with more sophisticated theoretical treatments.

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Appendix

In this study the smallest basis set used consists of (a) a triple-ζ (TZ) contraction of Van Duijneveldt's[38] (10s6p) primitive set for O and F and the (6s) primitive set for H according to the scheme (10s6p/6s) → [5s3p/3s]; (b) the addition of a set of polarization functions for each atom ($\alpha_d(O) = 0.85$, $\alpha_d(F) = 1.0$, $\alpha_p(H) = 0.75$); and (c) the addition of diffuse s- and p-type functions on O and F $\alpha_s(O) = 0.0840898$, $\alpha_p(O) = 0.0584002$, $\alpha_s(F) = 0.106753$, and $\alpha_p(F) = 0.0709406$; these exponents were obtained in an even tempered sense by using the ratios of the last two exponents of the (10s6p) primitive set and a diffuse s-type function on H ($\alpha_s(H) = 0.030155$[39]). This basis set, labeled TZP+diff, may be technically designated [6s4p1d/4s1p] and its use results in 62 contracted Gaussian functions (CGFs) for $F^{-}\cdot H_2O$.

The second basis set is labeled TZ2P+diff. We have previously described the formulation of this set for O and H.[34] The basis set for F is obtained in an exactly analogous manner and consists of a [7s4p] contraction of the (12s7p) primitive set of Van Duijneveldt[40] with the addition of two sets of polarization functions ($\alpha_d = 1.5$ and 0.35) and one set of diffuse s- and p-type functions ($\alpha_s = 0.0978$, $\alpha_p = 0.0649$). The TZ2P+diff basis set may be technically designed [8s5p2d/4s2p] and its use results in 90 CGFs for $F^{-}\cdot H_2O$.

Basis set three is labeled TZ4P+diff. It consists of the TZ2P+diff set but with four sets of polarization functions on O and F and three sets on H ($\alpha_d = 2.25$, 0.75, 0.25, and 0.083 for O and F, and $\alpha_p = 1.4$, 0.25, and 0.083 for H). This basis set may be designated [8s5p4d/4s3p] and results in 120 CGFs for $F^{-}\cdot H_2O$.

The last basis set used is labeled TZ4P+diff+d and consists of the TZ4P+diff basis set augmented by a set of d-type functions on H ($\alpha_d = 1.0$). Use of this basis set ([8s5p4d/4s3p1d]) results in 132 CGFs.

A Theoretical Study of the Reaction of Ketene Radical Cation with Ethylene: Nucleophilic Addition or Concerted [2 + 1] Cycloaddition?[†]

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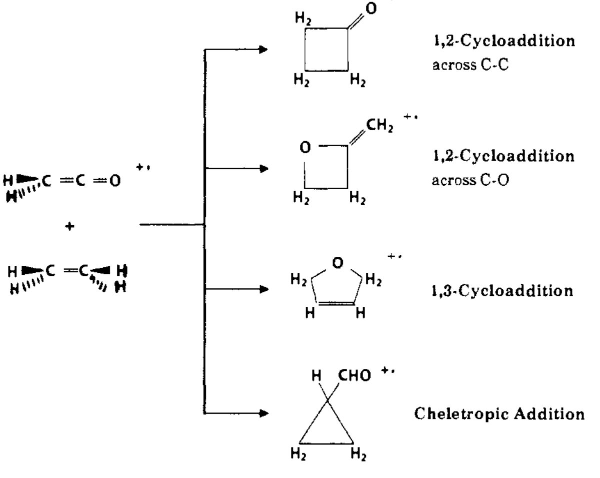
Contribution from the Institute of Organic Chemistry, Technical University Berlin, D-1000 Berlin 12, Federal Republic of Germany. *Received February 1, 1988*

