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The Thermal Energy Gas-Phase Reaction between D_2CC^- and O_2

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Rate constants and product branching ratios for the reaction between vinylidene anion, D_2CC^-, and molecular oxygen have been determined at 90 and 297 K. The overall measured rate constants are 3.8×10^{-10} and 4.5×10^{-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 O_2^-, O^-, C_2D^-, C_2OD^-, and 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 $O_2^- + C_2D_2$, suggests that this reaction is driven by the exothermic isomerization of vinylidene (D_2CC) to acetylene (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, H_2CC^-, 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 O_2^- ion product was observed. The rate constant reported was 3.0×10^{-10} cm^3 s^{-1} at 300 K. This rate constant increased to slightly greater than 5×10^{-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 O_2. Subsequently, the electron affinity of vinylidene was determined to be 0.490 ± 0.006 eV,[2,3] i.e., slightly greater than the electron affinity of $O_2 = 0.451 \pm 0.007$ eV.[4,5] Recently the rate constant for the reaction of H_2CC^- with 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

$$H_2CC^- + O_2 \rightarrow O_2^- + C_2H_2 \qquad (1)$$

to be the major channel and found minor channels leading to production of C_2H^- and C_2OH^-. The Langevin collision rate constant, $k_L = 2\pi e(\alpha/\mu)^{1/2}$, where α is the polarizability of O_2 and μ the reduced mass of the reactant pair, is 7.4×10^{-10} 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_1; i.e., the value of the rate constant is larger than $k_L \exp(-\Delta H/kT) = 1.65 \times 10^{-10}$ cm^3 s^{-1}. This seemed to imply one of two possibilities: either (a) the reported values of electron affinities and/or rate constant are in error or (b) the reaction is not a simple charge transfer to produce O_2^- and vinylidene, H_2CC, but rather an isomerization-driven charge transfer to produce O_2^- and acetylene, HCCH. In the latter case, the substantial isomerization exothermicity,[3] vinylidene → acetylene of ~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_1 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 realized. The present experiments were made with D_2CC^- for convenience (see below).

TABLE I: $D_2CC^- + O_2$ Reaction Rate Constants, in Units of 10^{-10} cm^3 s^{-1}

product	297 K	90 K
O_2^-	2.5	2.0
O^-	0.85	1.0
C_2D^-	0.12	0.10
C_2OD^-	0.050	0.085
OD^-	0.009	0.019
associative detachment	1.1	0.58
total	4.5	3.8

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 N_2O and deuterated ethylene. Deuterated ethylene was used because H_2CC^- and 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 O_2. The associative detachment channel was detected by using an electrometer attached to the nose cone at the sampling orifice. As 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 D_2CC^- 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

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efficiency with added O_2. The second is the possibility of the product ions diffusing to the walls at a different rate than the D_2CC^- 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 O_2 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, $k = 4.5 \times 10^{-10}$ cm^3 s^{-1} at 297 K, is slightly higher than the earlier values although in agreement within experimental uncertainty.[1,6] 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 H_2CC^- was used.

The suprise in the present results at 297 K is that only half of the reactions produce O_2^-. Since the total rate constant, determined from the D_2CC^- loss, was previously assumed to be for charge transfer only,[1,6] 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 ionic product, O^- (19%), was missed in earlier flowing afterglow experiments.[1,6] In these earlier experiments, ethylene was present in the flow tube as the source of the reactant H_2CC^- ion. Ethylene rapidly reacts with O^- to produce H_2CC^- (~30%) and products of associative detachment (~70%).[8]

$$O^- + H_2CCH_2 \rightarrow H_2CC^- + H_2O \quad (2a)$$

$$\rightarrow \text{neutrals} + e \quad (2b)$$

This secondary reaction is significantly faster than the reaction of H_2CC^- with O_2.[8]

In addition to the major products, the trace products C_2D^- (3%), C_2OD^- (1%), and OD^- (~0.2%) were observed in the present study, making the reaction of D_2CC^- with O_2 a remarkably complex (and rich) process. The observation of C_2D^- supports the findings of Guo and Grabowski.[6]

At 90 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 O_2^- channel (-20%) and the associative detachment channel (-53%). The O^- channel actually increases slightly (~+18%). Since the Langevin 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 C_2D_2O neutral may be either $D_2C{=}C{=}O$ or $DC{\equiv}C{-}OD$. The heat of formation of the latter neutral is unknown, but formation of this product should certainly be exothermic.

TABLE II: Reaction Energetics at 298 K (from References 3, 5, and 11) for the Reaction $D_2CC^- + O_2 \rightarrow$ Products

products	$-\Delta H$, kcal mol^{-1}
$O_2^- + D_2C{=}C$	-0.9 ± 0.23
$O_2^- + DC{\equiv}CD$	43
$O^- + D_2C{=}C{=}O$	126
$DC{\equiv}CO^- + OD$	92.6
$C_2D^- + DO_2$	21.8
$OD^- + DC{=}CO$	80
$O_2 + DC{\equiv}CD + e$	35
$O + D_2C{=}C{=}O + e$	41.5
$DC{\equiv}CO + OD + e$	38
$2DCO + e$	68.3
$D{-}CO{-}CO{-}D + e$	140
$D_2C{=}C{-}O{-}O + e$	~50 (est)

The charge-transfer reaction could lead either to vinylidene or to acetylene as the neutral C_2D_2 product, a point that warrants further discussion. In addition, there are six exothermic associative detachment channels available. These reactions are discussed below.

