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.

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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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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

Table I. Partial CAD Spectra of $[C_5H_8]^{+\cdot}$ Isomers[a]

	m/z															
precursor	53	52	51	50	49	42	41	40	39	38	37	29	28	27	26	15
isoprene	103	23	34	29	7	19	73	43	100	19	10	2	5	33	8	1
1-methylcyclobutene	105	17	27	24	6	22	68	49	100	23	11	2	7	29	8	1
1,3-pentadiene	77	15	22	18	4	18	68	36	100	19	9	2	5	27	7	1
3-methylcyclobutene	85	12	21	18	4	25	64	38	100	20	10	2	4	27	7	1
1,4-pentadiene	76	12	21	16	3	18	60	36	100	18	8	2	4	27	7	1
cyclopentene	69	10	15	12	3	25	69	48	100	22	10	2	6	21	7	1
methylenecyclobutane	49	11	17	16	5	11	49	90	100	23	11	2	8	21	8	1
pent-1-yne	82	14	23	20	5	39	51	142	100	25	12	20	7	33	8	1
pent-2-yne	150	30	50	43	10	15	75	36	100	25	14	6	4	43	10	2

[a] Peaks in the mass range *m/z* 63–67 are omitted due to metastable ion contribution. The precision of the measurements is better than ±5%.

investigations were to determine (a) whether the open-shell systems undergo electrocyclic reactions, a well-established phenomenon for neutral cyclobutenes, (b) what the energy barriers of the electrocyclic reactions are, and (c) what effects substituents have on the rate of the reaction. We now know that certain cyclobutene radical cations do indeed participate in electrocyclic reactions, and there exists an energy advantage for the rate of the reactions. On the basis of theoretical calculations, Bauld et al.[3] have shown recently that ionization exerts an analogous effect on other pericyclic reactions, and this has been confirmed by experimental studies.[4]

Substitution of a phenyl group on the carbon atoms of the double bond was shown to stabilize the cyclobutene radical cation in contrast to substitution of this group at carbons three and four. These effects parallel those of substitution on the electrocyclic ring opening of neutral cyclobutene.[5-8]

The electrocyclic ring opening of neutral cyclobutene and its derivatives to the corresponding 1,3-butadienes and the reverse process have been the subject of several experimental[5-7] and theoretical[8-11] studies. The pattern of their reactivity and the stereochemical course of the reactions have been explained in terms of the Woodward–Hoffmann rules of conservation of orbital symmetry[10] and on the basis of aromaticity and antiaromaticity of the transition state, a perturbation molecular orbital argument.[11] On the other hand, owing to the lack of experimental data, the applicability of such selection rules for pericyclic reactions of radical cations has not been thoroughly tested. Is there a correlation between reactions of radical cations and their neutral precursors? In some cases a close parallelism has been observed for pericyclic reactions of open-shell species and their neutral precursors. For example, the retro-Diels–Alder reaction of vinylcyclohexene observed in a mass spectrometer is similar to the corresponding thermal reaction of neutral vinylcyclohexene, suggesting a common mechanism.[12] Reactions of several analogues of ionized tetrahydronaphthalene resemble the thermal reactions of their neutral counterparts.[13] It has also been postulated that ions can undergo reactions which are analogous to photochemical reactions of the neutral molecules. As an example, Johnstone and Ward[14] and more recently Gooden and Brauman[15] have shown that cyclization of the *cis*-stilbene radical cation involves an electronically excited state. Isomeric cyclobutanedicarboxylic acids and corresponding ring-opened muconic acid radical cations undergo electrocyclic reactions that were postulated to occur via an electronically excited state.[16]

As a part of our continuing study of this subject, we report the electrocyclic reactions of 1-methyl- and 3-methylcyclobutene radical cations. This and other investigations are designed to provide additional evidence for the electrocyclic reactions of open-shell and closed-shell systems if the ring opening occurs. Furthermore, it is necessary to test the generality of our earlier findings with respect to the effects of substituents on the rate of the electrocyclic ring opening of cyclobutene radical cations.

In order to achieve these objectives, the gas-phase ions were investigated by using mass spectrometric techniques. In a mass spectrometer, gas-phase ions typically at a pressure of ca. 10^{-5} torr are studied. The effect of solvation, which can play a major role in determining the rate of a reaction, is no longer a factor. It is well-known that the unsaturated hydrocarbon radical cations undergo internal rearrangement with greater facility than other hydrocarbon- and heteroatom-containing radical cations. Therefore, the specific strategy is to use techniques that allow us to investigate ions that are stable to unimolecular decomposition and that possess low internal energies. Accordingly, we have employed (a) collisionally activated dissociation (CAD) spectroscopy,[17] (b) collisional ionization (charge stripping),[18] (c) low-pressure ion–molecule reactions conducted in the cell of a Fourier transform mass spectrometer (FTMS),[19] and (d) high-pressure ion–molecule reactions studied in a tandem mass spectrometer.[20,21] The radical ions were formed by electron ionization or by charge-exchange reactions.

