

sumption. However, after longer irradiation times, photouptake of O_2 always prevails, and this is attributed to the catalysts of reaction 3 by Pt deposits on the CdS particles formed during the photoreaction. At the same time, the Pt deposits also catalyze the formation of H_2 from water and conduction band electrons. This explains the appearance of H_2 in the gas chromatograms in Figure 1 after longer irradiation times.

Conclusions

Oxygen is generated when suspensions of CdS loaded with noble metal oxides are illuminated by visible light in the presence of an acceptor for conduction band electrons. An important result of the present investigation concerns the high catalytic activity of Rh_2O_3 in promoting water oxidation by valence band holes: Under alkaline condition the initial quantum yield for O_2 formation observed with CdS/ Rh_2O_3 exceeds that of CdS/ RuO_2 by a factor of 15.

A characteristic feature of CdS suspensions is rapid photoconsumption of oxygen involving reduction of O_2 by conduction band electrons,¹⁵ and this was shown to interfere with O_2 detection. As was suggested by Harbour et al.,¹⁷ a similar reaction is expected to take place also in water cleavage systems when the photolysis is performed in a closed vessel over long periods of time without

intermittent removal of gaseous products. Under such conditions the formation of a gaseous mixture of H_2 and O_2 in a 2:1 M proportion is unlikely to occur and one would expect to detect, apart from hydrogen, the products arising from the photouptake of O_2 by the CdS particles. A detailed analysis of these products will be given in a subsequent paper.²⁰ The present study was undertaken to identify unambiguously the valence band processes in illuminated CdS suspensions loaded with highly active water oxidation catalysts and to compare their efficiency in promoting oxygen generation.

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Registry No. CdS, 1306-23-6; RuO_2 , 12036-10-1; Rh_2O_3 , 12036-35-0; $PtCl_6^{2-}$, 16871-54-8; O_2 , 7782-44-7; H_2O , 7732-18-5; $H_2^{18}O$, 14314-42-2.

Cation Radical Diels–Alder Reaction of 1,3-Butadiene: A Two-Step Cycloaddition

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Abstract: The structure of the ion–molecule adduct produced in the reaction of 1,3-butadiene cation radical with neutral 1,3-butadiene has been investigated by collisionally stabilizing the adduct and then acquiring its collision-activated decomposition (CAD) spectrum by using a tandem mass spectrometer. The CAD spectrum of the adduct changed dramatically depending on the rate of the stabilization. This observation has been interpreted in terms of two distinct structures for the adduct. One which results at a total pressure of 13 mtorr has been identified as 4-vinylcyclohexene cation radical. This identification is based on the similarity of the CAD spectrum of 4-vinylcyclohexene and of the adduct. The second structure, stabilized at higher pressures (≤ 130 mtorr), is a branched, acyclic C_8H_{12} cation radical. The rate constant for the reaction has also been determined. The results of these experiments have been interpreted in terms of a stepwise mechanism for the formation of the 4-vinylcyclohexene cation radical instead of a concerted [4 + 1] cycloaddition mechanism.

1,3-Butadiene is an important molecule from a mechanistic viewpoint because it is the simplest diene component possible in a Diels–Alder cycloaddition. In fact, the reaction of neutral butadiene has served as a model for investigation of the cycloaddition.^{1–4} Two mechanistic alternatives for the thermal reaction are a one-step, concerted process and a two-step, nonconcerted one, in which acyclic octa-1,7-dien-3,6-diyl diradicals have been proposed as intermediates. Several studies have focused on

comparing the heat of formation of such diradicals with the heat of formation of the transition state of the Diels–Alder dimerization.¹ The mechanism of the reaction has also been probed by using deuterium labeling² and stereochemical³ and computational³ methods and by measuring the activation volume of the reaction.⁴

A diradical intermediate in the thermal Diels–Alder reaction cannot be unequivocally excluded. It is known that similar diradicals serve as intermediates in the formation of 1,2-divinylcyclobutanes, which are products of the photochemical dimerization of butadiene.⁵ The existence of an analogous acyclic radical cation species as an intermediate in the cation radical cyclization reaction is a reasonable possibility. The diradical intermediates characteristic of butadiene plus butadiene neutral chemistry are transitory and difficult to observe. In contrast, it may be possible to observe a cation radical intermediate in a gas-phase, ionic reaction by collisionally stabilizing it in a conventional high-pressure mass spectrometer source, provided the lifetime of the intermediate is on the order of 1–10 μs .

