electron affinities are inconsistent with the reported values of \( k_L \); i.e., the value of the rate constant is larger than \( k_L \). This seemed to imply one of two possibilities: either (a) the reported values of electron affinities and/or rate constants are in error or (b) the reaction is not a simple charge transfer to produce \( \text{O}_2^- \) and vinylidene, \( \text{H}_2\text{CC}^- \), but rather an isomerization-driven charge transfer to produce \( \text{O}_2^- \) and acetylene, \( \text{HCC} \). In the latter case, the substantial exothermicity,\(^3\) vinylidene \( \rightarrow \) acetylene \( \sim 44 \) kcal mol\(^{-1}\) must be utilized to drive the charge transfer.

The first point of the present study was simply to recheck the measured rate constant at room temperature, but the more critical test was planned to be a measurement of \( k_L \) at low temperature. If the product were neutral vinylidene, the energetics require that, at 90 K, the reaction must be extremely slow, with a maximum reaction probability of <1% for the reported electron affinities. The maximum reaction probability increases to 4% if the reported electron affinities with their maximum listed error limits are used. While the current experiment does resolve this point, the reaction has turned out to be far more complex than was previously recognized. The present experiments were made with \( \text{D}_2\text{CC}^- \) for convenience (see below).

2. Experimental Section

The measurements were made in the variable-temperature-selected ion flow drift tube at the Geophysics Laboratory. This instrument has been described in detail previously,\(^7\) and only details relevant to the present experiment are given here. The vinylidene anion was formed in an electron impact ion source from a mixture of \( \text{N}_2\text{O} \) and deuterated ethylene. Deuterated ethylene was used because \( \text{H}_2\text{CC}^- \) and \( \text{CN}^- \) have the same mass. The latter anion is a common impurity in our ion source and was observed to be present as an unreactive component when the ion at \( m/e = 26 \) was reacted with \( \text{O}_2 \). The associative detachment channel was detected by using an electrometer attached to the nose cone at the sampling orifice. As \( \text{O}_2 \) was added, the current to the nose cone decreased until the reaction achieved completion. This decrease is caused by the fact that electrons diffuse rapidly to the walls of our apparatus following associative detachment. After approximately 90% of the \( \text{D}_2\text{CC}^- \) had reacted, the nose-cone current leveled off to a constant value, indicating that the reaction had gone to completion. The leveling off of the nose-cone current upon completion of reaction eliminated two other possible causes of the decrease in current. The first is a change in the sampling pressure and the other is the gradual depletion of \( \text{D}_2\text{CC}^- \) as measured by the rate constant for the reaction with ionic oxygen. The measured efficiency (27% at 90 K) of the charge-transfer channel, which produces \( \text{O}_2^- + \text{D}_2 \) suggests that this reaction is driven by the exothermic isomerization of vinylidene (\( \text{D}_2\text{CC} \)) to acetylene (\( \text{DCCD} \)) within the complex. This charge-transfer reaction would be endothermic if the neutral product were vinylidene but is exothermic for production of neutral acetylene.

### Table I: \( \text{D}_2\text{CC}^- + \text{O}_2 \) Reaction Rate Constants, in Units of \( 10^{-10} \) cm\(^3\) s\(^{-1}\)

<table>
<thead>
<tr>
<th>Product</th>
<th>297 K</th>
<th>90 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O}_2^- )</td>
<td>2.5</td>
<td>2.0</td>
</tr>
<tr>
<td>( \text{O}^- )</td>
<td>0.85</td>
<td>1.0</td>
</tr>
<tr>
<td>( \text{CHD}^- )</td>
<td>0.12</td>
<td>0.10</td>
</tr>
<tr>
<td>( \text{COD}^- )</td>
<td>0.050</td>
<td>0.085</td>
</tr>
<tr>
<td>( \text{OD}^- )</td>
<td>0.009</td>
<td>0.019</td>
</tr>
<tr>
<td>Total</td>
<td>1.1</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>3.8</td>
</tr>
</tbody>
</table>