Results and Discussion

The primary goals of the present study were to determine whether the electrocyclic ring openings of 1-methyl- (1-MCB) and 3-methylcyclobutene (3-MCB) radical cations occur and, if so, to determine the effect of methyl substitution on the activation energy of the reaction. We also investigated $C_5H_8^{+\cdot}$ radical cations generated from methylenecyclobutane, 1,4-pentadiene, cyclopentene, pent-1-yne, and pent-2-yne to establish the specific chemical properties of cyclic and acyclic isomers. If substituted cyclobutene radical cations are formed with energies above the

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Table II. Collisional Ionization Spectra of $[C_5H_8]^{+\cdot}$ Isomers[a]

	m/z						
precursor	34	33.5	33	32.5	32	31.5	31
isoprene	8	9	22	23	12	5	21
1-methylcyclobutene		3	16	27	19	8	28
1,3-pentadiene	37	12	15	13	9	3	11
3-methylcyclobutene	7	6	18	18	18	8	25
1,4-pentadiene	4	5	23	17	18	8	25
cyclopentene	6	17	18	28	12	6	13
methylenecyclobutane	14	3	19	19	17	6	22
pent-1-yne	20	14	12	20	12	14	20
pent-2-yne	1	2	11	16	19	12	40

[a] Electron ionization at 70 eV. The precision of the measurements is better than ±5%.

Table III. Collisional Ionization Spectra of $[C_5H_8]^{+\cdot}$ Isomers[a]

		m/z						
precursor	ref	34	33.5	33	32.5	32	31.5	31
1-methylcyclobutene	*b*	2	8	19	19	15	9	29
	c	10	8	18	24	14	5	20
1,3-pentadiene	*b*	23	10	17	14	13	5	19
	c	34	14	15	14	9	3	12
3-methylcyclobutene	*b*	6	6	21	14	19	9	25
	c	29	12	15	15	11	3	14
1,4-pentadiene	*b*	4	5	23	17	17	8	26
	c	29	11	18	14	10	4	12

[a] $CS_2^{+\cdot}$ charge-exchange ionization. [b] Ion source pressure of 0.05 torr. [c] Ion source pressure of 0.4 torr.

activation energy of the electrocyclic reaction, then 1-$MCB^{+\cdot}$ and $iso^{+\cdot}$ (iso = isoprene) for example, should give identical CAD and collisional ionization spectra and undergo similar structurally specific ion–molecule reactions. These properties should not match those of other $C_5H_8^{+\cdot}$ ions. On the other hand, if the ions are formed with energies below the threshold for the electrocyclic reaction, then the properties of 1-$MCB^{+\cdot}$ and $iso^{+\cdot}$ should be different. In the following sections we present results and interpret them based on this reasoning.

Collisionally Activated Dissociation Spectroscopy Results. The major decomposition reactions of C_5H_8 radical cations as revealed by their CAD spectra (Table I) are the losses of CH_3 and C_2H_5 radicals to yield $C_4H_5^+$ and $C_3H_3^+$, respectively. Other important fragment ions are $C_3H_5^+$, $C_3H_4^{+\cdot}$, and $C_2H_3^+$. CAD spectra of some of the $C_5H_8^{+\cdot}$ ions have also been reported previously,[22-24] and our results are in agreement with those spectra.[22,23]

Although the CAD spectra of $C_5H_8^{+\cdot}$ ions appear to be qualitatively similar, there are still subtle differences which can be interpreted to assign structures of the isomeric ions. For example, the spectra of 1-$MCB^{+\cdot}$ and $iso^{+\cdot}$ are almost identical. Similarly, ionized 3-MCB, 1,3-pentadiene, 1,4-pentadiene, and cyclopentene yield virtually indistinguishable spectra. On the basis of differences in the relative abundances of C_4 fragments, the 1-$MCB^{+\cdot}$/$iso^{+\cdot}$ pair can be differentiated from the other cyclic/acyclic isomeric pair, i.e., the 3-$MCB^{+\cdot}$/1,3-$C_5H_8^{+\cdot}$ radical cations. The $C_5H_8^{+\cdot}$ radical cations derived from methylenecyclobutane, pent-1-yne, and pent-2-yne give distinctive spectra.

The similarities in the spectra of the ionized 1-MCB and isoprene pair and those of 3-MCB and 1,3-pentadiene can be explained if 1-$MCB^{+\cdot}$ and 3-$MCB^{+\cdot}$ undergo electrocyclic ring openings to isoprene and 1,3-pentadiene radical cations, respectively. Low-energy electron ionization did not accentuate the differences in the spectra of the cyclic and acyclic isomers, suggesting that the activation energies for the ring openings are relatively low.

Since the differences in the CAD spectra are not very pronounced, they should not be taken as strong evidence in support of the occurrence of an electrocyclic process. Furthermore, the CAD technique becomes relatively ineffective if the difference in the dissociation and isomerization energy thresholds is very large. Therefore, we decided to pursue the subject by using other diagnostic techniques, namely collisional ionization spectroscopy and structural-specific ion–molecule reactions. The latter experiments were conducted at low pressures in a trapped cubic cell of a FTMS, and the former were conducted by using tandem mass spectrometry.

Collisional Ionization (Charge Stripping) Results. Collisional activation of high translational energy ions can lead to further ionization to doubly charged species (eq 1).[18] The spectra of

$$M^{+\cdot} + N \rightarrow M^{2+} + N + e \qquad (1)$$

doubly charged ions are thought to be better for discerning isomeric ions as they permit investigation of ions that have internal energies close to the ground state.[25] The ions in the collisional ionization spectra of $C_5H_8^{+\cdot}$ ions (Table II) are the doubly charged molecular ions and the fragments formed by sequential hydrogen atom losses. Careful examination of the spectra shows that each $C_5H_8^{+\cdot}$ ion gives a distinct spectrum. Holmes et al.[22] have also reported collisional ionization spectra of some of the $C_5H_8^{+\cdot}$ ions in order to establish the structure of fragment ions resulting from water elimination of cyclopentanol, pentanal, and pent-1-en-3-ol ions. There is good agreement between the spectra reported here and those reported by Holmes et al.

