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Is the Elusive Trioxydehydroethene Neutral (O_2C-CO) Detectable in the Gas Phase?

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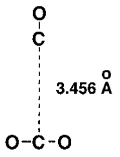
The covalently bound radical anion $[O_2C-CO]^{-\bullet}$ is formed when 1,3-dioxolane-2,5-dione captures an electron followed by retro-cleavage of CH_2O. Calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory indicate that there are a number of neutral isomers with formula C_2O_3, viz. van der Waals complex O_2C- - -CO (rel. energy = 0 kcal mol^{-1}), singlet oxiran dione (+60.9 kcal mol^{-1}), triplet OCOCO (+99.4 kcal mol^{-1}), covalently bound triplet O_2C-CO (+ 107.6 kcal mol^{-1}), singlet trioxapropellane (+171.9 kcal mol^{-1}) and triplet trioxapropellane (+ 222.4 kcal mol^{-1}). Of these, only triplet O_2C-CO is accessible by vertical Franck−Condon one-electron oxidation of $[O_2C-CO]^{-\bullet}$. Neutralization reionization experiments of $[O_2C-CO]^{-\bullet}$ (both $^-NR^+$ and $^-NR^-$) fail to produce recovery signals corresponding to ionized C_2O_3, which means that if neutral C_2O_3 is stable, the lifetime must be $<10^{-6}$ sec. The $^-NR^+$ spectrum of $[O_2C-CO]^{-\bullet}$ shows peaks corresponding to $CO^{+\bullet}$, $CO_2^{+\bullet}$ and to $[O{=}C{=}C{=}O]^{+\bullet}$. The last of these species can only be formed from a decomposing $C_2O_3^{+\bullet}$ radical cation by a process endothermic by 47 kcal mol^{-1} [at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory]. Calculations at this same level of theory indicate that the vertical one-electron oxidation of $[O_2C-CO]^{-\bullet}$ to triplet O_2C-CO ground state produces the neutral with essentially no excess energy. There are two dissociation pathways of this triplet neutral, (i) an endothermic process yielding $^3CO + {}^1CO_2$ (+ 28.9 kcal mol^{-1}), and (ii) an exothermic process (−6.8 kcal mol^{-1}) with a barrier of 5.4 kcal mol^{-1} yielding $^1CO + {}^3CO_2$. A combination of experimental and theoretical data, suggests that vertical oxidation of $[O_2C-CO]^{-\bullet}$ produces only one neutral C_2O_3 isomer; a transient triplet O_2C-CO neutral whose lifetime is less than 10^{-6} sec.

Introduction

Carbon monoxide and carbon dioxide cluster ions are important in atmospheric chemistry. Carbon dioxide cluster neutrals and ions have been studied extensively in the gas phase, including their photoelectron,[1−6] vibrational,[7−10] electron spin resonance,[11−13] and infrared[14,15] spectra. The van der Waals complex between carbon dioxide and carbon monoxide was first formed in a pulsed molecular beam using diode laser spectroscopy combined with Fourier transform microwave spectroscopy.[16] This CO_2-CO complex has since been studied extensively both experimentally and theoretically.[17−21] The complex is proposed to have the T-shaped geometry shown in **1**,[22] but infrared spectroscopy suggests that there may be two stable conformers of the complex.[20,21]



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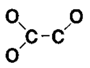

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We have used neutralization/reionization of negative ions ($^-NR^+$)[23] in a mass spectrometer to investigate the formation and characterization of short-lived neutrals in the gas phase.[e.g.24] Recently, we have shown that triplet ethylene dione ($O{=}C{=}C{=}O$) (which has been calculated to be stable with respect to dissociation to singlet and triplet carbon monoxide) cannot be observed using either $^-NR^+$ or $^-NR^-$ experiments from $[O{=}C{=}C{=}O]^{-\bullet}$.[25] Neutral $O{=}C{=}C{=}O$ is thus not detectable within the microsecond neutral lifetime of this experiment. This must mean that either the neutral is formed with sufficient excess energy to effect dissociation to carbon monoxide or the triplet neutral spin inverts to the singlet form of $O{=}C{=}C{=}O$, which is unstable with respect to dissociation to carbon monoxide.[25]

Our work on ethylene dione leads us to ask whether there is a stable trioxydehydroethene, with bond connectivity as shown in **2**. The van der Waals complex CO_2-CO (**1**) will certainly not be stable under the experimental conditions used for an NR experiment. Any C_2O_3 neutral detected during an NR experiment, must either be covalently bound or held together electrostatically. The aims of this study were therefore as follows: (i), to make a precursor anion radical $C_2O_3^{-\bullet}$ with bond connectivity corresponding to **2**, and (ii), to determine whether vertical one-electron oxidation of this anion radical forms a detectable trioxydehydroethene neutral.

Experimental Section

A. Mass Spectrometric Methods. For a detailed description of the experiment and the instrument used, see ref 26. In brief, the experiments were performed using a two-sector modified VG ZAB 2HF mass spectrometer with BE configuration, where B and E represent magnetic and electric sectors, respectively. The $C_2O_3^{-\bullet}$ radical anion was generated by chemical ionization (CI) in the negative ion mode, with typical source conditions as follows: source temperature 200 °C, repeller voltage −0.5 V, ion extraction voltage 7 kV, mass resolution $m/\Delta m \geq 1500$. The precursor, 1,3-dioxolane-2,5-dione, was placed in a small glass capillary tube which was then drawn out in a flame to create a very fine aperture, allowing for a slow steady release of sample vapor upon heating. The capillary was inserted into

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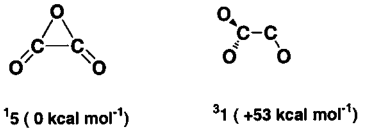
SCHEME 1



the CI source via the direct probe; the probe tip was heated to 60−80 °C to generate a background pressure of ca. 10^{-5} Torr inside the source housing. The $C_2O_3^{-\bullet}$ anion radical was formed by electron capture followed by loss of CH_2O as shown in Scheme 1, utilizing hexane as the CI reagent gas at a pressure of ca. 10^{-4} Torr inside the source housing.