\(^{1}\) On contract to GL from Systems Integration Engineering, Inc., Lexington, MA.

efficiency with added O₂. The second is the possibility of the product ions diffusing to the walls at a different rate than the D₂CC⁺ ions. As a further test, it was possible to derive a rate constant from the nose-cone-current data that agreed with the rate constant derived from the primary decay to within 20%, substantiating the associative detachment channel as the cause of the decrease in nose-cone current. The fraction of the reaction that proceeded by the associative detachment channel was taken as the fractional decrease in the nose-cone current when enough O₂ was added to drive the reaction to completion. The overall rate constants are accurate to 30%. No correction for mass discrimination was made. However, little mass discrimination is expected in the mass range of ions in this study. Individual rate constants for the major ion channels (>10% of the products) are accurate to 35% and the minor ion channels to 40%. The associative detachment channel is also accurate to 40%.

3. Results

The experimental results are listed in Table I. The total rate constant, \( k = 4.5 \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \) at 297 K, is slightly higher than the earlier values although in agreement within experimental uncertainty.¹ As noted above, the present experiments were performed using deuterated vinylidene anion for convenience. This may be the reason the present values are slightly higher than previous measurements where \( \text{H}_2\text{CC}^- \) was used.

The suprise in the present results at 291 K is that only half of the reactions produce \( \text{O}_2^- \). Since the total rate constant, determined from the \( \text{D}_2\text{CC}^- \) loss, was previously assumed to be for charge transfer only,¹ the charge-transfer rate constant was overestimated by a factor of 2.

The second most prominent reaction channel, 25%, is associative detachment to produce neutrals and free electrons. It is always difficult in this type of experiment to recognize a minor associative detachment channel because of the absence of a detectable ion product. Very careful considerations of mass discrimination are required to deduce the occurrence of a minor associative detachment channel from the imbalance of reactant ion loss and product ion production. Use of an electrometer, as in the present experiments, to measure the nose-cone current alleviates this problem.

The second most abundant ion product, \( \text{O}^- \) (19%), was missed in earlier flowing afterglow experiments.² In these earlier experiments, ethylene was present in the flow tube as the source of the reactant \( \text{H}_2\text{CC}^- \). Ethylene rapidly reacts with \( \text{O}^- \) to produce \( \text{H}_2\text{C}^- \) (∼30%) and products of associative detachment (∼70%).³

\[
\text{O}^- + \text{H}_2\text{C} = \text{H} \rightarrow \text{H}_2\text{CC}^- + \text{H}_2\text{O} \quad (2a)
\]

This secondary reaction is significantly faster than the reaction of \( \text{H}_2\text{CC}^- \) with \( \text{O}_2 \).⁴

In addition to the major products, the trace products \( \text{C}_2\text{D}^- \) (3%), \( \text{C}_2\text{OD}^- \) (1%), and \( \text{OD}^- \) (∼0.2%) were observed in the present study, making the reaction of \( \text{D}_2\text{CC}^- \) with \( \text{O}_2 \) a remarkably complex (and rich) process. The observation of \( \text{C}_2\text{D}^- \) supports the findings of Guo and Grabowski.⁶

At 297 K, the overall rate constant drops by about 16%. This decrease is largely in the two major channels (as it must be); i.e., the \( \text{O}_2^- \) channel (∼20%) and the associative detachment channel (∼53%). The \( \text{O}^- \) channel actually increases slightly (∼+18%). Since the Langewin collision rate constant is independent of temperature, the reaction efficiency decreases from 61% at 297 K to 51% at 90 K.