The dissimilarities in the collisional ionization spectra can be understood if a unique structure or a mixture of structures exists for each $C_5H_8^{+\cdot}$ ion under consideration. This interpretation is at odds with that drawn from the CAD spectra. Furthermore, the results do not provide any evidence for the electrocyclic reaction which is the main point of this study. Therefore, the collisional ionization spectra were investigated as a function of the internal energy of the ions.

Ionization by 70-eV electrons produces broad energy distributions (width of 2–8 eV)[26] of vibrationally and rotationally excited ions. The population of ions sampled for collisional activation will consist of a mixture of low-energy initially formed ions ($A^{+\cdot}$) and structurally equilibrating higher energy ions. If isomeric structure $B^{+\cdot}$ is accessible energetically, the fraction existing as $B^{+\cdot}$ depends on the internal energy distribution, the isomerization barrier, and the density of states of $A^{+\cdot}$ and $B^{+\cdot}$ with energy above the isomerization threshold. Thus, the CAD and collisional ionization spectra of this mixture may be considerably different than those of pure $A^{+\cdot}$ or $B^{+\cdot}$.

In view of these arguments, it is not clear whether the collisional ionization spectra of 1-$MCB^{+\cdot}$ and 3-$MCB^{+\cdot}$ (Table II) are characteristic of the un-isomerized cyclic structures or of a mixture of cyclic and ring-opened structures. The fraction that exists as ring opened will be internally excited because of the heats of formation (ΔH_f) of the acyclic ions are considerably lower than the corresponding cyclobutene radical cations (see Table IV). In order to clarify these uncertainties, 1-$MCB^{+\cdot}$ and 3-$MCB^{+\cdot}$ radical cations were produced by charge exchange with $CS_2^{+\cdot}$. The

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Table IV. Ionizing Energies[a] and Heats of Formation[b] of $C_5H_8^{+\cdot}$ Isomers

precursor	IE M^+	ΔH_f M[c]	ΔH_f M^+
isoprene	8.84[d]		222
1-methylcyclobutene	8.62[e]	29.33	228[f]
1,3-pentadiene	8.65[d]		216[g]
3-methylcyclobutene	9.08[e]	30.66	240[f]
1,4-pentadiene	9.62[d]	25.41	247
cyclopentene	9.02[d]		216[g]
methylenecyclobutane	9.35[d]	28.33	244
pent-1-yne	10.1[d]	34.72	268
pent-2-yne	9.25[d]	30.43	244

[a] Expressed in eV. [b] Expressed in kcal mol^{-1}. [c] $\Delta H_f(298)$ were calculated according to the group additivity rule by using the scheme of Benson and Buss.[28] [d] From ref 27. [e] Calculated from the estimated ΔH_f value of the radical cation and the ΔH_f value of the neutral molecule by using the formula $\Delta H_f(M^{+\cdot}) = \Delta H_f(M) + IE$. [f] See ref 29. [g] From ref 27b and 31.

initially formed ions now have a relatively narrow energy distribution centered at the difference in the recombination energy (RE) of the reagent ion and the ionizing energy (IE) of the C_5H_8 molecule under study. If the energy transferred is greater than the isomerization threshold, a substantial fraction of $A^{+\cdot}$ should rearrange to $B^{+\cdot}$. Moreover, if the pressure of the charge-exchange gas is high, $B^{+\cdot}$ will be stabilized by collisions with neutral gas molecules.

It is evident that the spectra of 1-$MCB^{+\cdot}$ and 3-$MCB^{+\cdot}$ acquired at low pressure of CS_2 (0.05 torr) have remained unchanged from those of the ions formed at 70 eV (see Table III), whereas the spectra of ions formed in the presence of high pressures (0.4 torr) of CS_2 have changed dramatically and have become identical with those of isoprene$^{+\cdot}$ and $C_5H_8^{+\cdot}$ ions, respectively.

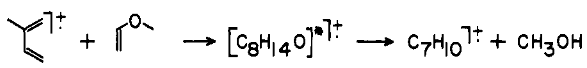
The low-pressure charge-exchange experiments produce evidence that the spectra are affected by internal energy which in turn affects the structure of the ions. The 1,3-pentadiene$^{+\cdot}$ ions formed by isomerization of 3-$MCB^{+\cdot}$ will possess 23 kcal mol^{-1} of excess energy (see Table IV) compared to the ions formed at a threshold energy by direct ionization of 1,3-pentadiene. These hot ions in admixture with a fraction of un-isomerized cyclic ions display different reaction channels upon collisional activation. If the spectra are a function of internal energy, then we expect 1,3-pentadiene radical cations generated by high-energy charge exchange at low pressures to exhibit different spectra compared to the thermally cool ions formed also by charge exchange but now at high ion source pressure. This is true as can be seen from the results in Table III, and the effect of internal energy on the structure and consequently on the collisional ionization spectra of $C_5H_8^{+\cdot}$ ions is now confirmed. Bowers and co-workers[32] have also noted a strong dependence of collisional ionization spectra on the internal energies of protonated ethylamine, dimethylamine, and ethanol.

