

A Combined Neutralization-Reionization Mass Spectrometric and Theoretical Study of Oxyallyl and Other Elusive $[C_3H_4O]$ Neutrals[☆]

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Five different anionic $[C_3H_4O]^{*-}$ isomers, i.e. the radical anions of acrolein, acetyl carbene, formyl methyl carbene, methoxy vinylidene, and oxyallyl are generated in an ion beam mass spectrometer and subjected to neutralization-reionization (NR) mass spectrometric experiments including neutral and ion decomposition difference (NIDD) mass spectrometry; the latter allows for the examination of the neutrals' unimolecular reactivity. Further, the anionic, the singlet and triplet neutral, and the cationic $[C_3H_4O]^{*+/+}$ potential-energy surfaces are calculated at the B3LYP/6-311++G(d,p)

level of theory. For some species, notably the singlet state of oxyallyl, the theoretical treatment is complemented by G2, CASSCF, and MR-CI calculations. Theory and experiment are in good agreement in that at the neutral stage (i) acrolein does not react within the μ sec timescale, (ii) acetyl and formyl methyl carbenes isomerize to methyl ketene, (iii) methoxy vinylidene rearranges to methoxy acetylene, (iv) singlet 1A_1 oxyallyl undergoes ring closure to cyclopropanone, and (v) triplet 3B_2 oxyallyl may have a lifetime sufficient to survive a NR experiment.

Introduction

For isomeric $[C_3H_4O]$ molecules, several unconventional connectivities are conceivable due to the low degree of saturation of the heavy-atom backbone, and the reader is invited to complement the selection of structures depicted in Chart 1. Besides more common isomers like acrolein **1**, methyl ketene **2**, methoxy acetylene **3**, or propargyl alcohol **4**, also hydroxy allene **5** or 1-hydroxy propyne **6** may be stable species^[1]. Experimental and theoretical evidence have been provided for the existence of strained rings like allene oxide **7**^[2], cyclopropanone **8**^{[2a][2g][3]}, methyl oxirene **9**^{[2g][4]}, and oxetene **10**^[5]. The ketocarbenes^[6] **11** and **12** were discussed with regard to the Wolff rearrangement of diazoketones and the intermediacy of oxirenones in these reactions^[7]. Further, unsaturated carbenes^[8] like methoxy vinylidene^{[9][10]} **13** may represent local minima on the $[C_3H_4O]$ potential-energy surface.

One of the most intriguing $[C_3H_4O]$ species is, however, the oxyallyl biradical **14**. This biradical and its substituted homologs have been proposed as intermediates or transition structures in (i) the Favorskii rearrangement [Scheme 1, path (a)]^[11], (ii) the disrotatory, degenerate isomerization of cyclopropanone **8** [path (b)]^[12] and the ring inversion in bicyclo[*n*.1.0]alkanones^[13], (iii) the isomerization of **7** to **8**

Chart 1

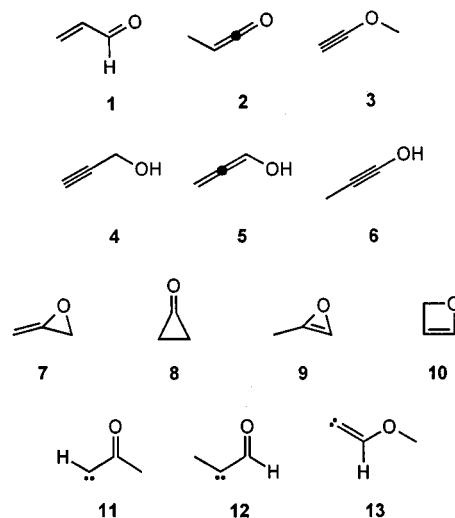
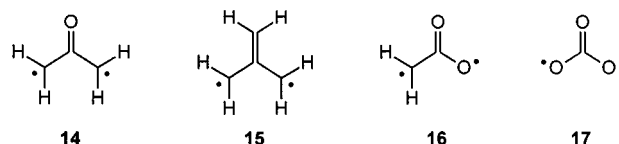


Chart 2



[paths (b) and (c)]^[14], (iv) the addition of diazomethane to ketenes yielding cyclopropanones^[15], and (v) in the photo-rearrangements of 2,5-cyclohexadienones (Scheme 2)^[16]. A recent synthetic method even provides an experimental

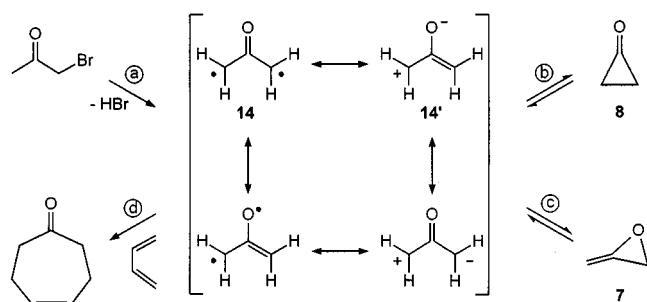
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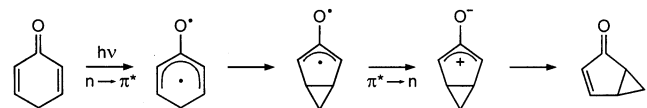
route to bicyclo[*n*,1,0]alkanones allowing for the study of the ring opening to the corresponding oxyallyl derivatives^[17]. The parent molecule **14**, however, has not been isolated yet. The analogy to isoelectronic trimethylenemethane **15** (TMM)^[18] as well as **16** and **17**, (Chart 2) is obvious.

Oxyallyl represents a non-Kekule molecule^[19], which like TMM is predicted to have a triplet 3B_2 ground state^{[20][21]} and is believed to be trapped chemically in cycloaddition reactions [Scheme 1, path (d)]^[22]. The lowest singlet state (1A_1) of **14** was calculated to be a local minimum which is only 1–2 kcal/mol above the 3B_2 ground state^{[20][21a]} and was described as a genuine biradical (**14**) rather than a zwitterion (**14'**)^{[20][21a]}. At the CASSCF(4,4)/6-31G(d) level of theory, the transition structure for symmetry allowed disrotatory ring closure to cyclopropanone was found to be as low as 0.3 kcal/mol^[23] relative to 1A_1 oxyallyl. It has thus been concluded that isolation and identification of singlet oxyallyl by experimental means should be at least extremely difficult, if not impossible.

Scheme 1



Scheme 2



One approach to experimentally generate and structurally characterize elusive and unconventional molecules uses the large potential of neutralization-reionization (NR) mass spectrometry^[24]. In these experiments, a beam of ionic precursor molecules is first neutralized in a high-energy collision and subsequently the fast moving neutrals are reionized in a second collision event. The experimental set-up is typically such that the lifetimes of the neutrals between the two collisions are in the range of microseconds. A recently developed method coined “neutral and ion decomposition difference” (NIDD) mass spectrometry^[25] allows to investigate the unimolecular decay of the transient neutrals formed^[26]. NIDD is based on the comparison of NR mass spectra with charge reversal (CR) spectra, in which the charge of the projectile is inverted by two-electron transfer in a single collision.

The NRMS approach to neutral molecules depends on the availability of appropriate, well characterized precursor ions. According to earlier results, acetylcarbene radical-cation **11** $^{\bullet+}$, for example, does not exist as a minimum on the cation surface^[4]. Instead, ionized methyl oxirene **9** $^{\bullet+}$ is

formed upon dissociative ionization of diazoacetone^[4]. Similarly, several attempts to generate the oxyallyl radical-cation **14** $^{\bullet+}$ failed^{[2d][2e]}. However, NR experiments provided evidence for the existence of neutral **7** and **9**^{[2d][2e][4]}. To get access to neutral oxyallyl, acetyl carbene, and other isomers by NR mass spectrometry, we decided to use $[C_3H_4O]^{\bullet-}$ radical-anions rather than the corresponding cations as precursors.

It is common knowledge that many positively charged ions give rise to extensive isomerizations, while most anions do not. Further, most carbenes have positive electron affinities and do not rearrange as radical anions^[27]. For example, the distonic^[28] radical anions of the non-Kekule molecules TMM and tetramethyleneethane have been studied^[29]. Similarly, the $^{\bullet}CH_2CO_2^-$ distonic radical-anion **16** $^{\bullet-}$ was examined by a variety of mass spectrometric techniques^[30], which also provided evidence that upon neutralization, **16** is formed in both the singlet and triplet states. Accordingly, negative ions appear as a promising approach to the isoelectronic oxyallyl system, rather than any route using radical cations as precursors.

In this paper, experimental data for the gas-phase existence of five neutral $[C_3H_4O]$ isomers are provided, i.e. acrolein **1**, acetyl carbene **11**, formyl methyl carbene **12**, methoxy vinylidene **13**, and oxyallyl **14**. The interpretation of the experiments is aided by extensive B3LYP/6-311++G(d,p) calculations on the anionic, the singlet and triplet neutral, and the cationic $[C_3H_4O]^{\bullet-}/0/^{\bullet+}$ potential-energy surfaces. Due to some fundamental shortcomings of this theoretical approach, additional calculations at higher levels of theory are included. The results shed new light on the questions concerning the existence, the singlet-triplet gap, and the probability of spin inversion for singlet and triplet oxyallyl.

Computational Details

In order to get an overview of the $[C_3H_4O]^{\bullet-}/0/^{\bullet+}$ potential-energy surfaces, the economic hybrid DFT/HF B3LYP method^[31] implemented in Gaussian 94^[32] with 6-311++G(d,p) basis sets^[33] was applied first. Geometry optimizations were performed with gradient procedures, and vibrational frequencies were calculated in order to determine the nature of stationary points as minima (no imaginary frequency), transition structures (one imaginary frequency), or higher order saddle points. In certain cases, intrinsic reaction coordinates (IRCs)^[34] were calculated with B3LYP/6-31G(d) in order to relate minima and transition structures; for the sake of brevity, we restrict this topic to the loss of CO from cyclopropanone as an example. Unscaled^[35] frequencies were used to derive zero-point vibrational energy (ZPVE) corrections. Selected geometrical data for calculated species are indicated in the Charts; a complete set of cartesian coordinates for each of the species is available upon request from the authors.

In general, the B3LYP approach is expected to provide an accuracy of ca. ± 5 kcal/mol for relative energies^[36], and even radical anions can be described quite well, provided the chosen basis set is sufficiently large^[37]. As will be shown by comparison of the theoretical results with known exper-

imental data for several key species (see below), the level of theory and the corresponding basis set chosen are appropriate for a qualitative, if not semiquantitative description of these systems; note however, that the electron affinity of CH_2 is overestimated by ca. 12 kcal/mol^[38]. For several stationary points, the energetics were cross-checked by performing calculations with the highly reliable G2 method^[39], which is expected to give the energetics within an error of ± 2 kcal/mol. The G2 method involves geometry optimization at the MP2/6-31G(d) level, and in all cases described further below these geometries were very similar to the B3LYP ones; accordingly, only the latter are reported.

The calculated relative energies were converted into heats of formation by anchoring them to known experimental data^[40] while keeping the deviations as small as possible. In general, a reasonable agreement of experiment and theory was found. Deviations larger than ± 5 kcal/mol were, however, obtained for the cumulenes such as methyl ketene or allene and their radical-cations (see below). These values were, therefore, not taken into account in the anchoring of the heats of formation. The consistency of the present calculations with earlier computational results obtained using MP2 and G2^{[41][42]} suggests that the experimental heats of formation of these cumulenes may need some refinement.

B3LYP was chosen, because it represents an economic and yet sufficiently accurate approach for most questions connected to this project. However, it is essentially a one-determinant procedure and additionally contains an "exact" Hartree-Fock (HF) exchange contribution. In fact, B3LYP turns out to be inappropriate for a quantitatively correct description of the biradicaloid, open-shell 1A_1 state of oxyallyl (see below)^{[20b][21a]}. Therefore, additional calculations were performed using four approaches: (i) The BP86 and BLYP density functionals implemented in Gaussian were explored because these do not contain an HF contribution. (ii) Complete active space self-consistent field (CASSCF) calculations were performed for the singlet state using several combinations of basis sets and active spaces. In addition to calculations without active electrons (RHF approach), the following combinations were considered: CASSCF(2,2) with the two unpaired electrons in the two valence orbitals of a_2 and b_1 symmetry, respectively, CASSCF(4,4) with the four valence π electrons in the four valence π orbitals (in order, of b_1 , b_1 , a_2 , and b_1 symmetry), CASSCF(6,5) where the in-plane oxygen lone-pair (b_2 symmetry) is also included in the active space, and CASSCF(6,7) in which two virtual orbitals (a_1 and b_2 symmetry) were added. This set of calculations was destined to determine whether or not the singlet state is a minimum. (iii) The relative energies of the singlet and triplet states at their respective CASSCF(6,5) geometries were examined using several correlated methods. These calculations were performed in Molpro94^[43] using the correlation-consistent polarized valence double zeta (cc-pVDZ) basis sets of Dunning et al.^[44] For oxygen, the corresponding augmented basis set including diffuse functions was used. The correlation methods considered included coupled cluster, MR-CI with and without a correction for higher excitations, multi-

reference averaged coupled-pair functional (MR-ACPF) calculations, and multi-reference perturbational theory. For the multi-reference methods, the active space chosen was the (6,5) combination described above. The MR-ACPF calculations were repeated with the larger correlation-consistent polarized valence triple zeta (cc-pVTZ) basis set, augmented on oxygen, and omitting the d polarization functions on hydrogen. (iv) Since the singlet and triplet states of oxyallyl are essentially degenerate at their minima, spin-inversion mediated surface-hopping could be expected to occur. In order to estimate the probability of the intersystem crossing, the spin-orbit coupling matrix element (H^{SO}) between the two states was calculated. For this purpose, a one-electron approximate spin-orbit Hamiltonian^[45] was used, as implemented in the Gamess for PC program package^[46]. The wavefunction of the singlet state was developed with the 6-31G(d) basis set as a fully optimized CASSCF(6,5) wavefunction. The triplet wavefunction was a CASSCF(6,5) wavefunction, where the orbitals of the active space were fully optimized, but the inner electrons were described in a frozen-core approximation by the corresponding singlet-optimized orbitals. Tests using other types of wavefunctions to describe the two states lead to almost identical results with respect to H^{SO} . The effective nuclear charges were taken from the literature^[45a].

Surface hopping may also be important for the singlet and triplet states of the acetyl and methyl formyl carbenes. In this case, however, the minimum geometries are substantially different, which means that it is not immediately obvious that the system can reach a crossing region. It is therefore necessary to explicitly locate the minimum energy crossing point (MECP) between the two surfaces. This was done for the acetyl carbene system at the B3LYP level of theory; the MECP in the formyl methyl carbene system is assumed to have similar properties. The method^[47] used to locate the MECP involves a geometry optimization with BECKE3LYP/6-311++G(d,p) following a composite energy gradient derived at each step from the energies and gradients of the singlet and triplet surfaces. This gradient is the sum of one term which points towards the crossing hyperline between the two surfaces, and one which points towards the minimum along the hyperline. The matrix element H^{SO} between the two states was calculated at the MECP using the same method as above. In this case, the active space included four electrons in four orbitals (the two orbitals at the carbene center and the π and π^* orbitals of the carbonyl group). Again, various other methods were used to determine H^{SO} , all giving very similar results. Due to the C_1 symmetry of this MECP, all three substates of the triplet state can couple to the singlet state, and the reported H^{SO} is the root-mean square of the coupling elements.

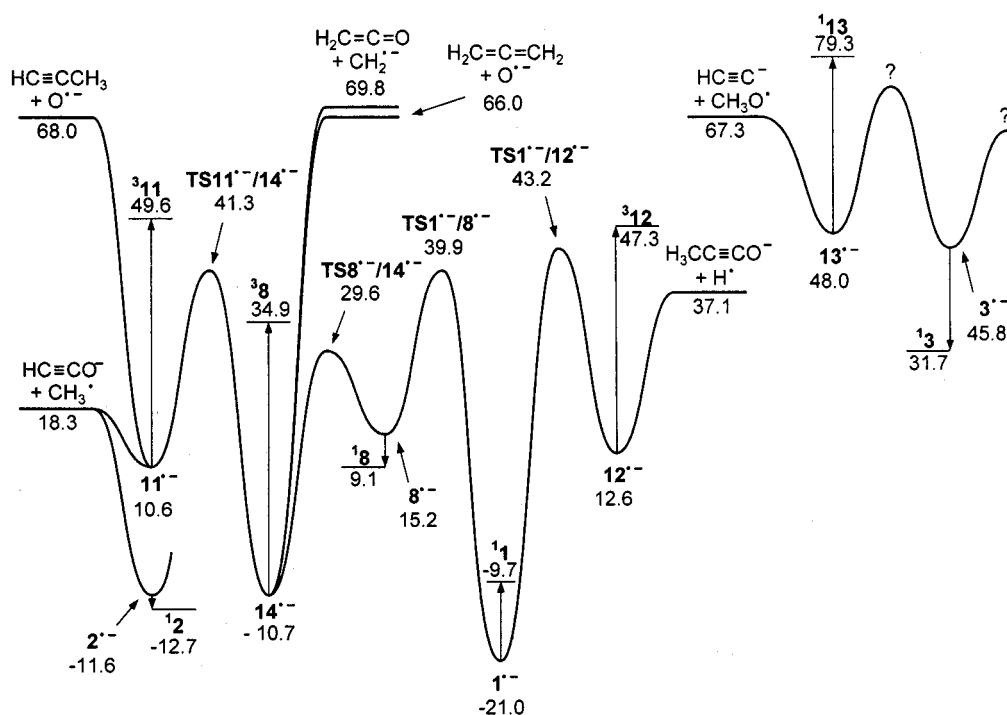
Theoretical Results

First, we shall consider the theoretical findings concerning the anionic, the singlet and triplet neutral, and the cationic $[C_3H_4O]^{*-10/+}$ potential-energy surfaces. These results will define the scope and serve as guidelines for the experiments. At the outset, let us, however, make a general

comment on the anionic species. In addition to the rearrangements, anions may undergo vertical electron detachment and thus escape detection. This may happen, if the relevant electron affinity (EA) is low enough and/or the internal energy of the anion is sufficiently large. Further, even anions which are stable against vertical electron detachment may correlate with neutrals of the same connectivity, but different geometry. Thus, some anions may exhibit negative adiabatic EAs and may undergo autodetachment within the μs timescale of the mass spectrometric experiments. Therefore, related neutrals have to be taken into account in evaluating the stability of anions^[37c].