4. Discussion

Table II gives the exothermicities for the observed reactions. The reaction products for the ion-atom interchange reactions appear to be unique, although the \( \text{C}_2\text{D}_2\text{O} \) neutral may be either

TABLE II: Reaction Energetics at 298 K (from References 3, 5, and 11) for the Reaction \( \text{D}_2\text{CC}^- + \text{O}_2 \rightarrow \text{Products} \)

<table>
<thead>
<tr>
<th>products</th>
<th>( -\Delta H ), kcal mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O}_2^- + \text{D}_2\text{CC}^- )</td>
<td>0.9 ± 0.23</td>
</tr>
<tr>
<td>( \text{O}_2^- + \text{D}_2\text{CC}=\text{CD} )</td>
<td>43</td>
</tr>
<tr>
<td>( \text{O}_2^- + \text{D}_2\text{CC}=\text{CO} )</td>
<td>126</td>
</tr>
<tr>
<td>( \text{D}_2\text{CC}=\text{CO} + \text{OD} )</td>
<td>92.6</td>
</tr>
<tr>
<td>( \text{D}_2\text{OD} + \text{CO} )</td>
<td>21.8</td>
</tr>
<tr>
<td>( \text{O}_2^- + \text{D}_2\text{CC}=\text{CO} + \text{e} )</td>
<td>80</td>
</tr>
<tr>
<td>( \text{O}_2^- + \text{D}_2\text{CC}=\text{CO} + \text{e} )</td>
<td>35</td>
</tr>
<tr>
<td>( \text{D}_2\text{CC}=\text{CO} + \text{OD} + \text{e} )</td>
<td>38</td>
</tr>
<tr>
<td>( \text{D}_2\text{CC}=\text{CO} + \text{e} )</td>
<td>68.3</td>
</tr>
<tr>
<td>( \text{D}_2\text{CC}=\text{CO} + \text{OD} + \text{e} )</td>
<td>140</td>
</tr>
<tr>
<td>( \text{D}_2\text{CC}=\text{CO} + \text{OD} + \text{e} )</td>
<td>68.3</td>
</tr>
</tbody>
</table>

\( \text{D}_2\text{CC}=\text{CO} + \text{OD} \) or \( \text{D}_2\text{CC}=\text{CO} + \text{OD} \). The heat of formation of the latter neutral is unknown, but formation of this product should certainly be exothermic.

The charge-transfer reaction could lead either to vinylidene or to acetylene as the neutral \( \text{C}_2\text{D}_2\text{O} \) product, a point that warrants further discussion. In addition, there are six exothermic associative detachment channels available. These reactions are discussed below.

4a. Charge-Transfer. The present finding of a lower rate constant than previously reported¹ for charge transfer at 297 K resolves, in part, the problem we set out to investigate; i.e., the present rate constant, \( k_1(297 \, \text{K}) = 2.5 \times 10^{-11} \, \text{cm}^3 \, \text{s}^{-1} \), is in better accord with the maximum allowable value for simple charge transfer, assuming that vinylidene is produced, \( k = k_1 \exp[-\Delta H/kT] = 1.65 \times 10^{-14} \, \text{cm}^3 \, \text{s}^{-1} \). The value of the endothermicity \( \Delta H = 0.9 \pm 0.23 \, \text{kcal mol}^{-1} \) just rules out vinylidene isomerization production. The model would be that the electron transfer occurs with high probability after capture. The latter process has a maximum impact parameter of 5.7 Å for the average thermal relative velocity at 297 K. The model also assumes that electron transfer takes place before a sufficiently intimate collision can occur that leads to ion-atom interchange, i.e., \( \text{O}^- \) production. This process presumably occurs at a distance comparable to stable molecular bond lengths (the order of 2–3 Å). There is no possibility of an experimental determination of the neutral product, since neutral vinylidene isomerizes to acetylene on an extremely short time scale, \( r = 0.04–0.2 \, \text{ps} \), and indeed has never been directly observed.

The situation at 90 K is quite different. The observed rate constant for charge transfer, \( 2 \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \), far exceeds the limiting value \( k = k_1 \exp[-\Delta H/kT] = 5.3 \times 10^{-12} \, \text{cm}^3 \, \text{s}^{-1} \) and indeed exceeds this limit even when the total uncertainty in the electron affinities of \( \text{D}_2\text{CC} \) and \( \text{O}_2 \), taken in the most favorable sense to give \( k_{\text{max}} = k_1 \exp[-\Delta H_{\text{max}}/kT] = 3.0 \times 10^{-11} \, \text{cm}^3 \, \text{s}^{-1} \). The conclusion is inescapable that the charge transfer at 90 K must produce \( \text{O}_2^- + \text{D}_2\text{CC} \), utilizing the large vinylidene → acetylene isomerization energy to drive the reaction, at least in a large percentage of the charge-transfer reactions. This is, to our knowledge, the first reported example of an isomerization-driven charge-transfer reaction.