Low-Energy Ion-Molcule Reactions. In this section, we present additional evidence for the electrocyclic ring opening of 1-MCB and 3-MCB radical cations which is based on the reactivity of the ions with diagnostic neutral reactants. The distinctive bimolecular reactions were conducted in a FTMS cubic trapped-ion cell under single collision conditions. Methyl vinyl ether (MVE) was chosen as the neutral reagent on the basis of its known reactivity with the 1,3-butadiene ion.[1,33] Due to exothermicity of the reaction, the collision complex could not be observed in the FTMS experiments. Thus, the structural identity of the $C_5H_8^{+\cdot}$ ions must be ascertained on the basis of specific decomposition reactions of the short-lived collision complex.

1-Methylcyclobutene and Isoprene Radical Cations. 1-$MCB^{+\cdot}$ reacts with its neutral precursor to produce an array of product ions. When the reaction is monitored at a pressure of 5×10^{-7} torr, and at variable time delays up to 700 ms, the major product ions were $C_9H_{13}^+$, $C_8H_{11}^+$, $C_7H_9^+$, and $C_5H_7^+$. In addition, product ions with compositions of $C_8H_{11}^{+\cdot}$, $C_7H_{11}^+$, $C_7H_{10}^{+\cdot}$, $C_6H_9^+$, $C_6H_7^+$, $C_6H_8^{+\cdot}$, and $C_5H_9^+$ of varying abundances were also noted.

Reaction of isoprene$^{+\cdot}$ radical cation with neutral isoprene leads to formation of identical reaction products, except that the relative abundances of the various fragments were different than those formed in the reaction of 1-$MCB^{+\cdot}$ and neutral 1-MCB. Unfortunately, these results cannot be used to assign the structures of the ions owing to the uncertainty of whether it is the ion or the neutral reactant which is responsible for the differences in the observed reactivities.

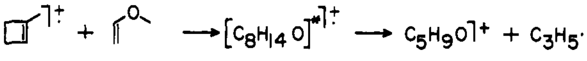
(a) Reaction with Methyl Vinyl Ether (MVE). The C_5H_8 ions (formed at 9-12 eV) were reacted in separate experiments with MVE at a partial pressure of 0.5×10^{-6} torr (total pressure was 1×10^{-6} torr). The major product of the reaction of isoprene radical cation with MVE was m/z 94 which presumably arises by expulsion of CH_3OH from the intermediate adduct (eq 2). In



(2)

addition, lower abundance products at m/z 111, 95, and 79 were also observed. An ion at m/z 93, probably due to the reaction of isoprene$^{+\cdot}$ with its neutral precursor, was also noted. The ratio of relative abundances of the ions m/z 94/93 was found to be 2.7 (Table V). The ion-ejection (double resonance) experiments revealed that both iso$^{+\cdot}$ and $MVE^{+\cdot}$ were reactants for all reaction pathways given.

The reaction of 1-$MCB^{+\cdot}$ and MVE yields new reaction products. The important product corresponds to loss of C_3H_5 (eq 3) from the adduct to give m/z 85. In addition, product ions



(3)

of compositions $C_7H_{11}O^+$, $C_7H_{11}^+$, $C_7H_{10}^{+\cdot}$, $C_7H_9^+$, $C_6H_7^+$, and $C_4H_7O^+$ were also observed. The process leading to the formation of m/z 94, $C_7H_{10}^{+\cdot}$, was of little importance. The ratio of the relative abundances of m/z 94/93 is 0.34 (Table V).

On the basis of comparative ion-molecule reactions with neutral MVE, it can be concluded that the chemical reactivity of the majority of 1-$MCB^{+\cdot}$ ions with lifetimes on the FTMS time frame (ca. 10^{-3}-1 s) is different than that of the isoprene$^{+\cdot}$ ion. We conclude that 1-$MCB^{+\cdot}$ maintains its cyclic structure under these experimental conditions.

(b) Gas-Pulsing Experiments. Although the existence of the un-isomerized 1-$MCB^{+\cdot}$ ions has been established in this work, we wish to provide more complete evidence for the electrocyclic ring opening. As discussed above, a significant population of ions may possess the initially formed structure, especially when low-energy electron ionization is employed. On the other hand, a large population of the ions formed by sufficiently energetic charge exchange may be the rearranged ions. If so, the ion-molecule reaction products should change to reflect the presence of the rearranged ions.

The investigation of ion-molecule reactions following charge-exchange ionization has been expedited by using a new experimental approach involving pulsed valve inlets for introduction of the charge-exchange reagent gas and the reactant neutral molecules into the FTMS cell. The application of pulsed valves was first demonstrated by Carlin and Freiser[34] and by Sack and Gross.[35] The present study is the first example of the use of two pulsed valves to perform consecutive ion-molecule reactions.

The choice of the pulsed valve strategy was based on the following considerations. First, the mass resolution obtained by using FTMS is an inverse function of the pressure in the cell.[36] Gas pulsing permits charge-exchange ionization, modest collisional stabilization (50-70 collisions), and subsequent ion-molecule

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Table V. Ratios of Relative Abundances of Ions *m/z* 94/93 and *m/z* 85/94

		reaction with neutral C_5H_8			reaction with neutral MVE		
ratio	precursor	*a*	*b*	*c*	*a*	*b*	*c*
m/z 94/93	1-methylcyclobutene	0.25	0.27	0.40	0.34	2.5	3.0
	isoprene	0.49	0.47	0.46	2.7	5.7	15.0
	3-methylcyclobutene	0.27	0.67		0.39	3.7	
	1,3-pentadiene	0.83	0.75		6.6	56.0	
m/z 85/94	1-methylcyclobutene				5.0	7.9	0.1
	3-methylcyclobutene				0.8	0.1	