Collisional induced dissociation (CID) of B mass selected $C_2O_3^{-\bullet}$ was effected in the first of the two tandem collision cells positioned between B and E. Argon was used as a target gas. The pressure of the collision gas in the cell was maintained such that 80% of the parent ion beam was transmitted through the cell. This corresponds to an average of 1.1−1.2 collisions per ion.[27] Product ions resulting from CID were recorded by scanning E.

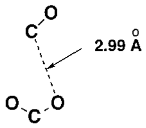
Neutralization-reionization[23] ($^-$NR$^+$ or $^-$NR$^-$ as appropriate) experiments were performed for B mass-selected $C_2O_3^{-\bullet}$ utilizing the dual collision cells located between sectors B and E. Neutralization of the anions was achieved by collisional electron detachment using O_2 at 80% transmittance as collision gas, whereas reionization to cations was achieved by collision of the neutrals with O_2, again at 80% transmittance. Ionization to anions in the second cell was performed using benzene as reagent gas at 80% transmttance. Any ions remaining after the first collision event were deflected from the primary neutral beam using an electrode maintained at a high voltage (1.5 kV) positioned before the second collision cell. To detect a reionization signal due to the parent, the neutral species must be stable for approximately one microsecond. Charge reversal ($^-$CR$^+$) spectra[28,29] were recorded using single collision conditions in collision cell 1 (O_2, 80%T).

B. Synthesis of the Precursor. 1,3-Dioxolane-2,5-dione was prepared by a reported method.[30]

C. Theoretical Methods. Geometry optimizations were carried out with the Becke 3LYP method[31,32] using a modest 6-31G(d) basis within the GAUSSIAN 98 suite of programs.[33] Stationary points were characterized as either minima (no imaginary frequencies) or transition structures (one imaginary frequency) by calculation of the frequencies using analytical gradient procedures. The minima connected by a given transition structure were confirmed by intrinsic reaction coordinate (IRC) calculations. The calculated frequencies were also used to determine zero-point vibrational energies which were then scaled[34] by 0.9804 and used as a zero-point correction for the electronic energies calculated at this and higher levels of theory. B3LYP/6-31G(d) has previously been used for geometry optimizations of anions and has demonstrated good correlation with structures calculated using high level coupled-cluster approaches.[35,36] Some problems have been highlighted in the literature regarding the use of the B3LYP method for the accurate prediction of molecular energies for carbon clusters,[37] even though the method continues to be used with success.[38,39] More accurate energies for the B3LYP geometries were determined using the CCSD(T) method[40−45] together with the Dunning aug-cc-pVDZ basis set.[46,47] The CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) approach predicts the adiabatic electron affinity of linear C_4 to be 3.65 eV[24] which is in reasonable agreement with the experimentally measured value of 3.88 eV.[48,49] All calculations were carried out on the Power Challenge Supercomputer or the AlphaServer SC at the Australian National University Supercomputing Facility (Canberra).

Results and Discussion

Experimental Approach to Neutral C_2O_3. The first task is to synthesize the precursor anion $C_2O_3^{-\bullet}$ by an unequivocal route. Anion radicals $C_2O_3^{-\bullet}$ have been reported previously on two occasions. The first study,[50] reports the formation of a $C_2O_3^{-\bullet}$ species by a dissociative process following capture of a low-energy electron by maleic anhydride. No structure was proposed for this species but the (initial) bond connectivity must be O−C−O−C−O. The second and more recent study[51] reports the formation of a stable radical anion $C_2O_3^{-\bullet}$ following laser ablation of transition metal targets with concurrent 11 K deposition of CO_2/CO/Ar mixtures. Theoretical calculations at a number of levels, including B3LYP/aug-cc-PVDZ and MP2/6-311+G(d), suggested that this $C_2O_3^{-\bullet}$ ion could have one of two structures of comparable energy; viz an electrostatic complex **3** and the covalently bound radical anion **4**. Consideration of the computed vibrational frequencies of these two structures with the infrared spectrum of the experimentally derived $C_2O_3^{-\bullet}$ anion suggested that it is structure **4**. The authors suggest that this anion radical is formed by electron capture of the van der Waals complex **1**.[51]



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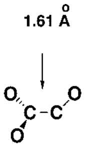

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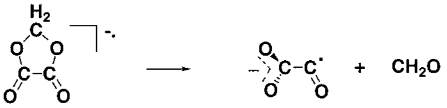
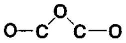
We approached the synthesis of $4^{-\bullet}$ from a precursor neutral which contained the appropriate bond connectivity. The anion radical was synthesized by electron capture of 1,3-dioxolane-2,5-dione, followed by a retro cleavage as shown in eqn **1**.



eqn. 1

The collisional induced mass spectrum of $C_2O_3^{-\bullet}$ (m/z 72) shows a pronounced molecular radical anion, but no fragment anions are observed in this spectrum. Possible fragment anions could be $O^{-\bullet}$ and $CO^{-\bullet}$ (electron affinities of $O^\bullet$ and CO are 1.461[52] and 1.37 eV[53] respectively), whereas the formation of $CO_2^{-\bullet}$ is unlikely under conditions of collisional activation (the electron affinity of CO_2 is − 0.60 eV,[53] but $CO_2^{-\bullet}$ can be observed under low energy conditions[10,54]). The stability of $C_2O_3^{-\bullet}$ is supportive of the formation of $4^{-\bullet}$: $3^{-\bullet}$ would decompose readily under conditions of collisional activation since the lowest energy dissociative pathway to CO_2 and CO is reported to be only some 3 kcal mol^{-1} endothermic.[51]



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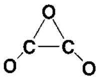

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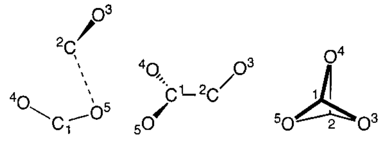
7