4.a. Charge-Transfer. The present finding of a lower rate constant than previously reported[1] 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 K) = 2.5×10^{-10} cm^3 s^{-1}, is in better accord with the maximum allowable value for simple charge transfer, assuming that vinylidene is produced, $k = k_L \exp(-\Delta H/kT) = 1.65 \times 10^{-10}$ cm^3 s^{-1}. The value of the endothermicity $\Delta H = 0.9 \pm 0.23$ kcal mol^{-1} is just the difference in electron affinities of D_2CC and O_2, obtained from high-precision photodetachment experiments.[3,5] These values are close enough to be inconclusive. The rate constant is larger than the maximum allowed, but the combined uncertainties in the rate constant and the endothermicity cannot rule out vinylidene 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., 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, $\tau \approx 0.04$-0.2 ps,[3] and indeed has never been directly observed.

The situation at 90 K is quite different. The observed rate constant for charge transfer, 2×10^{-10} cm^3 s^{-1}, far exceeds the limiting value $k = k_L \exp(-\Delta H/kT) = 5.3 \times 10^{-12}$ cm^3 s^{-1} and indeed exceeds this limit even when the total uncertainty in the electron affinities of (D_2CC) and (O_2) is taken in the most favorable sense to give $k_{max} = k_L \exp(-\Delta H_{max}/kT) = 3.0 \times 10^{-11}$ cm^3 s^{-1}. The conclusion is inescapable that the charge transfer at 90 K must produce O_2^- + DCCD, 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 O_2.[9] Following charge transfer, the exothermic vinylidene → acetylene isomerization, ΔH ~-44 kcal mol^{-1}, will rapidly blow the collision complex apart, yielding, of course, O_2^- and acetylene. The

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isomerization time $\sim 10^{-13}$ s[3] is comparable to a thermal "fly-by" time, $\tau \sim d/v \sim 10^{-8}$ cm/10^5 cm s^{-1}, and very much shorter than a typical orbiting collision complex lifetime for an ion complexed with O_2 or any neutral of comparable polarizability. Such lifetimes are typically $>10^{-12}$ s, as deduced from three-body-association rate constants. The D_2CC^-–O_2 complex lifetime could indeed be anomalously long as a result of the absorption of translational energy by the endothermic charge transfer, a process that has been called "endothermic trapping" and used successfully to explain several anomalously long ion–neutral complex lifetimes.[10]

Since the electrostatic well depth that drives the initial charge transfer at 90 K, ~5 kcal mol^{-1}, is large compared to kT at 297 K, ~0.6 kcal mol^{-1}, it seems likely that the mechanism of the reaction is the same at 297 and 90 K, i.e., an isomerization-driven charge transfer. We cannot be definite on this point at 297 K, since the endothermic product channel leading to O_2^- plus vinylidene could be driven by thermal energy alone at 297 K. In a sense this might appear to be almost a semantic point, since the vinylidene will isomerize to acetylene on a short time scale in either case. However, the mechanistic distinction seems to be a real one. A conceivable experimental test (although an extremely difficult one) might be to measure the kinetic energy release of products. If the separation requires the vinylidene isomerization, then the exothermicity should show up largely as kinetic energy of the products, ~1 eV for each of the O_2^- and DCCD products. Production of vinylidene would result in low-energy products. Guo and Grabowski[6] have also discussed a model in which vinylidene → acetylene isomerization occurs after electron transfer to O_2 in the complex, leading to both the O_2^- + HCCH and the HCC^- + HO_2 product channels.

4.b. Associative Detachment. The six possible, exothermic associative detachment reactions of Table II correspond in every case to an ion–atom interchange reaction in which the exothermicity is so large that the electron can be detached. The point of view that the reactions with and without detachment are variations of the same mechanistic process of bond rearrangements with different partitioning of the exothermicity may be helpful in deciding the most likely neutral products. The 2DCO + e channel does not have a counterpart DCO^- + DCO channel, in spite of its exothermicity, and might be excluded on this basis as well as via the more compelling argument against a reaction involving the concerted breaking of three bonds (and the making of three new bonds).

The most likely neutral products may be those that correlate with the most likely ion products, namely, O_2 + DC≡CD + e. 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 O_2^- (10.4 kcal mol^{-1})[3] 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 D_2C=C—O—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 D_2C=C=C=O + e.[6]

4.c. O^- + C_2D_2O Production. The most abundant product after charge transfer and associative detachment is that from the O^- + C_2D_2O production channel. The reaction to produce D_2C=C=O is very exothermic and relatively straightforward. A simple O^+ transfer to H_2CC^- from O_2, leaving O^-, is required. The slight increase upon lowering the temperature is consistent with the typical behavior of slow (i.e., $k \ll k_L$) reactions involving complexes. The number of competitive processes for the D_2CC^- + O_2 reaction makes any simple interpretation of the temperature dependence speculative, however.

4.d. C_2D^- + DO_2 Production. This 4% channel can be explained simply as a D atom abstraction by O_2 that decreases slightly with a lowering of the temperature.

4.e. C_2OD^- + DO and C_2OD + 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 O_2 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 O_2^- 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 O_2^- ion–vinylidene complex is blown apart by the very exothermic, very rapid vinylidene → acetylene isomerization.

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