Abstract: A thorough molecular orbital study of the potential energy surface of ionized cyclobutanone reveals that, in line with ESR data, this species does not appear to be a minimum on the MP2/6-31G**//6-31G* + ZPVE potential energy surface. While ring-opening by cleavage of the C(1)/C(2) bond (α-cleavage) has no barrier, the alternative reaction, i.e., cleavage of the C(2)/C(3) bond (β-cleavage), is predicted to be associated with a significant barrier. This is indicated by the fact that the β-cleavage product **4** is higher in energy than the sum of the heats of formation of the fission products C_2H_4 and $C_2H_2O^{\bullet+}$. The reverse reaction, i.e., the formal [2 + 1] cycloaddition of ionized ketene with ethylene, has been analyzed in detail. It has been found that this process should *not* be classified as a cycloaddition reaction but rather as a nucleophilic addition of C_2H_4 to the terminal carbon atom of the ketene radical cation. This type of reaction is governed by a 3-electron/2-orbital interaction as is the case with the recently described[15] nucleophilic addition of NH_3 to ionized ketene. The MO results present for the first time a coherent description of all experimental findings, including ESR studies at 77 K and ion/molecule reactions of $C_2H_4O^{\bullet+}$ with C_2X_4 (X = H, D) in the gas phase.

The reactivity and stereoselectivity patterns in cycloaddition reactions of neutral organic molecules have been impressively accounted for by the Woodward–Hoffmann rules[1] and the Frontier Molecular Orbital (FMO) approach introduced by Fukui.[2] On the basis of simple symmetry considerations and energy differences of interacting molecular orbitals, these models provide a qualitative classification of reactions as being high-("forbidden") and low-energy processes ("allowed"). Much less is known, however, about these features in cycloadditions involving radical cations. As the occupation of the orbitals of reacting species is changed upon ionization, a change of the reaction mechanism is likely to result.[3] The last few years have witnessed a growing interest of both experimentalists and theoreticians on "hole" catalyzed cycloadditions. Bauld and co-workers[4] demonstrated that radical cation catalyzed Diels–Alder reactions occur with considerably enhanced reaction rates and selectivities, compared to the respective neutral

Scheme I



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[*] Author to whom correspondence should be addressed.

[†] Dedicated to Dr. V. Hanuš, Prague, on the occasion of his 65th birthday.

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Table I. Absolute Energies (in hartrees) and Zero-Point Vibrational Energies (ZPVE, in kcal mol^{-1}) of Some $C_4H_6O^{\bullet+}$ Isomers

species	point group	HF/6-31G*	6-31**/ 6-31G*	MP2/ 6-31G*//6-31G*	MP2^a/ 6-31G**//6-31G*	ZPVE^b (6-31G*)
1	C_{2v}	−229.493 76	−229.503 85	−230.151 47	−230.174 98	53.4
2	C_1	−229.509 47	−229.519 76	−230.177 40	−230.201 74	52.3
3	C_s	−229.508 30	−229.518 58	−230.175 75	−230.200 27	52.3
4	C_1	−229.463 67	−229.474 35	−230.109 28	−230.133 12	52.0
5	C_s	−229.450 36	−229.461 29	−230.113 49	−230.137 08	51.0
ketene radical cation	C_{2v}	−151.425 16	−151.429 12	−151.822 93	−151.824 88	18.6
ethylene	D_{2h}	−78.031 72	−78.038 84	−78.293 69	−78.316 82	30.6
TS **1**/**2**	C_s	−229.488 35	−229.498 42	−230.167 27	−230.191 07	52.9
TS **2**/**2**	C_s	−229.504 20	−229.514 46	−230.172 10	−230.196 34	52.2
TS **2**/**3**	C_1	−229.503 24	−229.513 60	−230.171 03	−230.195 57	52.1
TS **4**/**4**	C_s	−229.447 10	−229.457 69	−230.094 22	−230.118 53	50.6

^{a}Frozen core approximation ^{b}Given in kcal mol^{-1}; the values have been scaled by a factor of 0.89.

Table II. Relative Energies (given in kcal mol^{-1}) for Some $C_4H_6O^{\bullet+}$ Isomers

species	HF/6-31G*	6-31G**/6-31G*	MP2/6-31G*//6-31G*	MP2/6-31G**//6-31G*	"best"^{a}
1	0	0	0	0	0
2	−9.9	−10.0	−16.3	−16.8	−17.9
3	−9.1	−9.3	−15.3	−15.9	−17.0
4	18.9	18.5	26.5	26.3	24.9
5	27.3	26.8	23.9	23.8	21.4
TS **1**/**2**	3.4	3.4	−9.9	−10.1	−10.6
TS **2**/**2**	−6.6	−6.7	−13.0	−13.4	−14.6
TS **2**/**3**	−6.0	−6.1	−12.3	−12.9	−14.2
TS **4**/**4**	29.3	29.0	36.0	35.5	32.7
(C_2H_4 + $CH_2CO^{\bullet+}$)	23.2	22.6	21.9	20.9	16.7

^{a}MP2/6-31G**//6-31G* + ZPVE.

reactions. Gross et al.[5] reported several studies of cycloadditions involving radical cations in the gas phase. In particular, they provided circumstantial evidence that many of these processes occur in a stepwise fashion, and in some cases they were able to characterize structurally the encounter complexes by quenching the reactive intermediates with neutral bath molecules.