[a] Results of static experiments (9.5-eV ionization). [b] Results of charge-exchange ionization by $C_6H_6^{+\cdot}$ in the gas-pulsing experiments. [c] Results of charge-exchange ionization by $CS_2^{+\cdot}$ in the gas-pulsing experiments.

reactions to be conducted at high pressure followed by mass analysis at low pressure. Second, increasing the internal energy by raising the electron energy caused considerable decomposition of $C_5H_8^{+\cdot}$ radical cations and increased the complexity of the situation due to reactions of the fragment ions with both the neutral C_5H_8 and the diagnostic neutral molecule. The situation was even more complicated when a mixture of C_5H_8, the diagnostic neutral molecule, and the charge-exchange gas was ionized by electron impact. The situation is simplified considerably by admitting first the charge-exchange gas and later the diagnostic neutral reactant and pulsing on the electron beam only when the charge-exchange gas is present. Thus, the neutral reagent is not ionized directly.

Third, the reactions of $C_5H_8^{+\cdot}$ radical cations and its corresponding neutral molecules can be minimized by keeping the pressure of C_5H_8 low. Furthermore, the predominant mode of ionization can be ensured to be charge exchange rather than direct ionization by pulsing the electron beam during the large-pressure pulse of the charge-exchange gas. This produces a large number of charge-exchange ions which in turn transfer their charge to C_5H_8 thereby giving a large number of $C_5H_8^{+\cdot}$ ions, more than could be produced by direct electron ionization.

The actual experiments were conducted in the following way. 1-MCB was admitted to the cell in the usual way at a low pressure of 4×10^{-8} torr. The charge-exchange gas (first benzene) was then pulsed into the cell to give an instantaneous maximum pressure of 3×10^{-6} torr (measured outside the cell; the pressure inside the cell is estimated to be two to three times the outside pressure) and ionized by a 10-eV pulse coincident with its peak pressure. After a suitable delay to allow complete charge exchange and pump out of excess charge-exchange gas, the diagnostic neutral reactant (MVE) was pulsed into the cell and allowed to react with 1-MCB$^{+\cdot}$. Any MVE ions formed by the unconsumed reagent ions and the $C_5H_8^{+\cdot}$ ions were removed from the cell by continuous ion ejection.

The results obtained by reacting 1-MCB$^{+\cdot}$ and isoprene$^{+\cdot}$ with MVE by using pulsed valves for addition of the reagents are reported as the ratios of relative abundances of the ions *m/z* 94/93 and *m/z* 85/94 (Table V). For comparison, the abundance ratios of the ions *m/z* 94/93 obtained in the static experiments and by using pulsed valve inlets in the absence of MVE (i.e., due to reaction of $C_5H_8^{+\cdot}$ and neutral C_5H_8) are also included. Enhanced abundance for *m/z* 94 was found when MVE is pulsed into the cell, and this can be interpreted in terms of electrocyclic ring opening of 1-MCB$^{+\cdot}$ to iso$^{+\cdot}$. However, an ion at *m/z* 85 was the major fragment ion when benzene$^{+\cdot}$ (RE = 9.3 eV)[37] was employed as the charge-exchange reagent, suggesting that only a small fraction of 1-MCB$^{+\cdot}$ has isomerized to isoprene$^{+\cdot}$. The product analysis of the reaction of 1-MCB$^{+\cdot}$ formed by pulsing CS_2 (RE CS_2 = 10 eV)[37] showed *m/z* 85 to be of very low abundance. Clearly, a considerable proportion of 1-MCB$^{+\cdot}$ formed by energetic charge exchange by $CS_2^{+\cdot}$ undergoes ring opening to isoprene radical cation.

3-Methylcyclobutene and *trans*-1,3-Pentadiene Radical Cations. We now wish to test for the corresponding electrocyclic reaction of 3-MCB$^{+\cdot}$. Bimolecular reactions of 3-MCB$^{+\cdot}$ and $C_5H_8^{+\cdot}$ with MVE were used to establish the structural identities. The reactions were conducted under the same conditions employed for the corresponding reactions of 1-MCB$^{+\cdot}$.

The reaction of 3-MCB$^{+\cdot}$ with neutral 3-MCB produces the same fragment ions that were observed for the reactions of 1-MCB$^{+\cdot}$ and neutral 1-MCB with the exception that now *m/z* 93, 81, 79, and 67 were the predominant products. The "dimer" formed by the reaction of 1,3-pentadiene radical cation and its neutral precursor fragmented to form mainly ions at *m/z* 121, 107, 94, and 93 with low yields of ions at *m/z* 108, 80, 69, and 67. The product ions of *m/z* 81 and 79 were not observed.

When MVE was admitted as the neutral reactant, 1,3-pentadiene radical cation reacted to form principally *m/z* 94 along with low yields of *m/z* 79, 95, and 111. On the other hand, the ion at *m/z* 93 was the predominant product for reaction of 3-MCB$^{+\cdot}$ and MVE. This product ion also results by the reaction of 3-MCB$^{+\cdot}$ and neutral 3-MCB and of $C_5H_7^+$, a major fragment ion when 3-MCB is ionized, and MVE (by loss of CH_3OH from the adduct). In addition, *m/z* 94, 85, 79, and 71 were also observed. The ion at *m/z* 85, a characteristic product from reaction of the cyclic radical cation, is not as abundant as for the corresponding reaction of 1-MCB$^{+\cdot}$. The reaction of MVE$^{+\cdot}$ with neutral 3-MCB, monitored while ejecting 3-MCB$^{+\cdot}$, showed mainly *m/z* 85 with low-abundance ions at *m/z* 93 and 94.