The C_{2v} symmetric oxyallyl radical-anion $14^{\bullet-}$ corresponds to a deep local minimum which is separated from the isomeric structures $8^{\bullet-}$ and $11^{\bullet-}$ by large barriers. Fragmentation of $14^{\bullet-}$ into $\text{H}_2\text{CCCH}_2 + \text{O}^{\bullet-}$ or $\text{H}_2\text{CCO} + \text{CH}_2^{\bullet-}$ is quite energy demanding (>70 kcal/mol) and thus unlikely to occur. A 1,3-hydrogen migration via $\text{TS}11^{\bullet-}/14^{\bullet-}$ leads to the acetyl carbene radical-anion $11^{\bullet-}$, but the barrier is more than 50 kcal/mol above $14^{\bullet-}$. In addition to the fragmentation into propyne and $\text{O}^{\bullet-}$ which is endothermic by ca. 60 kcal/mol relative to $11^{\bullet-}$, loss of methyl radical concomitant with formation of HCCO^- provides a low-lying exit channel for $11^{\bullet-}$ with an energy demand of

Figure 1. Relevant parts of the anionic $^2[\text{C}_3\text{H}_4\text{O}]^{\bullet-}$ potential-energy surface calculated at the B3LYP/6-311++G(d,p) level of theory. Vertical arrows indicate adiabatic transitions to the corresponding neutrals of lowest heat of formation



The Anionic $^2[\text{C}_3\text{H}_4\text{O}]^{\bullet-}$ Potential-Energy Surface

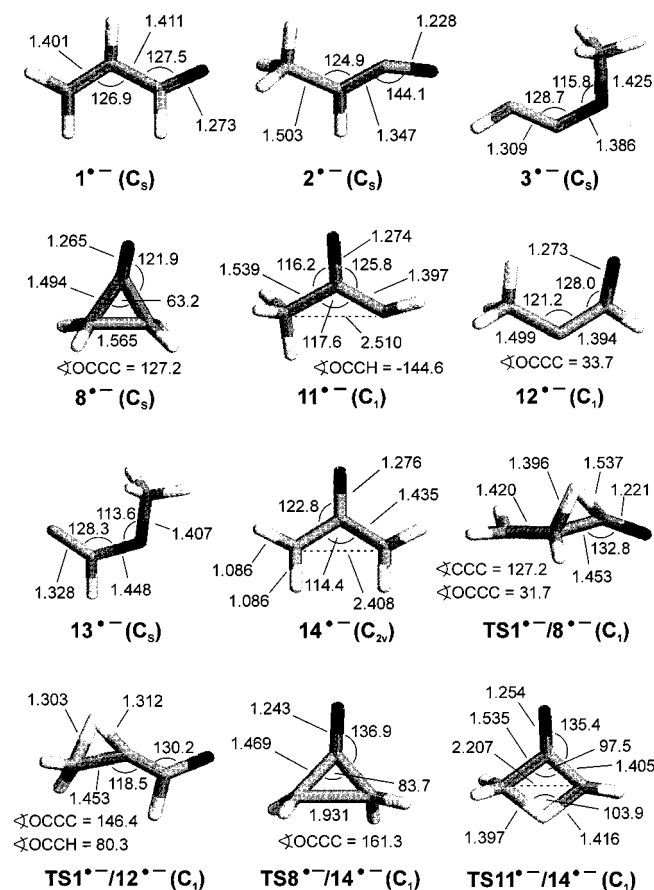
Several $^2[\text{C}_3\text{H}_4\text{O}]^{\bullet-}$ isomers and their mutual transition structures (Chart 3) were found at the B3LYP/6-311++G(d,p) level of theory. The energetics (Table 1) and the resulting potential-energy surface also include some fragmentation channels as well as relevant neutral species. The arrows connecting anions and neutrals in Figure 1 indicate the adiabatic EA and, thus, provide information with regard to the stability of the anions against electron detachment.

Eight local $^2[\text{C}_3\text{H}_4\text{O}]^{\bullet-}$ minima were found (Figure 1) with three, however, being less stable than the corresponding neutrals. While electron detachment from the radical anions of acrolein $1^{\bullet-}$, acetyl carbene $11^{\bullet-}$, methyl formyl carbene $12^{\bullet-}$, methoxy vinylidene $13^{\bullet-}$, and oxyallyl $14^{\bullet-}$ is predicted to have considerable energy demands, electron losses from the radical anions of methyl ketene $2^{\bullet-}$, methoxy acetylene $3^{\bullet-}$, and cyclopropanone $8^{\bullet-}$ are exothermic, though probably associated with kinetic barriers due to the necessity of geometrical reorganization.

only 7.7 kcal/mol above the minimum. The latter result is consistent with the observation of methyl loss under ICR conditions^[50]. Ring closure of $14^{\bullet-}$ to the cyclopropanone radical-anion $8^{\bullet-}$ via $\text{TS}8^{\bullet-}/14^{\bullet-}$ has an energy demand of more than 40 kcal/mol relative to $14^{\bullet-}$ and proceeds in a symmetry allowed, conrotatory movement of the CH_2 groups. The disrotatory process is symmetry forbidden, and all attempts to locate a transition structure for the disrotatory ring closure of $14^{\bullet-}$ failed. In C_s symmetric $8^{\bullet-}$ the oxygen is not located in the CCC plane due to the radical center at C(1). The negative adiabatic electron affinity of neutral cyclopropanone 18 implies, however, that ring closure of $14^{\bullet-}$ is most likely associated with electron detachment instead of generating long-lived $8^{\bullet-}$.

Among the isomers considered in this study, the radical anion of acrolein $1^{\bullet-}$ corresponds to the deepest minimum. $1^{\bullet-}$ is located ca. 10 kcal/mol below $14^{\bullet-}$ and is connected to $8^{\bullet-}$ via $\text{TS}1^{\bullet-}/8^{\bullet-}$ which is probably a spurious transition structure in the sense discussed above, because neither 1 nor 8 have electron affinities large enough to allow the

Chart 3

Table 1. Calculated total energies (E_t), zero-point vibrational energies (ZPVE), and calculated as well as experimental heats of formation (ΔH_f°) of anionic [C₃H₄O]^{•-} isomers and relevant fragmentation reactions^[a]

	$E_t^{[b]}$ (hartree)	ZPVE (hartree)	$\Delta H_f^{[c]}$ (kcal/mol)	$\Delta H_f^{[d]}$ (kcal/mol)
CH ₂ CHCHO ^{•-} (1 ^{•-})	-191.928179	0.056847	-21.0	
CH ₃ CCO ^{•-} (2 ^{•-})	-191.913221	0.057328	-11.6	
CH ₃ OCCH ^{•-} (3 ^{•-})	-191.821696	0.056849	45.8	
c-CH ₂ CH ₂ CO ^{•-} (8 ^{•-})	-191.870588	0.057338	15.2	
CH ₃ COCH ^{•-} (11 ^{•-})	-191.877830	0.056658	10.6	
CH ₃ CCHO ^{•-} (12 ^{•-})	-191.874634	0.056760	12.6	
CH ₃ OCHC ^{•-} (13 ^{•-})	-191.818321	0.057669	48.0	
•CH ₂ COCH ₂ ^{•-} (14 ^{•-})	-191.911810	0.055994	-10.7	<32 ^[e]
TS1 ^{•-} /8 ^{•-}	-191.831112	0.051170	39.9	
TS1 ^{•-} /12 ^{•-}	-191.825790	0.051601	43.2	
TS8 ^{•-} /14 ^{•-}	-191.847600	0.053444	29.6	
TS11 ^{•-} /14 ^{•-}	-191.828888	0.050643	41.3	
HCCO ^{•-} + CH ₃ [•]	-191.865581	0.048008	18.3	22.7
CH ₃ CCO ^{•-} + H [•]	-191.835633	0.046970	37.1	
CH ₂ CCH ₂ [•] + O ^{•-}	-191.789574	0.054844	66.0	71.5
CH ₃ CCH [•] + O ^{•-}	-191.786372	0.055491	68.0	70.5
CH ₂ CO ^{•-} + CH ₃ [•]	-191.795913	0.046839	69.8	77.0
HCC ^{•-} + CH ₃ O [•]	-191.787556	0.050581	67.3	69.8
HCC [•] + CH ₃ O ^{•-}	-191.729137	0.048624	103.9	101.7

[a] The total energies of the fragments are given in Table 2. – [b] Total energies based on B3LYP/6-311++G(d,p) optimized structures including ZPVE corrections (unscaled). – [c] Calculated heats of formation on the basis of literature data (see Computational Details). – [d] Reference data as given in Table 2 and ref.^[40]. – [e] Upper limit calculated from the reaction of [D₃]acetone with O^{•-} as described in ref.^[50].

Table 2. Calculated total energies (E_t), zero-point vibrational energies (ZPVE), and experimental heats of formation (ΔH_f°) of fragments used in this study

	$E_t^{[a]}$ (hartree)	ZPVE (hartree)	$\Delta H_f^{[b]}$ (kcal/mol)	$\Delta H_f^{[c]}$ (kcal/mol)
H [•]	-0.502257	–		52.1
³ O	-75.089880	–		59.6
¹ O ^[d]				104.9
O ^{•-}	-75.149014	–	22.5	25.9
¹ CH ₂	-39.130248	0.016496	104.8	103.5 ^[e]
³ CH ₂	-39.148992	0.017125		93.0
CH ₂ ^{•-}	-39.175824	0.015329	76.2	88.4
CH ₃ [•]	-39.825553	0.029635		34.8
HCC [•]	-76.616825	0.014122		134.2
HCC ^{•-}	-76.731381	0.014512	62.3	65.7
HCC [•]	-77.329674	0.026988		54.5
HCC ^{•+}	-76.916019	0.026085	314.1	317.4
H ₂ CC:	-77.264329	0.023530	104.0	
H ₂ CC ^{•+}	-76.850938	0.021604	363.4	
C ₂ H ₃ [•]	-77.892692	0.036308		63.4
H ₂ CCH ₂	-78.564764	0.050773		12.5
H ₂ CCH ₂ ^{•+}	-78.185446	0.048288	250.5	254.9
H ₃ C–CH	-78.448053	0.046475	85.7	
CO	-113.344010	0.005041		-26.4
HCO [•]	-113.878377	0.012954		10.7
HCO ⁺	-113.567343	0.014473	205.8	207.9
CH ₂ O	-114.515350	0.026498		-26.0
CH ₂ O ^{•+}	-114.117602	0.023838	223.6	224.7
CH ₃ O [•]	-115.056175	0.036069		3.7
CH ₃ O ^{•-}	-115.112312	0.034502	-31.5	-32.5
HCCO [•]	-151.954398	0.018388		42.4
HCCO ^{•-}	-152.040028	0.018373	-11.3	-12.1
HCCO ⁺ [f]	-151.587535	0.018300	272.6	262.0
CH ₃ CCO ^{•-}	-191.333376	0.046970		-11.4
CH ₂ CO	-152.620089	0.031510		210.2
CH ₂ CO ^{•+}	-152.265089	0.031177	211.4	210.2
CH ₃ CCH	-116.637358	0.055491		44.6
CH ₃ CCH ^{•+}	-116.268204	0.050947	276.2	283.5
CH ₂ CCH ₂	-116.640560	0.054844		45.6
CH ₂ CCH ₂ ^{•+}	-116.292902	0.052349	261.7	269.0
CH ₂ CHCO ^{•+}	-191.012770	0.050586		

[a] Total energies based on B3LYP/6-311++G(d,p) optimized structures including ZPVE corrections (unscaled). – [b] Reference data as given in ref.^[40]. – [c] Heats of formation of ions and excited state species calculated from the difference in B3LYP/6-311++G(d,p) total energies of these and the corresponding ground-state neutrals. – [d] Since B3LYP calculations are problematic with the excited singlet state of oxygen atoms, the excitation energy of 1.967 eV (see ref.^[48]) relative to the triplet ground state has been added to the calculated energy of the triplet species. – [e] This value is derived from MR-CI calculations on the singlet-triplet gap of methylene (ref.^[49a]). – [f] HCCO⁺ is predicted to exhibit a triplet ground state with the singlet being ca. 30 kcal/mol higher in energy.

rearrangement to compete with electron loss. Similar arguments apply to the 1,2-hydrogen migration via TS1^{•-}/12^{•-} in that electron detachment is predicted to precede the formation of formyl methyl carbene anion 12^{•-} which is ca. 34 kcal/mol less stable than 1^{•-}. In analogy to 11^{•-}, the carbene 12^{•-} can decompose to CH₃CCO^{•-} anions and a hydrogen atom. Although 13^{•-} represents the isomer of highest energy studied here, the methoxy vinylidene radical-anion 13^{•-} is predicted to be a stable species in the gas phase^[51], as the EA of the corresponding neutral exceeds 30 kcal/mol. Below the threshold for electron detachment from 13^{•-}, C–O bond cleavage can proceed to yield HCC^{•-} and CH₃O[•], also providing a potential route for the isomerization to 3^{•-} via an ion-dipole complex of the type [HCC/CH₃O]^{•-}. Passage from the methoxy vinylidene/

methoxy acetylene part of the $^2[\text{C}_3\text{H}_4\text{O}]^{\bullet-}$ potential-energy surface to the other isomers requires extensive rearrangements, and we did not search for reaction pathways connecting both parts, but assume that isomerizations other than that of $13^{\bullet-}$ to $3^{\bullet-}$ do not occur.

From these calculations two major conclusions can be drawn. (i) It should be possible to generate at least five different $^2[\text{C}_3\text{H}_4\text{O}]^{\bullet-}$ isomers, i.e. $1^{\bullet-}$, $11^{\bullet-}$, $12^{\bullet-}$, $13^{\bullet-}$, and $14^{\bullet-}$, provided that appropriate precursors can be found. This set of anions therefore defines the structural scope of this study. (ii) Three of these isomers have fragmentation channels below the threshold for electron detachment and are expected to undergo unimolecular dissociation. $11^{\bullet-}$ can undergo facile loss of methyl radical^[50], $12^{\bullet-}$ can generate CH_3CCO^- anions by expulsion of a hydrogen atom, and for $13^{\bullet-}$ the occurrence of C–O bond cleavage is expected to yield HCC^- anions concomitant with neutral methoxy radicals. Instead, for the other two isomers, i.e. $1^{\bullet-}$ and $14^{\bullet-}$, no significant metastable ion decompositions are expected to be observed experimentally.

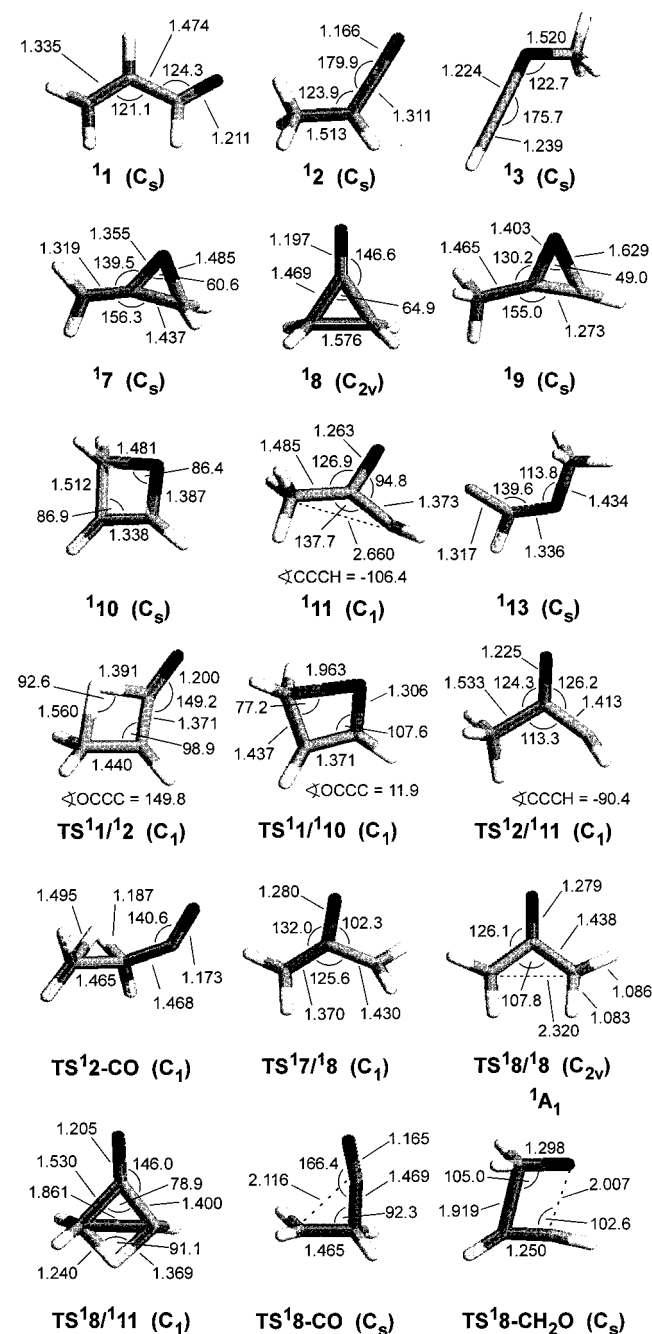
The Neutral Singlet $^1[\text{C}_3\text{H}_4\text{O}]$ Potential-Energy Surface

Owing to the fact that the singlet-triplet gaps of some neutrals, e.g. oxyallyl^{[20][21a]} and the carbenes^[52], are small, singlet and triplet surfaces need to be considered. Before discussing some particular questions concerning neutral oxyallyl in more detail, let us first provide an overview of the $^1[\text{C}_3\text{H}_4\text{O}]$ and $^3[\text{C}_3\text{H}_4\text{O}]$ potential-energy surfaces starting with the singlet isomers.