Among the many "hole"-catalyzed cycloaddition processes studied in the gas phase, the reaction of ketene radical cation and neutral ethylene was investigated some years ago by Dass and Gross[6] using tandem mass spectrometry and Fourier transform mass spectrometry. The primary reaction adduct arising from the ion/molecule reaction was collisionally stabilized by quenching it with inert neutral bath molecules (CS_2) under high-pressure conditions (150–500 mTorr). The adduct was then characterized by collisionally activated dissociation (CAD) and metastable ion mass spectrometry. For a structural assignment of the adduct ions, a variety of isomeric $C_4H_6O^{\bullet+}$ species were studied, and their CA characteristics were taken as references for comparison. Some of these reference compounds are displayed in Scheme I. Their choice was dictated by chemically feasible, potential modes of reactions between ketene radical cation and ethylene.

It was shown[6] that only ionized cyclobutanone gives rise to a CA spectrum matching that of the ion/molecule reaction adduct; all other $C_4H_6O^{\bullet+}$ candidates showed distinctly different CA characteristics. The authors, therefore, concluded that the adduct most probably corresponds to the cyclobutanone radical cation (**1**). However, there is no clear-cut evidence whether or not cyclobutanone itself has retained its cyclic structure upon ionization. For instance, the $C_4H_6O^{\bullet+}$ generated upon ^{60}Co γ-radiation at 77 K of cyclobutanone has an ESR spectrum that is not compatible with a cyclic structure **1** but rather indicates that in the course of ionization α-cleavage of the C(1)/(2) bond has occurred to generate a species of the type $^{\bullet}CH_2CH_2CH_2CO^+$.[7] Thus, it can only be stated that the ion/molecule reaction and the ionization of cyclobutanone most probably result in the same $C_4H_6O^{\bullet+}$ ion, the actual structure of which, however, is still uncertain.

In this paper, we report our results of an ab initio molecular orbital (MO) study of the cycloreversion mechanism of ionized cyclobutanone **1** to generate $C_2H_2O^{\bullet+}$ and C_2H_4. According to the principle of microscopic reversibility this kind of analysis will provide information pertinent on the mechanism of the ion/molecule reaction as well.

Computational Details

All computations have been performed with the CRAY version of the Gaussian 82[8] series of programs. Open-shell species were treated in the unrestricted Hartree–Fock (UHF) formalism.[9] The geometries were fully optimized with a polarized 6-31G* basis set[10] with use of analytical gradient procedures. All stationary points have been characterized to correspond either to local minima or transition structures by having zero or one negative eigenvalue in the analytically computed force constant matrix, respectively. Zero-point vibrational energies (ZPVE) have been calculated from the 6-31G* harmonic normal frequencies which were scaled by a factor of 0.89 in order to account for the systematic overestimation of normal frequencies by Hartree–Fock calculations.[11] Single-point calculations were performed by using a 6-31G** basis set,[12] and the effects of valence electron correlation were accounted for by means of Møller–Plesset perturbation theory[13] terminated at second order

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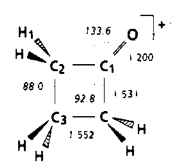
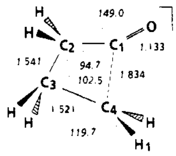
Chart I



1 (C_{2v})

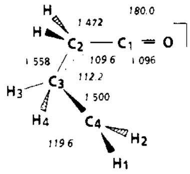
Charge density		Spin density	
C_1	+0.48	C	-0.33
C_2	-0.30	C_2	0.18
C_3	-0.26	C_3	-0.02
O	-0.08	O	1.11



TS **1/2** (C_s)