We have calculated the structures of $3^{-\bullet}$ and $4^{-\bullet}$ at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. The results are listed in Table 1, and are similar to those obtained earlier by Zhou et al.[51,55] We have also investigated whether there are other stable radical anions of formulas $C_2O_3^{-\bullet}$; viz those corresponding to structures **5** to **7**. These results are also

TABLE 1: Anion Structures ($3^{-\bullet}$), ($4^{-\bullet}$), and ($7^{-\bullet}$)



	$3^{-\bullet}$	$4^{-\bullet}$	$7^{-\bullet}$
state		2A′	$2A_2''$
symmetry	C_1	C_s	D_{3h}
energy (Hartrees)[a]	−301.22629	−301.23312	−301.04053
Rel. energy (kcal mol^{-1})	4.3	0.0	120.9
dipole moment (Debye)[a]	2.89	1.31	0.00
bond length (Å)[b]or angle (°)[b]			
C^1C^2	3.03	1.62	1.64
C^2O^3	1.15	1.20	1.47
C^1O^4	1.24	1.24	1.47
C^2O^4	3.03	2.39	1.47
C^2O^5	2.57		
C^1O^5	1.25	1.24	1.47
$C^1C^2O^3$	106.4	124.4	56.3
$C^2C^1O^4$	78.1	112.6	56.3
$C^2C^1O^5$	56.6	112.6	56.3
$O^3C^2O^5$	104.5		
$O^4C^1O^5$	134.6	134.8	92.2
$O^3C^2C^1O^4$	89.3	91.3	120.0
$O^3C^2C^1O^5$	−88.8	−91.3	−120.0

[a] CCSD(T)/aug-cc-pVDZ level of theory including zero point energy (calculated from vibrational frequencies at the B3LYP/6-31G(d) level of theory and scaled by 0.9804.[34]) [b] Geometries at B3LYP/6-31G(d) level of theory.

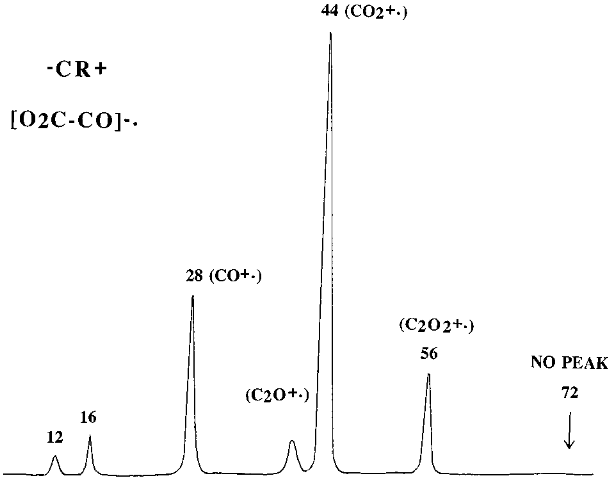


Figure 1. Charge reversal ($^-CR^+$) spectrum of $[O_2C{-}CO]^{-\bullet}$ ($4^{-\bullet}$). VG ZAB 2HF mass spectrometer. For experimental details see Experiment Section.

summarized in Table 1. Anions $5^{-\bullet}$ and $6^{-\bullet}$ are unstable at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory, and $7^{-\bullet}$ though stable, lies 121 kcal mol^{-1} above $4^{-\bullet}$, and is eliminated on energetic grounds. We have not considered isomers of $C_2O_3^{-\bullet}$ which contain −O−O− functionality: such species would be unstable under the reaction conditions used for the neutralization experiments. We conclude on both experimental and theoretical grounds, that the synthesis shown in eqn 1 does produce radical anion $4^{-\bullet}$, the precursor anion required for this investigation.

The charge reversal ($^-CR^+$) and neutralization reionization ($^-NR^+$) mass spectra of $[O_2C{-}CO]^{-\bullet}$ are shown in Figures 1 and 2, respectively. The charge reversal experiment is considered to involve a vertical Franck−Condon synchronous two-electron oxidation of the radical anion to the corresponding radical cation.[23,24] As can be seen from a consideration of the $^-CR^+$ spectrum, there is no recovery signal corresponding to the parent radical cation: only peaks corresponding to decomposition of the parent cation are observed. This means that if we produce a neutral C_2O_3 species in the neutralization reionization experiment, we cannot use positive ion mass spectroscopy to identify the neutral, because under the reaction conditions, ionization of that neutral will not give rise to a detectable recovery signal [i.e., we will not see a peak corresponding to an ion $C_2O_3^{+\bullet}$ (m/z 72)].[56] The $^-NR^+$ experiment involves stepwise vertical one-electron Franck−Condon oxidation processes from $C_2O_3^{-\bullet}$ to the neutral and then to the cation. The $^-CR^+$ and $^-NR^+$ spectra show some similarities. The major peaks in this spectrum are due to ionized CO and CO_2. As expected, there is no recovery signal at m/z 72 in the $^-NR^+$ spectrum, which means that we cannot use a peak at m/z 72 as a specific probe to detect the formation (or absence) of neutral C_2O_3.

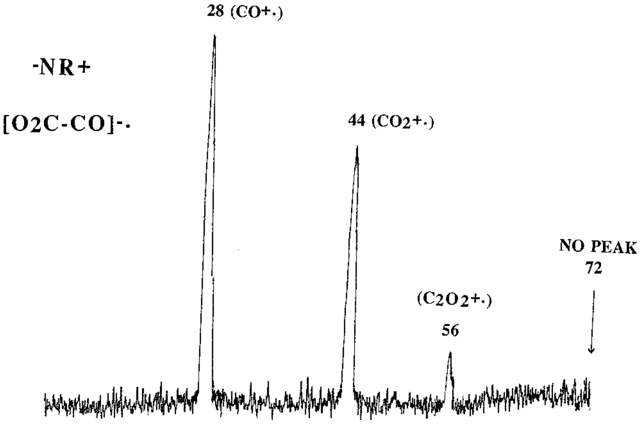


Figure 2. Neutralization reionization ($^-NR^+$) mass spectrum of $[O_2C{-}CO]^{-\bullet}$ ($4^{-\bullet}$). VG ZAB 2HF mass spectrometer. For experimental details see Experimental Section.