18 stationary points on the $^1[\text{C}_3\text{H}_4\text{O}]$ surface were optimized (Chart 4). The minima of lowest energy (Figure 2) are acrolein **1** ($\Delta H_f = -11.6$) and methyl ketene **2** ($\Delta H_f = -12.7$), which are almost comparable in energy (Table 3)^[53]. These two more conventional isomers are connected by 1,3-hydrogen transfer via **TS¹1/2** having a substantial energy demand (ca. 70 kcal/mol) but still lying below the $\text{CO} + \text{CH}_3\text{CH}$ and $\text{CH}_3^{\bullet} + \text{HCCO}^{\bullet}$ exit channels. The thermodynamically most favorable exit channel corresponds to formation of carbon monoxide and ethene, but the energy demand of the associated **TS¹2-CO** is huge. Accordingly, the interconversion $13 \rightleftharpoons 12$ is not facile, but feasible provided that a sufficient amount of internal energy is available.

Singlet oxetene **10** is ca. 30 kcal/mol higher in energy than **1** and can be accessed via **TS¹1/10** with an energy demand of 56 kcal/mol. It should be noted that acrolein exists in *s-cis* or *s-trans* conformations. Of course, ring closure to **10** involves the *s-cis* conformer as a starting point. As the *s-cis* and *s-trans* structures of **1** do not differ much in energy^[54] and the rotational barrier can be expected to be located below **TS¹1/10**, we take the *s-trans* isomer as representative for both conformers and refrain from discussing this aspect further. **10** appears to be a good candidate for fragmentation into $\text{CH}_2\text{O} + \text{C}_2\text{H}_2$, another exit channel which is not too high in energy. However, this reaction corresponds to a symmetry forbidden [2+2] cycloreversion proceeding via **TS¹10-CH₂O** reflected by the sizable barrier of 71 kcal/mol.

Chart 4

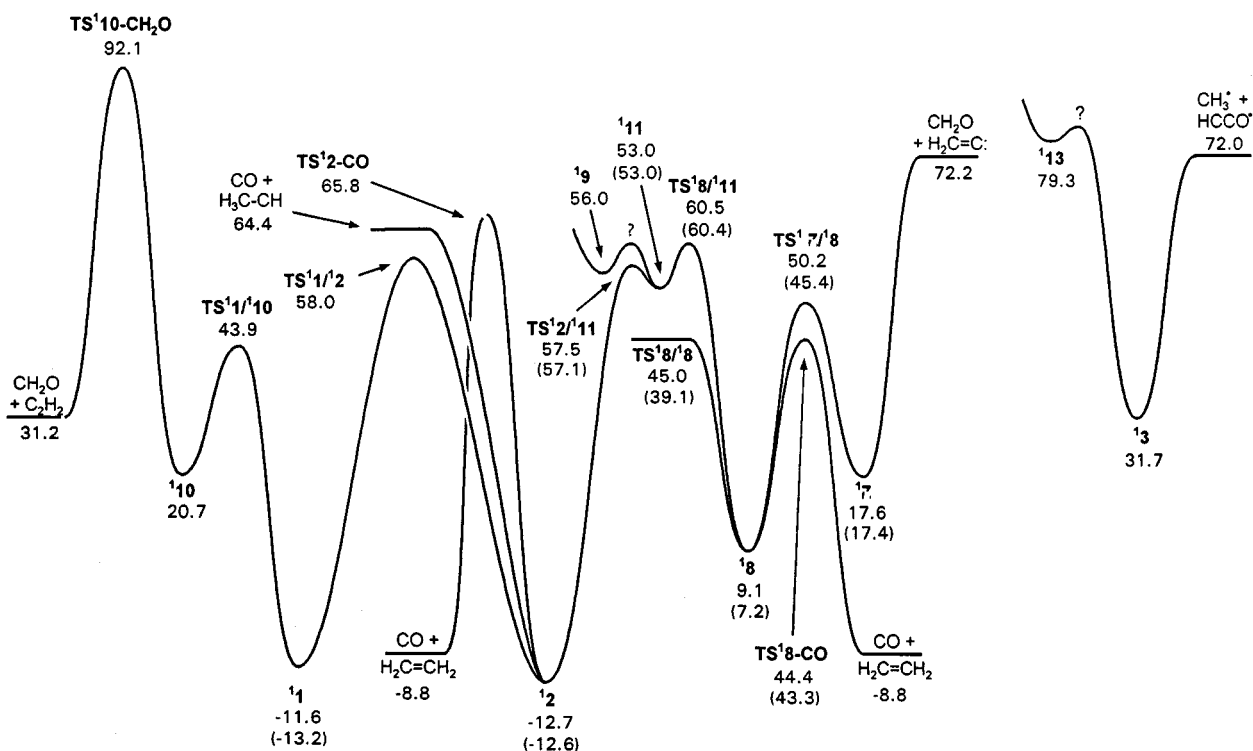


Methyl ketene **2** is also connected to acetyl carbene **11**, which is higher in energy by 65 kcal/mol. The associated **TS²1/11** for the well-known Arndt-Eistert rearrangement^{[6][7]} demands an energy of only 4.5 kcal/mol relative to the carbene. This result is in agreement with the large body of experimental studies^{[6][7]} which describe the formation of transient keto carbenes from diazo ketones to yield the corresponding ketenes as reaction products. Experiments with ^{13}C labeled diazo ketones^[6] revealed that the label is distributed between the former carbene and carbonyl carbon atoms, and oxirenes have been postulated as reaction intermediates^[2g]. In fact, methyl oxirene **19** has been generated and identified by neutralization-reionization

Table 3. Calculated total energies (E_t), zero-point vibrational energies (ZPVE), and calculated as well as experimental heats of formation (ΔH_f) of neutral singlet $^1[C_3H_4O]$ isomers and relevant fragmentation reactions^[a]

	$E_t(\text{B3LYP})^{[b]}$ (hartree)	ZPVE (hartree)	$\Delta H_f(\text{B3LYP})^{[c]}$ (kcal/mol)	$E_t(\text{G2})$ (hartree)	$\Delta H_f(\text{G2})$ (kcal/mol)	$\Delta H_f^{[e]}$ (kcal/mol)
CH ₂ CHCHO (¹ 1)	-191.913197	0.061062	-11.6		-13.2 ^[d]	-18.0
CH ₃ CHCO (¹ 2)	-191.914879	0.060763	-12.7		-12.6 ^[d]	-25.0
CH ₃ OCCH (¹ 3)	-191.844234	0.060446	31.7			
c-CH ₂ C(=CH ₂) (¹ 7)	-191.861719	0.061254	17.6	-191.539543	17.4	
c-CH ₂ CH ₂ CO (¹ 8)	-191.880069	0.060537	9.1		7.2 ^[d]	4.0
c-OCHC(-CH ₃) (¹ 9)	-191.805322	0.057272	56.0			
c-OCHCHCH ₂ (¹ 10)	-191.861616	0.062463	20.7			
CH ₃ COCH (¹ 11)	-191.810174	0.057601	53.0	-191.482789	53.0	
CH ₃ OCHC: (¹ 13)	-191.768328	0.058537	79.3			
TS ¹ ₁ / ₂	-191.802213	0.055580	58.0			
TS ¹ ₁ / ₁₀	-191.824641	0.059951	43.9			
TS ¹ ₂ / ₁₁	-191.803533	0.056119	57.5	-191.476214	57.1	
TS ¹ ₂ -CO	-191.789822	0.055123	65.8			
TS ¹ ₇ / ₈	-191.814573	0.057748	50.2	-191.494922	45.4	
TS ¹ ₈ / ₁₈ (*CH ₂ COCH ₂ *)	-191.822957	0.057756	45.0	-191.504859	39.1	
TS ¹ ₈ / ₁₁	-191.798161	0.056033	60.5	-191.471029	60.4	
TS ¹ ₈ -CO	-191.823775	0.057725	44.4	-191.498198	43.3	
TS ¹ ₁₀ -CH ₂ O	-191.747946	0.054674	92.1			
CO + H ₂ CCH ₂	-191.908774	0.055814	-8.8			-13.9
CH ₂ O + HCCH	-191.845024	0.053485	31.2			28.5
CO + H ₃ CCH	-191.792063	0.051516	64.4			
CH ₃ * + HCCO*	-191.779951	0.048023	72.0			
CH ₂ O + H ₂ CC:	-191.779679	0.050027	72.2			
HCO* + C ₂ H ₃ *	-191.771069	0.049262	77.6			
CH ₂ CO + ¹ CH ₂	-191.750337	0.048012	90.5			
CH ₂ CCH ₂ + ¹ O ^[f]			148.3			150.5

[a] The total energies of the fragments are given in Table 2. – [b] Total energies based on B3LYP/6-311++G(d,p) optimized structures including ZPVE corrections (unscaled). – [c] Calculated heats of formation on the basis of literature data (see Computational Details). – [d] G2 data taken from ref.^[39]; the data were adopted to the ΔH_f scale. – [e] Reference data as given in Table 2 and ref.^[40]. – [f] Since B3LYP calculations are problematic with the excited singlet state of oxygen atoms, the excitation energy of 1.967 eV (see ref.^[48]) relative to the triplet ground state has been added to the calculated energy of the $^1\text{CH}_2=\text{C}=\text{CH}_2 + ^3\text{O}$ exit channel.

Figure 2. Relevant parts of the singlet neutral $^1[C_3H_4O]$ potential-energy surface calculated at the B3LYP/6-311++G(d,p) level of theory. Values in brackets are heats of formation derived from G2 calculations (in part taken from ref.^[39])

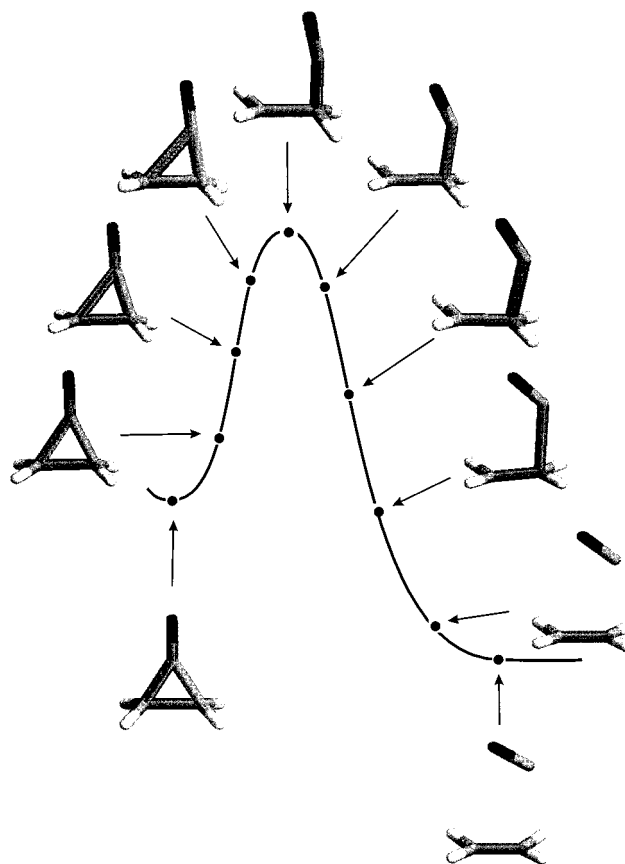
mass spectrometry^[4]. At the B3LYP/6-311++G(d,p) level of theory **19** corresponds to a local minimum energetically close to **11**. Although we did not succeed in locating the transition structure connecting **19** and **11**, this part of the potential-energy surface is assumed to be rather flat, because otherwise the exchange of the isotopic labels could not compete with the isomerization to **12**. Ring opening of **19** can either lead to acetyl carbene **11** or formyl methyl carbene **12**. While the Arndt-Eistert reaction of the former involves a methyl migration with a 4.5 kcal/mol barrier, the same reaction of **12** proceeds by a 1,2-hydrogen shift which can be expected to be even more facile. All attempts to locate **12** at the B3LYP/6-311++G(d,p) level failed and led to methyl ketene instead. This finding is in conflict with the result that photolysis of 2-diazo-[2-¹³C]propanal^[6] leads to a distribution of the ¹³C-label over the C(1) and C(2) positions of the methyl ketene formed. Accordingly, these experiments predict formyl methyl carbene as an intermediate with a lifetime long enough to undergo the isomerization **12** $\rightleftharpoons$ **19** $\rightleftharpoons$ **11**, and it remains an open question, whether or not **12** represents a genuine minimum.

With regard to singlet oxyallyl **14** (see below), we also searched for a transition structure connecting it with acetyl carbene **11** via a 1,3-hydrogen migration as found for the radical anions. Indeed, a TS was found only 7.5 kcal/mol higher in energy than the carbene, but an IRC calculation revealed that this transition structure, **TS18/11**, connects **11** with cyclopropanone **18** rather than oxyallyl. In fact, this finding is already indicated by the short C(1)–C(3) distance in **TS18/11** (1.861 Å, Chart 4) as compared to the much longer ones in **TS11^{•-}/14^{•-}** (2.207 Å, Chart 3) and **TS311/14** (2.209 Å, Chart 5, see below) of the radical anion and the triplet neutral, respectively. As **TS12/11** and **TS18/11** are quite close in energy, we performed G2 calculations^[55] (Figure 2, values in brackets) in order to verify the energetics. The G2 energies are in excellent agreement with the B3LYP results. Thus, in line with experimental data^{[6][7]} the Arndt-Eistert reaction **11** $\rightarrow$ **12** is more favorable than isomerization of **11** to cyclopropanone **18**.

Cyclopropanone **18** may decompose unimolecularly via **TS18-CO** into carbon monoxide and ethene which is exothermic by 18 kcal/mol and associated with a 35 kcal/mol barrier. According to the Woodward-Hoffmann rules^[56], the cycloreversion corresponds to a concerted [2+1] process which is thermally allowed due to the particular orbital situation at the carbene-like CO subunit. Unlike **18** itself, **TS18-CO** is, however, far from being *C*_{2v} symmetric (Chart 4)^[57]. In order to ensure that this transition structure indeed connects **18** with the CO + C₂H₄ exit channel, an IRC calculation was performed (Figure 3). Accordingly, loss of CO from cyclopropanone occurs as a concerted reaction in that no intermediate 1,3-biradical is involved, nevertheless it proceeds in an extremely asynchronous fashion. The first C–C bond is almost completely broken (*r*_{CC} = 2.116 Å) in the TS, while the second C–C bond is exactly as long as in **18** (*r*_{CC} = 1.469 Å). At this sort of geometry, some biradical character cannot be excluded, and some doubt could be cast upon the accuracy of the single-reference B3LYP

method; the very similar geometric and energetic results obtained with the G2 method are, however, comforting in this respect.

Figure 3. IRC calculation for the reaction **18** $\rightarrow$ **TS18-CO** $\rightarrow$ C₂H₄ + CO

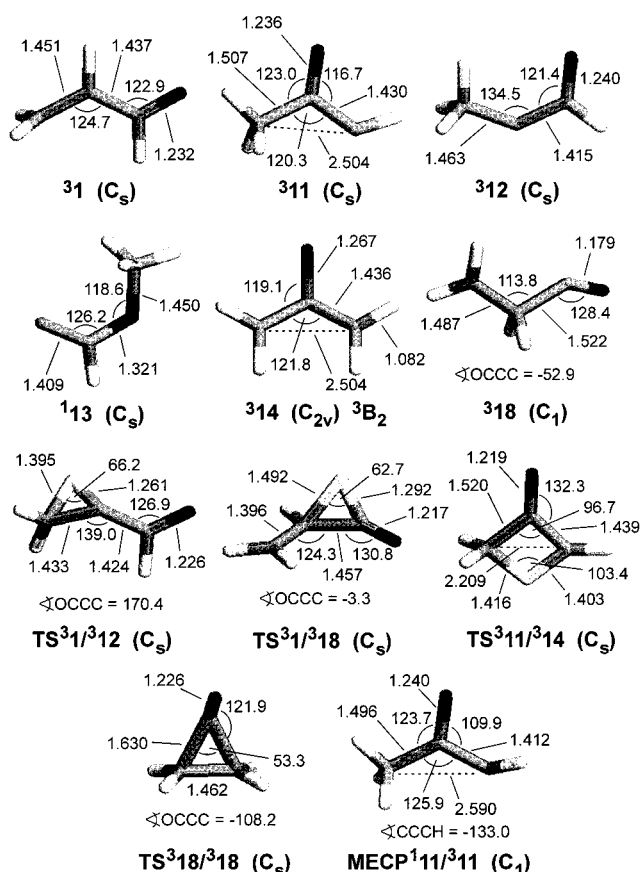


Cyclopropanone can also rearrange to allene oxide **17** via **TS17/18**. Allene oxides have long been predicted to be intermediates in the formation of cyclopropanones by oxidation of allenes with peracids^{[2][14]}, and experimental evidence for the existence of **17** has been provided by neutralization-reionization mass spectrometry^{[24][2e]} as well as matrix-isolation techniques^[2g]. The barrier for formation of cyclopropanone **TS17/18** is higher than **TS18-CO** by 6 kcal/mol at the B3LYP/6-311G++(d,p) level, but this difference diminishes to ca. 1 kcal/mol using the G2 method. Therefore, rearrangement to **17** starting with **18** might compete with the loss of CO, but **17** constitutes a dead end because the fragmentations into either H₂CO + H₂CC, H₂CCO + ¹CH₂, or H₂CCCH₂ + ¹O are quite high in energy (55, 73, and 131 kcal/mol relative to **17**, respectively). Methoxy acetylene **13** and methoxy vinylidene **13** were found as local minima. In accordance with the thermochemistry of other vinylidenes^[9], **13** is more stable than **13** by ca. 48 kcal/mol. While all attempts failed to locate a TS connecting these minima, it seems reasonable to assume that it is close in energy to **13** due to the presence of a hydrogen atom in the vinylidene unit.