Charge density		Spin density	
C_1	+0.46	C	-0.26
C_2	-0.28	C_2	0.24
C_3	-0.28	C_3	-0.04
C_4	-0.25	C_4	0.60
O	-0.17	O	0.67

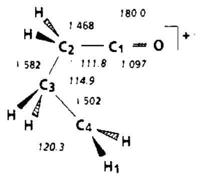
∡$H_1C_4C_3C_2$ 103.9°



2 (C_1)

Charge density		Spin density	
C	+0.73	C	-0.11
C_2	-0.36	C_4	1.33
C_3	-0.27		
C_4	-0.29		
O	-0.17		

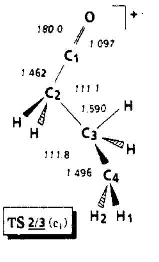
∡$H_1C_4C_3C_2$ 140.1°
∡$H_2C_4C_3C_2$ -58.6°
∡$H_3C_3C_2C_1$ 179.7°
∡$H_4C_3C_2C_1$ -65.4°
∡$C_4C_3C_2C_1$ 57.6°



TS **2/2** (C_s)

Charge density		Spin density	
C	+0.72	C_2	0.14
C_2	-0.36	C	-0.11
C_3	-0.26	C_4	1.32
C_4	-0.31		
O	-0.18		

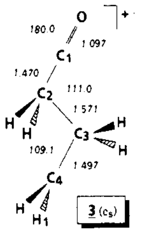
∡$H_1C_4C_3C_2$ 95.7°



TS **2/3** (C_1)

Charge density		Spin density	
C_1	+0.72	C_1	0.16
C_2	-0.36	C_4	1.33
C	-0.29		
C_4	-0.25		
O	-0.18		

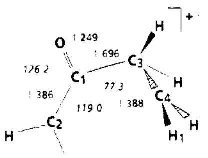
∡$H_1C_4C_3C_2$ -90.3°
∡$H_2C_4C_3C_2$ 91.4°
∡$C_4C_3C_2C_1$ 120.8°



3 (C_s)

Charge density		Spin density	
C_1	+0.72	C	-0.13
C_2	-0.36	C_4	1.32
C_3	-0.27		
C_4	-0.25		
O	-0.18		

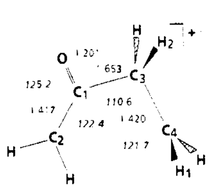
∡$H_1C_4C_3C_2$ 89.9°



4 (C_1)

Charge density		Spin density	
C	+0.24	C	-0.55
C	-0.19	C	0.86
C	-0.24	C	-0.11
C	-0.08	O	0.90
O	-0.28		

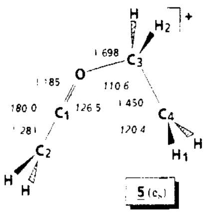
∡H C C C -21.4°
∡H C C C 213.4°
∡C C C C 95.8°
∡C C C O 169.1°
∡H C C C -86.2°



TS **4/4** (C_1)

Charge density		Spin density	
C	+0.45	C	1.09
C	-0.24	C	-0.54
C	-0.44	O	0.70
C	+0.08		
O	-0.34		