Several examples of solution-phase cycloaddition reactions involving a cation radical partner have been reported recently by

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Bauld and co-workers.⁶ These authors have also analyzed the radical cation Diels-Alder reaction by using computational methods^{7a} and have interpreted the results in terms of a [4 + 1] (and not a [3 + 2])⁸ nonsynchronous concerted cycloaddition mechanism. In addition, some gas-phase cation radical cycloadditions have recently been investigated, and these have involved the cation radicals of *o*-quinodimethane,⁹ fulvene,¹⁰ styrene,¹¹ and 1,3-butadiene and ethyl and methyl vinyl ethers.¹²

Several papers have been published on gas-phase reactions of the 1,3-butadiene cation radical and its corresponding neutral.¹³ Barker, Hamill, and Williams,^{13a} working at lower pressures than were used in the present work (<1 mtorr), observed that the abundances of the decomposition products of the intermediate $C_8H_{12}^{+\cdot}$ were similar to those of the 4-vinylcyclohexene cation radical. They were not able to observe a stable C_8H_{12} intermediate, but their results were qualitatively the same as those of Koyano, Omura, and Tanaka (who were also unable to observe a stable, butadiene cation radical dimer).^{13b} Gross et al.¹⁴ and Henis¹⁵ used ion cyclotron resonances (ICR) spectrometry to investigate the ion chemistry of 1,3-butadiene at a lower pressure regime (approximately 10^{-5} torr) and found that the distribution of products was qualitatively similar to those observed earlier.¹³

One purpose of the present work is to investigate directly the products of the reactions of the 1,3-butadiene cation radical with neutral butadiene; specifically, we wish to determine if the 1,3-butadiene cation radical participates in cycloadditions which are analogous to those observed for neutral molecules. In this investigation, a variety of mass spectrometric techniques were employed. The most structurally informative experiments involved the formation and collisional stabilization of the [1,3-butadiene cation radical + neutral butadiene) adduct in the source of a mass spectrometer. The adduct was then mass selected by using the first stage of a tandem mass spectrometer, collisionally activated, and a spectrum of its decomposition products taken by scanning the second stage.¹⁶ This spectrum is commonly referred to as a collision-activated decomposition (CAD) spectrum and is known to be structurally specific.¹⁷ The CAD spectrum of the adduct was then compared to CAD spectra of molecular ions of isomeric reference compounds,¹⁶ which were chosen on the basis of analogies with neutral chemistry. The structures of the adduct ion are assigned on the basis of these comparisons.¹⁷

The butadiene radical cation chemistry was also investigated by examining (1) the distributions of the product ions formed in a chemical ionization source at pressures between 10 and 500 mtorr and (2) the distributions of the product ions formed in a Fourier transform mass spectrometer¹⁸ (FTMS) at a pressure of

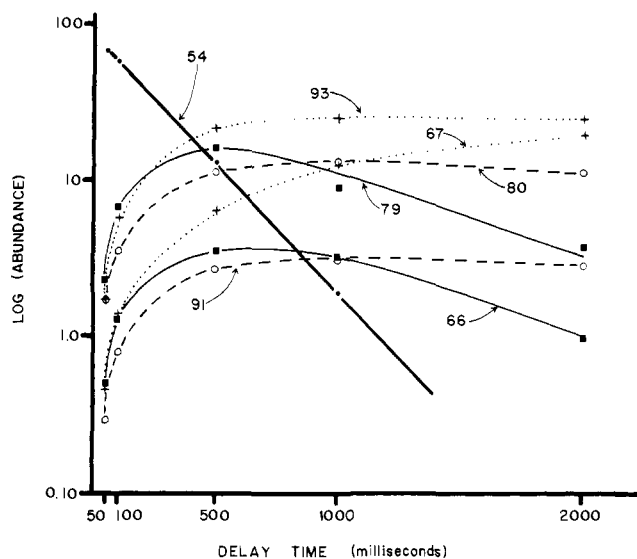


Figure 1. Log (abundance) of product ions formed in the 1,3-butadiene ion-molecule reaction vs. time at a pressure of 5×10^{-7} torr.

Table I. Distributions of Product Ions Formed in the 1,3-Butadiene Ion-Molecule Reaction Conducted in a High-Pressure Source

<i>m/z</i>	mtorr of butadiene					
	8	13	26	65	130	390
93	33	57	53	72	82	77
91	23	36	34	30	35	436
80	60	57	63	73	87	44
79	100	100	100	100	100	100
78	24	25	16	7.2	4.7	77
67	32	43	47	61	85	159
66	44	36	31	32	30	21

5×10^{-7} torr by varying the reaction time from 50 to 3000 ms. Pulsed ion cyclotron resonance mass spectrometry was used to determine the reaction rate constant, and the thermochemistry of the 1,3-butadiene ion-molecule reaction was examined by measuring ionization and appearance energies.