The parts of the [¹C₃H₄O] potential-energy surface described so far are in reasonable agreement with previous

calculations and known experimental data. However, there exists one major problem which is directly connected to a central topic of this study. Thus, ¹A₁ oxyallyl **14** is predicted to be a transition structure for the symmetry allowed, disrotatory **18** → **TS^{18/18}** → **18** stereomutation of cyclopropanone rather than being a genuine minimum. As a consequence, acetyl carbene **11** and allene oxide **17** are also not connected to oxyallyl, but directly to cyclopropanone. The prediction of ¹A₁ oxyallyl as a saddle point is in marked contrast to earlier studies^{[20][21]}, shedding some doubt on the performance of B3LYP in accurately describing ¹A₁ oxyallyl (see below).

Chart 5



The Neutral Triplet ³[C₃H₄O] Potential-Energy Surface

For the neutral triplet surface (Figure 4), six local minima (Chart 5) have been located which correspond to acrolein **31**, acetyl carbene **311**, formyl methyl carbene **312**, methoxy vinylidene **313**, oxyallyl **314**, and the C-CO ring opened biradical **318**. Thus, exactly those five structures which correspond to stable anions (see above) are local minima on the triplet surface of the neutral species^[58].

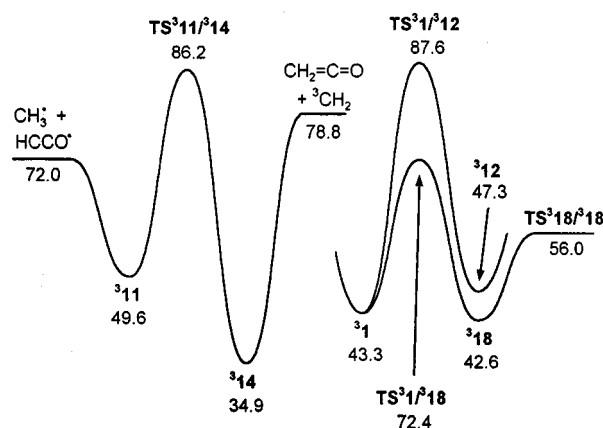
Surprisingly, ³B₂ oxyallyl **314** represents the most stable of these, being separated by a barrier of 51 kcal/mol with respect to 1,3-hydrogen shift via **TS^{311/314}** to yield triplet acetyl carbene **311** (Table 4). The lowest exit channel proceeds from **311** to CH₃• + HCCO• with an energy demand of 22 kcal/mol relative to the carbene. The isomerization **314** ⇌ **311** is, however, unlikely because the formation of

Table 4. Calculated total energies (*E_t*), zero-point vibrational energies (ZPVE), and calculated as well as experimental heats of formation (Δ*H_f*) of neutral triplet ³[C₃H₄O] isomers and relevant fragmentation reactions^[a]

	<i>E_t</i> ^[b] (hartree)	ZPVE (hartree)	Δ <i>H_f</i> ^[c] (kcal/mol)	Δ <i>H_f</i> ^[d] (kcal/mol)
³ CH ₂ CHCHO (31)	-191.825675	0.056509	43.3	
³ CH ₃ COCH (311)	-191.815498	0.057920	49.6	
³ CH ₃ CCHO (312)	-191.819235	0.058379	47.3	
³ CH ₃ OCHC: (313)	-191.732148	0.058825	102.0	
³ •CH ₂ COCH ₂ •	-191.839073	0.056839	34.9	
(³ B ₂) (314)				
³ •CH ₂ CH ₂ CO• (318)	-191.826711	0.056385	42.6	
TS^{31/312}	-191.750100	0.052037	90.6	
TS^{31/318}	-191.779254	0.053445	72.4	
TS^{311/314}	-191.757155	0.051756	86.2	
TS^{318/318}	-191.805137	0.058083	56.0	
(³ C-CH ₂ CH ₂ CO)				
CH ₃ • + HCCO•	-191.779951	0.048023	72.0	
CH ₂ CO + ³ CH ₂	-191.769081	0.048635	78.8	81.6
CH ₂ CCH ₂ + ³ O	-191.730440	0.054844	103.0	105.2

[a] The total energies of the fragments are given in Table 2. — [b] Total energies based on B3LYP/6-311++G(d,p) optimized structures including ZPVE corrections (unscaled). — [c] Calculated heats of formation on the basis of literature data (see Computational Details). — [d] Reference data as given in Table 2 and ref.^[40].

Figure 4. Relevant parts of the triplet neutral ³[C₃H₄O] potential-energy surface calculated at the B3LYP/6-311++G(d,p) level of theory



ketene and triplet methylene provides an exit channel which is directly accessible from triplet oxyallyl requiring 7 kcal/mol less energy than **TS^{311/314}**.

Rearrangement of formyl methyl carbene **312** into the lowest triplet state of acrolein **31** is exothermic by ca. 4 kcal/mol and proceeds via **TS^{31/312}** having an energy demand of ca. 45 kcal/mol. Similarly, a 1,2-hydrogen shift via **TS^{31/318}** connects **31** and **318** which are close in energy with a mutual barrier of about 30 kcal/mol. Triplet cyclopropanone does not correspond to a local minimum and can rather be regarded as the transition structure for the degenerate exchange of the two methylene groups in **318** which is expected to be facile because **TS^{18/18}** is located only 13 kcal/mol above **318**.

Due to the significant singlet-triplet gaps of 53 and 23 kcal/mol, respectively, the triplet isomers **31** and **313** are not

likely to be formed by electron detachment of the corresponding radical anions in NR experiments. Instead, the triplet state of acetyl carbene **311** is calculated to be ca. 4 kcal/mol more stable than the singlet. This result is in agreement with previous calculations as well as experimental work on π -acceptor substituted carbenes such as dicyano methylene and others^[52]. Due to the energetic proximity of singlet and triplet **11**, spin inversion shall be considered too. Both states have geometries differing particularly with respect to the HCCO dihedral and the CCC and CCO angles. Therefore, a reasonable description of the spin inversion requires the determination of the minimum-energy crossing point (MECP) between these two states. MECP **111/311** was located ca. 9 kcal/mol above **311**. The geometry (Chart 5) corresponds almost to an averaged structure of both minima. At the MECP, the matrix element for spin inversion was computed as $H^{SO} = 5.5 \text{ cm}^{-1}$. The magnitude of H^{SO} tends to increase with the atomic number,^{[45][59]} and the size of the computed value can be regarded as being typical for carbon; for example, H^{SO} of methylene was determined^[60] as 8 cm^{-1} . Although small, these matrix elements may still account for an efficient spin crossing under the experimental conditions (see below).

Table 5. Frequencies for the dis- and conrotatory movements of the CH_2 groups at the C_{2v} optimized geometry of the $^1\text{A}_1$ state of singlet oxyallyl **14**

	ν_1 (disrot)	ν_2 (conrot)
RHF/3-21G	410i	779 (ν_5)
RHF/6-31G	329i	766 (ν_5)
RHF/6-31G(d)	419i	779 (ν_5)
BHLYP/6-311++G(d,p)	402i	724 (ν_5)
B3LYP/6-311++G(d,p)	405i	954 (ν_9)
BLYP/6-311++G(d,p)	1098i, 302i ^[c]	638 (ν_5)
BP86/6-311++G(d,p)	1141i, 340i ^[c]	640 (ν_5)
CASSCF(2,2)/3-21G	140	471 (ν_3)
CASSCF(4,4)/6-31G(d) ^[a]	132	411
CASSCF(6,5)/3-21G ^[b]	170	230
CASSCF(6,5)/3-21G	116i	374
CASSCF(6,5)/6-31G	128i	376
CASSCF(6,5)/6-31G(d)	87i	403
CASSCF(6,5)/D95*	95i	404
CASSCF(6,7)/6-31G(d)	76	449 (ν_3)

^[a] Taken from ref.^[23]. — ^[b] From numerical differentiation of analytical gradients. Taken from ref.^[20b]. — ^[c] The vibrational analysis of C_{2v} symmetric $^1\text{A}_1$ oxyallyl with pure density functionals leads to two imaginary frequencies. The larger of these corresponds to a C_2 symmetric out of plane movement of the four hydrogen atoms.

Table 6. Characteristic geometrical parameters of the C_{2v} symmetric $^3\text{B}_2$ and $^1\text{A}_1$ States of oxyallyl **14** at various levels of theory

	$^3\text{B}_2$	$^1\text{A}_1$				
	r_{cc}	r_{co}	a_{cco}	r_{cc}	r_{co}	a_{cco}
BP86/6-311++G(d,p)	1.446	1.275	119.2	1.452	1.245	126.1
BLYP/6-311++G(d,p)	1.447	1.280	119.2	1.455	1.248	125.8
B3LYP/6-311++G(d,p)	1.436	1.267	119.1	1.438	1.238	126.1
BHLYP/6-311++G(d,p)	1.424	1.259	119.0	1.421	1.229	126.4
HF/6-31G(d)	1.425	1.275	118.6	1.413	1.231	126.8
MP2/6-31G(d)	1.443	1.243	119.5	1.451	1.236	126.5
CASSCF(6,5)/6-31G(d)	1.440	1.250	119.2	1.467	1.211	122.9

Table 7. Total energies (E_t) of $^1\text{A}_1$ oxyallyl (**14**) and energies (E_{rel}) of $^3\text{B}_2$ oxyallyl (**314**) and cyclopropanone (**18**) relative to $^1\text{4}$ at various levels of theory

	$^1\text{A}_1$ Oxyallyl $E_t^{[a]}$	$^3\text{B}_2$ Oxyallyl $E_{\text{rel}}^{[b]}$	Cyclo- propanone $E_{\text{rel}}^{[b]}$
ZPVE	0.059988	0.060220	0.065149
(CASSCF(6,5)/6-31G(d))			
HF/cc-pVDZ	−190.660187	−40.0	−51.2
MP2/cc-pVDZ	−191.270594	−17.7	−40.1
CCSD/cc-pVDZ	−191.299715	−13.5	−39.7
CCSD(T)/cc-pVDZ	−191.338351	−1.6	−29.6
G2 ^[c]	−191.504859	−0.8	−31.9
BHLYP/6-311++G(d,p) ^[d]	−191.751742	−21.6	−43.4
B3LYP/6-311++G(d,p) ^[d]	−191.839073	−10.1	−35.9
BLYP/6-311++G(d,p) ^[d]	−191.826946	−2.2	−31.8
BP86/6-311++G(d,p) ^[d]	−191.882780	−3.3	−36.7
CASSCF(6,5)/6-31G(d)	−190.734961	−4.8	−23.1
CASSCF(6,5)/cc-pVDZ	−190.758435	−3.8	−28.8
CASPT2/cc-pVDZ	−191.291950	−1.6	−23.3
CASPT3/cc-pVDZ	−191.317058	−1.2	−28.9
MR-CISD/cc-pVDZ	−191.252650	−1.7	−28.4
MR-CISD(+Q)/cc-pVDZ	−191.325658	−1.1	−28.2
MR-ACPF/cc-pVDZ	−191.330166	−0.9	−27.9
MR-ACPF/cc-pVTZ	−191.492953	−0.3	−30.1

^[a] Total energies of the $^1\text{A}_1$ state of oxyallyl from single-point calculations at CASSCF(6,5)/6-31G* geometry. — ^[b] Energies relative to the $^1\text{A}_1$ state of oxyallyl from single-point calculations at CASSCF(6,5)/6-31G* geometries, and including the (unscaled) CASSCF zero-point energy. — ^[c] Standard G2 procedure. — ^[d] Geometries fully optimized at the levels of theory given here.

Neutral Oxyallyl: A Challenge for Computational Chemistry

In view of the note by Osamura et al.^[20b] that “the electronic state for this system is not necessarily best described by a one-configuration wave function”, the failure of B3LYP in describing neutral $^1\text{A}_1$ oxyallyl is not surprising, as the method is essentially a one-determinant procedure and contains an “exact” Hartree-Fock exchange contribution. This conjecture is further supported by the fact that RHF calculations with different basis sets (Table 5) lead to similar results with respect to the imaginary frequency for the disrotatory ring closure and predict singlet oxyallyl as a saddle point.

Three questions shall be addressed in this section: (i) Is $^1\text{A}_1$ oxyallyl a transition structure or a local minimum? (ii) How large is the singlet-triplet splitting? (iii) What is the probability of spin crossing from $^3\text{B}_2$ to $^1\text{A}_1$ oxyallyl? In contrast to the hybrid method B3LYP, pure density functional theory might be expected to correctly describe the electronic structure of $^1\text{A}_1$ oxyallyl, and therefore the BLYP and BP86 functionals have been applied. As a reference, we have chosen the frequencies (Table 5), geometries (Table 6), and relative energies of $^1\text{A}_1$ and $^3\text{B}_2$ oxyallyl as well as cyclopropanone (Table 7) obtained with CASSCF or MR-CI methods (bold entries). In general, the geometrical parameters of the $^3\text{B}_2$ state are similar for all methods, while for the $^1\text{A}_1$ state all density functionals used show deviations of up to ca. 0.05 Å and 3° , respectively, as compared to the CASSCF results. As far as the singlet-triplet splitting is concerned, the pure density functionals BLYP and BP86 are in reasonable agreement with CASSCF calculations

(Table 7). The more Hartree-Fock exchange is taken into consideration, the larger the singlet-triplet splitting, i.e. -10.1 kcal/mol for B3LYP, -21.6 kcal/mol for BHLYP, and -40.0 kcal/mol for a HF calculation. Similar arguments hold true for the energy difference between 1A_1 oxyallyl and cyclopropanone, for which we consider a value of ca. -30 kcal/mol as derived from MR-CI as a good estimate. In accord with the change in the singlet-triplet splitting, 1A_1 oxyallyl becomes destabilized the more HF character is included. Interestingly, the BLYP and BP86 density functionals even lead to two imaginary frequencies in the vibrational analysis of C_{2v} symmetric 1A_1 oxyallyl, one corresponding to the disrotatory ring closure ($302i$ cm^{-1} and $340i$ cm^{-1} , respectively), the second, even larger one ($1098i$ cm^{-1} , $1141i$ cm^{-1}) describing a C_2 symmetric out-of-plane movement of the four hydrogen atoms. At these levels the 1A_1 state is neither a local minimum, nor a transition structure, but a higher-order saddle point. Hence, we conclude that these density functionals cannot describe singlet oxyallyl.

From earlier vibrational analyses at the CASSCF(4,4)/6-31G(d)^[23] and CASSCF(6,5)/3-21G levels with numerical differentiation of analytical gradients^[20b], 1A_1 oxyallyl has been predicted to be a local minimum. The lowest, real frequency has been assigned to disrotatory movement of the two methylene groups. However, the transition structure associated with ring closure to cyclopropanone was only 0.33 kcal/mol above the minimum. We could reproduce these results qualitatively, but obtain one imaginary frequency with CASSCF(6,5)/3-21G (additional inclusion of the in-plane oxygen lone-pair (b_2) in the active space), if the frequencies are calculated analytically. The situation is not very sensitive to the size of the basis set for a given active space, i.e. all analytical frequency calculations at the CASSCF(6,5) level (Table 5) predict imaginary frequencies of about $100i$ cm^{-1} . Upon further increase of the active space in a CASSCF(6,7)/6-31G(d) calculation (addition of two virtual (a_1 , b_2) orbitals in the active space) the frequency becomes real again (76 cm^{-1}), thus, predicting singlet oxyallyl as a genuine intermediate. In conclusion, there is no obvious trend which correlates the size of either the active space or the basis set with the nature of 1A_1 oxyallyl. In fact, these calculations cannot decide whether 1A_1 oxyallyl is a local minimum or a transition structure, but only lead to the conclusion that the $^1[C_3H_4O]$ potential-energy surface is rather flat around 1A_1 oxyallyl. Moreover, even if 1A_1 oxyallyl represents a real minimum on the potential-energy surface, rearrangement to cyclopropanone is expected to be very facile. In conclusion, 1A_1 oxyallyl is very likely to escape all attempts of its generation and identification by neutralization-reionization mass spectrometry, although very flat potential-energy surfaces with wells of less than a few kcal/mol have been successfully probed using this method^{[61][62]}.

The singlet-triplet splitting was studied by a series of energy calculations at higher levels using the optimized CASSCF(6,5)/6-31G(d) geometry (Table 7). Starting from -4.8 kcal/mol with CASSCF(6,5)/6-31G(d), the splitting of

the 1A_1 and 3B_2 states diminishes to -1.6 and -1.2 kcal/mol upon inclusion of perturbation theory in CASPT2 and CASPT3 calculations, respectively, to only -0.3 kcal/mol at the MR-ACPF level of theory using the sizable cc-pVTZ basis set. In fact, both states are almost isoenergetic, although the triplet remains the ground state at all levels applied here.