∡H C C C -121.0°
∡H C C C -88.4°

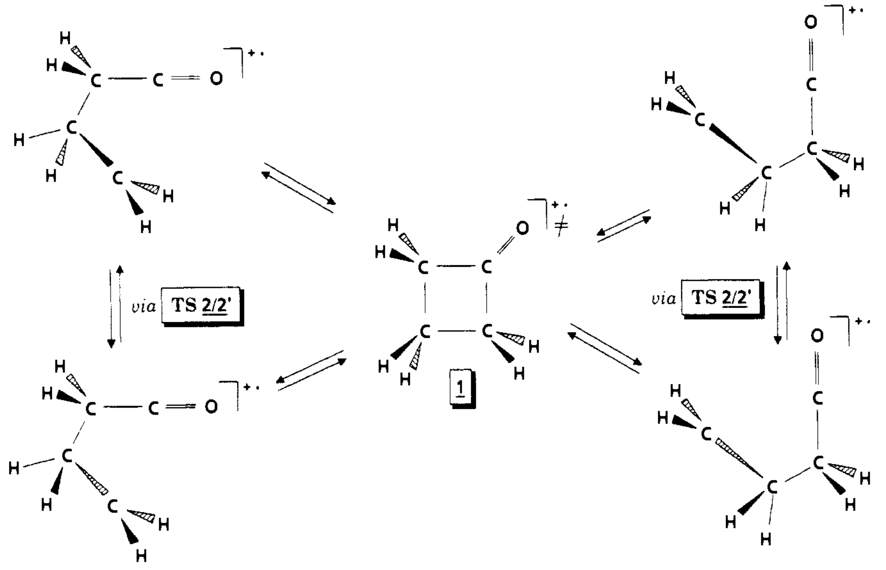


5 (C_s)

Charge density		Spin density	
C	+0.59	C	1.12
C	-0.33	O	0.19
C	+0.03		
C	-0.25		
O	-0.52		

∡H C OC -122.5°
∡H C C O -90.1°

Scheme II



(MP2). Thus, the highest level of theory used is indicated by the notation MP2/6-31G**//6-31G* + ZPVE. Total and relative energies are listed in Tables I and II, respectively; optimized geometries (bond length in Å; bond angles in deg) of the species of interest are given in Chart I.

Results and Discussion

At the HF/6-31G* level of theory, we were able to localize the C_{2v} symmetric cyclobutanone radical cation **1** as a local minimum. The minimal energy requirement path (MERP) for ring opening of **1** was analyzed by varying the most flexible reaction parameter with respect to the two competing opening modes via an α- or β-cleavage, i.e., the distance between the midpoints of the two opposite C_1–C_2 and C_3–C_4 bonds. This parameter was changed in steps of 0.05 Å. The transition structure TS **1/2**, which corresponds to an α-cleavage process, was found to be only 3.4 kcal/mol above **1** in energy (HF/6-31G*). The open-chain structure **2** (C_1), the 1-oxotetramethylene radical cation, was found to be 9.9 kcal/mol more stable than **1** at this level of theory (see Figure 1a). As shown in Chart I, the structure is twisted around the C_2–C_3 bond by 57.6° (staggered conformation), whereas a corresponding C_s symmetric, ecliptic conformation turned out to be the transition structure (TS **2/2**) of a degenerate conformational change upon C_2–C_3 twisting. A further conformational isomer, 0.7 kcal mol^{-1} less stable than **2**, corresponds to the anti-structure **3**, and at the HF/6-31G* level of theory **3** is separated from **2** by a barrier of 3.2 kcal/mol.

When one turns to the "best" level used in this study, i.e., MP2/6-31G**//6-31G* + ZPVE, the picture changes quite drastically (Figure 1b). The most notable difference is that TS **1/2** is not any longer a stationary point on the potential energy surface; with a 6.31G* geometry it is calculated to be 10.6 kcal mol^{-1} *more* stable than ionized cyclobutanone **1**. Most interestingly, **1** appears to be the transition structure connecting the various α-cleavage processes with each other (Scheme II). The result that **1** is not likely to correspond to a minimum structure substantiates the ESR findings on ionized cyclobutanone.[7]

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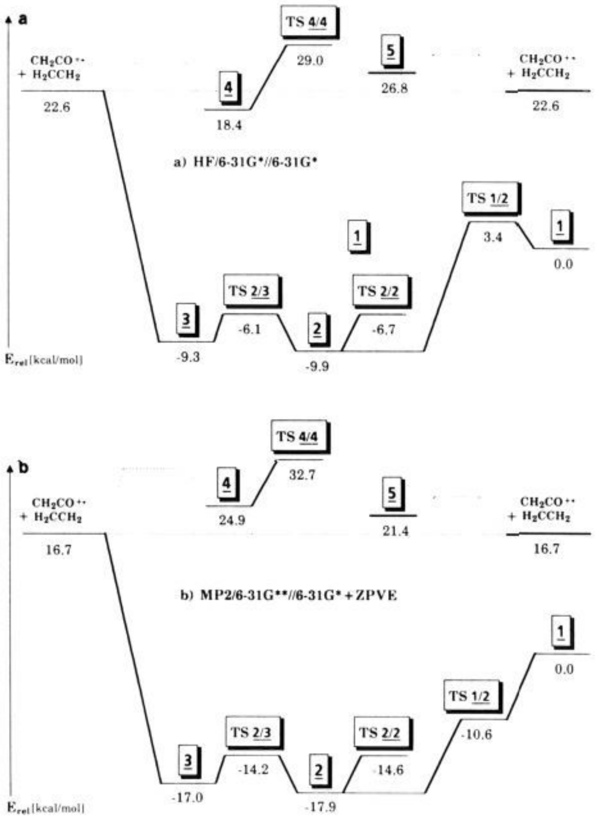