There is however, a small peak in the $^-NR^+$ spectrum which can only be formed from a decomposing $C_2O_3^{+\bullet}$ radical cation: the peak at m/z 56, $C_2O_2^{+\bullet}$ (see Figure 2). We have shown previously that although the radical anion and cation of O=C=C=O (ethylene dione) are stable species, neutral O=C=C=O cannot be detected under the conditions used for the neutralization reionization experiment.[25] Because $[O{=}C{=}C{=}O]^{-\bullet}$ is not formed on collisional activation of the precursor anion $C_2O_3^{-\bullet}$, $[O{=}C{=}C{=}O]^{+\bullet}$ is likely to be formed from a decomposing $C_2O_3^{+\bullet}$ radical cation in the $^-NR^+$ experiment, and the decomposing $C_2O_3^{+\bullet}$ radical cation can only be formed by ionization of a transient C_2O_3 neutral. Calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory show that $[O_2CCO]^{+\bullet}$ ($4^{+\bullet}$) is not a stable minimum on the cation potential surface. The $^-NR^+$ spectrum of $[O_2C{-}CO]^{-\bullet}$ (Figure 2) identifies three decomposition products, $CO_2^{+\bullet}$, $CO^{+\bullet}$, and $C_2O_2^{+\bullet}$: these processes are summarized in Table 2. The processes forming $CO_2^{+\bullet}$ and $CO^{+\bullet}$ are exothermic by 18.0 and 18.2 kcal mol^{-1} respectively (at the level of theory used), whereas the formation of $C_2O_3^{+\bullet}$ is calculated to be endothermic by 47 kcal mol^{-1}.

We have shown above that we cannot use $4^{+\bullet}$ as a probe to detect the presence of neutral O_2CCO in a $^-NR^+$ experiment because the cation radical $4^{+\bullet}$ is not a stable species. However, if some C_2O_3 neutrals can survive for a microsecond, they should be observable in a $^-NR^-$ experiment, i.e., where we use the stable radical anion $4^{-\bullet}$ as a probe to detect the neutral C_2O_3.

In the $^-NR^-$ study, we first carried out a standard experiment using PhCOCOPh to check the sensitivity of the instrument. Conversion of $[PhCOCOPh]^{-\bullet}$ to neutral PhCOCOPh followed by electron capture by the neutral to reform $[PhCOCOPh]^{-\bullet}$

TABLE 2: Thermochemical Data for Decompositions of C_2O_3

cation[a]	kcal mol^{-1}	neutrals	kcal mol^{-1}
$C_2O_3^{+\bullet} \rightarrow C_2O_2^{+\bullet} + O^\bullet$	+47.0	$^3\mathbf{4} \rightarrow {}^1CO + {}^3CO_2$	−6.80
$C_2O_3^{+\bullet} \rightarrow CO_2^{+\bullet} + CO$	−18.0	$^3\mathbf{4} \rightarrow {}^3CO + {}^1CO_2$	28.90
$C_2O_3^{+\bullet} \rightarrow CO_2 + CO^{+\bullet}$	−18.2	$^3\mathbf{5} \rightarrow {}^1CO + {}^3CO_2$	2.12

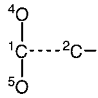
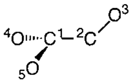
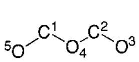
[a] Calculations at the CCSD(T)/aug-cc-pVDZ level of theory indicate that $\mathbf{4}^{+\bullet}$, the radical cation of O_2CCO, does not exist as a potential minimum, but undergoes immediate dissociation. The energy value for $C_2O_3^+$. given in the Table is that of the species with the geometry of neutral triplet **4** on the cation radical surface (following vertical Franck−Condon oxidation of the neutral). Energy values are determined from the following theoretically calculated values (Hartrees): $C_2O_3^{+\bullet}$ = −300.742 94, $C_2O_2^{+\bullet}$ = −225.706 04, $CO_2^{+\bullet}$ = −187.666 28, $CO^{+\bullet}$ = −113.068 94, $O^\bullet$ = −74.925 65, ^1CO = −188.174 43, ^3CO = −188.014 50, $^1CO_2$ = −188.174 43, $^3CO_2$ = −188.014 50 [at CCSD(T)/aug-cc-pVDZ level of theory (calculated from vibrational frequencies at the B3LYP/6−31G* level of theory and scaled by 0.9804 [34])].

gives a pronounced recovery signal. Using this as a standard, it is still possible to increase the signal intensity by a factor of 10^4 in a $^-NR^-$ experiment with the instrument operating at optimal conditions of sensitivity. We then performed the $^-NR^-$ experiment with $[O_2C{-}CO]^{-\bullet}$ on some fifty occasions. Several times, we thought we could see a small signal for $C_2O_3^{-\bullet}$ at maximum sensitivity of the instrument, but the noise level was very high under these conditions, and we were not able to reproduce these results. We conclude, on a statistical basis, that there is no signal for $C_2O_3^{-\bullet}$ in repeated $^-NR^-$ experiments using the instrument at maximum sensitivity and using various collision conditions in the tandem collision cell facility. Thus we are unable to directly detect neutral C_2O_3 in a neutralization reionization experiment. We conclude from the experimental evidence that a transient C_2O_3 neutral is formed, but the lifetime of this neutral must be less than 10^{-6} sec. following neutralization of the radical anion.[57]

Theoretical Consideration of the Structure of Neutral C_2O_3. There are a number of neutral C_2O_3 isomers that we must consider in the context of this study, viz **1** and **4**−**7**. In principle, all of these may have singlet and triplet states. These isoforms have all been investigated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory: details of energies and geometries of stable structures are listed in Tables 3 and 4. Some of these structures can be eliminated as possible products of the NR process from $\mathbf{4}^{-\bullet}$. For example, the singlet and triplet of **7** are high energy structures (Table 4) and are considered no further, whereas the triplet of **6** is unstable at the level of calculation used. That leaves the van der Waals complex **1**, the singlet and triplet of **4**, triplet **5**, and singlet **6** to be considered as possible neutral isoforms of C_2O_3, that might, in principle, be accessed by vertical oxidation of $[O_2C{-}CO]^{-\bullet}$.

