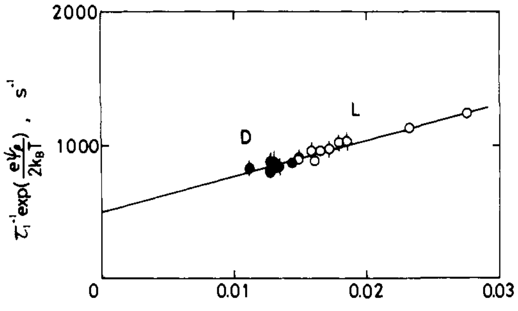

Figure 7. Plots of τ_1^{-1} $\exp(e\Psi_\beta/2k_BT)$ vs. $\exp(e\Psi_\beta/k_BT)([\mathrm{S(His)}] + [\mathrm{Cl}^-])$ in eq 7.

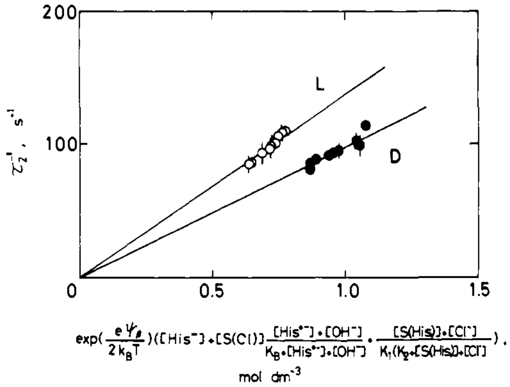

Figure 8. Plots of τ_2^{-1} vs. the concentration term in eq 8.

lines through the origin in both the Mg–HT(Cl)–L- and D-histidine systems. The value of the rate constant k_1^{int} was obtained from the slope of the straight line, and the value of the rate constant k_{-1}^{int} was evaluated by using the equilibrium constant K_1^{int}. The values of the rate constants obtained are also given in Table I. The good linearities for both the L- and D-histidine systems shown in Figures 7 and 8 lead to the conclusion that the two relaxations observed can be reasonably attributed to reaction III.

From the comparison of the obtained rate constants, one can see that the difference in the rate constants of the optical isomers is revealed in the value of the intercalation–deintercalation rate of step 1. It appears that the intercalation–deintercalation rate of L- and D-histidines is governed mainly by the geometric factors of the interlayer spacing and the intercalating molecule, since the size of the interlayer spacing of Mg–HT(Cl) is nearly equal to that of intercalating histidine. In the present study, Table I shows that the value of the rate constants of the intercalation–deintercalation of D-histidine is less than that for L-histidine. Taking into account that the values of the rate constants of step 2 for L-histidine are the same as that for D-histidine, it is concluded that the difference in the kinetic and static data may be due to the difference in the rates of the intercalation–deintercalation of L- and L-histidines, resulting from the different chirality of the optical isomers.

Finally, it can be seen from the present study that the stereoselective adsorption of the configurational isomers of L- and D-histidines was achieved by the Mg–hydrotalcite-like compound despite the fact that the clay itself is optically inactive. This fact indicates that the stereoselectivity of the hydrotalcite clay must be due to properties in the interlayer region. The results of this study show that the selectivity of clays for biological significant isomers results from differences in rates of intercalation. The reasons for the selection of L-amino acid by the Mg–hydrotalcite-like compound and, in general, the selection of the L form in biological systems may be revealed by further studies in which the properties of the interlayer region are varied.

Registry No. Cl$^-$, 16887-00-6; L-histidine, 71-00-1; D-histidine, 351-50-8.

[2 + 1] Cycloaddition of Ketene Radical Cation and Ethylene

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Abstract: The reaction of the ketene radical cation and neutral ethylene has been investigated by using tandem mass spectrometry and Fourier transform mass spectrometry. The reaction was conducted at high pressures (150–500 mtorr) in the presence of an inert bath gas which permitted collisional stabilization and isolation of the adduct for study by collisionally activated dissociation (CAD) and metastable ion spectroscopy. The structure of the adduct was established to be that of the cyclobutanone radical cation. Thus, the mechanism of the reaction is a facile [2 + 1] cycloaddition across the carbon–carbon double bond of the ketene radical cation.

Studies of cycloadditions of neutral molecules have substantially increased our understanding of pericyclic reactions. Their mechanisms have been impressively accounted for by the Woodward–Hoffman rule[1] and by the frontier molecular orbital (FMO) approach developed by Fukui.[2] However, few reports have appeared in the literature that describe cycloaddition reactions involving radical cations as one of the reactants. In 1969, Ledwith et al.[3] were first to demonstrate a radical cation catalyzed cyclodimerization. Recently, Bauld and co-workers[4,5] have shown convincingly that ionization of one partner has considerable advantage in enhancing the rate of cycloaddition. Similar observations have been made by us[6] and others.[7]

However, the mechanistic aspects of cycloaddition reactions involving radical cations are not yet perfectly understood. The

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[1] Woodward, R. B.; Hoffmann R. *J. Am. Chem. Soc.* **1965**, *87*, 395.

[2] Fukui, K. *Acc. Chem. Res.* **1971**, *4*, 57.

[3] Bell, F. A.; Crellin, R. A.; Fujii, N.; Ledwith, A. *Chem. Commun.* **1969**, 251.

[4] Bauld, N. L.; Bellville, D. J.; Pabon, R.; Chelsky, R.; Green, G. *J. Am. Chem. Soc.* **1983**, *105*, 2378. Bauld, N. L.; Pabon, R. *Ibid.* **1983**, *105*, 634.

[5] Bellville, D. J.; Wirth, D. D.; Bauld, N. L. *J. Am. Chem. Soc.* **1981**, *103*, 718. Bauld, N. L.; Bellville, D. J. *Ibid.* **1982**, *104*, 2665.

[6] Dass, C.; Gross, M. L. *J. Am. Chem. Soc.* **1983**, *105*, 5724. Gross, M. L.; Russell, D. H. *Ibid* **1979**, *101*, 2082.

[7] Haselbach, E.; Bally, T.; Lanyiova, Z. *Helv. Chim. Acta* **1979**, *62*, 577.