Figure 1. Minimal energy requirement paths for isomerization processes of some $C_4H_6O^{\cdot+}$ and dissociation to C_2H_4 and $C_2H_2O^{\cdot+}$: (a) HF/6-31G*//6-31G*; (b) MP2/6-31G**//6-31G* + ZPVE. (For details see text and for structural assignments Chart I.)

We further note the following from Figure 1b: The rotational isomers **2** and **3** are 17.9 and 17.0 kcal/mol below **1**, which itself is 16.7 kcal/mol more stable relative to completely separated C_2H_4 and $C_2H_2O^{\cdot+}$. The barrier for rotational isomerism **2** ⇄ **3** via TS **2/3** and the degenerate isomerization of **2** via TS **2/2** are not significantly affected by the level of theory and are of the order of ca. 3 kcal/mol. According to the calculations, **3** decomposes continuously endothermically to the fragments $CH_2CO^{\cdot+}$ and C_2H_4 with a heat of reaction of 33.7 kcal/mol. From Figure 1b it is also obvious that the internal energy gained in the formation of the encounter complex $CH_2CO^{\cdot+}/C_2H_4$ would be more than sufficient "freely" to interconvert **2** (via **1** and TS **2/2**) and **3** (via TS **2/3**). Moreover, the approach of ionized ketene and ethylene in a manner that would proceed via the formation of **3**, i.e., reaction of C_2H_4 with the *terminal* carbon atom of ionized ketene, does not involve a barrier. Before discussing this important finding and its implications for the mechanism of the addition reaction $C_2H_2O^{\cdot+} + C_2H_4 \rightarrow C_4H_6O^{\cdot+}$, we will briefly mention the results obtained for the product of breaking the C(2)/C(3) bond of **1** (i.e., the β-cleavage product **4**). The 2-oxotetramethylene radical cation **4** is calculated to be 24.9 kcal/mol higher in energy than **1**. Thus, even if **1** were to have a finite lifetime, it would not isomerize via β-cleavage to form **4** but rather undergo ring opening to form **2**. With regard to the formation of $C_4H_6O^{\cdot+}$ from $C_2H_2O^{\cdot+}$ and C_2H_4, it is important to note that **4** is 8.2 kcal/mol *less* stable than the separated $C_2H_4/CH_2CO^{\cdot+}$ species. Though we did not succeed (poor convergence, spin contamination of the UHF wave function) in locating the transition structure for the formation of **4** from separated $C_2H_4/CH_2CO^{\cdot+}$, there can be no doubt that the minimal energy requirement path for the combination of C_2H_4 and $CH_2CO^{\cdot+}$ will not proceed via **4** but rather via **3**!

The last structure to be considered concerns **5**, which corresponds to the interaction of the ethylene–carbon atom with the oxygen atom of ionized ketene. Although we did not calculate the transition structure for the reaction $C_2H_4 + C_2H_2O^{\cdot+} \rightarrow$ **5**, the fact that **5** is 4.7 kcal/mol *above* the isolated reactants leaves no doubt that this reaction path, like the process $C_2H_4 + C_2H_2O^{\cdot+} \rightarrow$ **4**, can be excluded from further discussion.