Results and Discussion

Time and Pressure Dependence of Products. As a prelude to the CAD studies of stabilized butadiene ion-molecule adducts, the time dependence of the product ion distributions was investigated by using Fourier transform mass spectrometry¹⁸ (FTMS). FTMS was used because time-resolved measurements cannot be conducted by using the tandem mass spectrometer in our laboratory. At a pressure of 5×10^{-7} torr and after 1000 ms, the 1,3-butadiene radical cation (*m/z* 54) has decreased exponentially to less than 2% of its initial abundance (see Figure 1). The 1,3-butadiene cation radical reacts with neutral 1,3-butadiene to yield on activated ion-molecule adduct which rapidly decomposes in the absence of collisional stabilization. The important decomposition products of the adduct are *m/z* 93, 91, 80, 79, 67, and 66 which correspond to the losses of $\cdot CH_3$, $\cdot CH_3 + H_2$, C_2H_4 , $\cdot C_2H_5$, $\cdot C_3H_5$, and C_3H_6 , respectively. As time was increased, *m/z* 93, 80, and 67 became more abundant relative to the other decomposition products. It is possible that this result is signaling the formation of a second 1,3-butadiene adduct, but a more reasonable explanation is that some of the product ions are reacting further while others are relatively inert.

The pressure dependence of the 1,3-butadiene product ions was examined by using the tandem mass spectrometer equipped with a high-pressure, chemical ionization source. The distribution of product ions was qualitatively the same as that observed via FTMS

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Table II. Partial CAD Spectra of Adducts Stabilized at Different Pressures^a

<i>m/z</i>	mtorr of butadiene						mtorr of CS ₂	
	13	26	65	130	260	650	390	650
93	13.0	15.0	26.0	38.0	36.0	27.0	38.0	32.0
91	5.9	5.6	6.5	11.0	15.0	18.0	14.0	18.0
80	9.6	9.9	6.9	3.0	1.8	1.0	1.6	1.3
79	20.0	19.0	16.0	8.8	7.8	8.5	7.8	8.1
67	2.3	2.5	1.9	1.2	1.1	1.5	1.5	1.3
66	19.0	17.0	13.0	3.6	1.9	1.6	2.6	2.0
54	1.3	2.0	1.8	0.3	0.3	0.5	0.5	0.5

^aAbundances are expressed relative to the total fragment ion current. Ions of low abundance are not reported.

except an adduct C₈H₁₂⁺ was observed. The abundances of the adduct and its fragmentation products corresponding to the losses of ·CH₃ (to yield *m/z* 93), C₂H₄ (*m/z* 80), ·C₂H₅ (*m/z* 79), and C₃H₆ (*m/z* 66) were observed to increase with pressure up to approximately 130 mtorr (see Figure 2). Decreases in the abundances of the product ions were observed as the pressure was increased beyond 130 mtorr. The decreases occur in part because these products can undergo further reaction (vide supra) and also because of the increasing stabilization of the C₈H₁₂⁺ adduct at higher pressures (i.e., the rate of collisional stabilization has become more competitive with the rate of fragmentation). These data agree with the results reported in earlier, more limited studies of 1,3-butadiene.¹³⁻¹⁵

The FTMS spectra recorded at shorter times and the high-pressure 1,3-butadiene mass spectra are similar to the mass spectrum of 4-vinylcyclohexene (see Table I), which is in accord with the earlier findings of Barker, Hamill, and Williams.^{13a} However, the agreement between the 1,3-butadiene spectra and that of the reference compound is not complete: the abundances of *m/z* 93, 91, and 67 are notably greater in the FTMS and in the high-pressure mass spectrum than in the 4-vinylcyclohexane spectrum. Although these differences could arise from variations in the internal energy of the adduct, a more likely possibility is the presence of a small amount of a second adduct structure whose characteristic decompositions give rise to *m/z* 93, 91, and 67 (vide infra). The FTMS and the high-pressure 1,3-butadiene data cannot be used to distinguish unequivocally between these possibilities.

CAD Spectra of Stabilized Intermediates. The C₈H₁₂⁺ adduct was sufficiently abundant at pressure ≥10 mtorr for study by the CAD technique. The use of collisional activation is preferred in lieu of monitoring unimolecular decompositions in the source or flight tube (metastable decompositions) because CAD spectra are known to be nearly independent of the internal energy¹⁷ of the ions under study. Furthermore, metastable (noncollision activated) spectra of the adducts formed at the lower pressures were too weak to be useful.