On the basis of these results, we postulate that a significant fraction of 3-MCB$^{+\cdot}$ isomerizes to $C_5H_8^{+\cdot}$. More proof of the electrocyclic ring opening was obtained by performing the ion–molecule reaction with MVE by using pulsed valve inlets for addition of the reagents. Ionization was by charge exchange with benzene. The enhanced abundance of ion at *m/z* 94 (Table V) is taken as confirmation that 3-MCB$^{+\cdot}$ undergoes electrocyclic ring opening to $C_5H_8^{+\cdot}$. The experiments in which $CS_2^{+\cdot}$ was used as the ionizing agent were not successful because CS_2 charge exchange caused unimolecular decomposition of 3-MCB$^{+\cdot}$.

High-Pressure Ion–Molecule Reaction Studies. The reactions of $C_5H_8^{+\cdot}$ ions with MVE under high pressures in a tandem mass spectrometer were investigated as the final test of the ring-opening hypothesis. In these experiments, the two reactants were mixed in a high-pressure CI source of the triple-analyzer instrument in the presence of nitric oxide which serves as inert bath gas and a source for NO$^{+\cdot}$ to charge exchange the C_5H_8 hydrocarbons. The stabilized adduct at *m/z* 126 was characterized by obtaining its CAD spectrum. Since the CAD spectra of the reactant $C_5H_8^{+\cdot}$ ions are not different, this approach may be more fruitful for discerning the structure of the $C_5H_8^{+\cdot}$ ions.

The CAD spectra of the adducts formed from the reactions of 1-MCB$^{+\cdot}$ and its ring-opened isomer, isoprene radical cation, with MVE are identical (Figure 1) and distinct from the spectra of the adducts formed by other $C_5H_8^{+\cdot}$ ions (Table VI). Likewise, the spectra of the adducts formed in the corresponding reactions of 3-MCB$^{+\cdot}$ and 1,3-$C_5H_8^{+\cdot}$ ions with neutral MVE are also nearly identical (Figure 2). Because the spectra were obtained after mixing the two reactants in 1:1 ratio, they may also have features of the adduct formed via a reaction of MVE$^{+\cdot}$ radical cation and neutral C_5H_8. However, the spectra did not change even when the partial pressure of the hydrocarbon was increased to 5 times that of MVE. These data may be interpreted in terms of identical structures of various reactant $C_5H_8^{+\cdot}$ radical cations, an interpretation consistent with the electrocyclic ring opening of 1-MCB$^{+\cdot}$

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Table VI. CAD Spectra of Stabilized Adducts

	m/z																				
precursor	111	110	97	95	94	93	81	79	77	68	67	65	55	53	51	45	43	41	39	29	27
isoprene	100	3	9	6	9	3	4	9	7	3	5	3	4	3	2	2	3	7	4	2	2
1-methylcyclobutene	100	2	8	7	10	3	5	9	6	3	5	2	5	4	1	2	2	7	4	2	2
1,3-pentadiene	43	4	100	7	7	4	8	9	6	6	8	4	6	7	2	4	2	10	7	2	3
3-methylcyclobutene	61	6	100	9	18	8	9	10	8	10	12	5	8	10	2	6	5	12	10	3	4
1,4-pentadiene	55	6	100	9	31	10	10	11	9	11	13	5	8	8	4	5	4	12	10	3	4
cyclopentene	30	4	45	10	100	19	11	12	8	18	19	3	6	4	3	9	3	8	5	2	3
methylenecyclobutane	100	6	19	11	17	7	10	15	10	5	14	6	10	9	4	5	6	13	11	4	4
pent-1-yne	88	3	100	11	8	8	7	10	10	6	20	6	8	10	3	5	4	15	8	4	4
pent-2-yne	100	3	9	12	6	6	8	13	10	7	13	4	11	9	3	3	6	13	9	3	3

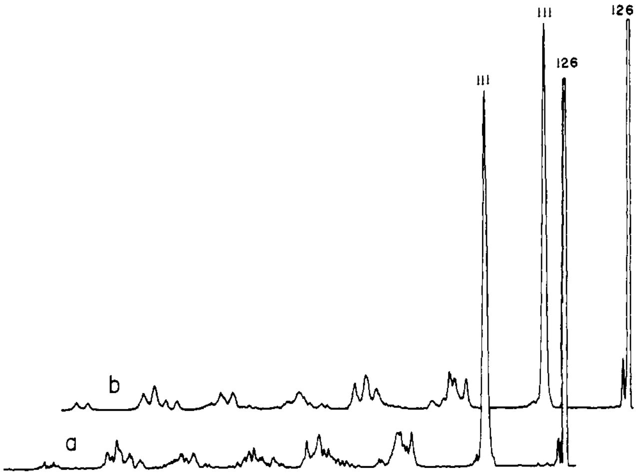

Figure 1. CAD spectrum of (a) iso$^{+\cdot}$ + MVE adduct and (b) 1-MCB$^{+\cdot}$ + MVE adduct.