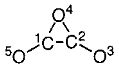
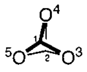
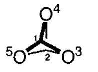
The van der Waals complex **1** has the most negative energy of all the neutral isomers of C_2O_3. However, it is stable with respect to dissociation to CO_2 and CO by only 1.2 kcal mol^{-1} at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. We also calculate at the same level of theory, that following one-electron Franck−Condon vertical oxidation of $\mathbf{4}^{-\bullet}$, a species corresponding to singlet $O_2C{-}CO$ (the singlet neutral with the same geometry as $\mathbf{4}^{-\bullet}$) is formed with an excess energy of 62.8 kcal mol^{-1} with respect to the van der Waals structure **1**. This will initiate immediate dissociation to CO_2 and CO. Van der Waals neutral **1** will not survive the NR experiment.

TABLE 3: Neutral Structures (1), (4), and (5)

	 **1**	 **4**	 **5**
state	1A′	3A″	3A′
symmetry	C_s	C_s	C_s
energy (Hartrees)[a]	−301.245 30	−301.072 61	−301.086 81
rel. energy (kcal mol^{-1})	0.0	108.4	99.5
adiabatic electron affinity (eV)	−0.52	4.37	
dipole moment (Debye)[a]	0.235	0.950	1.350
bond length (Å)[b] or angle (°)[b]			
C^1C^2	3.19	1.51	2.34
C^2O^3	1.14	1.2	1.18
C^1O^4	1.17	1.26	1.39
C^2O^4	3.41	2.42	1.39
C^1O^5	1.17	1.26	1.18
$C^1C^2O^3$	179.9	133.8	156.7
$C^2C^1O^4$	90.5	122.0	32.4
$C^2C^1O^5$	90.4	122.0	156.7
$O^4C^1O^5$	179.1	116.0	124.3
$O^3C^2C^1O^4$	180.0	97.4	0.0
$O^3C^2C^1O^5$	180.0	−97.4	0.0
Total atomic charges			
C^1		0.278	
C^2		0.576	
O^3		−0.248	
O^4		−0.303	
O^5		−0.303	
Sum of Mulliken charges		0.000	

[a] CCSD(T)/aug-cc-pVDZ level of theory including zero point energy (calculated from vibrational frequencies at the B3LYP/6-31G(d) level of theory and scaled by 0.9804.[34]). [b] Geometries at B3LYP/6-31G(d) level of theory.

TABLE 4: Neutral Structures (^{1}6), (^{1}7), and (^{3}7)

	 ^{1}**6**	 ^{1}**7**	 ^{3}**7**
state	1A1	1A1′	3A1″
symmetry	C_{2v}	D_{3h}	D_{3h}
energy (Hartrees)[a]	−301.148 28	−300.971 42	−300.890 94
rel. energy (kcal mol^{-1})	60.9	171.9	222.4
adiabatic electron affinity (eV)	2.31	1.88	4.07
dipole moment (Debye)[a]	0.07	0.00	0.000
bond length (Å)[b] or angle (°)[b]			
C^1C^2	1.44	1.49	1.71
C^2O^3	1.18	1.43	1.46
C^1O^4	1.42	1.43	1.46
C^2O^4	1.42	1.43	1.46
C^1O^5	1.18	1.43	1.46
$C^1C^2O^3$	163.5	58.7	54.2
$C^2C^1O^4$	59.5	58.7	54.2
$C^2C^1O^5$	163.5	58.7	54.2
$O^4C^1O^5$	137.0	95.5	89.2
$O^3C^2C^1O^4$	180.0	120.0	120.0
$O^3C^2C^1O^5$	0.0	−120.0	−120.0

[a] CCSD(T)/aug-cc-pVDZ level of theory including zero point energy (calculated from vibrational frequencies at the B3LYP/6-31G(d) level of theory and scaled by 0.9804.[34]). [b] Geometries at B3LYP/6-31G(d) level of theory.

The singlet neutral corresponding to structure **4** does not exist as a minimum on the potential surface of C_2O_3. Singlet **4** is unstable with respect to decomposition to CO_2 and CO. The situation is different for triplet **4**, which is calculated to be a stable species. The structural details of triplet **4** are contained in Table 3. The structure of triplet **4** (C_s) is similar to that of $\mathbf{4}^{-\bullet}$ (C_s), except for minor differences in the dihedral angles $O^3C^2C^1O^4$ and $O^3C^2C^1O$,[5] which are 97.4° and −97.4° for the neutral, and 91.3° and −91.3° for the radical anion. Triplet **4** has a dipole moment of 0.94 D, and an adiabatic electron affinity of 4.37 eV. The central C−C bond length of 1.506 Å implies

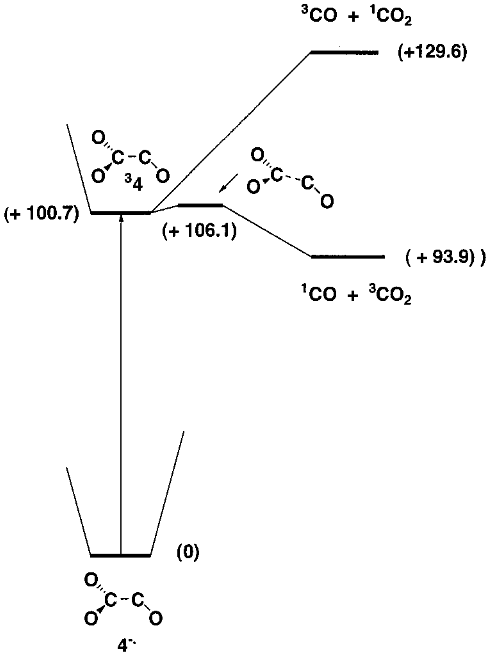


Figure 3. Vertical Franck−Condon oxidation of $[O_2C-CO]^{-\bullet}$ to triplet O_2C-CO, and dissociation pathways for triplet O_2C-CO. CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory.