The CAD spectrum of the butadiene ion-molecule intermediate changes as a function of the total pressure of the gas in which the intermediate was formed (see Table II). The major decompositions of the adduct formed at 13 mtorr correspond to the elimination of ·C₂H₅ (to give *m/z* 79) and C₃H₆ (*m/z* 66), which together account for 39% of the total fragment ion current (TIC). The adduct formed at pressures from 130 to 390 mtorr undergoes extensive ·CH₃ loss to give *m/z* 93, which alone accounts for approximately 38% of the TIC, and the importance of the ethyl and propene losses is dramatically decreased.

We could not be sure that the C₈H₁₂ ion is a simple biomolecular adduct of butadiene cation radical and neutral 1,3-butadiene when the pressure of butadiene was high. Therefore, the higher order reactions were minimized without significantly changing the extent of collisional stabilization by using CS₂ as a bath gas. CS₂ is a useful reagent for this purpose because CS₂⁺ ionizes the butadiene by low-energy charge exchange (CS₂ IP ≈ 10 eV),²⁰

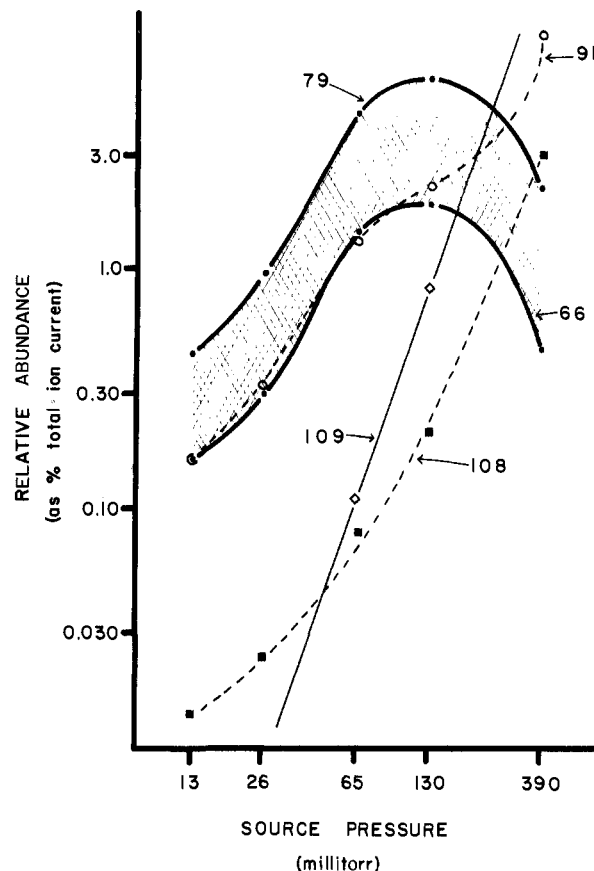


Figure 2. Relative abundances of ions formed in a high-pressure ion source as a function of source pressure. Ions of *m/z* 93, 80, and 67 have profiles similar to that of *m/z* 79 and fall in the shaded region. Not pictured are the 1,3-butadiene molecular ion and its fragments which account for most of the ion current.

and it provides a nonreactive background for collisional stabilization. The efficacy of this strategy to reduce higher order reactions is demonstrated by the behavior of the *m/z* 109 ion, which at a pressure of 260 mtorr and in the absence of CS₂ is more than 4 times as abundant as the butadiene adduct (*m/z* 108). At the same pressure in a 10:1 mixture of CS₂ and 1,3-butadiene, the *m/z* 109 ion is approximately 4 times less abundant than the *m/z* 108 ion. The spectrum of the adduct formed under these high-pressure conditions is nearly identical with those of adducts formed in excess 1,3-butadiene alone.

The observation of distinct CAD spectra at high and low pressure is accounted for in terms of at least two, clearly distinguishable structural adducts which result from the reaction of the 1,3-butadiene cation radical with neutral 1,3-butadiene. This observation is similar to that of Frey on the effect of pressure on the reactions of gas-phase methyl with 1,3-butadiene.¹⁹

CAD Spectra of Reference Compounds. The CAD spectra of 14 reference compounds were acquired in an attempt to find to a match for the CAD spectra of the intermediates. The compounds (Table III) were ionized by electrons (70 eV) at low pressure and by CS₂⁺, high-pressure charge exchange (CE). Both

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Table III. Relative Abundances of CAD Ions of C₈H₁₂ Reference Compounds^a