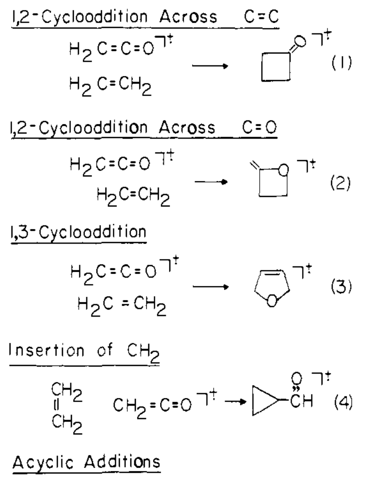
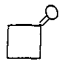


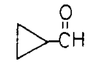
Figure 1. Possible modes of reaction of the ketene radical cation and neutral ethylene.

cyclodimerization of *N*-vinylcarbazole was postulated to occur in a stepwise fashion.[8,9] Bauld and co-workers,[4,5] however, have proposed a concerted path for the cation radical catalyzed [4 + 1] Diels–Alder reaction and for [2 + 1] cyclodimerization of olefins. Two-step mechanisms for the gas-phase cycloaddition of butadiene radical cation + butadiene,[10] methyl vinyl ether radical cation + butadiene,[10] and styrene radical cation + styrene[11] have been demonstrated recently in work done in this laboratory.

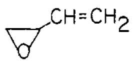
In this study, we report on the structure of the adduct formed in the gas-phase reaction of the ketene radical cation ($I^{+}\cdot$) and ethylene. The experimental strategy adopted by us makes use of tandem mass spectrometry (MS/MS), involving collisionally activated dissociation (CAD) spectroscopy[12] and unimolecular metastable ion spectroscopy.[13] Ionized ketene was reacted with neutral ethylene in a high-pressure chemical ionization (CI) source. This permits collisional stabilization of the adduct which, at low pressure (10^{-6} torr), would dissociate due to the exothermicity of the reaction. The structure of the adduct was determined by comparison of its CAD spectrum with those of structurally reasonable reference compounds. The reference compounds were cyclobutanone (II), cyclopropanecarboxaldehyde (III), butadiene monoxide (IV), methyl vinyl ketone (V), 3-methoxypropyne (VI), methoxyallene (VII), ethoxyacetylene (VIII), crotonaldehyde (IX), methacraldehyde (X), and 2,5-dihydrofuran (XI). The choice of these compounds was dictated by the possibility of a variety of mechanisms such as those shown Figure 1.



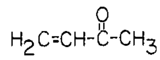
II



III



IV



$H_2C=CH-C(=O)-CH_3$

V

$HC\equiv C-CH_2-O-CH_3$

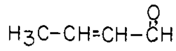
VI

$H_2C=C=CH-O-CH_3$

VII

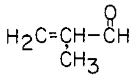
$HC\equiv C-O-C_2H_5$

VIII



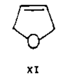
$H_3C-CH=CH-CH(=O)$

IX



$H_2C=C(CH_3)-CH(=O)$

X

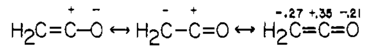


XI

The experimental approach is a more direct method of investigating the structure of an ion–molecule reaction adduct than the use of ion cyclotron resonance (ICR) spectrometry and isotopic labeling which have been extensively used in the past. Recent studies from our laboratory have successfully utilized this methodology to investigate the adducts formed in the reactions of *o*-quinodimethane radical cation + styrene,[14] styrene radical cation + styrene,[11] and benzene radical cation + 2-iodopropane.[15]

We have also studied the ketene$^{+}\cdot$–ethylene ion-molecule reaction at low pressure by using Fourier transform mass spectrometry (FTMS).[16] These investigations at low pressure permit us to show unequivocally which species is the reactant ion.

Neutral ketene acts as a powerful electrophile because of significant positive charge on the central carbon (see structures a, b and c).[17] As a result, ketenes undergo concerted [$_{\pi}2_s$ + $_{\pi}2_a$) cycloadditions in an antarafacial fashion.[18] Okada et al.[19] have shown the reaction to be symmetry allowed. The cycloaddition occurs with ease when electron-withdrawing groups are present on the ketene or when the olefin is relatively electron rich. Sustmann and co-workers[20] have postulated that it is the carbon–carbon double bond which should participate in [2 + 2] cycloadditions leading to cyclobutanone derivatives. Experimental results are in excellent accord with this expectation.[21-26] The reaction has been shown to occur in a concerted fashion.[23-26] However, cycloaddition at the carbonyl group can be observed when highly electron-rich olefins are involved[26,27] or when strongly electron-withdrawing groups are substituted on the ketene.[28] We expect that ionization of ketene will produce an even more reactive electrophile, and as a result, cycloadditions with unreactive olefins will be promoted. This possibility is explored in this paper.



$$H_2C=\overset{+}{C}-\overset{-}{O} \leftrightarrow H_2\overset{-}{C}-\overset{+}{C}=O \leftrightarrow H_2\overset{-.27}{C}=\overset{+.35}{C}=\overset{-.21}{O}$$

a b c

The properties of ionized ketene have been explored less extensively. Beauchamp and co-workers[29] investigated the ion–molecule reactions of $I^{+}\cdot$ by using ICR and photoionization mass spectrometry. The major reaction sequence initiated by $I^{+}\cdot$ involved sequential incorporation of CH_2 into the ionic product with the loss of CO. The ionic products arising from fragmentation

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(8) Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133.

(9) Neunteufel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 4080.

(10) Groenewold, G. S.; Gross, M. L. *J. Am. Chem. Soc.*, in press.

(11) Groenewold, G. S.; Chess, E. K.; Gross, M. L. *J. Am. Chem. Soc.* **1984**, *106*, 539.