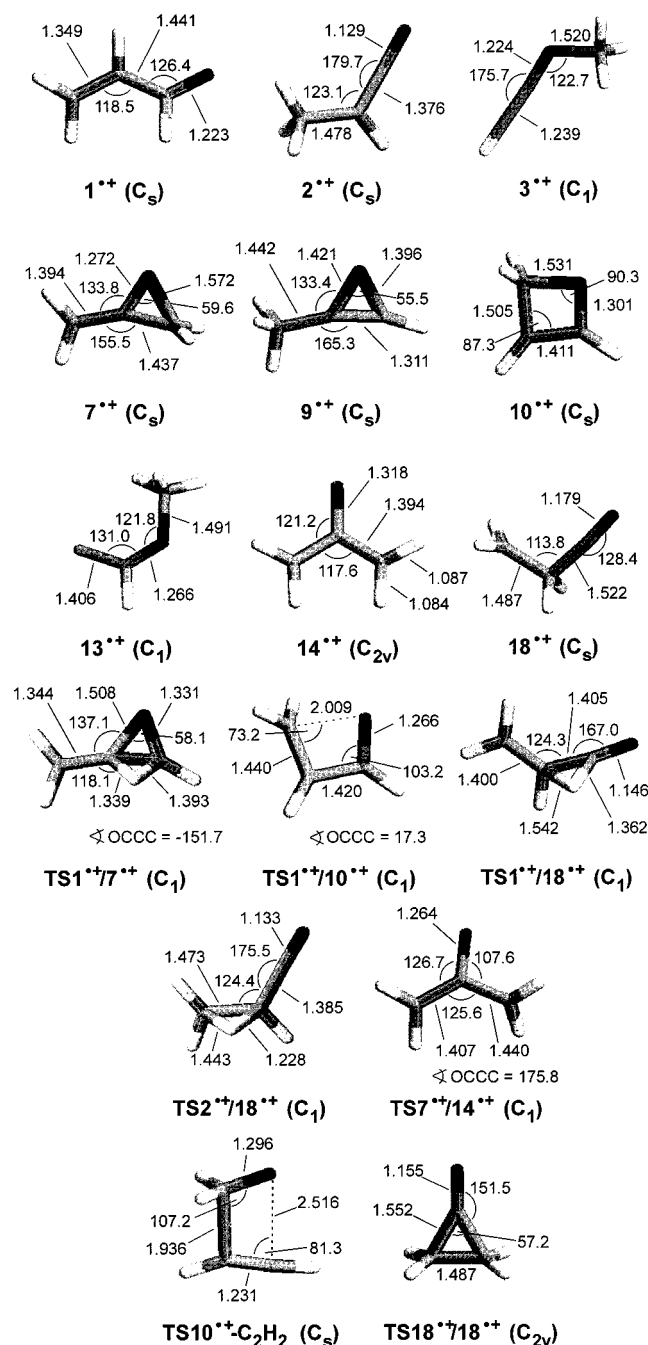
Thus, the 1A_1 and the 3B_2 states of oxyallyl are very similar not only with respect to their geometries, but also as far as their relative energy is concerned. Surface hopping from the triplet to the singlet surface may therefore play a role. Accordingly, 3B_2 oxyallyl could undergo spin inversion to the singlet surface, followed by ring closure to cyclopropanone. Provided that this process is efficient, also 3B_2 oxyallyl would represent a short-lived species. The highest probability for spin crossing can be expected at the minimal-energy crossing point (MECP)^{[47][63]} on the crossing seam of both potential-energy surfaces. Unlike in the case of the acetyl carbene system, the triplet and singlet minima in the oxyallyl system are very close, and since their energies are nearly degenerate, the MECP can be assumed to lie very close to both minima, and does not need to be located. The spin-orbit coupling element H^{SO} calculated at the singlet minimum is extremely small (ca. 0.05 cm^{-1}) whatever the wavefunction used to calculate it^[64]. The calculated H^{SO} of **14** is two orders of magnitude smaller than that for acetyl carbene (see above), suggesting that interconversion of the 1A_1 and 3B_2 states of oxyallyl may be inefficient in the μs timescale. In summary, the triplet state of oxyallyl is predicted to be experimentally accessible, because the thresholds for isomerization and/or fragmentation are sufficiently large and the triplet lifetime may suffice for its detection.

The Cationic $^2[C_3H_4O]^{++}$ Potential-Energy Surface

With respect to the NR experiments reported further below, some knowledge about the cationic surface is required (Figure 5)^{[2d][2e][4][41]}. 16 stationary points (Chart 6) were located and their energetics as well as those of a variety of exit channels were evaluated (Table 8).

Ionized methyl ketene 2^{++} represents the most stable isomer, and its geometry resembles much the corresponding singlet neutral. Direct cleavage of a terminal C–H bond in 2^{++} , leading to $H_2CCHCO^+ + H^\bullet$, is quite favorable in energy and lies only ca. 9 kcal/mol above $CO + C_2H_4^{++}$. Two 1,2-hydrogen shifts lead from 2^{++} via $TS2^{++}/18^{++}$ to 18^{++} , a prototype distonic ion^{[28][65]}, and from 18^{++} via $TS1^{++}/18^{++}$ to ionized acrolein 1^{++} . The *s-cis* form of 1^{++} can undergo ring closure via $TS1^{++}/10^{++}$ to the oxetene radical cation 10^{++} . Due to the similar energetics of $TS1^{++}/10^{++}$ and $TS1^{++}/18^{++}$ the isomerizations $1^{++} \rightarrow 10^{++}$ and $1^{++} \rightarrow 18^{++}$ might compete to some extent. With respect to a mass spectrometric characterization, the formation of 10^{++} is, however, a dead end, as no low-lying, direct exit channels are accessible for this radical cation. For example, the most probable fragmentation into acetylene and ionized formaldehyde via $TS10^{++}-C_2H_2$ requires 50 kcal/mol more than $TS1^{++}/10^{++}$. Instead, energized 1^{++} and 10^{++} are likely to reach the $H_2CCHCO^+ + H^\bullet$ exit channel.

Chart 6



A different situation is found for allene oxide 7^{++} and oxyallyl radical-cations 14^{++} which are located 39 and 60 kcal/mol above 2^{++} , respectively. In line with earlier results^[2c], the oxyallyl radical-cation 14^{++} represents a high-energy minimum on a rather flat part of the $^2[C_3H_4O]^+$ potential-energy surface. It is connected to the more favorable allene oxide cation 7^{++} by $TS7^{++}/14^{++}$, and calculations at the MP4/6-31G(d) level have predicted a barrier of no more than 2 kcal/mol^[2c]. At the B3LYP/6-311++G(d,p) level, $TS7^{++}/14^{++}$ is unambiguously characterized by a single imaginary frequency corresponding to the ring closure $14^{++} \rightarrow 7^{++}$, but it is found to be slightly

lower in energy than 14^{++} . This result is obviously wrong, but still within the error margins of ± 5 kcal/mol. Notwithstanding, the qualitative conclusion remains unchanged in that ionized oxyallyl is predicted to rapidly rearrange to allene oxide radical-cations. The earlier experiments^[2c] also revealed an intense loss of CH_2 concomitant with the formation of ionized ketene from allene oxide radical-cations 7^{++} . Owing to the fact that this exit channel is ca. 70 kcal/mol higher in energy than $CO + C_2H_4^{++}$, appreciable barriers and/or dynamic bottlenecks must prevent isomerization of 7^{++} and/or 14^{++} to any of the other isomers which can decompose into CO and $C_2H_4^{++}$. Indeed, a concerted 1,2-hydrogen shift via $TS1^{++}/7^{++}$ was located which is more than 60 kcal/mol above 7^{++} and only 6 kcal/mol below the threshold of the $^3CH_2 + H_2CCO^{++}$ exit channel. If one takes into account that rearrangements are entropically less favorable as compared to direct bond cleavages, it is obvious that both pathways compete in high-energy collisions. Hence, it appears as if 7^{++} and 14^{++} are somewhat separated from the other parts of the potential-energy surface. Nevertheless, there might exist other feasible reaction pathways with lower energy demands. A plausible candidate would be the formation of ionized cyclopropanone from 7^{++} , which then could decompose to $CO + C_2H_4^{++}$. However, in analogy to the triplet neutral, ionized cyclopropanone does not correspond to a local minimum, but to $TS18^{++}/18^{++}$ which describes the degenerate interchange of the two methylene groups in the acyclic distonic ion 18^{++} . Further, all attempts to locate a transition structure for C–C ring closure from 14^{++} or a concerted C–O ring cleavage/C–C closure from 7^{++} failed. $TS18^{++}/18^{++}$ is 10 kcal/mol lower than the $CO + C_2H_4^{++}$ exit channel which is consistent with the observation^[2c] of partial exchange of the two methylene groups in unsymmetrically labeled 18^{++} .

With respect to the radical cations of acetyl and formyl methyl carbenes, several attempts to optimize their geometries always lead only to ionized methyl oxirene 9^{++} . This result is again in accord with experimental studies^[4], which demonstrated that upon ionization of diazo acetone 9^{++} instead of ionized acetyl carbene is formed. Finally, though quite energetic the radical cations of methoxy acetylene 3^{++} and methoxy vinylidene 13^{++} were located as local minima; again, the transition structure connecting these isomers could not be located.

Predictions Emerging from the Calculations

The presentation of the theoretical results so far described the potential-energy surfaces one by one in a kind of “horizontal” view. Neutralization-reionization (NR) and charge-reversal (CR) experiments involve, however, transitions from one surface to another by electron transfer. Accordingly, we shall attempt to draw some conclusions from the theoretical results in order to make predictions for the experiments.

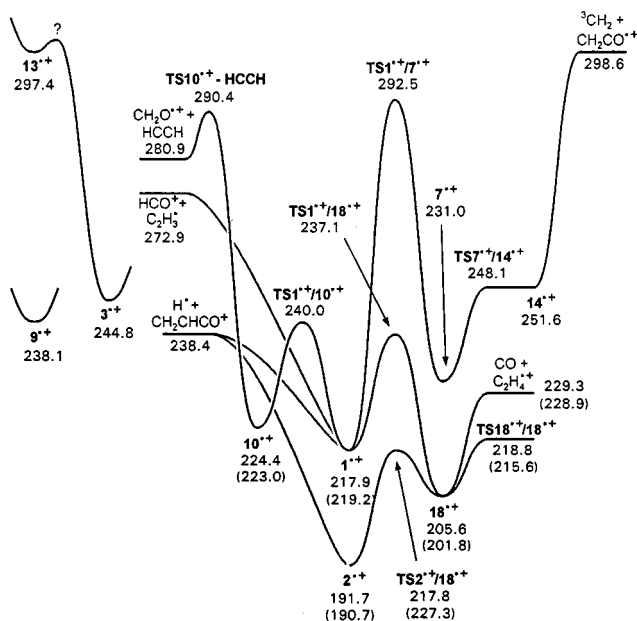
The electron-transfer processes occurring in NR and CR experiments can be considered to occur as vertical processes which proceed without any significant geometrical changes^[66]. Hence, Franck-Condon factors may play a cru-

Table 8. Calculated total energies (E_t), zero-point vibrational energies (ZPVE), and calculated as well as experimental heats of formation (ΔH_f) of cationic [C₃H₄O]^{•+} isomers and relevant fragmentation reactions^[a]

	$E_t^{[b]}$ (hartree)	ZPVE (hartree)	$\Delta H_f^{[c]}$ (kcal/mol)	$\Delta H_f^{[d]}$ (kcal/mol)	$\Delta H_f^{[e]}$ (kcal/mol)
CH ₂ CHCHO ^{•+} (1 ^{•+})	-191.549037	0.059192	217.9	215.0	208.6(B), 219.2(M)
CH ₃ CHCO ^{•+} (2 ^{•+})	-191.589240	0.059695	191.7	181.4	193.4(B), 190.7(M)
CH ₃ OCCH ^{•+} (3 ^{•+})	-191.504748	0.059186	244.8		
c-OCH ₂ C(=CH ₂) ^{•+} (7 ^{•+})	-191.526705	0.060290	231.0		228.5(T)
c-OCHC(-CH ₃) ^{•+} (9 ^{•+})	-191.515201	0.058519	238.1		232.1(T)
c-OCHCHCH ₂ ^{•+} (10 ^{•+})	-191.537224	0.062190	224.4		222.5(B); 223.0(M)
CH ₃ OCHC ^{•+} (13 ^{•+})	-191.420971	0.057865	297.4		
*CH ₂ COCH ₂ ^{•+} (14 ^{•+})	-191.493849	0.059510	251.6		251.7(T)
*CH ₂ CH ₂ CO ^{•+} (18 ^{•+})	-191.567123	0.058848	205.6		200.5(B,T), 201.8(M)
TS1 ^{•+} /7 ^{•+}	-191.428682	0.052529	292.5		
TS1 ^{•+} /10 ^{•+}	-191.512368	0.059647	240.0		
TS1 ^{•+} /18 ^{•+}	-191.517064	0.054396	237.1		
TS2 ^{•+} /18 ^{•+}	-191.532597	0.055826	217.8		227.3(M)
TS7 ^{•+} /14 ^{•+}	-191.499332	0.057386	248.1		253.7(T)
TS10 ^{•+} -C ₂ H ₂	-191.432045	0.054536	290.4		
TS18 ^{•+} /18 ^{•+}	-191.546097	0.058868	218.8	213.8 ^[f]	226.4(B), 221.8(T) 215.6(M)
CO + C ₂ H ₄ ^{•+}	-191.529456	0.053329	229.3	228.5	224.2(T), 228.9(M)
CH ₂ CHCO ^{•+} + H [•]	-191.515027	0.050586	238.4		
HCO ^{•+} + C ₂ H ₃ [•]	-191.460035	0.050781	272.9	271.3	
CH ₂ O ^{•+} + HCCH	-191.447276	0.050826	280.9	279.2	
CH ₂ O + HCCH ^{•+}	-191.431369	0.052583	290.9	291.0	
CH ₂ O ^{•+} + H ₂ CC:	-191.381931	0.047368	321.9		
CH ₂ O + H ₂ CC: ^{•+}	-191.366288	0.048102	331.7		
CH ₂ CO ^{•+} + ³ CH ₂	-191.414081	0.048302	298.6	303.2	
CH ₂ CO ^{•+} + ¹ CH ₂	-191.395337	0.047673	313.4		
CH ₂ CCH ₂ ^{•+} + ³ O	-191.382782	0.052349	321.3	328.6	

^[a] The total energies of the fragments are given in Table 2. – ^[b] Total energies based on B3LYP/6-311++G(d,p) optimized structures including ZPVE corrections (unscaled). – ^[c] Calculated heats of formation on the basis of literature data (see Computational Details). – ^[d] Reference data as given in Table 2 and ref.^[40]. – ^[e] Computed data at the UHF/6-31G(d) (B), MP4/6-31G(d) (T), and G2 (M) levels taken from ref.^[4], ref.^[39], and ref.^[41], respectively. The data were adopted to the ΔH_f scale. – ^[f] Although ionized cyclopropanone corresponds to TS18^{•+}/18^{•+}, the vertical ionization energy of the neutral has been measured. See ref.^[40].

Figure 5. Relevant parts of the cationic ²[C₃H₄O]^{•+} potential-energy surface calculated at the B3LYP/6-311++G(d,p) level of theory. Values in brackets are heats of formation derived from G2 calculations as taken from ref.^[39]. For clarity, some high-energy exit channels have been omitted (see Table 8)



cial role^[67] not only with respect to the efficiency of the electron-transfer processes, but also for the amount of in-

ternal energy imparted in the species formed. As qualitative rules, the efficiency of electron transfer decreases the larger the geometry differences of the different charge states are, and the amount of internal energy stored in the species formed by vertical electron transfer increases with the geometry differences. Thus, significant geometry differences will not only be associated with low efficiencies, but also with the formation of excited products and thus enhanced fragmentation. Having made these general remarks, let us consider the behavior of the five stable radical-anions in ⁻NR⁺ and ⁻CR⁺ experiments; for the time being it seems to be too ambitious to predict ⁻NIDD⁺ spectra.

(i) Due to the large singlet-triplet gap, singlet acrolein is most probably formed upon neutralization of 1^{•-}. As the radical anion and the singlet neutral have similar geometries, **1** will also be formed with little internal energy. Further, the barriers associated with any isomerizations are large. Hence, **1** is expected to survive as an intact entity in the μ s regime and will be then reionized to 1^{•+}. These considerations predict an intense survivor signal in the NR mass spectrum due to reionized **1**, accompanied by fragmentation via α -cleavages to yield H₂CCHCO⁺, HCO⁺, and C₂H₃⁺ fragments, respectively.

(ii) Due to the small singlet-triplet gaps, acetyl carbene **11** and formyl methyl carbene **12** can be formed from their radical anions in their triplet ground states or in the corresponding singlet states. Both singlet carbenes are predicted

to easily rearrange to methyl ketene $^1\mathbf{2}$. Due to the significant spin-orbit coupling constants, the triplet states may interconvert to the singlets also followed by isomerization to $^1\mathbf{2}$ within the μs regime. All these four routes lead to $^1\mathbf{2}$ containing a significant amount of excess energy (more than ca. 70 kcal/mol), such that within the lifetime of the neutral partial isomerization to acrolein $^1\mathbf{1}$ as well as fragmentation may occur despite the large energy demands. Due to these substantial differences between the anions and neutrals, weak survivor signals are expected for the radical anions of both carbenes. Instead, the structural features of energized $^1\mathbf{2}$ imply formation of the fragments H_2CCHCO^+ , H_nCO^+ ($n = 0, 1$), and C_2H_n^+ ($n = 0-4$) upon reionization to cations. In contrast to case (i), however, a significant amount of methyl radical loss concomitant with the HCCO^+ fragment is also expected. Based on these arguments, $^1\mathbf{1}^{\bullet-}$ and $^1\mathbf{2}^{\bullet-}$ are predicted to have similar, though certainly not identical $^- \text{NR}^+$ spectra.