<i>m/z</i>	1		2		3		4		5		6		7	
	EI	CS ₂	EI	CS ₂	EI	CS ₂	EI	CS ₂	EI	CS ₂	EI	CS ₂	EI	CS ₂
93	25.0	25.0	43.0	36.0	47.0	31.0	41.0	35.0	9.2	19.0	20.0	19.0	43.0	26.0
91	8.8	11.0	5.8	7.8	12.0	17.0	8.5	11.0	5.9	13.0	4.8	9.4	12.0	14.0
80	4.5	4.6	2.1	2.1	3.4	3.6	2.0	n.a.	26.0	5.7	8.9	8.0	1.3	1.9
79	26.0	22.0	15.0	14.0	7.2	9.2	19.0	20.0	17.0	16.0	19.0	21.0	12.0	17.0
67	1.4	1.8	1.0	1.1	0.7	0.9	0.8	0.9	7.7	3.0	3.6	3.8	0.8	1.3
66	4.7	3.7	1.9	2.2	1.6	1.9	0.5	1.0	6.6	3.2	11.0	7.9	0.8	1.0
54	0.5	0.8	0.3	0.4	0.3	0.6	0.2	0.5	1.3	3.2	8.8	2.0	0.4	0.6

<i>m/z</i>	8		9		10		11		12		13		14	
	EI	CS ₂	EI	CS ₂	EI	CS ₂	EI	CS ₂	EI	CS ₂	EI	CS ₂	EI	CS ₂
93	14.0	19.0	10.0	12.0	34.0	33.0	34.0	28.0	6.3	5.7	17.0	18.0	40.0	32.0
91	5.5	7.7	9.5	12.0	11.0	13.0	15.0	13.0	6.0	7.7	7.2	11.0	7.5	8.5
80	12.0	7.7	1.2	2.2	5.1	4.7	3.8	3.1	31.0	19.0	14.0	9.9	9.8	11.0
79	23.0	22.0	41.0	36.0	17.0	14.0	12.0	15.0	15.0	17.0	21.0	20.0	12.0	16.0
67	1.8	2.1	0.7	1.0	2.2	2.1	1.2	1.8	11.0	13.0	6.4	5.0	1.8	3.1
66	18.0	14.0	1.8	2.1	1.9	1.3	1.0	1.2	5.3	6.4	3.0	2.5	1.5	2.4
54	1.0	1.0	0.3	0.4	0.8	1.0	0.4	0.6	0.7	0.6	1.0	0.9	0.3	0.5

^aElectron impact (EI) ionization at pressure = 2×10^{-6} torr. CS₂ ionization at pressure = 650 mtorr.

ionizing techniques were employed because the CAD spectra of some of the reference compounds vary depending on the amount of internal energy deposited in the compounds as a consequence of ionization. The adducts also show this dependence because they were formed under ionizing conditions which result in the deposition of widely varying amounts of internal energy. The amount of internal energy primarily affects the unimolecular (metastable) contributions to the CAD spectra. For example, the metastable contribution to the loss of $\cdot\text{CH}_3$ from 5-methyl-1,3,6-heptatriene varies from 30% to 10% depending on the ionization conditions. In general, charge exchange accompanied by collisional stabilization deposits a smaller, more uniform amount of energy into the ions and adducts, whereas electron ionization produces ions possessing a wide spectrum of internal energies.

The CAD spectra of most of the reference compounds in Table III vary only slightly depending on the mode of ionization. The changes can be understood in terms of internal energy differences discussed above. An exception is *cis*-1,2-divinylcyclobutane (5), for which the principal fragmentation involving loss of C₂H₄ to give *m/z* 80 when ionized by electrons changes to the loss of a methyl radical (to give *m/z* 93) when ionized by CS₂ charge exchange. The similarity of the CAD spectra of electron-ionized *cis*-1,2-divinylcyclobutane and 1,5-cyclooctadiene (12) may point to a Cope-type rearrangement, but more experiments are necessary to verify this hypothesis.

The dramatic changes that occur in the CAD spectra of the 1,3-butadiene ion-molecule intermediate must be a result of structural changes. The structure of the butadiene ion-molecule adduct formed and stabilized at the lowest pressures may be assigned by comparing its CAD spectrum obtained at 13 mtorr with the spectra in Table III. The CAD spectrum of that adduct matches best with that of 4-vinylcyclohexene ionized by EI. The abundant loss of C₃H₆ (*m/z* 66) consistently accounts for $16 \pm 3\%$ of the total ion current (TIC) in the CAD spectra of 4-vinylcyclohexene, regardless of the method of ionization. The loss of C₃H₆ similarly accounts for $18 \pm 1\%$ of the TIC in the spectra of the adduct generated at the lower pressures studied. The only other reference compound for which collision-activated C₃H₆ elimination is an important process is *trans*-1,2-divinylcyclobutane (11–7.9%, compound 6), but 6 does not have the same structure as the 1,3-butadiene ion-molecule reaction adduct because the CAD spectra do not match. The qualitative similarity observed between the CAD spectrum of *trans*-1,2-divinylcyclobutane (6) and that of 4-vinylcyclohexene (8) may indicate that the cation radicals are partially interconverting or isomerizing to a common structure. This possibility has been suggested previously.²¹