(12) (a) Haddon, W. F.; McLafferty, F. W. *J. Am. Chem. Soc.* **1968**, *90*, 4745. (b) McLafferty, F. W.; Bente, P. F., III; Kornfeld, R.; Tsai, S.-C.; Howe, I. *Ibid.* **1973**, *95*, 2120. (c) McLafferty, F. W.; Kornfeld, R.; Haddon, W. F.; Levsen, K.; Sakai, I.; Bente, P. F., III; Tsai, S.-C.; Schuddemage, H. D. R. *Ibid.* **1973**, *95*, 3886. (d) Levsen, K.; Schwarz, H. *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 509.

(13) Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. "Metastable Ions"; Elsevier: Amsterdam, 1973.

(14) Chess, E. K.; Ping-Huang, L.; Gross, M. L. *J. Org. Chem.* **1983**, *48*, 1522.

(15) Miller, D. L.; Gross, M. L. *J. Am. Chem. Soc.* **1983**, *105*, 3783.

(16) Wilkins, C. L.; Gross, M. L. *Anal. Chem.* **1981**, *53*, 1661A.

(17) Houk, K. N.; Strozier, R. W.; Hall, A. *Tetrahedron Lett.* **1974**, 897.

(18) Reference 1, p 163. Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: New York, 1976; p 143.

(19) Okada, T.; Yamaguchi, K.; Fueno, T. *Tetrahedron* **1974**, *30*, 2293.

(20) Sustmann, R.; Ansmann, A.; Vahrenholt, F. *J. Am. Chem. Soc.* **1972**, *94*, 8099.

(21) Stevens, H. C.; Reich, D. A.; Brandt, D. R.; Fountain, K. R.; Gaughan, E. J. *J. Am. Chem. Soc.* **1965**, *87*, 5257.

(22) Rey, M.; Roverts, S.; Dieffenbacher, A.; Dreiding, A. S. *Helv. Chim. Acta* **1970**, *53*, 417. Brady, W. T.; Roe, R., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 1662. Brady, W. T.; Parry, F. H., III; Roe, R., Jr.; Holf, E. F., Jr. *Tetrahedron Lett.* **1970**, 819. Brady, W. T.; Harrison, J. M.; Duke, A. J. *Chem. Commun.* **1970**, 589.

(23) Huisgen, R.; Feiler, L. A.; Binsch, G. *Chem. Ber.* **1969**, *3460*. Huisgen, R.; Feiler, L. A. *Ibid.* **1969**, 3391. Huisgen, R.; Feiler, L. A.; Otto, P. *Ibid.* **1969**, 3405, 3444. Huisgen, R.; Otto, P. *Ibid.* **1969**, 3475.

(24) Martin, J. C.; Goodlett, V. W.; Burpitt, R. D. *J. Org. Chem.* **1965**, *30*, 4309.

(25) Brady, W. T.; O'Neal, H. R. *J. Org. Chem.* **1962**, *32*, 612. Montaigne, R.; Ghosez, L. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 221.

(26) Martin, J. C.; Gott, P. G.; Goodlett, V. W.; Hasek, R. N. *J. Org. Chem.* **1965**, *30*, 4175.

(27) Hoffmann, R. W.; Bressel, U.; Gelhaus, J.; Hauser, H. *Chem. Ber.* **1971**, *104*, 873.

(28) England, D. C.; Krespan, C. G.; Delaunois, M. *J. Org. Chem.* **1970**, *35*, 3312. Ghosez, L. *Angew. Chem.*, **1969**, *81*, 33. DoMinh, T.; Strausz, O. P. *J. Am. Chem. Soc.* **1970**, *92*, 766.

(29) Williamson, A. D.; Vogt, J.; Beauchamp, J. L. *Chem. Phys. Lett.* **1977**, *47*, 330. Vogt, J.; Williamson, A. D.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 3478.

Table I. CAD Spectra of C_4H_6O Radical Ions

precursor	69	68	55	54	53	52	51	50	43	42	41	40	39	38	37	31	29	28	27	26	15
$A^{+\cdot}$	1	2	1		<1		<1	1	1	100	10	3	14	4	2		<1	3	5	3	<1
II	1	2	1		<1		<1	1	1	100	12	3	16	4	3		<1	3	6	4	<1
III	158	12	100	2	9	27	18	18	44	58	41	23	52	12	8	6	11	3	20	8	3
IV	12	13	31		2	1	2	2	7	99	34	26	100	23	10	4	13	3	12	7	2
V	1		100	2	1		1	1	21	7	2		3	1	1		<1	8	4	<1	1
VI	66	4	100	8	12	1	1	1	2	31	9	8	27	32	13	7	13		10	7	3
VII	312	11	33	15	17	1	1	1	4	100	37	34	93	33	16	4	34		31	20	7
VIII	5	1	27						2	100	8	2	4				21	2	8	2	<1
IX	659	23	16	3	5	4	10	11	5	63	80	17	100	22	11	4	22	3	16	10	3
X	256	17	13	2	5	4	10	11	11	63	73	19	100	21	11	4	18		14	7	2
XI	126	28	2		1	<1	2	2	2	100	64	24	89	19	9	2	17	2	12	7	2
a	102	12	126		9	11	20	20	60	100	52	15	48	12	7	3	9	2	32	12	4
$A^{+\cdot b}$	63	11	99		8	6	18	16	54	100	44	18	44	9	4	3	8	2	25	9	5
$A^{+\cdot c}$	49	6	72		7	6	13	14	36	100	26	11	29	7	4	3	5	2	17	6	2

(column header *m*/*z* spans 69–15)

[a] From the reaction of ketene radical cation + ketene. [b] Ketene radical cation + ethylene adduct formed at 30-mtorr source pressure. [c] Ketene$^{+\cdot}$ + ethylene adduct formed at 80-mtorr source pressure.

of the unstable dimer were $C_2H_4^{+\cdot}$, $C_3H_4O^{+\cdot}$, and $C_2H_3O^+$. The major product $C_3H_4O^{+\cdot}$ ion, reacted further with neutral ketene forming $C_2H_3O^+$ (eq 1) and $C_4H_6O^{+\cdot}$ (eq 2). Similar results were obtained by Debrou et al.[30] who used a quadrupole ion trap (QUISTOR).