(iii) The situation is less complicated for the radical-anion of methoxy vinylidene $^1\mathbf{3}^{\bullet-}$. The size of the singlet-triplet gap implies that neutralization leads predominantly to the singlet neutral, which subsequently suffers a facile 1,2-hydrogen shift to yield methoxy acetylene $^1\mathbf{3}$. Due to the significant exothermicity of this rearrangement, extensive fragmentation of $^1\mathbf{3}$ appears likely. Accordingly, the $^- \text{NR}^+$ and $^- \text{CR}^+$ spectra are expected to be dominated by the HCCO^+ fragment, along with signals characteristic for a methoxy moiety, i.e. H_nCO^+ ($n = 0-3$)^[63], as well as a weak recovery signal.

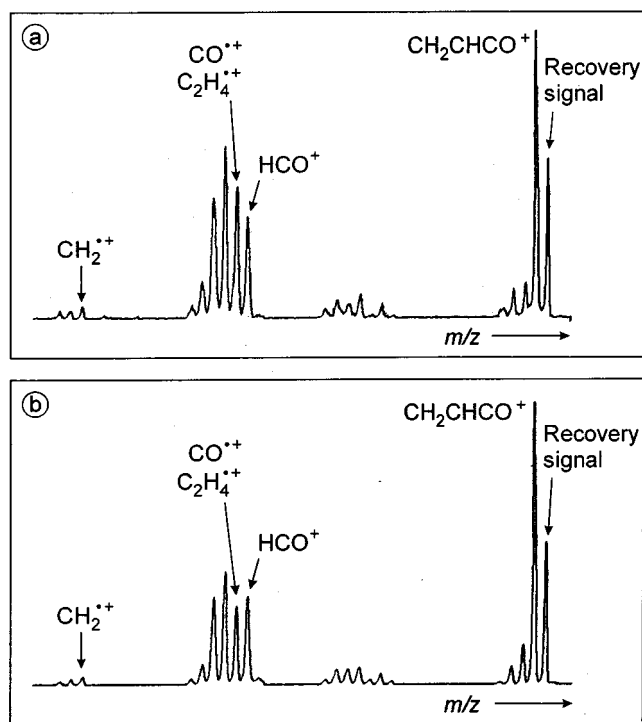
(iv) For neutral oxyallyl $^1\mathbf{14}$, the near degeneracy of the singlet and triplet states suggests that both neutrals are formed upon electron detachment from the radical anion. For the $^1\text{A}_1$ state the calculations predict isomerization to cyclopropanone, which can subsequently decompose to carbon monoxide and ethene due to the excess energy deliberated in the rearrangement $^1\mathbf{14} \rightarrow ^1\mathbf{8}$. As far as the formation of singlet oxyallyl as transient neutral is concerned, we thus expect a $^- \text{NR}^+$ spectrum which hardly shows a recovery signal, but is dominated by CO^+ and C_2H_n^+ ($n = 0-4$) fragments formed either by reionization of the neutral fragments or by fragmentation of the distonic ion $^1\mathbf{18}^{\bullet+}$. However, spin inversion of triplet oxyallyl to the singlet surface may be slow such that the $^3\text{B}_2$ ground state, $^3\mathbf{14}$, may survive at the neutral stage of a NR experiment. Reionization of this species to the radical-cation surface should then inter alia give rise to loss of methylene together with ionized ketene, H_2CCO^+ , as a characteristic fragmentation arising from the oxyallyl structure. The overall $^- \text{CR}^+$ and $^- \text{NR}^+$ spectra are then predicted to be superpositions of the processes described for each of the two states.

Experimental Results

$^- \text{NR}^+$, $^- \text{CR}^+$, and $^- \text{NIDD}^+$ methods have been applied to the radical-anions of acrolein $^1\mathbf{1}^{\bullet-}$, acetyl and formyl methyl carbenes $^1\mathbf{11}^{\bullet-}$ and $^1\mathbf{12}^{\bullet-}$, methoxy vinylidene $^1\mathbf{13}^{\bullet-}$, and oxyallyl $^1\mathbf{14}^{\bullet-}$. It turns out that these radical anions are distinguishable from each other by some structurally indica-

tive peaks in their CR mass spectra. Thus, one prerequisite for a successful application of NR experiments is fulfilled in that the anions under study are experimentally accessible and do not give rise to extensive isomerizations. In addition to the systems described further below, we examined a series of other reagent combinations also including positive ions. These results are, however, not included here as the ions formed were either isomeric mixtures or dealt with parts of the $[\text{C}_3\text{H}_4\text{O}]^{\bullet-/\bullet+}$ potential-energy surfaces which are not relevant for the oxyallyl system^{[2d][2e][4][41]}.

Figure 6. (a) $^- \text{NR}^+$ mass spectrum (O_2 , 80% T, O_2 , 80% T) and (b) $^- \text{CR}^+$ mass spectrum (O_2 , 80% T) of acrolein radical-anions $^1\mathbf{1}^{\bullet-}$ generated by NICI of a mixture of acrolein and N_2O

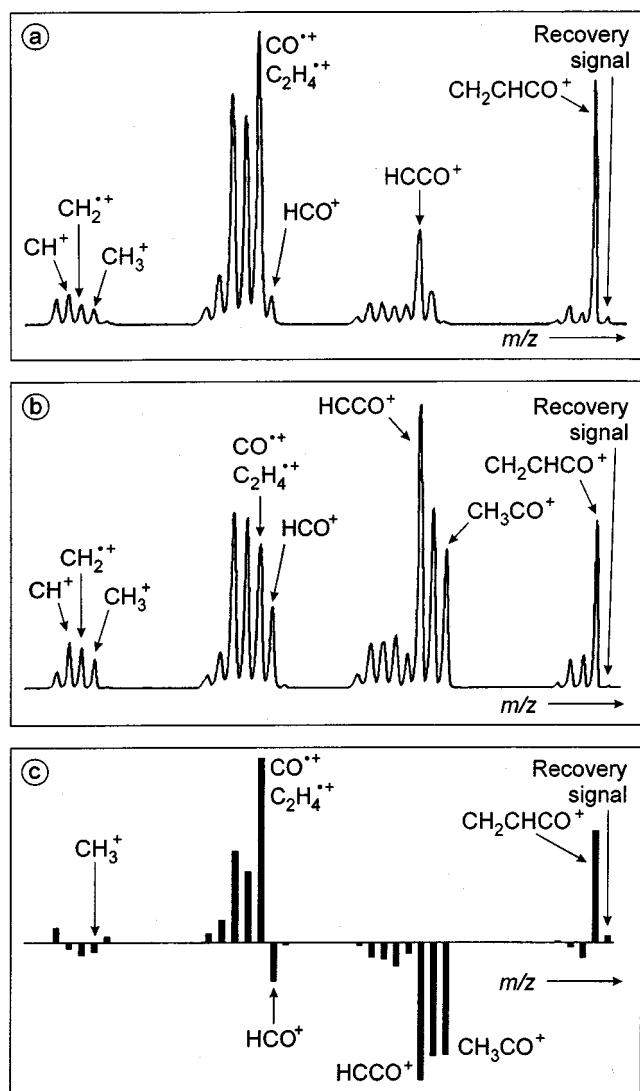


Acrolein Radical-Anion

The radical anion $^1\mathbf{1}^{\bullet-}$ can easily be generated by electron capture in negative ion chemical ionization (NICI) of acrolein with N_2O as reagent gas. As expected from the calculations, significant metastable ion decompositions are not observed for $^1\mathbf{1}^{\bullet-}$. The $^- \text{NR}^+$ and $^- \text{CR}^+$ mass spectra of $^1\mathbf{1}^{\bullet-}$ (Figure 6) are very similar. The most important features are: (i) a large recovery signal, (ii) the base peak corresponding to the loss of hydrogen, and (iii) less intense signals for HCO^+ and C_2H_4^+ or isobaric CO^+ , respectively. In fact, the minor differences between the $^- \text{NR}^+$ and $^- \text{CR}^+$ mass spectra are insignificant in terms of the NIDD scheme^[25], suggesting that the neutral does not rearrange extensively within the μs timescale as predicted above. Thus, the equilibrium structures of $^1\mathbf{1}^{\bullet-}$, $^1\mathbf{1}$, and $^1\mathbf{1}^{\bullet+}$ are similar to each other, such that the vertical electron-transfer processes are expected to proceed without imparting large amounts of internal energy into the neutral or the cation for the majority of these species. Formation of the triplet neutral $^3\mathbf{1}$

can rigorously be excluded due to the large singlet-triplet splitting. As a consequence, fragmentations as well as rearrangements are minor for acrolein, accounting for the intense recovery signals observed in both spectra. Among the fragment ions, those arising from the energetically and entropically favored α -cleavages prevail, i.e. H_2CCHCO^+ , HCO^+ , and $C_2H_3^+$. Though low in energy, the entropically disfavored rearrangement to 18^{*+} , which subsequently decomposes to $C_2H_4^{*+} + CO$, can only compete to a smaller extent. Overall, acrolein represents a system which is stable in the anionic, neutral and cationic forms and we consider **1** as a reference for the other $[C_3H_4O]$ isomers.

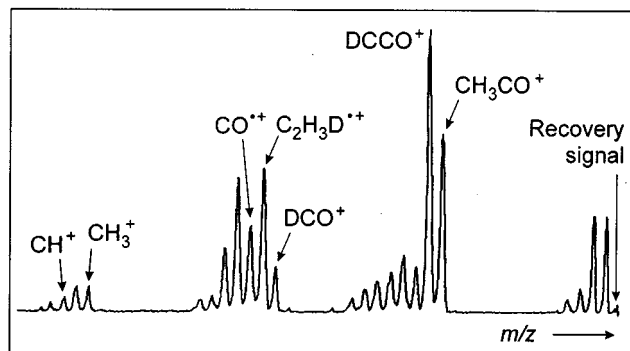
Figure 7. (a) $^{-}NR^+$ mass spectrum (O_2 , 80% T, O_2 , 80% T), (b) $^{-}CR^+$ mass spectrum (O_2 , 80% T), and (c) $^{-}NIDD^+$ spectrum of acetyl carbene radical-anions 11^{*-} generated by NICI of a mixture of diazoacetone and N_2O



Acetyl Carbene Radical-Anion

The generation of a pure ion beam of 11^{*-} is a straightforward matter if NICI of diazoacetone with N_2O as a reagent gas is applied. Electron capture of the diazo compound followed by loss of N_2 gives rise to an intense peak

Figure 8. $^{-}CR^+$ (O_2 , 80% T) mass spectrum of $[1-D_1]$ acetyl carbene radical-anions $11a^{*-}$ generated by NICI of a mixture of $[1,1,1-D_3]$ acetone and N_2O



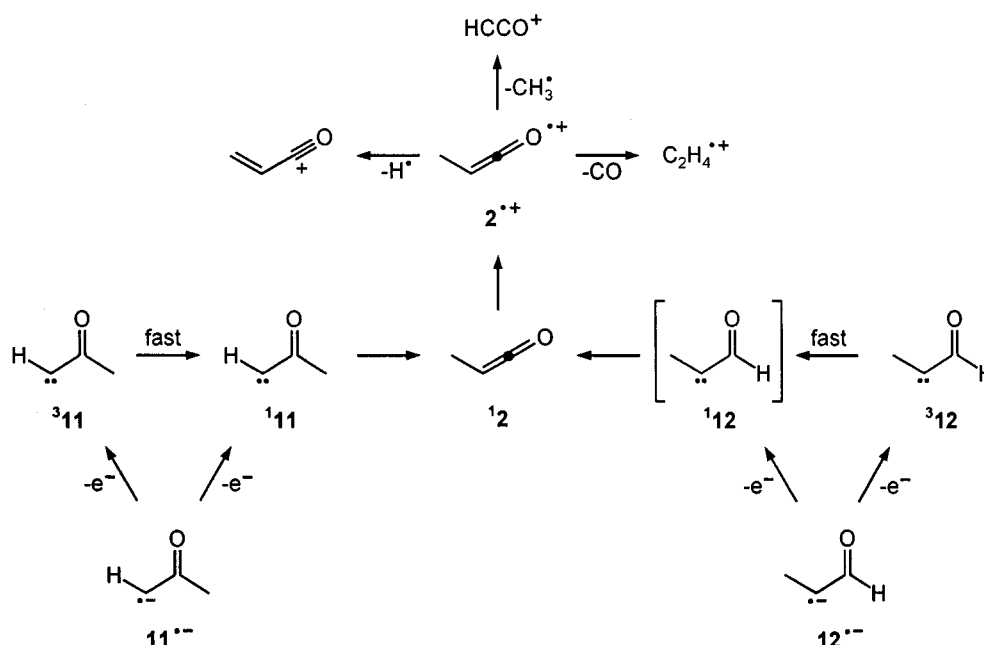
for 11^{*-} which exhibits characteristic methyl losses in its MI and CA spectra^[50]. As far as connectivity is concerned, the $^{-}CR^+$ mass spectrum (Figure 7b) shows losses of CH and CH_3 fragments, leading to CH_3CO^+ and $HCCO^+$ cations, respectively. In particular, the acetyl ion is characteristic for 11^{*-} as it involves loss of the high-energy methin unit and is only observed as a major fragment ion for this ion. However, the $^{-}CR^+$ spectrum contains some fragments, e.g. the reasonably large HCO^+ signal, which imply the occurrence of some rearrangements (see below).

In order to further cross-check the structural assignment and also to study possible intramolecular rearrangements, we took advantage of the following procedure. It is well known^{[50][68]} that the reaction of acetone with O^{*-} yields a ca. 1:1 mixture of acetyl carbene 11^{*-} and oxyallyl radical-anions 14^{*-} via competing 1,1- and 1,3-abstractions of " H_2^{*+} " from acetone. Thus, acetyl carbene radical-anion can be made by NICI of $[1,1,1-D_3]$ acetone with N_2O as reagent gas. Reaction of O^{*-} should accordingly lead to the 1,1-abstractions of " D_2^{*+} " and " H_2^{*+} " leading to the D_1 - and D_3 -labeled ions $11a^{*-}$ and $11b^{*-}$, respectively. Due to the labeling, the 1,3-abstraction of " HD^{*+} " to yield $[1,1-D_2]$ oxyallyl, $14a^{*-}$, does not interfere any more with the 1,1-abstraction products. While loss of " H_2^{*+} " yields $11b^{*-}$ which is isobaric with the D_3 -labeled acetone enolate, " D_2^{*+} " loss should lead to pure $11a^{*-}$. Except for the label, the corresponding $^{-}CR^+$ spectrum (Figure 8) is indeed in complete agreement with that of the unlabeled ion generated from diazoacetone/ N_2O . Thus, the expulsions of CD and CH_3 moieties lead to intense signals due to CH_3CO^+ and $DCCO^+$, respectively, while loss of CH is practically absent. In summary, we conclude that both precursors lead to ion beams consisting of the genuine radical anions of acetyl carbene.

In agreement with the predictions derived from the theoretical results (see above), the $^{-}NR^+$ spectrum (Figure 7a) of 11^{*-} differs completely from the corresponding $^{-}CR^+$ spectrum. While the methyl loss corresponds to the base peak in the $^{-}CR^+$ spectrum, the most abundant signal in the $^{-}NR^+$ spectrum is due to $CO^{*+}/C_2H_4^{*+}$. Further, the HCO^+ signal becomes less intense in the $^{-}NR^+$ spectrum as compared to the $^{-}CR^+$ experiment. Most significantly,

the abundant, and structurally indicative CH loss in the $^{-}\text{CR}^{+}$ spectrum vanishes almost completely, if the $^{-}\text{NR}^{+}$ procedure is applied. These findings indicate that the neutral carbene initially formed upon collisional electron detachment of its radical anion is no longer present in the neutral beam. This conclusion is confirmed by the $^{-}\text{NR}^{-}$ spectrum of $11^{\bullet-}$, in which HCCO^{-} represents the base peak while the recovery signal for $11^{\bullet-}$ hardly exceeds the signal-to-noise ratio. Due to the positive electron affinities of carbenes, one would instead expect a fair recovery signal for acetyl carbene if reionized to anions^[4]. The qualitative differences of the $^{-}\text{NR}^{+}$ and $^{-}\text{CR}^{+}$ spectra are expressed quantitatively in the $^{-}\text{NIDD}^{+}$ spectrum (Figure 7c). Thus, the structurally indicative peaks, i.e. the losses of $\text{CH}^{\bullet}$ and $\text{CH}_3^{\bullet}$, are negative, while the $\text{H}_2\text{CCHCO}^{+}$ and $\text{C}_2\text{H}_4^{\bullet+}/\text{CO}^{\bullet+}$ appear as intense positive peaks. In conjunction with the weak recovery signal, the NIDD pattern very much suggests the occurrence of an isomerization at the neutral stage.