The CAD spectrum of the 1,3-butadiene ion-molecule adduct that is formed at the highest pressures matches best with the spectrum of 5-methyl-1,3,6-heptatriene ionized by charge exchange with CS₂⁺ (3). The reference spectra of ions produced by CS₂ CE are better for comparison with the spectra of the adduct stabilized at higher pressure because the conditions for ionization are similar, and all ions are subjected to collisional stabilization in the source. The adduct formed at 650 mtorr decomposes to give an abundant ion (18%) corresponding to the loss of $\cdot\text{CH}_3 + \text{H}_2$ (*m/z* 91), an abundant $\cdot\text{CH}_3$ loss, and only a few ions (<10%) corresponding to loss of $\cdot\text{C}_2\text{H}_5$ (*m/z* 79). None of the reference compounds except 5-methyl-1,3,6-heptatriene exhibit these features.

The CAD spectrum of the 1,3-butadiene ion-molecule adduct is observed to change slightly even when stabilized at the higher pressures. For example, the propensity for loss of a methyl radical achieves a maximum at pressures between 130 and 390 mtorr and then decreases. Presumably this is because extensive collisional stabilization reduces the internal energy and hence the metastable ion contribution to the total $\cdot\text{CH}_3$ elimination. The same effect can be observed by comparing the spectra of 5-methyl-1,3,6-heptatriene ionized by electrons or by CS₂ charge exchange (vide supra).

Rate Constant and Thermochemistry. Additional experiments were performed in order to determine the efficiency of the 1,3-butadiene cation radical reaction and to examine its thermochemistry. Pulsed ion cyclotron resonance (ICR) spectrometry was used to determine the reaction rate constant which was calculated from the disappearance curve of the C₄H₆ molecular ion at a pressure of 1.1×10^{-6} torr. The experimental rate constant is $0.74 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This value may be compared with the Langevin collision constant which was calculated to be $1.3 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ according to the method of Gioumoussis and Stevenson.²² In addition, a plot of $\log(I/I_0)_{54}$ vs. time was linear for more than 95% of the reaction. This observation is consistent with an interpretation that the reacting species has a single structure, although two or more structures would not be detected if their reactions with neutral 1,3-butadiene have the same rate constant.

The pressure-dependent structural preferences of the 1,3-butadiene ion-molecule adduct indicated by the CAD spectra might

(21) For a discussion of the 4-vinylcyclohexene cation radical fragmentation pathways, see: Brittain, E. F. H.; Wells, C. H. J.; Paisley, H. M. *J. Chem. Soc. B* 1969, 503.

(22) Gioumoussis, G.; Stevenson, D. P. *J. Phys. Chem.* 1958, 29, 294.

Table IV. Thermochemistry²³ of Reference Compounds Representing the Two Intermediates Formed in the 1,3-Butadiene Ion-Molecule Reaction

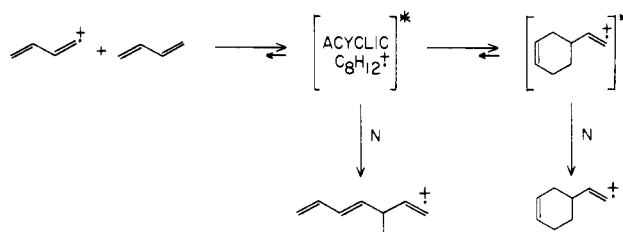
4-Vinylcyclohexene	
$\Delta H_f^\circ = 17.5$ kcal/mol	$AP_{79} = 9.5 \pm 0.1$ eV
$IP = 8.8 \pm 0.1$ eV	$AP_{93} = 9.8 \pm 0.1$ eV
$AP_{66} = 9.2 \pm 0.1$ eV	$AP_{54} = 10.9 \pm 0.1$ eV
$AP_{80} = 9.4 \pm 0.1$ eV	
5-Methyl-1,3,6-heptatriene	
$\Delta H_f^\circ = 32.2$ kcal/mol	$AP_{93} = 8.8 \pm 0.1$ eV
$IP = 8.4 \pm 0.1$ eV	