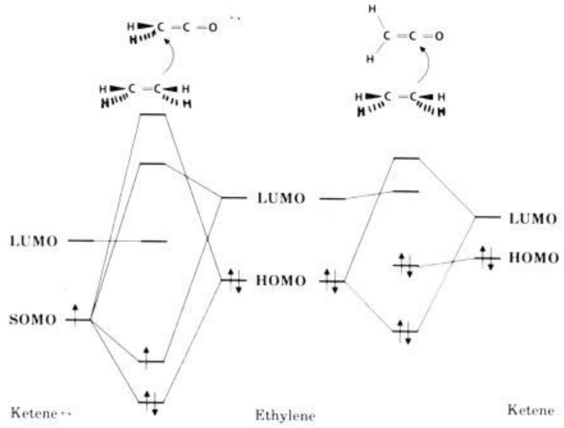
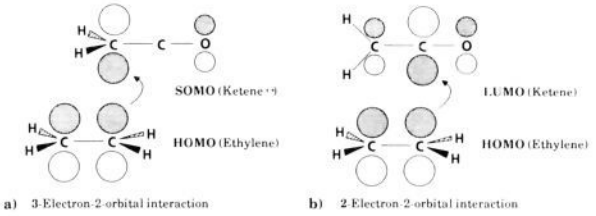
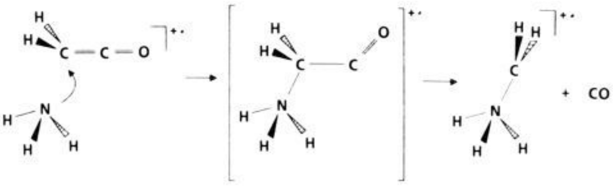


Figure 2. Schematic orbital interactions of ethylene approaching *ionized* (left) and neutral (right) ketene.

Chart II



Scheme III



According to the MO calculations the most favored approach of ionized ketene and ethylene would involve **3**, the anti conformation of ring-opened cyclobutanone radical cation. This conclusion, however, is in disagreement with the mechanistic proposal put forward by Dass and Gross,[6] who postulated an approach toward the carbonyl carbon atom of ketene radical cation, i.e., via structure **4**. They claimed that, "since the ketene reactant is a radical cation, it is logical to expect that the first interaction involves its central carbon atom because of its electrophilicity and large LUMO coefficient...". This assumption is, however, by no means justified, as we are dealing with radical cations, and an orbital interaction scheme derived from the neutral (closed shell) case is not a priori valid for the open-shell system.

When one analyzes the MOs of **3** it becomes obvious that the dominant orbital interaction between the two reacting subunits $C_2H_2O^{\cdot+}$ and C_2H_4 involves the SOMO of ketene radical cation and the HOMO of ethylene as well as the SOMO of $C_2H_2O^{\cdot+}$ with the LUMO of C_2H_4 (Figure 2). The former is energetically the more important one and represents a 3-electron/2-orbital interaction, a special feature in odd electron systems (see Chart II). In neutral systems, this approach would involve an antibonding 4-electron/2-orbital interaction. Therefore, ethylene approaches the central carbon in *neutral* ketene in the early stage of the reaction (Chart IIb) before finally rotating the methylene group for ring closure.[14] This approach is governed by a HOMO–LUMO interaction as shown in Chart IIb and Figure

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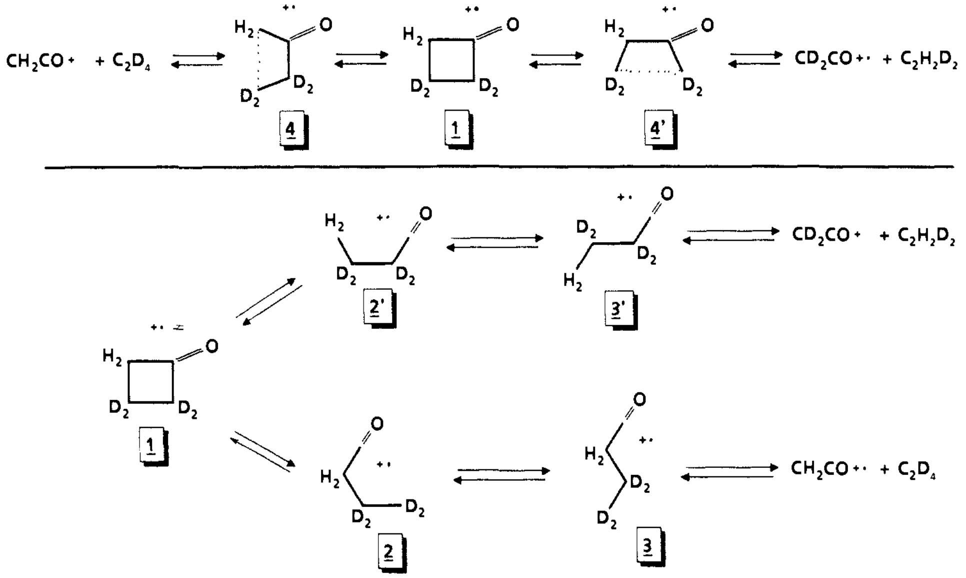
[14] Burke, L. A. *J. Org. Chem.* **1985**, *50*, 3149.