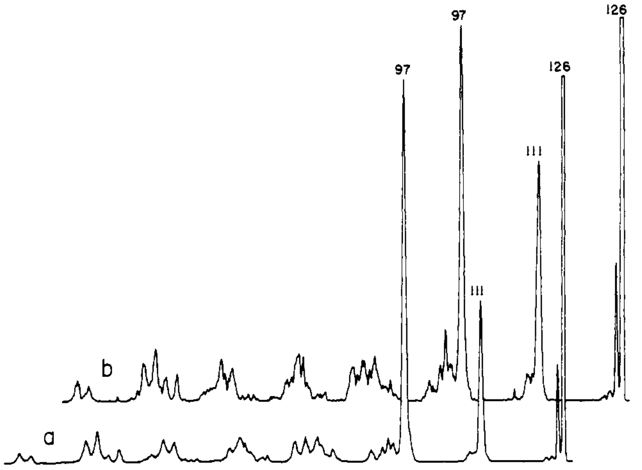

Figure 2. CAD spectrum of 1,3-$C_5H_8^{+\cdot}$ + MVE adduct and (b) 3-MCB$^{+\cdot}$ + MVE adduct.

and 3-MCB$^{+\cdot}$ to isoprene and 1,3-pentadiene radical cations, respectively. The presence of a small amount of cyclobutene radical cations cannot be ruled out under the conditions of this experiment because we cannot be sure that the adduct leading to $C_5H_9O^+$ (*m/z* 85) can be stabilized and studied.

The decomposition products observed in the present experiment contrast with those seen in the low-pressure FTMS studies. The short-lived adduct formed by the reaction of isoprene$^{+\cdot}$ and MVE at low pressures (FTMS conditions) underwent loss of CH_3OH, whereas the adduct intercepted at high pressures decomposed principally by loss of a methyl group. Similar observations pertain for the adduct of the reaction of 1,3-pentadiene and MVE; the losses of CH_3 and C_2H_5 were the only major reactions induced by collisional activation of the stabilized adduct. On the basis of these differences, it is suggested that the structures of the adducts formed at low pressures and at high pressures are different. A tentative proposal, consistent with the study of 1,3-butadiene and MVE,[38] is that the collisionally stabilized adducts are acyclic, but, in the absence of stabilizing collisions, the adduct adopts a cyclic structure.

Activation Energy Estimates. Benzene charge exchange of 1-MCB in the FTMS cell caused only a small fraction of 1-MCB$^{+\cdot}$ to isomerize to the acyclic isomer, which suggests that the energy transferred by benzene radical cation is close to the onset of ring opening of 1-MCB$^{+\cdot}$. On the other hand, only a small proportion of 1-MCB$^{+\cdot}$ retained the cyclic structure when $CS_2^{+\cdot}$ was employed as the charge-exchange reagent. The excess energies transferred to 1-MCB$^{+\cdot}$ by $C_6H_6^{+\cdot}$ and $CS_2^{+\cdot}$ are approximately 0.68 and 1.4 eV, respectively. Thus, the activation barrier for electrocyclic ring opening of 1-MCB$^{+\cdot}$ should be less than 14 kcal mol^{-1} (0.6 eV).

Similar experiments performed for 3-MCB have shown that even the energy deposited by benzene radical cation charge exchange (0.22 eV) is large enough to cause the ring opening of 3-MCB$^{+\cdot}$. We assign an upper limit of 4 kcal mol^{-1} as the energy barrier for the electrocyclic ring opening of 3-MCB$^{+\cdot}$.

These estimates of activation energies are similar to those for 1-phenyl- and 3-phenylcyclobutene radical cations.[2] The ring opening of 3-phenylcyclobutene radical cation was shown to be complete at energies close to the threshold for ionization, whereas the barrier for the reaction of 1-phenylcyclobutene ion is ca. 14 kcal mol^{-1}. Thus, substitution of methyl or phenyl at the double bond of cyclobutene radical cation stabilizes it, whereas substitution at the allylic position causes it to ring open with greater ease.

The energy advantage gained upon ionization is evident if we compare the activation energies with the corresponding values for neutral 1-MCB (35.10 kcal mol^{-1})[5b] and 3-MCB (31.55 kcal mol^{-1}).[5b]

Experimental Section

The CAD spectra were acquired by using a triple-analyzer Kratos MS-50 TA mass spectrometer of EBE geometry.[39] The C_5H_8 hydrocarbons were ionized at 70 eV (500 μA of emission) and low-energy electron ionization, selected at a mass resolution of 16 000 (10% valley definition) by using MS I (comprised of electrostatic and magnetic analyzers), and collisionally activated in the third field-free region by using He as the neutral target. The high-mass resolution ensures that contribution to the main beam by the ^{13}C of $[M - 1]^+$ ions, which are of significant abundance in the 70-eV mass spectra of C_5H_8 hydrocarbons,[31] is minimized. The He pressure was adjusted to attenuate the main beam intensity by 50%. The CAD spectra were acquired as described previously.[2] The ion source was operated at <70 °C to avoid thermal isomerization of methylcyclobutenes. Samples were introduced through a glass inlet maintained at ambient temperature for the same reason. The ions were extracted from the source at 8 kV.

The collisional-ionization spectra were obtained in a similar way except the second electrostatic analyzer voltage was scanned over a narrow range covering *m/z* 30–35.