be better understood through a consideration of the ion energetics of the 4-vinylcyclohexene and 5-methyl-1,3,6-heptatriene cation radicals (Table IV).²³ Both cation radicals are very similar in energy and with respect to fragmentation.²¹ The ΔH_f° of the 5-methyl-1,3,6-heptatriene cation radical is about 225 kcal/mol and will tolerate up to 9 kcal before expelling a methyl radical. The ΔH_f° of the 4-vinylcyclohexene cation radical is 4 kcal/mol lower in energy than that of the 5-methyl-1,3,6-heptatriene cation radical, but only 8 kcal/mol is required for elimination of C_3H_6 from the 4-vinylcyclohexene cation radical. However, the elimination of C_3H_6 is necessarily a rearrangement and is expected to be slow compared to a methyl cleavage. Therefore, the 4-vinylcyclohexene cation radical is easier to observe than is the 5-methyl-1,3,6-heptatriene cation radical.

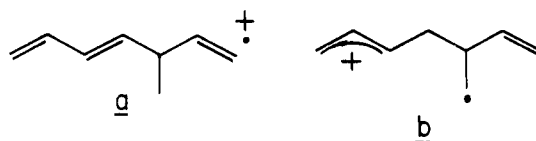
The appearance energy (AE) for m/z 54 (corresponding to the 1,3-butadiene) cation radical arising from the 4-vinylcyclohexene cation radical is *at most* only 7 kcal/mol greater than the ΔH_f° of the 1,3-butadiene cation radical plus neutral 1,3-butadiene (262 kcal/mol). The AE value of 269 kcal/mol represents an upper limit and is probably too high because of kinetic and competitive shifts. The reaction of the 1,3-butadiene cation radical with neutral 1,3-butadiene to form the 4-vinylcyclohexene cation radical occurs with negligible activation energy, and this conclusion is in accord with the high efficiency observed for the reaction.

Mechanism. The reaction of 1,3-butadiene cation radical and neutral 1,3-butadiene has both high efficiency and noncomposite dynamics. The high efficiency rules out extensive back reaction and is not in accord with direct formation of a cyclic intermediate, which would have high orientation requirements for the reactants. Nevertheless, the 4-vinylcyclohexene cation radical intermediate does form and is observable under conditions of minimal collisional stabilization. As the collisional stabilization is increased by increasing the pressure of 1,3-butadiene or the bath gas CS_2 , another intermediate, which is acyclic in structure, is detected. This is manifested in both the spectra of the product ions formed in the high-pressure source and in the CAD spectra of the intermediates, both taken as a function of the extent of collisional stabilization.

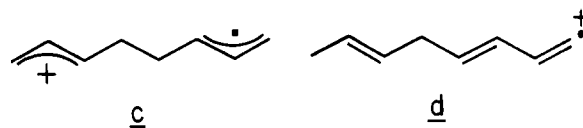
An important consideration for proposing a mechanism is whether the cyclic structure, which is more readily stabilized, is formed in parallel or in series with the acyclic adduct. As the pressure is increased from 13 to 130 mtorr, the abundance of the observable adduct increases by approximately 1 order of magnitude (see Figure 2). The proportion of adduct structures which are cyclic at 130 mtorr is estimated to be approximately 5% based on a consideration of the relative abundance of m/z 66 in the CAD spectrum of the adduct stabilized. This fragment ion is most characteristic of the cyclic structure, and its relative abundance is observed to decrease as the pressure is increased. Therefore, the *absolute* amount of cyclic intermediate did not increase, and probably decreased, as the stabilizing gas pressure was increased from 13 to 130 mtorr. These considerations are consistent with a serial, and not a parallel, mechanism for formation of the cyclic and acyclic intermediates. The cyclic intermediate becomes more difficult to observe under the higher pressure conditions because its formation is preempted by collisional stabilization of its acyclic precursor.

Scheme I

The precise structure of the acyclic adduct is now addressed. The CAD spectrum of the adduct stabilized at high pressure (i.e., the acyclic adduct) matches best with that of 5-methyl-1,3,6-heptatriene, a. This structure most closely resembles an adduct



produced by condensation at the 1-position of neutral butadiene and the 2-position of the cation radical (structure b). We note that this structure adduct would not be expected to be as favored as structure c, which has been postulated to resemble the lowest



energy transition state or intermediate connecting the reactants and the 4-vinylcyclohexene cation radical product.⁷ The reference compound which bears the closest resemblance to structure c is d (compound 1), but its CAD spectrum does not match those of the adducts stabilized at high pressure. Ring opening of the 1,2-bond of *cis*- or *trans*-1,2-divinylcyclobutane cation radicals would be a route for production of c.^{11a} However, the CAD spectra of these reference compounds did not match that of the acyclic adduct. The divinylcyclobutane cation radicals may isomerize by routes other than the desired ring opening, e.g., a Cope rearrangement (vide supra). The best interpretation of the data in hand is that the adduct stabilized at high pressure possesses a branched acyclic structure such as a. However, structure c cannot be ruled out because we cannot be certain that the reference compounds are accurate models or precursors for this structure. Furthermore, structure c may serve as a precursor for the branched structure which has higher propensity to decompose by losing methyl.