Scheme IV



2. This type of interaction is of minor importance for the reaction of $C_2H_2O^{\bullet+}$ with C_2H_4.

Note, that although ketene radical cation is a charge-bearing partner, the favorable addition goes in an *orbital*-controlled fashion toward the electrophilic center of the ketene radical ion; the latter corresponds to the *terminal* carbon, in contrast to neutral ketene, where orbital and charge-controlled modes of the approach coincide, favoring an initial approach at the central carbon atom.

This change of electrophilic reactivity has also recently been found for the ion/molecule reaction between ketene radical cation and NH_3.[15] Here, evidence has been presented for an "S_N2-type" reaction in which the nucleophile (NH_3) attacks the terminal carbon atom of ionized ketene, as shown in Scheme III. For the reaction of NH_3 with neutral ketene it is, not surprisingly, the central carbon atom of C_2H_2O that is attacked by NH_3. Similarly, it was recently reported[16] that 1,3-hydrogen migrations in closed-shell and open-shell systems differ significantly with regard to the energy requirements.

Let us now return to the central question of which species is initially formed when C_2H_4 interacts with $C_2H_2O^{\bullet+}$. In order to support their conclusions that the species formed is ionized cyclobutanone **1** and that in the initial phase of the reaction intermediate **4** is generated, Dass and Gross[6] carried out ion/molecule reactions employing $C_2H_2O^{\bullet+}$ and C_2D_4. From the fact that from the (isolated) adduct ion, upon collisional activation, C_2D_4 and $C_2H_2D_2$ are nearly equally eliminated, they arrive at the following conclusions: "An acyclic intermediate would give loss of only C_2D_4. The deuterium labeling results can only be rationalized if the adduct possesses a symmetrical cyclic structure (**1**) or is a mixture of unsymmetrical one-electron or long-bond cyclobutanone radical cations (**4** and **4'** in the present Scheme IV). We are unable to judge whether the cyclobutanone ion exists as an energy minimum or maximum". We disagree, as this conclusion is based on the assumption that the favored ring-cleavage of **1** leads to **4**. As outlined above, this is *not* the case. In fact, the deuterium labeling experiments are perfectly in line with what one expects from Figure 1b, and what is shown in Scheme IV (lower part).

Conclusions

The reaction of ionized ketene and ethylene is a simple nucleophilic addition leading to an open-chain 1-oxotetramethylene radical cation. The process is governed by a 3-electron/2-orbital interaction. The cyclic structure of ionized cyclobutanone **1** is likely to be a transition structure on the potential energy surface, and, therefore, the term [2 + 1] cycloaddition is not an appropriate classification for the reaction of ionized ketene with ethylene. When one compares the reactions of C_2H_4 with neutral and ionized ketenes, one sees that the centers of reactivity (electrophilicity) have moved from the central carbon in neutral ketene to the terminal carbon in the radical cation, thus resulting in different adduct structures. The theoretical results are in perfect agreement with Symons' ESR study on ionized cyclobutanone[7] and they also give for the first time a consistent description of the labeling data of Dass and Gross.[6]

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Registry No. 1, 115461-80-8; **2**, 93250-35-2; **4**, 115481-59-9; **5**, 115461-81-9; ketene radical cation, 64999-16-2.

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(15) Drewello, T.; Heinrich, N.; Maas, W. P. M.; Nibbering, N. M. M.; Weiske, T.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 4810.

(16) (a) Clark, T. *J. Am. Chem. Soc.* **1987**, *109*, 6838. (b) See also: Heinrich, N.; Schwarz H. *Int. J. Mass Spectrom. Ion Proc.* **1987**, *79*, 295 and references cited therein. (c) For a detailed analysis of the properties of "odd-electron" bonds, see: Clarc, T. *J. Am. Chem. Soc.* **1988**, *110*, 1672 and references cited therein.