$$C_3H_4O^{+\cdot} + CH_2CO \rightarrow C_2H_3O^+ + C_3H_3O \quad (1)$$

$$C_3H_4O^{+\cdot} + CH_2CO \rightarrow C_4H_6O^{+\cdot} + CO \quad (2)$$

Results and Discussion

Our first goals were to ascertain whether a reaction can be observed between ketene radical cation and ethylene (eq 3) and, if the reaction did occur, to investigate the structure of the adduct, $A^{+\cdot}$. The structure of the adduct, $A^{+\cdot}$, was studied by using CAD

$$CH_2CO^{+\cdot} + C_2H_4 \rightarrow A^{+\cdot} \quad (3)$$

spectroscopy. The efficiency of the CAD technique as a diagnostic tool for structure determinations of gas-phase ions is well established.[12] This is due largely to the fact that the method permits sampling of ions with energies below the threshold for dissociation. The CAD spectrum of an adduct, formed from an ionic reagent prepared by low-energy charge exchange and stabilized by collisions with the inert bath gas, should be characteristic of its structure.

Structure of the ($CH_2{=}C{=}O^{+\cdot} + C_2H_4$) Adduct. The facility of the [2 + 2] cycloaddition of ketene and ethylene compared to ethylene + ethylene is attributed to the additional interaction of the olefin π electrons with the vacant p orbital (p_y) of the central carbon atom in ketene.[18,20] This contributes two strong bonding interactions which are absent in the $[_\pi2_s + {}_\pi2_a]$ reaction path for simple olefins. In addition, there is less steric hindrance for effective orbital overlap as a consequence of substitution of two hydrogens of ethylene by oxygen. Although the extra stabilization favors the cycloadditions of ketenes with olefins, not many cycloaddition reactions are known involving unsubstituted ketene. Cycloadditions are only observed when the energies of the LUMO–HOMO pair of the reacting partners are brought closer together by substituting either ketene with electron-withdrawing groups or the olefins with electron-donating groups.[21-26]

Ionization of ketene should make the central carbon atom even more electrophilic in nature and, thus, enhance its ability for cycloadditions with olefins. This premise was tested by reacting ketene with ethylene in a high-pressure CI source. Ketene (IE = 9.6 eV[31]) was ionized by charge exchange with $CS_2^{+\cdot}$ (IE = 10.0 eV[31]) as the reagent ion. The maximum energy transferred to $I^{+\cdot}$ by ionization with $CS_2^{+\cdot}$ is $\simeq$0.4 eV. The CS_2 also acts as a buffer gas and permits the partial pressures of the reacting gases to be lowered which minimizes side reactions such as consecutive additions leading to polymerization (for examples, see eq 1 and 2). The reference compounds were also ionized in separate experiments by using $CS_2^{+\cdot}$ charge exchange. The low-energy ionization should maintain the structure integrity of the ions.

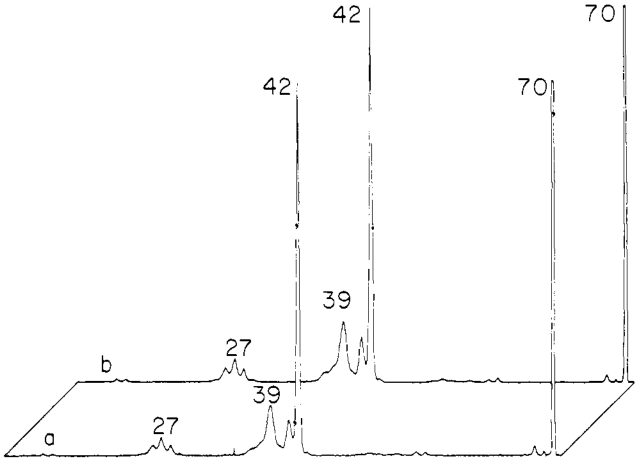

Figure 2. CAD spectra of (a) the adduct of the ion–molecule reaction of ionized ketene and neutral ethylene and (b) the cyclobutanone radical cation.

Under high-pressure conditions, the ions suffer several collisions (ca. 100) with the neutral bath gas which serve to stabilize the ion–molecule adduct. Specifically, at pressures above 150 mtorr in the CI source, the adduct could be intercepted and its CAD spectrum obtained. The dominant fragment ion in the CAD spectrum of the adduct, $A^{+\cdot}$, is *m*/*z* 42 (see Figure 2 and Table I), which could arise by the loss of C_2H_4 or CO (eq 4 and 5, respectively). Only ionized cyclobutanone gives a CAD spectrum

$$A^+ \rightarrow CH_2CO^{+\cdot} + C_2H_4 \quad (4)$$

$$A^{+\cdot} \rightarrow C_3H_6^{+\cdot} + CO \quad (5)$$

which matches that of the adduct (Figure 2). All other C_4H_6O reference compounds give molecular ions which have CAD spectra that are readily distinguished from those of $A^{+\cdot}$ and $II^{+\cdot}$ (Table I). These other $C_4H_6O^{+\cdot}$ radical cations give extensive losses of H (except V and VIII) and CH_3 unlike the adduct and the cyclobutanone radical cations. Moreover, other significant differences are the relative abundances of ions *m*/*z* 42, 41, 40, 39, 38, 29, and 27.

Before we conclude that the adduct has the cyclobutanone radical cation structure, we need to examine the nature of the *m*/*z* 42 fragment ion. Ionized cyclobutanones, which fragment in the source of a mass spectrometer, are known to undergo a cycloreversion reaction to lose C_2H_4 or a substituted ethylene and produce principally $CH_2CO^{+\cdot}$ at *m*/*z* 42.[32] The collisionally

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[30] Debrou, G. B.; Fulford, J. E.; Lewars, E. G.; March, R. E. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *26*, 345.

[31] Levin, R. D.; Lias, S. G. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1982**, NSRDS-NBS 71.

Table II. CAD Spectra of Deuterium-Labeled Adducts

	m/z																					
	71	70	69	60	58	57	56	46	45	44	43	42	41	40	39	32	30	29	28	27	26	15
a[a]	2	1		2	2	1	<1	100	13	76	4	48	22	10		4	11	8	10	4	2	2
b[b]	2	2	2		1	2	<1			100	9	41	7	8	4		2	2	4	3	1	<1

[a] Ketene radical cation + ethylene-d_4 adduct. [b] Ketene-d_2 radical cation adduct.