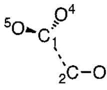
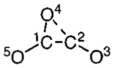
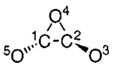
a single bond; the two equivalent CO bonds (1.261 Å) indicate significant double bond character, whereas the other C−O bond (1.178 Å) must have some triple bond character. Mulliken charge analysis (Table 3)[58] shows excess electron density on each of the three oxygen atoms with the carbon bearing the single oxygen surprisingly being the most electropositive atom.

The results of calculations for the neutralization of $4^{-\bullet}$ to triplet **4** [at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory] are shown in Figure 3 with details of structures listed in Tables 1 and 3. The vertical one-electron oxidation in this case gives the triplet neutral with essentially no excess energy resulting from that process. There are two dissociative processes of this neutral: (i) an endothermic process (+28.9 kcal mol^{-1}) yielding ^3CO and $^1CO_2$, a process which is unlikely to be accessible, and (ii) the formation of ^1CO and $^3CO_2$ by an exothermic process (−6.8 kcal mol^{-1}), but one which has a well-defined barrier (see Figure 3 and Table 5) of 5.4 kcal mol^{-1}. These data suggest that should there be triplet neutrals of structure **4** formed with insufficient energy to surmount the barrier of 5.4 kcal mol^{-1}, then those neutrals should be detectable in the NR experiment if their lifetimes are $\geq 10^{-6}$ sec.

Finally, calculations show that neither triplet **5** nor singlet **6** are accessible by vertical Franck−Condon oxidation of $[O_2C-CO]^{-\bullet}$ ($4^{-\bullet}$). Let us deal first with singlet **6** because it is the simpler of the two systems. The structure corresponding to singlet O_2C-CO [the (unstable) singlet neutral with the same geometry as $4^{-\bullet}$] does not occur on the reaction coordinate for the ring opening of singlet **6** followed by dissociation to CO_2 and CO. This process is shown in Figure 4. We have calculated many points along the reaction coordinate for dissociation of singlet **6**. During the ring opening of **6** and the subsequent dissociation, the CO_2 and CO units remain planar. There is no rotation to produce orthogonal orientation of the CO_2 and CO moieties (as in $4^{-\bullet}$).

The situation with triplet neutral **5** is different and more complex. In principle, triplet **5** may be accessible via triplet **4**, if the barrier of conversion of triplet **4** to triplet **5** is less than that of the barrier (+5.4 kcal mol^{-1}) for the dissociation of triplet **4** to ^1CO and ^3CO. We have carried out extensive potential surface calculations on this system, considering two scenarios, viz (i) a synchronous rearrangement of triplet **4** to triplet **5**, and (ii) a stepwise process whereby triplet **4** partially dissociates to a loosely bound CO_2/CO intermediate followed by reorienation of CO_2 and CO within that complex in order to effect formation of triplet **5**. We can find no stepwise pathway to triplet **5**; dissociation to CO and CO_2 always occurs in preference to any rearrangement. Neither could we find any concerted pathway from triplet **4** to triplet **5**. Cyclization via a transition state corresponding to symmetrical but unstable triplet **6**, did not proceed to triplet **5**, but led directly to dissociation to CO and CO_2. The only transition state we could find [apart from that for direct dissociation of triplet **4** to $^3CO_2$ and ^1CO (see Figure 3)], is a non planar cyclic saddle point for the degenerate rearrangement of triplet O_2C-CO to triplet $OC-CO_2$. This transition state lies 30 kcal mol^{-1} above triplet O_2C-CO, has

TABLE 5: Transition State Structures

	 **see Figure 3**	 **see Figure 4**	 **8**
state	3A″	1A′	
symmetry	C_s	C_s	C_1
energy (Hartrees)[a]	−301.06402	−301.14837	−301.01677
bond length (Å)[b] or angle (°)[b]			
C^1C^2	2.03	1.47	1.39
C^2O^3	1.15	1.16	1.21
C^1O^4	1.25	1.32	1.48
C^2O^4	2.84	1.66	1.48
C^1O^5	1.25	1.19	1.21
$C^1C^2O^3$	122.3	180.0	156.2
$C^2C^1O^4$	117.6	72.9	61.8
$C^2C^1O^5$	117.6	145.8	156.2
$O^4C^1O^5$	117.5	141.3	140.9
$O^3C^2C^1O^4$	−105.3	180.0	−164.8
$O^3C^2C^1O^5$	105.3	0.0	30.5

[a] CCSD(T)/aug-cc-pVDZ level of theory including zero point energy (calculated from vibrational frequencies at the B3LYP/6-31G(d) level of theory and scaled by 0.9804.[34]). [b] Geometries at B3LYP/6-31G(d) level of theory.

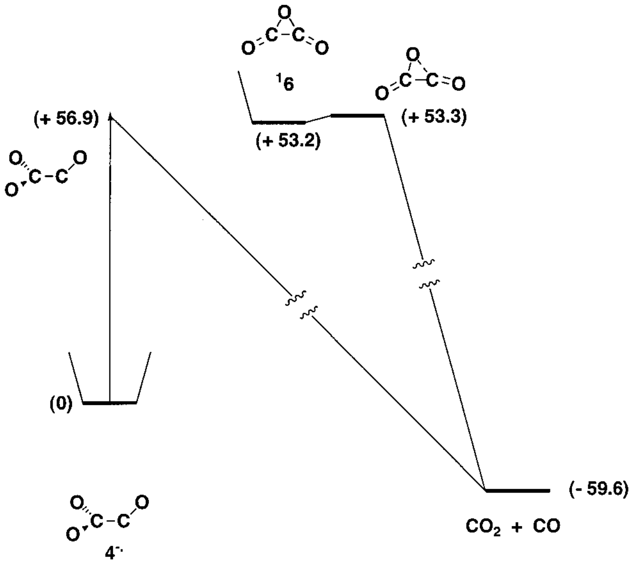
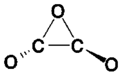


Figure 4. Dissociation pathways for singlet O_2C-CO (^{1}**4**) and ^{1}**6**. CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory.

the structure **8** shown below and defined in detail in Table 5. This process cannot compete energetically with the dissociation pathway to ^1CO and $^3CO_2$ (Figure 3). We cannot find any pathway whereby triplet OCOCO is accessible from $[O_2C-CO]^{-\bullet}$ under vertical oxidation conditions.