The charge-exchange and the high-pressure ion–molecule reactions were conducted in a Kratos CI source. The charge-exchange gases were admitted through an all-metal reagent gas inlet and ionized at 280 eV. MVE was admitted through a custom-built gas probe and the hydrocarbons as described above. Relative partial pressures of NO, MVE, and C_5H_8 hydrocarbons (10:1:1) were adjusted to give 0.1–0.3 torr of pressure

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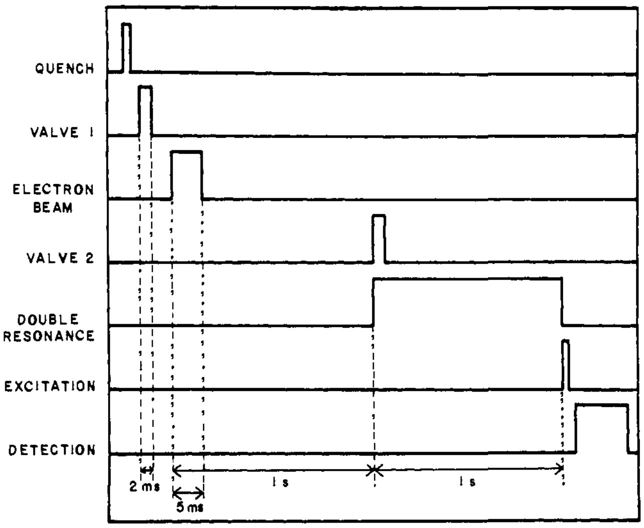

Figure 3. Sequence of events in the FTMS gas-pulsing experiments.

in the ion source. The source pressure was measured by using an ion gauge which was calibrated by a Hasting gauge mounted on a regular probe. When CS_2 was used as a charge-exchange gas, its pressure was varied in the range 0.05–0.4 torr.

The apparatus used for low-pressure ion–molecule reaction studies was a home-built FTMS[40] controlled by a Nicolet FTMS-1000 data system. The cell was located in a magnetic field of 1.2 T. The trapping voltage was to 1 V. The ions were formed by an electron beam biased at 9–15 eV and pulsed for 5 ms. The ions were excited by a 800-kHz excitation bandwidth "chirp" and measured by acquiring the mass spectrum over the mass range 20–150 amu at variable time delays ranging from 1 to 700 ms. Double-resonance pulses were set for continuous ejection of the ions of interest throughout the reaction period. The reactants (1:1) at a total pressure of 1×10^{-6} torr were introduced into the cell through metal inlets maintained at ambient temperature.

The consecutive reactions in the FTMS were performed by using a pulsed reagent inlet technique. The pulsed valve inlet setup has been described in detail previously[35] and will not be discussed here. The C_5H_8 hydrocarbons were admitted into the cell to a static pressure of 4×10^{-8} torr as described above. The experimental sequence is shown in Figure 3. Benzene, used as a charge-exchange reagent, was admitted via a pulse of 2-ms duration. The second valve pulse was delayed 1 s from the first pulse in order to allow thorough removal of the excess neutral reagent. Detection was then delayed 1 s in order to permit adequate time for reaction of the stored ions and the neutral reagent. The reagents were introduced to the valves from stainless steel reservoirs at 0.5–1 torr, producing pressure pulses with a maximum amplitude of 3×10^{-6} torr in the vacuum chamber containing the cell.

1-Methylcyclobutene was synthesized by isomerization of methylenecyclobutane by using the procedure of Shabtai and Gil-Av.[41] The reaction was conducted over freshly prepared Na/alumina catalyst at 2–3 °C. Methylenecyclobutane was freshly distilled over sodium metal under vacuum. The product was purified by preparative GC by using a 4 m × 6 mm stainless steel column packed with 20% TCEP coated on 60/80 Chromosorb (Supelco). The column was operated at ambient temperature with the injector and detector at 60 °C. When He was used as a carried gas at a flow rate of 22 mL min^{-1}, the 1-MCB emerged from the column at 11.0 min and the unreacted methylenecyclobutane at 14.4 min.

3-Methylcyclobutene was prepared by a photochemical-induced isomerization of *trans*-1,3-pentadiene (99%) according to the procedure of Frey[5a] except cyclohexane was used as a solvent in place of *n*-hexane and isopentane was not added to the reaction mixture. *n*-Hexane interfered with the purification of 3-MCB when the above-mentioned GC method was used.

All other chemicals were purchased from commercial sources (Wiley Organics) as >99% purity grade and used without further purification.

Acknowledgment. This 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. 1-Methylcyclobutene radical cation, 91631-62-8; 3-methylcyclobutene radical cation, 91738-63-5; isoprene radical cation, 50535-53-0; (*E*)-1,3-pentadiene radical cation, 84847-89-2; 1,4-pentadiene radical cation, 91631-63-9; cyclopentene radical cation, 34512-37-3; methylenecyclobutane radical cation, 91631-64-0; 1-pentyne radical cation, 77742-02-0; 2-pentyne radical cation, 91631-65-1.

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Molecular Dynamics Study of Solvation in Urea–Water Solution

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Abstract: In order to study the effect of urea on water structure, a molecular dynamics simulation of a dilute aqueous urea solution has been carried out. A rigid body model is used to represent urea, and the intermolecular potentials are given by Lennard-Jones and electrostatic terms. Only very small differences are observed between the properties of water molecules in the solvation region of urea and the bulk, and these differences can be assigned to direct urea–water interactions, with no substantial perturbation of water–water interactions. Implications for the mechanism of solubilization of hydrocarbons by urea are discussed.

I. Introduction

Aqueous urea solutions have interesting and anomalous properties. Urea forms nearly ideal mixtures with water.[1] Yet, is a strong protein denaturant,[2] increases the solubility of hydrocarbons,[3] and inhibits micellar aggregation.[4] Due in large part to this protein denaturing ability, aqueous urea solutions have been studied extensively. In spite of this, the mechanism by which urea acts remains unresolved.

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