Scheme 3



As outlined above, the theoretical treatment suggests rearrangement of singlet acetyl carbene 111 to methyl ketene 12 (Scheme 3). Single-point calculations reveal an internal energy content of at least 19 kcal/mol for 111 if formed upon vertical electron detachment of the radical anion. Accordingly, the barrier associated with methyl shift via $\text{TS}^{12/11}$ can easily be surmounted, and formation of 12 at the neutral stage can account for the experimental findings. Upon reionization methyl ketene gives rise to losses of atomic hydrogen atom as well as carbon monoxide. The corresponding fragments give rise to positive signals in the $^{-}\text{NIDD}^{+}$ spectrum and identify the $111 \rightarrow 12$ rearrangement as occurring at the neutral stage. The fact that the fragmentations occur after reionization is not at all an objection against the NIDD method, because these dissociations can only proceed, if the $111 \rightarrow 12$ rearrangement occurs at the neutral stage of the NR experiment^{[25a][25c]}.

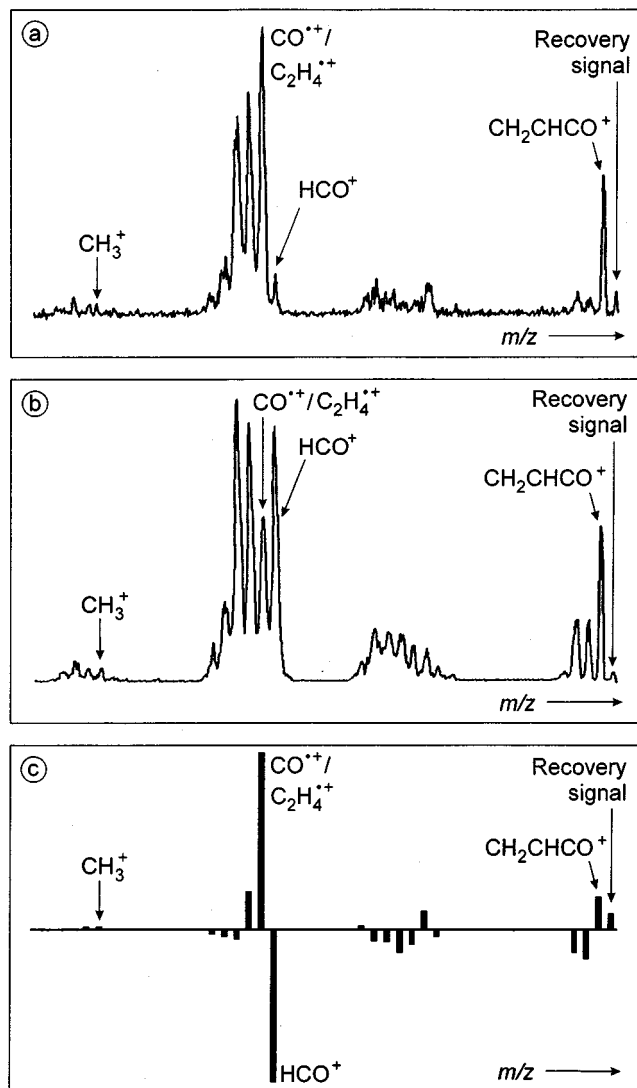
When formed from 111 via $\text{TS}^{12/11}$, neutral 12 contains an excess energy of about 70 kcal/mol which is stored in vibrations and rotations. This amount of energy not only accounts for the weak recovery signal in the $^{-}\text{NR}^{+}$ spectrum, but it may also suffice for a partial isomerization of 12 to 11 , which must, nevertheless, occur to a minor extent due to the much more intense recovery signals in the $^{-}\text{CR}^{+}$ and $^{-}\text{NR}^{+}$ spectra of $11^{\bullet-}$. Indeed, the recovery signal in the $^{-}\text{NR}^{+}$ spectrum of $11^{\bullet-}$ could also be completely due to non-fragmenting methyl ketene or to the triplet species 311 (see below). As mentioned above, the HCO^{+} fragment indicates some type of structural rearrangement which is, however, not accounted for by the formation of 12 . The observation of HCO^{+} as a negative signal in the $^{-}\text{NIDD}^{+}$ spectrum of $11^{\bullet-}$ points towards an origin from ionic species. Indeed, formation of HCO^{+} can be rationalized by isomerization to methyl oxirene radical-cations $9^{\bullet+}$ upon charge inversion, because acetyl carbene is not a minimum

on the cation surface^[4]. Subsequently, $9^{\bullet+}$ undergoes fragmentation to afford HCO^{+} . This interpretation is not only in line with the negative $^{-}\text{NIDD}^{+}$ signal for HCO^{+} , but also accounts for the shift of this fragment to DCO^{+} for the D_1 -labeled ion $11\text{a}^{\bullet-}$ (see Figure 8).

The electronic ground state of acetyl carbene is, however, predicted to be a triplet, and there is no reason why 311 should not be formed upon electron detachment. The intact carbene structure would, however, (i) yield recovery signals in $^{-}\text{NR}^{-}$ and $^{-}\text{NR}^{+}$ experiments, and (ii) lead to some loss of CH in the $^{-}\text{NR}^{+}$ experiment. These criteria are not met experimentally, and in accord with the theoretical prediction we conclude that 311 is unstable on the microsecond time-scale of the experiment, presumably due to crossing from the triplet to the singlet state. In fact, a single point calculation reveals that 311 is formed with an excess energy of ca. 9 kcal/mol upon vertical electron detachment from

$11^{\bullet-}$ such that the neutral may overcome the MECP to the singlet surface. Overall, surface hopping from 311 to 111 seems to occur easily followed by the isomerization $^111 \rightarrow ^12$, such that neither state of 11 exhibits a lifetime sufficient for its unequivocal detection by NRMS.

Figure 9. (a) $^-NR^+$ mass spectrum (O_2 , 80% T, O_2 , 80% T), (b) $^-CR^+$ mass spectrum (O_2 , 80% T), and (c) $^-NIDD^+$ spectrum of formyl methyl carbene radical-anions $12^{\bullet-}$ generated by by NICI of a mixture of $[2,2-D_2]$ -propanal and N_2O



Formyl Methyl Carbene Radical-Anions

A pure ion beam of $12^{\bullet-}$ can be generated by reacting $[2,2-D_2]$ propanal with $O^{\bullet-}$, leading to loss of D_2O concomitant with formation of unlabeled $12^{\bullet-}$. The $^-CR^+$ mass spectrum (Figure 9b) exhibits some signals which are indicative for the anticipated anion structure. The intense HCO^+ and $C_2H_3^+$ signals point to the occurrence of an α -cleavage of the C–C bond adjacent to the carbonyl group upon charge inversion, and also hydrogen-atom loss can be attributed α -C–H bond cleavage. Further, the presence of weak signals due to methyl loss and methyl cation reveal the presence of methyl as a structural subunit. Moreover,

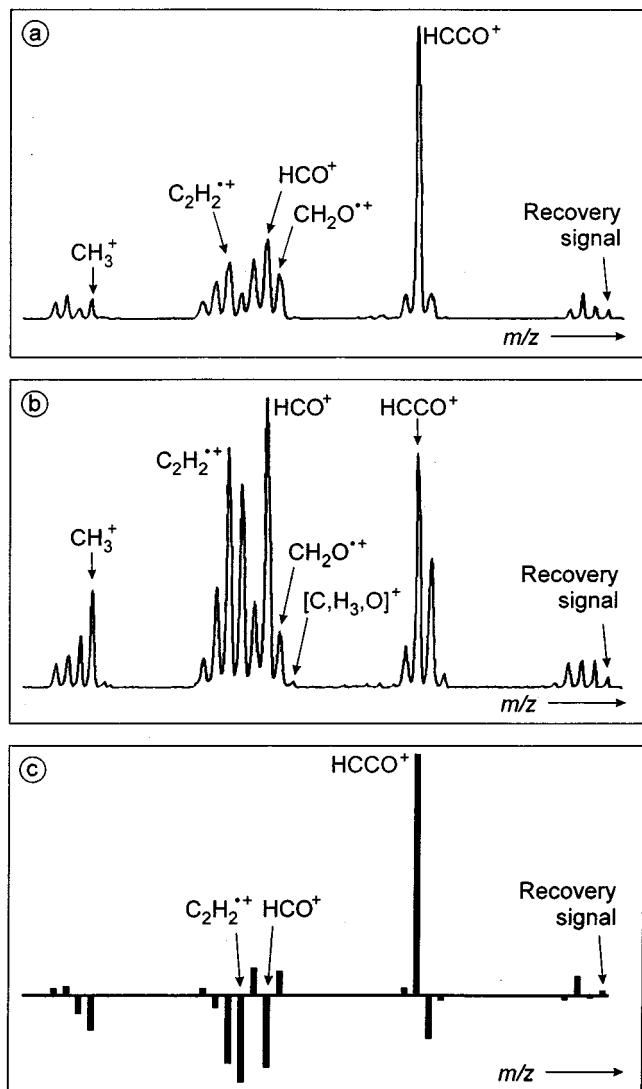
the absence of some fragments which are observed for the other radical anions under study, i.e. the losses of CH and CH_2 in particular, confirms this structural assignment.

The $^-CR^+$ and $^-NR^+$ spectra of $12^{\bullet-}$ (Figure 9) show some pronounced differences. In particular, the HCO^+ signal becomes much smaller in the NR experiment, while the losses of $H^{\bullet}$, $CH_3^{\bullet}$, and C_2H_4/CO , respectively, gain in intensity. The $^-NIDD^+$ spectrum (Figure 9c) provides some quantitative information in this respect. Thus, the dominant positive signal is due to $C_2H_4^{\bullet+}/CO^+$, while HCO^+ prevails on the negative scale. In analogy to acetyl carbene (see above), we conclude that formyl methyl carbene formed upon vertical electron detachment undergoes the rearrangement $^112 \rightarrow ^12$ at the neutral stage and further assume that the spin inversion $^312 \rightarrow ^112$ is efficient. Thus, the carbenes 11 and 12 , while being separated on the anion surface, are predicted to by and large collapse to the same neutral upon electron detachment (Scheme 3). This conjecture is fully in line with the comparison of the $^-CR^+$ and $^-NR^+$ spectra of the carbenes (Figures 7 and 9). Thus, the $^-CR^+$ spectra of $11^{\bullet-}$ and $12^{\bullet-}$ are completely different from each other, while the corresponding $^-NR^+$ spectra are rather similar, though not identical^[69]. The slight difference of the two $^-NR^+$ spectra may be attributed to the amount of internal energy stored in 12 depending on its generation from 11 or 12 together with some minor contributions from other isomers, e.g. 11 or residual amounts of 'cold' triplet species below the respective MECPs. In conclusion, the two keto carbenes 11 and 12 represent well characterized, stable species as radical anions, but neither spin state of the neutral carbenes is long-lived enough to be detected by NRMS due to the facility of spin-inversion as well as rearrangement at the neutral stage.

Methoxy Vinylidene Radical-Anions

For the generation of $13^{\bullet-}$, methyl vinyl ether was subjected to NICI with N_2O . This route follows earlier studies^[51] which have demonstrated that the abstraction of " $H_2^{\bullet+}$ " by $O^{\bullet-}$ proceeds as a 1,1-elimination from the methylene group; the methyl group was found not to be involved. While the presence of a methyl group is apparent from the $^-CR^+$ mass spectrum (Figure 10b), we cannot rigorously exclude the presence of isomeric methoxy acetylene, because the structurally indicative C^+ and CH^+ fragments are obscured by those arising from the methyl group. Notwithstanding, we exclude formation of the radical anion $3^{\bullet-}$ due to the negative electron affinities of acetylenes^{[9b][70]}. Formation of $13^{\bullet-}$ is also suggested by the CA mass spectrum in which the three most intense peaks correspond to $HCC^{\bullet-}$ (100%), $H_2CC^{\bullet-}$ (60%), and $CH_3O^{\bullet-}$ (10%). These signals can be attributed to the initial formation of an $[HCC/CH_3O]^{\bullet-}$ ion/dipole complex by C–O bond cleavage of $13^{\bullet-}$. The different electron affinities of $HCC^{\bullet}$ (2.97 eV) and $CH_3O^{\bullet}$ (1.57 eV) are reflected in the intensities of the corresponding fragment ions. In addition, the $[HCC/CH_3O]^{\bullet-}$ ion/dipole complex can undergo hydrogen transfer followed by the loss of formaldehyde in which the anionic product must be the radical anion of vinylidene^[9b]

Figure 10. (a) $^{-}\text{NR}^{+}$ mass spectrum (O_2 , 80% T, O_2 , 80% T), (b) $^{-}\text{CR}^{+}$ mass spectrum (O_2 , 80% T), and (c) $^{-}\text{NIDD}^{+}$ spectrum of methoxy vinylidene radical-anions $\text{13}^{\bullet-}$ generated by NICI of a mixture of methyl vinyl ether and N_2O



rather than that of acetylene. The presence of a methoxy group in the ion formed upon NICI of methyl vinyl ether with N_2O is further confirmed by the characteristic pattern observed in the $^{-}\text{CR}^{+}$ mass spectrum. Thus, a minor signal for $[\text{C},\text{H}_3,\text{O}]^{+}$ is accompanied by an intense HCO^{+} and two smaller CH_2O^{+} and CO^{+} signals. This pattern is typical for the methoxy cation more or less irrespective of the way of its formation in CR, CR/CA, or CIDI experiments^{[25a][25c][63][71]}. In conclusion, we assume that NICI of methyl vinyl ether with N_2O leads to a ion beam of genuine $\text{13}^{\bullet-}$.

While the $^{-}\text{NR}^{+}$ spectrum of $\text{13}^{\bullet-}$ differs very much from the $^{-}\text{CR}^{+}$ spectrum, the fragmentation pattern is indeed quite similar except that in Figure 10a the HCCO^{+} signal is drastically increased at the expense of all other signals. This is also reflected in the $^{-}\text{NIDD}^{+}$ spectrum (Figure 10c) in which the HCCO^{+} is the only significant signal with a positive intensity while no pronounced peaks

appear on the negative scale. Consequently, the reactivity of neutral 13 is characterized by an intense methyl loss. According to the NIDD scheme^[25b], such a situation implies that a substantial fraction of the neutrals formed upon electron detachment of the radical anion undergoes dissociation into a specific channel, i.e. methyl loss, rather than structural rearrangements etc.

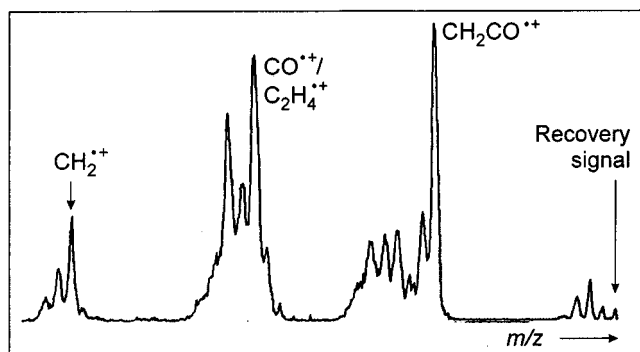
These results are in pleasing agreement with the theoretical predictions. Formation of 313 can be excluded due to the size of the singlet-triplet gap, and 13 is expected to rearrange easily into methoxy acetylene 13 which is more stable by ca. 47 kcal/mol. Assuming that the barrier connecting 13 with 3 is in the range of a few kcal/mol^[9], 13 is generated with an internal energy of about 50 kcal/mol. This amount of energy is more than sufficient to promote fragmentation which has an energy demand of ca. 40 kcal/mol relative to 13 to afford $\text{CH}_3^{\bullet} + \text{HCCO}^{\bullet}$ radicals. Subsequently, these neutral fragments are reionized giving rise to the intense HCCO^{+} signal in the $^{-}\text{NR}^{+}$ spectrum. It should be noted that the CH_3^{+} signal is expected to appear on the positive scale of the $^{-}\text{NIDD}^{+}$ spectrum like the HCCO^{+} signal, but yet the CH_3^{+} peak is negative. As discussed previously for a different example^[72], this apparent failure of NIDD to detect both neutrals formed as positive signals can be traced back to differences in collection efficiencies of the complementary fragments. Thus, two-electron transfer in the $^{-}\text{CR}^{+}$ experiment is likely to afford comparable amounts of CH_3^{+} and HCCO^{+} fragments, due to the similar ionization energies of $\text{CH}_3^{\bullet}$ (9.8 eV) and $\text{HCCO}^{\bullet}$ (9.9 eV). Instead, reionization of the neutral fragments is much more efficient for $\text{HCCO}^{\bullet}$ as compared to the methyl radical which has only about third the mass and kinetic energy. Thus, methyl is much more discriminated in $^{-}\text{NR}^{+}$ than in $^{-}\text{CR}^{+}$, such that the latter overcompensates the NR component and CH_3^{+} appears as a negative signal in the $^{-}\text{CR}^{+}$ spectrum.

The question remains whether the existence of 13 can be deduced from the experimental data alone. In the $^{-}\text{NR}^{+}$ spectrum, a recovery signal is observed which is, unfortunately, too weak for further characterization aimed at probing the presence of the vinylidene structure in the reionized species^[10b]. The fragmentation pattern in the $^{-}\text{NR}^{+}$ spectrum is also in accord with structure 13 and separates this from the other isomers except for a clear-cut distinction from isomeric 3 which definitely cannot be made using the experimental data. Single-point calculations indicate that a few kcal/mol excess energy are deposited in the molecule in the consecutive one-electron oxidations from the radical anion to the neutral and further to the radical cation, the barrier associated with rearrangement to the acetylene can be assumed to be rather low for the neutral and cationic species. However, methyl loss from 13 should proceed rather fast due to the internal energy imparted in 13 , if formed from 13 (see above). Nevertheless, we cannot provide any definitive evidence to decide whether the weak recovery signal is due to genuine 13 or to small amounts of "hot" 13 which survive the passage from the first to the second collision cell.