8

Conclusions

1. The radical anion $[O_2C-CO]^{-\bullet}$ (**4**$^{-\bullet}$) has been synthesized in the source of a modified ZAB 2HF mass spectrometer by electron capture of 1,3-dioxolane-2,5-dione followed by loss of CH_2O.

2. Neutralization reionization experiments (both $^-NR^+$ and $^-NR^-$) on the precursor radical anion **4**$^{-\bullet}$ give spectra containing no recovery signals corresponding to ionized C_2O_3. If a neutral C_2O_3 is formed in these experiments, the neutral must have a lifetime less than 10^{-6} sec.

3. The $^-NR^+$ spectrum of $[O_2C-CO]^{-\bullet}$ shows a peak corresponding to $[O{=}C{=}C{=}O]^{+\bullet}$. This can only originate from a decomposing species $C_2O_3{}^{+\bullet}$.

4. A combination of experimental and theoretical data suggests that neutralization of $[O_2C-CO]^{-\bullet}$ (**4**$^{-\bullet}$) produces a transient covalently bound species corresponding to triplet O_2C-CO (**4**) with a lifetime $<10^{-6}$ sec.

Acknowledgments. We thank the Australian Research Council for funding our negative ion program. S.D. and S.P. thank the ARC for a research associateship and a Ph.D. scholarship, respectively. We thank the Australian National University Supercomputing Facility (Canberra) for a generous allowance of computer time.

References and Notes

(1) Smith, G. P.; Cosby, P. C.; Mosely, J. T. *J. Chem. Phys*. **1977, *67*, 3838.**

(2) Jones, G. G.; Taylor, J. W. *J. Chem. Phys.* **1978**, *68*, 1768.

(3) Linn, S. H.; Ng, C. Y. *J. Chem. Phys.* **1981**, *75*, 4921.

(4) Illies, A. J.; Jarrod, M. F.; Inagner-Redeker, W.; Bowers, M. T. *J. Chem. Phys.* **1988**, *88*, 5204.

(5) DeLuca, M. J.; Niu, B.; Johnson, M. A. *J. Chem. Phys.* **1988**, *88*, 5857.

(6) Tsukuda, T.; Johnson, M. A.; Nagata, T. *Chem. Phys. Lett.* **1997**, *268*, 429.

(7) Jacox, M. E.; Thompson, W. E. *J. Chem. Phys.* **1989**, *91*, 1410.

(8) Thompson, W. E.; Jacox, M. E. *J. Chem. Phys*. **1991**, *95*, 735.

(9) Jacox, M. E.; Thompson, W. E. *J. Phys. Chem*. **1991**, *95*, 2781.

(10) Thompson, W. E.; Jacox, M. E. *J. Chem. Phys.* **1999**, *111*, 4487, and references cited therein.

(11) Knight, L. B.; Steadman, J. *J. Chem. Phys*. **1982**, *77*, 1750.

(12) Giamello, E.; Murphy, D.; Marchese, L.; Marta, G,; Zeechina, A. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3715.

(13) Knight, L. B.; Hill, D.; Berry, K.; Babb, R.; Fetter, D. *J. Chem. Phys.* **1996**, *105*, 5672.

(14) Zhou, M. F.; Andrews, L. *J. Chem. Phys.* **1999**, *110*, 2414.

(15) Zhou, M. F.; Andrews, L. *J. Chem. Phys*. **1999**, *110*, 6820.

(16) Legon, A. C.; Suckley, A. P. *J. Chem. Phys.* **1989**, *91*, 4440.

(17) Randall, R. W.; Summersgill, J. P. L.; Howard, B. J. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 1943.

(18) Xu, Y.; McKellar, A. R. W.; Howard, B. J. *J. Mol. Spectrosc.* **1996**, *179*, 345.

(19) Muenter, J. S.; Bhattacharjee, R. *J. Mol. Spectrosc.* **1998**, *190*, 290.

(20) Raducu, V.; Gauthierroy, B.; Dahoo, R.; Abouafmarguin, L.; Langlet, J.; Caillet, J.; Allavena, M. *J. Chem. Phys.* **1995**, *102*, 9235.

(21) Langlet, J.; Caillet, J.; Allavena, M.; Raducu, V.; Gauthier-Roy, B.; Dahoo, R.; Abouaf-Marguin, L. *J. Mol. Struct.* **1999**, *484*, 145.

(22) Structures drawn in the text or the figures indicate the bond connectivity and the overall geometry. These structures do not indicate the bond order except when indicated to the contrary (e.g., in eqn 1). Bond lengths are listed in Tables 1 and 3−5.

(23) Wesdemiotis, C.; McLafferty, F. W. *Chem. Rev.* **1987**, *26*, 805; Holmes, J. L. *Mass Spectrom Rev.* **1989**, *8*, 513; For recent reviews of the neutralization/reionization technique and nomenclature see Shalley, C. A.; Hornung, G.; Schröder, D.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1998**, *172*, 181. Zagorevskii, D. V.; Holmes, J. L. *Mass Spectrom. Rev.* **1999**, *18*, 87.

(24) Blanksby, S. J.; Schröder, D.; Dua, S.; Bowie, J. H.; Schwarz, H. *J. Am. Chem. Soc.* **2000**, *122*, 7105, and references therein.

(25) Schröder, D.; Heinemann, C.; Schwarz, H.; Harvey, J. N.; Dua, S.; Blanksby, S. J.; Bowie, J. H. *Chem. Eur. J.* **1998**, *4*, 2550.