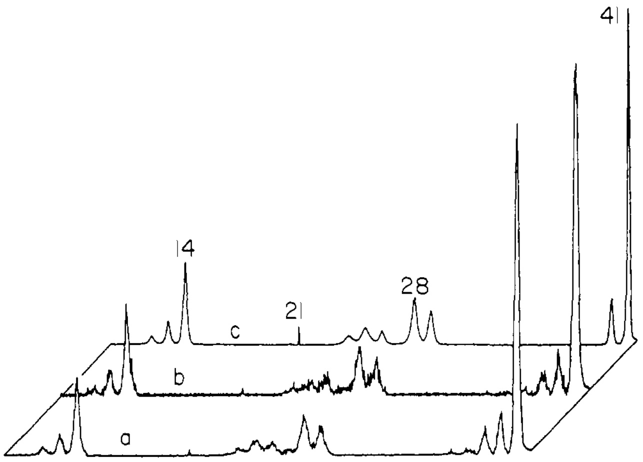

Figure 3. CAD spectra of *m/z* 42 (lower mass) formed in I FFR from (a) the adduct of the ion–molecule reaction of ionized ketene and neutral ethylene and (b) cyclobutanone radical cation and (c) the CAD spectrum of ketene radical cation.

activated adduct, however, undergoes loss of both C_2H_4 and CO to give $CH_2CO^{+\cdot}$ and $C_3H_6^{+\cdot}$, respectively, at *m/z* 42. This was established by monitoring the reaction between $I^{+\cdot}$ and deuterated ethylene (vide infra) and by studying the consecutive reactions of the adduct $C_4H_6O^{+\cdot}$ by using an MS/MS/MS technique.[33] The latter strategy involved collisional activation of the adduct $A^{+\cdot}$ to produce *m/z* 42 in the collision cell located just outside the ion source (first field free region (FFR)). The *m/z* 42 fragment ions were then mass analyzed by using the double focusing MS-I, and two different mass ions were observed. The lower mass species had a CAD spectrum, taken by activating the ion in the second collision cell located after the double-focusing analyzer (third FFR), which is identical with that of ionized ketene (Figure 3). The higher mass ion at *m/z* 42 has a structure represented by either ionized propene or cyclopropane or a mixture of the two as confirmed by examining the CAD spectrum.[34] The relative abundances of $CH_2CO^{+\cdot}$ and $C_3H_6^{+\cdot}$ were 1.0:1.1.

Ionized cyclobutanone ($II^{+\cdot}$) decomposed almost exclusively to $CH_2CO^{+\cdot}$ if only the reactions in the ion source were considered. However, collisional activation of $II^{+\cdot}$ in the first FFR region caused formation of $CH_2CO^{+\cdot}$ and $C_3H_6^{+\cdot}$ in the abundance ratio of 1.0:1.1. The CAD spectra of these ions are identical with those of ionized ketene (Figure 3) and $C_3H_6^{+\cdot}$, respectively, as was observed for the adduct. McLafferty et al.[12c] have also reported other examples of ions which give different CAD vs. electron ionization mass spectra.

The unimolecular or metastable decompositions of the adduct and the cyclobutanone ion are also identical. For example, the loss of 28 mass units from these $C_4H_6O^{+\cdot}$ ions gave a composite metastable peak shape consistent with the fact that both neutral C_2H_4 and CO were expelled. The shapes of peaks, determined by the kinetic energy releases and by the relative extents of loss of C_2H_4 and CO, are identical (Figure 4). Other $C_4H_6O^{+\cdot}$ ions ($III^{+\cdot}$–$XII^{+\cdot}$) show different metastable ion characteristics for loss of 28 mass units. The kinetic energy release measured at the width of the peak at half height varied from 35 to 230 meV compared to 6.1 meV for the adduct $A^{+\cdot}$ and the ionized cyclobutanone.

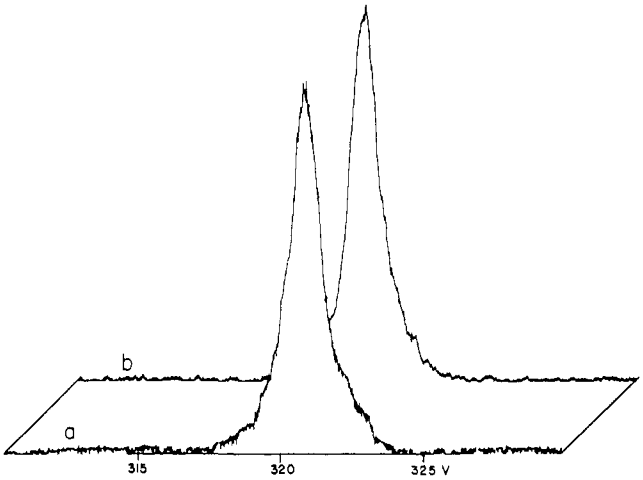

Figure 4. Peak shapes of the unimolecular transition *m/z* 70 → 42 from (a) the adduct of the ion–molecule reaction of ionized ketene and neutral ethylene and (b) the cyclobutanone radical cation. ESA voltage corresponding to the transmission of main beam was 534 V.