The mechanism for utilizing the isomerization energy to drive the reaction is straightforward. The endothermic charge transfer can occur in the collision complex, wherein the endothermicity of 0.9 kcal mol⁻¹ is supplied by the electrostatic interaction potential. The well depth of this potential is about 5 kcal mol⁻¹, as deduced from typical electrostatic bonds for small ions clustered to neutrals with polarizabilities comparable to that of \( \text{O}_2 \). Following charge transfer, the exothermic vinylidene → acetylene isomerization, \( \Delta H \sim -44 \, \text{kcal mol}^{-1} \), will rapidly blow the collision complex apart, yielding, of course, \( \text{O}_2 \) and acetylene. The

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The most likely ion products, namely, the six possible, exothermic rearrangement with the electron remaining on the other product. The rate constants for both reactions increase significantly with temperature, which may reflect the barrier associated with the initial endothermic charge transfer. The subsequent vinylidene isomerization may simply collisionally detach the weakly bound electron on O₂⁺ (10.4 kcal mol⁻¹) in the dissociation process, with 22% efficiency at 90 K and 33% at 297 K, rather naturally increasing with energy.

The most exothermic associative detachment channel, to produce D-CO-CO-D + e + 140 kcal mol⁻¹ can be rejected out of hand due to the complexity of rearrangement required. A straightforward associative detachment process is the simple addition to produce D₂C=C=O + e + with an estimated exothermicity of ~50 kcal mol⁻¹. This is somewhat analogous to the CO association with the vinylidene anion, known to be fast to produce D₂C=C=O + e +.

4c. O⁺ + C₂D₂O Production. The most abundant product after charge transfer and associative detachment is that from the O⁺ + C₂D₂O production channel. The reaction to produce D₂C=C=O is very exothermic and relatively straightforward. A simple O⁺ transfer to H₂CC⁻ from O₂⁺, leaving O⁺, is required. The slight increase upon lowering the temperature is consistent with the typical behavior of slow (i.e., k ≪ k_l) reactions involving complexes. The number of competitive processes for the D₂C⁺ + O₂ reaction makes any simple interpretation of the temperature dependence speculative, however.

4d. C₂D⁺ + O₂ Production. This 4% channel can be explained simply as a D atom abstraction by O₂ that decreases slightly with a lowering of the temperature.

4e. C₂OD⁺ + DO and C₂OD⁺ + DO⁺ Production. The 1-2% DCCO⁺ + DO channel appears to be more complex than the previous, more abundant channels. Two concerted bond breakings, C-D and O-O, and two new bond formations, O-D and C-O, are required. The DCCO⁺ + DO⁺ reaction is the same bonding rearrangement with the electron remaining on the other product.

5. Summary

The thermal (and 90 K) reaction between the vinylidene anion and O₂ is found to be far more complicated than originally reported, with five negative ion products observed, together with a substantial associative detachment channel to produce free electrons. The substantial reaction efficiency for O₂⁺ production at 90 K, 27%, requires that the neutral product be acetylene, not vinylidene, since otherwise the reaction would be endothermic. This appears to be the first observation of an isomerization-driven charge transfer, i.e., a reaction in which simple electron transfer is endothermic but for which the energy deficit is supplied by an exothermic isomerization of the product neutral. The mechanism proposed for this is straightforward: the endothermic initial charge transfer is driven by the electrostatic (ion-induced dipole) attraction, and then the trapped O₂⁺ ion-vinylidene complex is blown apart by the very exothermic, very rapid vinylidene → acetylene isomerization.

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