(26) Peppe, S.; Blanksby, S. J.; Dua, S.; Bowie, J. H. *J. Phys. Chem.* **2000**, *104*, 5817, and references therein.

(27) Holmes, J. L. *Org. Mass Spectrom.* **1985**, *20*, 169.

(28) Bowie, J. H.; Blumenthal, T. *J. Am. Chem. Soc.* **1975**, *97*, 2959. Szulejko, J. E.; Bowie, J. H.; Howe, I.; Beynon, J. H. *Int J. Mass Spectrom. Ion Phys.* **1980**, *13*, 76.

(29) Bursey, M. M. *Mass Spectrom. Rev.* **1990**, *9*, 555.

(30) Serck-Hanssen, K. *Acta Chem. Scand*. **1969**, *23*, 2000

(31) Becke, A. D. *J. Phys. Chem.* **1993**, *98*, 5648.

(32) Stevens, P. J.; Devlin, F. J.; Chablowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11 623.

(33) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A. *GAUSSIAN 98*; GAUSSIAN Inc.: Pittsburgh, PA, 1998.

(34) Wong, M. W. *Chem. Phys. Lett.* **1996**, *256*, 391.

(35) Szczepanski, J.; Ekern, S.; Vala, M. *J. Phys. Chem.* **1997**, *101*, 1841.

(36) Crawford, T. D.; Stanton, J. F.; Saeh, J. C.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1999**, *121*, 1902.

(37) Plattner, D. A.; Houk, K. N. *J. Am. Chem. Soc.* **1995**, *117*, 4405.

(38) Martin, L. M. L.; El-Yazal, J.; Trancois, J.-P. *Chem. Phys. Lett.* **1996**, *252*, 9.

(39) Masqualine, E. E.; Lopez, M. *Chem. Phys. Lett.* **2000**, *320*, 415.

(40) Cizek, J. *Adv. Chem. Phys.* **1969**, *14*, 35.

(41) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* **1978**, *4*, 545.

(42) Hampel, C.; Peterson, K.; Werner, H.-J. *Chem. Phys. Lett*. **1992**, *190*, 1.

(43) Watts, J. D.; Gauss, J.; Bartlett, R. J. J. *J. Chem. Phys*. **1993**, *98*, 8718.

(44) Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1993**, *99*, 5219.

(45) Deegan, M. J. O.; Knowles, P. J. *Chem. Phys. Lett.* **1994**, *227*, 321.

(46) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

(47) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, *98*, 1358.

(48) Arnold, D. W.; Bradforth, S. E.; Kitsopoulos, T. N.; Neumark, D. M. *J. Chem. Phys*. **1991**, *95*, 8753.

(49) Xu, C.; Burton, G. R.; Taylor, T. R.; Neumark, D. M. *J. Chem. Phys*. **1997**, *107*, 3428.

(50) Cooper, C. D.; Compton, R. N. *J. Chem. Phys*. **1974**, *59*, 3550.

(51) Zhou, M.; Zhang, L.; Chen. M.; Qin, Q. *J. Chem. Phys*. **2000**, *112*, 7089, and references cited therein.

(52) Neumark, D. M.; Lykke, K. R.; Andersen, T.; Lineberger, W. C. *Phys. Rev.* **1985**, *32*, 1890.

(53) Bartmess, J. E. Negative Ion Energetics. NIST Standard Reference Database − Number 69. http://webbook.nist.gov/cgi/cbook.exe? EA=3−3.5&Units=SI.

(54) Schröder, D.; Schalley, C. A.; Harvey, J. N.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1999**, *187*, 25.

(55) There are numbering errors in Table 2 of ref 51 with regard the structure of **3**$^{-\bullet}$, and so it is difficult to assess the reported geometry of the system. We have repeated the calculation of this system at one of the reported levels used by Zhou et al, viz at the B3LYP/6-311+G(d) level of theory. We obtain the same energy but some differences to their reported bond lengths and angles. Our results for **3**$^{-\bullet}$ at the B3LYP/6−311(d) level of theory are (using the numbering system for **3**$^{-\bullet}$ shown in Table 1) are as follows: energy, −301.988524 Hartree; state $^2A'$; C^1O^4 (1.23 Å), C^1O^5 (1.22), C^2O^3 (1.16), C^2O^4 (3.63), $C^2O^4C^1$ (63.5°), $O^4C^1O^5$ (139.2). The CO_2 and CO units are planar to each other using this level of theory. When **3**$^{-\bullet}$ is examined at the level of theory used in this paper [CCSD(T)/aug-cc-

pVDZ//B3LYP/6-31G(d)] the dihedral angle between CO_2 and CO is different, with the two units essentially orthogonal to each other (see Table 1).

(56) A reviewer has asked why the $^-CR^+$ spectrum of $C_2O_3^{-\bullet}$ contains no peak due to $C_2^{+\bullet}$ (*m*/*z* 24), when the corresponding spectrum of $C_2O_2^{-\bullet}$ does show a peak corresponding to *m*/*z* 24.[25] The answer is that in $C_2O_2^{+\bullet}$, CC is essentially a double bond,[25] whereas that of unstable $O_2CCO^{+\bullet}$ is a 'long' single bond which undergoes facile cleavage to give CO and CO_2 species (see Table 2).

(57) A reviewer has asked whether it is possible that some $(O_2CCO)^{-\bullet}$ ions are 'metastable' with respect to electron loss. To check this proposal, we have carried out a 'neutralization'/reionization experiment as follows. The parent radical anion $(O_2CCO)^{-\bullet}$ is fired through the first collision cell which contains no collision gas. The deflector between the two cells is charged, and the second cell contains O_2 (as in a normal $^-NR^+$ experiment). Thus only neutrals formed by 'metastable' electron loss from $(O_2CCO)^{-\bullet}$ can enter the second collision cell. No positive ion signals result from this [$^-$('metastable' N)R^+] experiment. We make no conclusion about the negative results of this experiment, because there is the possibility that a small yield of such neutrals could be formed but the instrument may not be sensitive enough to detect them.

(58) Mulliken, R. S. *J. Chem. Phys*. **1962**, *36*, 3428.