We also investigated the adducts formed by the reactions of ionized ketene-d_2 with ethylene and $I^{+\cdot}$ with ethylene-d_4. The CAD spectra of these adducts (Table II) are similar to that of the adduct formed from ketene$^{+\cdot}$ and ethylene (Figure 2a) except now the composite peak at *m/z* 42 was split. The ion at *m/z* 46 in the spectrum of the adduct formed in the reaction of ketene$^{+\cdot}$ and ethylene-d_4 corresponds to the loss of CO, while the ions at *m/z* 42 and 44 are the results of cycloreversion reactions to expel C_2D_4 and $C_2H_2D_2$, respectively. After the contribution of the signal due to the loss of CDO[35] was corrected for, the two ions arising by the losses of C_2D_4 and $C_2H_2D_2$ are approximately of equal abundance. We also note the ions at *m/z* 58 and 60 (due to eliminations of CD_2 and CH_2) and the absence of anion at *m/z* 59. Similarly, ions at *m/z* 43 (loss of C_2HD_3) and 31 ($C_2HD_3^+$) are absent, while ions at *m/z* 42, 44 (losses of C_2D_4 and $C_2H_2D_2$), 30 ($C_2H_2D_2^{+\cdot}$) and 32 ($C_2D_4^{+\cdot}$) are conspicuous. This is rationalized to mean that H/D rearrangements are not occurring in the adduct prior to or concurrent with collisional activation. The other reference compounds, if isotopically labeled, must undergo H/D rearrangements to a certain extent prior to formation of ketene ion.

All of the above observations constitute strong evidence that the adduct has the structure of the cyclobutanone radical cation. Only the adduct $A^{+\cdot}$ and the cyclobutanone radical cation show identical CAD spectra and metastable characteristics, and these spectra differ drastically from those of other $C_4H_6O^{+\cdot}$ ions.

It may be argued that the $C_4H_6O^{+\cdot}$ ions were formed by reaction 2 and not by the reaction of ketene$^{+\cdot}$ with ethylene. This ambiguity was resolved by investigating the reaction of ionized ketene and neutral ketene in the CI source in the absence of ethylene. A $C_4H_6O^{+\cdot}$ ion of comparatively low abundance was observed. Its CAD spectrum, acquired after forming the adduct at a source pressure of 500 mtorr (same as that used to study the adduct $A^{+\cdot}$), is different from that of the cycloadduct $A^{+\cdot}$ (Table I). Variation of ion source pressure had no effect on the spectrum of this $C_4H_6O^{+\cdot}$. However, in the presence of ethylene, the cycloadduct was observed only at pressures above 150 mtorr. At

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(32) Schwarz, H.; Koppel, C. In "The Chemistry of Ketenes, Allenes and Related Compounds"; Patai, S., Ed.; Wiley: New York, 1980; Part I, p 189.

(33) Burinsky, D. J.; Cooks, R. G.; Chess, E. K.; Gross, M. L. *Anal. Chem.* **1982**, *54*, 295.

(34) Williams, R. B. *J. Am. Chem. Soc.* **1942**, *64*, 1395.

(35) The probability of the loss of CDO is twice that of CHO. Therefore, the correction to the abundance of *m/z* 44 amounts to two times the intensity of *m/z* 45.

lower pressures, the abundance of the adduct $A^{+\cdot}$ was considerably lower, and the CAD spectra were identical with or had contribution from the $C_4H_6O^{+\cdot}$ formed by reaction 2 (Table I). Moreover, the experiments involving the deuterated analogues have also eliminated this uncertainty. The adduct from the ketene radical cation–ethylene reaction was now studied without interference of the product from reaction 2.

Reaction at Low Pressure. Throughout the foregoing discussion, we have assumed that the reactant is ionized ketene and not ionized ethylene. When the propensity of ketene to undergo cycloaddition reactions because of the electrophilicity of the central carbon atom is considered, this assumption seems justified. Moreover, the charge exchange reaction of $CS_2^{+\cdot}$ with ethylene is endothermic (IE of ethylene is greater than that of CS_2), and as a result, few ions of ethylene were present under the experimental conditions, typically less than 7% of $I^{+\cdot}$ when the partial pressures of CS_2, ketene, and ethylene were in the ratio of 10:1:1 and the total ion source pressure was 500 mtorr. Nevertheless, we can obtain additional evidence concerning this question by investigating low-energy ion–molecule reactions by using a Fourier transform MS.

Ketene ($P = 3 \times 10^{-7}$ torr) and ethylene ($P = 7 \times 10^{-7}$ torr) were ionized in separate experiments at 9.5–11.0 eV. It was observed that the rate of disappearance of ketene radical cation was greater when it reacted with ethylene and ketene compared to its reaction with neutral ketene only. In addition to $C_3H_4O^{+\cdot}$, ions at m/z 54 and 55 were also observed. However, it could not be ascertained whether the cycloaddition was occurring because the adduct could not be detected, and its major decomposition products, $C_3H_6^{+\cdot}$ and $CH_2CO^{+\cdot}$, have the same mass as the reactant (ketene radical cation). Unequivocal evidence for the participation of the ketene radical cation as the reacting species was obtained by reacting it with ethylene-d_4. The following sequence was observed.

$$\mathrm{CH_2CO^+ + CH_2CO \longrightarrow C_3H_4O^+ + CO} \qquad (6)$$

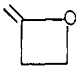
$$\mathrm{CH_2CO^+ + C_2D_4} \begin{array}{ll} \longrightarrow \mathrm{C_3H_2D_4^+ + CO} & (7) \\ \longrightarrow \mathrm{C_3HD_2O^+ + CHD_2} & (8) \\ \longrightarrow \mathrm{C_3D_3O^+ + CH_2D} & (9) \\ \longrightarrow \mathrm{CH_2CO^+ + C_2D_4} & (10) \\ \longrightarrow \mathrm{CD_2CO^+ + C_2H_2D_2} & (11) \end{array}$$

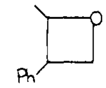
$$\mathrm{CD_2CO^+ + CH_2CO^+ \longrightarrow C_3H_2D_2O^+ + CO} \qquad (12)$$

$$\mathrm{CD_2CO^+ + C_2D_4} \begin{array}{ll} \longrightarrow \mathrm{CD_2CO^+ + C_2D_4} & (13) \\ \longrightarrow \mathrm{C_3D_6^+ + CO} & (14) \\ \longrightarrow \mathrm{C_3D_3O^+ + CD_3} & (15) \end{array}$$

Generation of $C_3H_2D_4^{+\cdot}$ and $CD_2CO^{+\cdot}$, which subsequently react with neutral ketene and ethylene-d_4, establishes the participation of ionized ketene in the cycloaddition reaction.