Oxyallyl Radical-Anions

The reaction of acetone with $O^{\bullet-}$ is known to yield a mixture of acetyl carbene $11^{\bullet-}$ and oxyallyl $14^{\bullet-}$ radical-anions via formal 1,1- and 1,3-abstractions of " $H_2^{\bullet+}$ "^[50]. Therefore, other ways of generating a pure beam of oxyallyl radical-anions $14^{\bullet-}$ had to be explored. One possible way is the complete desilylation of 1,3-bis(trimethylsilyl)acetone by NICI in a NF_3/F_2 plasma. In analogy to the generation of TMM radical-anion^{[29b][29c]}, this process can be assumed to proceed very specifically to yield pure $14^{\bullet-}$. In fact, the $^{-}CR^+$ mass spectrum (Figure 11) reveals loss of CH_2 concomitant with the generation of ketene radical-cations as the most abundant process. Contribution of $11^{\bullet-}$ to the ion beam can be ruled out, due to the practical absence of the characteristic loss of CH in Figure 11. Unfortunately, intensity of oxyallyl radical-anions achieved upon desilylation of bis(trimethylsilyl)acetone was not sufficient for reliable NR experiments and a NIDD analysis. Nevertheless, the $^{-}CR^+$ spectrum of unlabeled $14^{\bullet-}$ shall serve as a reference in the following discussion.

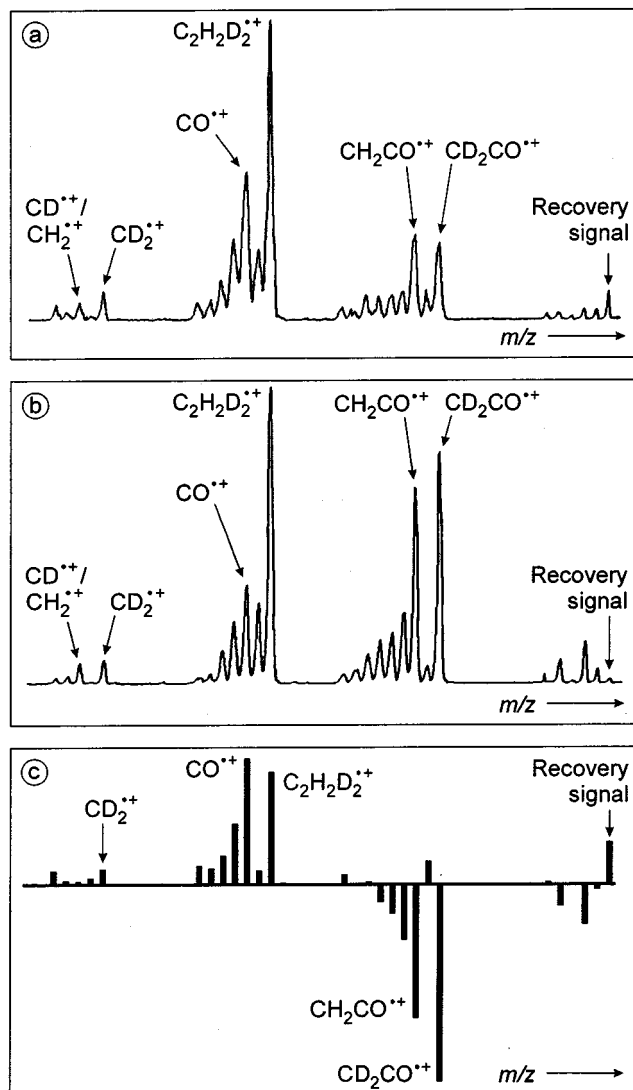
Figure 11. $^{-}CR^+$ (O_2 , 80% T) mass spectrum of oxyallyl radical-anions $14^{\bullet-}$ generated by NICI of a mixture of 1,3-bis(trimethylsilyl)acetone, NF_3 , and F_2 . Due to low intensities, the spectrum was recorded using B(1) only for mass selection followed by charge inversion in the subsequent field-free region. As the products were monitored with E(1), the peaks are broader as compared to the other spectra, which were obtained under double-focussing conditions.



The further arguments are derived from experiments carried out with $[1,1-D_2]$ oxyallyl anions $14a^{\bullet-}$ generated by NICI of $[1,1,1-D_3]$ acetone with N_2O as reagent gas (see above). Except for the mass shifts due to labeling, the $^{-}CR^+$ spectrum of $14a^{\bullet-}$ (Figure 12b) is in good agreement with that of the unlabeled oxyallyl. Thus, CH_2 and CD_2 losses are observed as abundant processes, while no signal due to the expulsion of CH is observed. The oxyallyl structure is further confirmed to be intact by the fact that the signal for CHD loss is marginal and, thus, no abundant H/D exchange is observed between the two methylene groups. In conclusion, $14^{\bullet-}$ and $14a^{\bullet-}$ are well characterized with respect to their ion structures and can be examined by NR experiments. In line with the theoretical predictions both anions do not show significant metastable ion decompositions.

As predicted by theory, the $^{-}NR^+$ spectrum of $14a^{\bullet-}$ (Figure 12a) differs very much from the $^{-}CR^+$ spectrum. Thus, the losses of CH_2 and CD_2 decrease in intensity, but

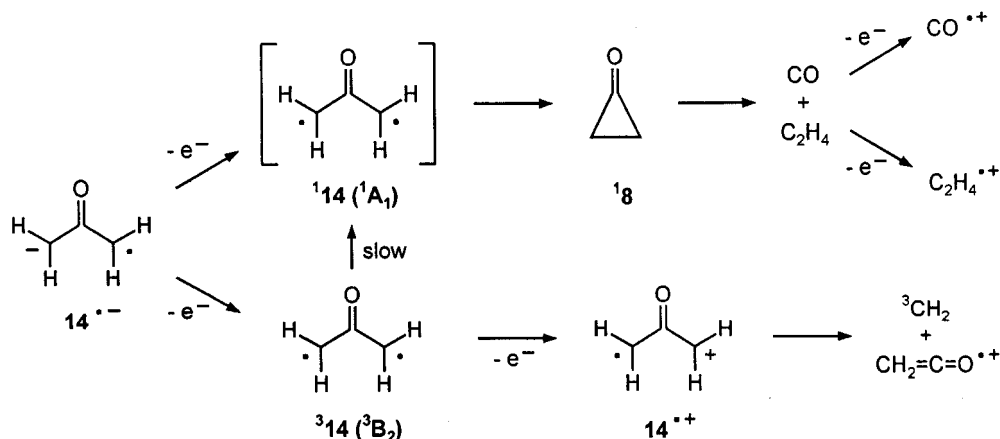
Figure 12. (a) $^{-}NR^+$ mass spectrum (O_2 , 80% T, O_2 , 80% T), (b) $^{-}CR^+$ mass spectrum (O_2 , 80% T), and (c) $^{-}NIDD^+$ spectrum of $[1,1-D_2]$ oxyallyl radical-anions $14a^{\bullet-}$ generated by by NICI of a mixture of $[1,1,1-D_3]$ acetone and N_2O



are still present as distinct signals. Vice versa, the peaks due to $CO^{\bullet+}$ and $C_2H_2D_2^{\bullet+}$ increase. Consequently, the latter two fragments appear as positive signals in the $^{-}NIDD^+$ spectrum (Figure 12c), indicating the formation of CO and $C_2H_2D_2$ at the neutral stage of the experiment^[73]. Accordingly, $H_2CCO^{\bullet+}$ and $D_2CCO^{\bullet+}$ give rise to large negative peaks suggesting that loss of methylene occurs after reionization to the cation radical. Nevertheless, it is notable that loss of methylene is observed *at all* in the $^{-}NR^+$ spectrum (see below). Moreover a decent recovery signal is observed in the $^{-}NR^+$ spectrum of $14a^{\bullet-}$, and also the $^{-}NR^-$ spectrum of $14a^{\bullet-}$ exhibits a signal due to the reionized parent ion.

The theoretical analysis presented above suggests that electron detachment from $14^{\bullet-}$ leads to both the singlet 1A_1 and triplet 3B_2 states of oxyallyl. Under the experimental conditions, 114 is predicted to immediately collapse to cyclopropanone 18 . Due to the excess energy of about 30

Scheme 4



kcal/mol deliberated in the rearrangement ${}^1\mathbf{14} \rightarrow \mathbf{18}$, a substantial fraction of the neutral $\mathbf{18}$ is expected to reach the $\text{CO} + \text{C}_2\text{H}_4$ exit channel. These fragments are subsequently reionized and thus show up as positive peaks in the ${}^-\text{NIDD}^+$ spectrum. Notwithstanding, $\mathbf{18}$ cannot be the *only* neutral species formed in the ${}^-\text{NR}^+$ experiment, because neither the present calculations nor earlier experimental data^[2e] can explain the distinct loss of methylene upon reionization by involving $\mathbf{18}$ alone. Triplet oxyallyl, however, can easily account for the fragmentation into $\text{CH}_2 + \text{H}_2\text{CCO}^{\bullet+}$. Theory predicts (i) formation of ${}^3\mathbf{14}$ as the ground state neutral upon electron detachment from the anion, (ii) inefficient intersystem crossing to the singlet surface due to the small magnitude of H^{SO} , and (iii) reionization of ${}^3\mathbf{14}$ to the cation radical of allene oxide for which loss of methylene is characteristic^[2e]. In summary, the ${}^-\text{NR}^+$ and ${}^-\text{NIDD}^+$ spectra of $\mathbf{14a}^{\bullet-}$ are in agreement with the prediction that these represent superpositions of components arising from singlet and triplet oxyallyl (Scheme 4).

It is therefore tempting to attribute the recovery signals in the NR spectra to the formation of ${}^3\text{B}_2$ oxyallyl which survives the NR procedure intact. Unfortunately, however, detailed consideration of the respective potential-energy surfaces reveals that none of the recovery signals provides *unambiguous* evidence for intermediate ${}^3\mathbf{14}$. In particular, the depth of the potential-energy well of neutral cyclopropanone implies that besides fragmentation via the $\text{CO} + \text{C}_2\text{H}_4$ exit channel, some $\mathbf{18}$ may remain intact. Therefore, neutral $\mathbf{18}$ could account for the recovery signals observed in both types of NR experiments, because it is expected to undergo reionization to the cation and anion surfaces, i.e. $\mathbf{18} \rightarrow \text{TS}\mathbf{18}^{\bullet+}/\mathbf{18}^{\bullet+} \rightarrow \mathbf{18}^{\bullet+}$ and $\mathbf{18} \rightarrow \mathbf{8}^{\bullet-}$, respectively; the latter process would involve formation of a metastable anion, but due to its non-planar geometry (see above), it may be accessible from excited $\mathbf{18}$ and electron detachment may be prevented by a kinetic barrier. The losses of CH_2 and CD_2 observed in the ${}^-\text{NR}^+$ mass spectrum of $\mathbf{14a}^{\bullet-}$ cannot arise from neutral $\mathbf{18a}$, and these signals provide strong, but indirect evidence for the formation of long-lived, neutral ${}^3\mathbf{14}$. However, formation of neutral $\mathbf{17}$ upon electron

detachment from the radical anion could provide an alternative for the methylene losses. Nevertheless, there exists no reason why ${}^3\mathbf{14}$ should not be formed in the neutralization step and this would – if spin inversion occurs at all – rearrange to $\mathbf{18}$ rather than $\mathbf{17}$. In summary, the CR and NR spectra of $\mathbf{14}^{\bullet-}$ can be rationalized by a superposition of fragments due to the formation of neutral singlet ${}^1\text{A}_1$ and triplet ${}^3\text{B}_2$ oxyallyl, but other explanations are possible and cannot rigorously be excluded.

Conclusions

This study underlines the conceptual advantage of using anionic precursors in probing the structure and reactivity of elusive neutrals by mass spectrometric means. In particular, rearrangements are much less frequent for anions than for cations while neutralization of anions, viz. electron detachment, is more facile than neutralization of cations. This approach has enabled the identification of the radical anions of acrolein, acetyl carbene, formyl methyl carbene, methoxy vinylidene, and oxyallyl. Further, the recently developed NIDD approach allows for the examination of the unimolecular reactivity of the neutral species generated in NR experiments. Thus, evidence is presented for the rearrangement of acetyl and formyl methyl carbenes to methyl ketene. The rearrangement of methoxy vinylidene to methoxy acetylene and the loss of CO from singlet oxyallyl via cyclopropanone as an intermediate constitute – although predicted by theory – hitherto unknown reactions.

The present results also pose some questions to the NR methodology. The mere observation of a recovery signal has often been considered as significant evidence for the existence of the neutral under study. The present study reveals, however, that the assignment of the neutral structure can be rather difficult, if a further characterization of the survivor ions cannot be made. For example, there is no doubt that acrolein exists as a neutral, but for the acetyl and formyl-methyl carbenes it is quite certain that the survivor ions do not correspond to the reionized carbenes, but rather to ionized methyl ketene formed via isomerization at the neutral stage. Similarly, the survivor ions observed for methoxy vinylidene anion-radicals cannot provide direct evidence for

the existence of the corresponding neutral, and also the possible existence of ³B₂ oxyallyl can only be deduced from a combination of theory and experiment. Thus, just as the absence of a recovery signal does not necessarily mean that the neutral under study is non-existent, the *observation* of a recovery signal does not prove the existence of the neutral, because it may be due to rearranged species.

Finally, it should be pointed out that the analysis of NR and CR spectra benefits much from theoretical models of the potential-energy surfaces involved. In fact, some experimental data can only be interpreted by explicit reference to the theoretical predictions, e.g. spin inversions. For the bulk of our calculations, the B3LYP/6-311++G(d,p) level of theory was chosen on pragmatic grounds due to its moderate expense. This method is, however, not appropriate for all parts of the potential-energy surface. In particular, the singlet biradicaloid ¹A₁ state of oxyallyl is not accurately described with B3LYP as demonstrated by the rather different results obtained using other methods. In general, complementary calculations are therefore recommended in any study where the performance of DFT is either unknown or expected to be poor.

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Experimental Section

The experiments were performed with a modified VG ZAB/HF/AMD four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sectors) which has been described in detail previously^[74]. In brief, the anions of interest were generated by negative ion chemical ionization (NICI, repeller voltage ca. 0 V, electron energy 50–100 eV) of mixtures of the corresponding precursors with N₂O. For the generation of a pure beam of oxyallyl radical-anions, 1,3-bis(trimethylsilyl) acetone was subjected to NICI with mixture of NF₃ and F₂^{[29b][29c][75]}; elemental fluorine was generated inside the ion source by thermolysis of silver(II) fluoride.

The ions were accelerated to 8 keV translational energy and mass-selected by means of B(1)/E(1) at mass resolutions of m/Δm = 2000–5000. Unimolecular decompositions of metastable ions (MI) occurring in the field-free section preceding B(2) were recorded with this sector. For collisional activation (CA) experiments^[76], the ions were collided in the field-free region between E(1)/B(2) with helium at 80% transmission (T) of the incident beam; these conditions approximate single-collision conditions^[77].

In neutralization-reionization ([−]NR⁺)^[78] experiments, the radical anions were neutralized by high-energy collisions with molecular oxygen (80% T) in the first of two differentially pumped collision cells located in the field-free region between E(1) and B(2). Unreacted ions were deflected away from the beam of neutral species by applying a voltage of 1 kV on a deflector electrode located

between the two collision chambers. Subsequent reionization to cations occurred in the second cell by collision with oxygen (80% T). The resulting mass spectra were recorded by scanning B(2). Charge-reversal mass spectra^[79] of the anions to cations ([−]CR⁺) were obtained by colliding the ion beam with oxygen (80% T) in the field-free region preceding B(2). Under these conditions, the [−]CR⁺ process can be treated as a vertical, two-electron oxidation occurring in a single step, although some species may undergo multiple collisions. For direct comparison with the [−]NR⁺ spectra, the [−]CR⁺ experiments were also recorded under [−]NR⁺ conditions (i.e. O₂/O₂, each 80% T), but no severe differences to the [−]CR⁺ spectra obtained under single-collision conditions were found for the systems under study. The spectra were accumulated and on-line processed with the AMD-Intectra data system; usually, 10 to 50 scans were averaged to improve the signal-to-noise-ratio.

[−]NIDD⁺ spectra^{[25][26]} were obtained by subtracting the normalized peak heights of the [−]CR⁺ spectra from those of the corresponding [−]NR⁺ spectra according to equation (1).

$$I_i(\text{NIDD}) = [I_i(\text{NR}) / \sum_i I_i(\text{NR})] - [I_i(\text{CR}) / \sum_i I_i(\text{CR})] \quad (1)$$

In this normalization scheme positive intensities in the difference spectra indicate products whose formation involves either decompositions or rearrangements of the intermediate neutral species^[25c], while decompositions of the projectile and/or recovery ions which do not involve processes at the neutral stage appear as negative peaks in the [−]NIDD⁺ spectra.

Diazoacetone was synthesized from acetyl chloride and diazomethane as described in the literature^[80]. 1,3-Bis(trimethylsilyl)acetone was obtained by oxidation of the corresponding alcohol with Ag₂CO₃/celite^[81]. [1,1,1-D₃]acetone was prepared by reaction of CD₃MgI with acetaldehyde followed by Jones oxidation of the alcohol formed. Immediate distillation and usage of the product is recommended in order to obtain highest isotopic purities; otherwise the deuterium label may undergo complete intermolecular equilibration within a few hours or days depending on the purity of the sample. [2,2-D₂]propanal was made by repeated isotopic exchanges of the unlabeled aldehyde with D₂O in refluxing pyridine. ¹⁸O-labeled acetone was generated by hydrolysis of the corresponding cyclohexylimine^[82] with H₂¹⁸O in the inlet system of the mass spectrometer. All other substances were commercially available and used without further purification.

☆ Dedicated to Professor M. H. Zenk on the occasion of his 65th birthday.

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