Mechanism. 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,[17] and the π electrons at one of the carbons of ethylene. Subsequent cyclization occurs by interaction of the second carbon of the ethylene with the terminal carbon atom of the ketene and not with the oxygen atom. The cyclization at oxygen would generate 2-methyleneoxetane (XII) radical cation. Although,


XII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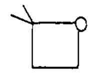
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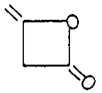
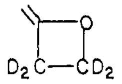

XV

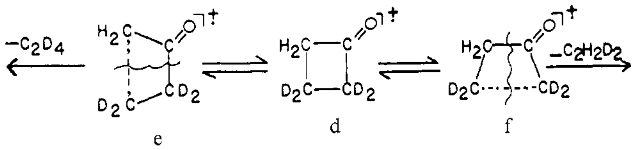

XVI

we did not investigate $XII^{+\cdot}$, its formation can be ruled out on the basis of its expected fragmentation pattern which can be predicted by analogy with the mass spectra of 2-methyl-3-phenyloxetane (XIII),[36] 2,2-dimethyloxetane (XIV),[36b] 2,4-dimethyloxetane,[37] and diketene (XVI).[38] We would expect to observe m/z 40 (allene$^{+\cdot}$) formed by the loss of CH_2O by the decomposition of this cycloadduct, but this is not the case. Moreover, if 2-methyleneoxetane-d_4 (XVI) was the cycloadduct formed from ionized ketene and ethylene-d_4, the only major fragment ion expected in its decomposition would be m/z 42 formed by elimination of C_2D_4. This structure should not undergo elimination of CO and $C_2H_2D_2$.

The other possibility for cycloaddition involves the two terminal atoms (carbon and oxygen, reaction 3 in Figure 1) of ketene to give, after a hydrogen atom rearrangement, ionized 2,5-dihydrofuran. This clearly does not occur as can be seen by comparing the CAD spectra of $A^{+\cdot}$ and of $XI^{+\cdot}$. Similarly, the possibility of insertion of CH_2 in the double bond of ethylene (reaction 4 in Figure 1) can be ruled out on the basis of different CAD spectra of the adduct $A^{+\cdot}$ and ionized cyclopropanecarboxaldehyde ($III^{+\cdot}$). The acyclic structures are also dismissed on the basis of CAD spectral comparisons.

The fact that the cycloaddition is occurring at the carbon–carbon double bond and does not involve the carbonyl moiety is reminiscent of the chemistry of neutral ketene and corroborates the theoretical analysis of Sustmann and co-workers.[20] Cycloaddition at the carbonyl bond involves less stabilization resulting from the interaction of the HOMO ethylene–LUMO >C=C< of ketene than that achieved by the interaction of HOMO ethylene–LUMO >C=O orbitals for the cycloaddition involving the carbon–carbon double bond.[20]

According to Bauld and co-workers[4] [2 + 1] cycloadditions are symmetry forbidden. Nevertheless, these reactions do occur presumably through the intermediacy of a long-bond four-membered ring.[4] Another possibility is a two-step mechanism involving formation of an acyclic radical cation. We now know that the final structure observed in this study cannot be acyclic by considering the results obtained with deuterium-labeled reactants. For example, the adduct formed in the reaction of $CH_2CO^{+\cdot}$ and ethylene-d_4 undergoes nearly equal losses of C_2D_4 and $C_2H_2D_2$ and no detectable loss of C_2HD_3. 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 (d) or is a mixture of unsymmetrical one-electron or long-bond cyclobutanone radical cations (e and f; eq 16). We



(16)

are unable to judge, based on the evidence gathered here, whether the cyclobutanone ion exists as an energy minimum or maximum on the potential surface connecting the two long-bond structures.

We did seek evidence for the existence of an acyclic structure which forms prior to ring closure. The experiments involved the increase of the bath gas pressure in an attempt to stabilize and isolate that structure. This was a successful strategy in the study of the radical cation dimerization of butadiene.[10] However, the adduct formed by the reaction of the ketene radical cation and ethylene gave invariant CAD spectra as a function of pressure quite unlike the dimer produced in the butadiene radical cation cyclodimerization.

In conclusion, ionization of ketene promotes a facile cycloaddition with neutral ethylene. The corresponding reaction of neutral ketene and neutral ethylene to form cyclobutanone has been observed but only under very vigorous experimental conditions.[39] Ionization of ketene presumably lowers the energies of both its HOMO and LUMO and brings its LUMO and the

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(36) (a) Jones, G., II; Mcdonnell, L. P. *Tetrahedron Lett.* **1975**, 4633. (b) *J. Org. Chem.* **1978**, *43*, 2184.

(37) Pihlaja, K.; Polviander, K.; Kesninen, R.; Jalonen, J. *Acta Chem. Scand.* **1971**, *25*, 765.

(38) Friedman, L.; Long, F. A. *J. Am. Chem. Soc.* **1953**, *75*, 2832.

(39) Hall, H. K., Jr.; Plorde, D. E. U.S. Patent 3 646 150, 1972; *Chem. Abstr.* 1973, *76*, P112787 n.

HOMO of ethylene closer, thereby enhancing the rate of the cycloaddition reaction. Thus, the advantage of the radical cation catalyzed cycloaddition, pointed out recently by Bauld and coworkers,[4] has been confirmed.

Experimental Section

All the CAD spectra were acquired by using a Kratos MS-50 triple analyzer of EBE geometry,[40] which has the advantage of allowing the acquisition of CAD spectra after choosing the parent ion at high-mass resolution. For example, we observed three isobaric ions at *m/z* 70 (the mass of the adduct $A^{+\cdot}$) in the study of the ketene$^{+\cdot}$–ethylene reaction. The signal due to $A^{+\cdot}$ was separated from the interfering signals at a resolution of 5000 (10% valley definition). The composition of the ion was verified to be $C_4H_6O^{+\cdot}$ by peak matching with the $CS_2^{+\cdot}$ ions (*m/z* 76). The $C_4H_6O^{+\cdot}$ ion was more substantial than the other two interfering ions. Similarly, while studying the cycloadduct formed between $I^{+\cdot}$ and deuterated ethylene, a mass resolution of $\simeq$10 000 was required to eliminate obtrusive signals, especially that due to the $C_4H_{10}O^{+\cdot}$ ion. Collisional activation was effected in the third FFR by using helium as the target gas. Its pressure was adjusted to give a 50% suppression of the main beam intensity. The unimolecular or the CAD spectra were acquired by scanning the second electrostatic analyzer (ESA) voltage. Each spectrum was the average of 3–5 determinations, and each consisted of 7–20 scans that were acquired and averaged by using a Data General Nova 4X computer. The relative standard deviations for relative intensities were less than ±3%.

The kinetic energy release measurements were made with the energy resolution slit located after the second ESA set to 0.125 mm. The second ESA voltage was scanned over a narrow range (312–328 V) so as to monitor only the ion formed by metastable decomposition.

The ion–molecule reactions were conducted in a Kratos high-pressure CI source at pressures of 150–500 mtorr and a temperature of 150 °C. Source pressures were estimated by using an ion gauge located in the source pumping manifold which was calibrated by using a Hastings gauge mounted on a regular sample probe. CS_2 was admitted through a reagent gas inlet system and ethylene through a custom-built CI probe to which was attached a $\simeq$50-mL reservoir. The ethylene pressure was regulated by a fine metering valve. Ketene was admitted through an all-glass inlet maintained to avoid polymerization. The reagent gas was ionized by 280-eV electrons. The relative partial pressures of CS_2:CH_2CO:C_2H_4 were 10:1:1. The reference compounds were introduced through the glass inlet at a partial pressure of 5–10% that of CS_2 and ionized by charge exchange with $CS_2^{+\cdot}$. Their CAD spectra were acquired as described earlier.

For the examination of the consecutive reactions of the cycloadduct, a MS/MS/MS technique was employed.[29] The ions emerging from the ion source were collisionally activated in the first FFR. The fragment ion *m/z* 42 (m_2) formed by decomposition of the adduct $A^{+\cdot}$ (m_1) was selected by decoupling the accelerating voltage and first ESA voltage and setting the first ESA to $E = E_0(m_2/m_1)$, where E_0 is the first ESA voltage necessary to transmit the parent ion, and the magnet to m_2^2/m_1. This transmitted only those *m/z* 42 ions which were formed from the adduct $A^{+\cdot}$ in the first FFR. The spectra of the *m/z* 42 product ions formed in the consecutive reaction were acquired in the third FFR as described above.

The low-energy ion–molecule reactions were investigated in a trapped cubic cell by using a home-built FTMS[16] controlled by a Nicolet 1000 data system and associated electronics. The reagent gases were admitted through a standard metal inlet system maintained at ambient temperature. The cell was located in a magnetic field of 1.2 T. The ions were formed by an electron beam pulse of 5 ms; experiments were performed over a 9.5–11.5-eV range of electron energies. The trap voltage was 1 V, and the emission current was 2.0 μA. The ions were excited by using an excitation bandwidth of 800 kHz and sweep rate of 2 kHz μs^{-1}. The spectra obtained from 100 time domain sweeps were acquired at variable time delays ranging from 1 to 700 ms.

All the reference compounds were procured from commercial sources except methoxyallene[41] and cyclopropanecarboxaldehyde[42] which were synthesized by using methods reported in the literature. Ketene was synthesized by using low-pressure pyrolysis of acetic anhydride which was flowed through a quartz tube held at 500–520 °C.[43] The unreacted starting material and the involatile products were collected in a trap immersed in a dry ice–isopropyl alcohol bath. The ketene was collected in a second trap cooled to liquid nitrogen temperature and was further purified by trap-to-trap vacuum distillation. It was prepared fresh each time before use.

Acknowledgment. The work was supported by the National Science Foundation (Grant CHE-8320388) and by the Midwest Center for Mass Spectrometry, a National Science Foundation Regional Instrumentation Facility (Grant CHE-82-11164).

Registry No. $I^{+\cdot}$, 64999-16-2; II, 1191-95-3; III, 1489-69-6; IV, 930-22-3; V, 78-94-4; VI, 627-41-8; VII, 13169-00-1; VIII, 927-80-0; IX, 4170-30-3; X, 78-85-3; XI, 1708-29-8; $H_2C{=}CH_2$, 74-85-1.

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(40) Gross, M. L.; Chess, E. K.; Lyon, P. A.; Crow, F. W.; Evans, S.; Tudge, H. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *42*, 243.

(41) Brandsma, L. "Preparative Acetylenic Chemistry"; Elsevier: Amsterdam, 1971.

(42) Young, B.; Trahanovsky, W. S. *J. Org. Chem.* **1967**, *32*, 2349.

(43) Blake, P. G.; Davies, H. H. *J. Chem. Soc. B* **1971**, 1727.

Electrocyclic Reactions of Gas-Phase 1-Methyl- and 3-Methylcyclobutene Radical Cations

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Abstract: The facile electrocyclic ring opening of gas-phase 1-methyl- and 3-methylcyclobutene radical cations has been demonstrated by using collisional activation decomposition spectroscopy and Fourier transform mass spectrometry (FTMS). The effect of internal excitation on the isomerization was investigated by employing both electron- and charge-exchange ionization to form the ions with various internal energies. Both the collisional ionization spectra and the bimolecular reactivities of the methyl-substituted cyclobutene ions change with increasing excitation to reflect the onset of ring opening. The variations of reactivity in structurally specific ion–molecule reactions were probed by utilizing a new experimental approach involving pulsed introduction of reactants into the cell of an FTMS. The results of these experiments permit an approximate assignment of the activation energies for isomerization of 1-methylcyclobutene and 3-methylcyclobutene radical cations to be less than 16 and 4 kcal mol^{-1}, respectively. The activation energies are considerably lower than those of the corresponding electrocyclic reactions of neutral molecules, but the effects of substitution parallel those found for the neutral cyclobutenes.

The behavior of open-shell species in electrocyclic reactions is a subject of current interest. Recently, we reported on the electrocyclic ring opening of cyclobutene[1] and 1-phenyl- and 3-phenylcyclobutene[2] radical cations. The principal aims of these

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