In summary, the butadiene cation radical reacts with neutral 1,3-butadiene to produce an acyclic intermediate which isomerizes to an activated 4-vinylcyclohexene cation radical²⁴ in the absence of collisional stabilization (see Scheme I). Subsequent decompositions in the collision-free environment of the FTMS and of the chemical ionization source at 13 mtorr give a distribution of products which is similar but not identical with that found in the reference mass spectrum of 4-vinylcyclohexene. A small fraction of the initially formed intermediates either lose a methyl radical directly or isomerize to another acyclic intermediate such as 5-methyl-1,3,6-heptatriene cation radical and then decompose via methyl radical elimination. The enhancement of the loss of $\cdot CH_3$ (m/z 93) in the FTMS spectrum and in the mass spectrum acquired at 13 mtorr may be attributed to decompositions of the acyclic intermediate.

As the pressure is increased, the collisional stabilization rate increases and the acyclic product is intercepted before it can isomerize to the 4-vinylcyclohexene cation radical. A potential energy diagram can be drawn in accord with the mechanism proposed in Scheme I and with the thermochemical measurements

(23) ΔH_f° values were calculated according to the group additivity method of: Benson, S. W. "Thermochemical Kinetics"; Wiley: New York, 1968.

(24) For an example of cyclizing gas-phase cations, see: Hall, D. G.; Morton, T. H. *J. Am. Chem. Soc.* **1980**, *102*, 5686.

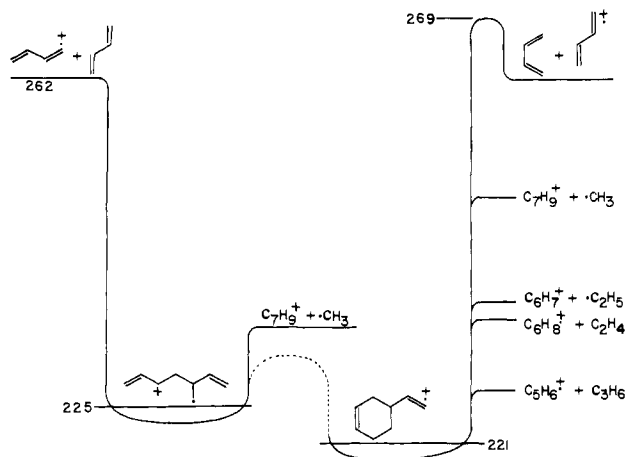


Figure 3. Simplified potential energy surface for the 1,3-butadiene ion-molecule reaction.

(see Figure 3). The activation barrier for isomerization of the initially formed acyclic intermediate must be comparable to that for loss of a methyl group since evidence for both processes is found in the FTMS and in the lower pressure mass spectral data. Once isomerization occurs, the properties of the rearranged intermediate are nearly identical with those of 4-vinylcyclohexene. However, the isomerization can be prevented by increasing the rate of collisional stabilization, thereby effectively "freezing out" the intermediate in an acyclic form.

This mechanism has consequences in terms of cycloaddition reactions of cation radicals both in the gas phase and in solution. Because the intermediate formed initially in a collision-free environment is acyclic, the ultimate cycloaddition cannot be concerted. This may be because the driving force for concerted cycloadditions, namely a six-electron aromatic transition state, has been lessened by removal of one electron from one of the reactants. The two-step mechanism proposed here is consistent with the mechanisms postulated for the cation radical reactions of 1,3-butadiene plus vinyl methyl ether^{12a} and styrene plus styrene^{11a} and with the theoretical calculations of Turecek and Hanus.^{7b}

Experimental Section

Mass Spectrometry. The CAD spectra and the mass spectra of the ions formed in the 13–650-mtorr pressure range were recorded by using a Kratos MS-50 triple analyzer mass spectrometer of EBE design, which has been described previously.²⁵ Ion-molecule reactions were run in a commercially available (Kratos Scientific Instruments) chemical ionization source which was operated at ambient temperature to reduce arcing. Source pressures were estimated by using an ion gauge located in the source-pumping manifold which was calibrated by using a Hastings gauge, which was mounted on a probe and mated directly with one of the reentrants of the CI source. This calibration was tested by recording the methane spectrum at various pressures and matching the i_{41}/i_{43} ratios to those reported earlier.²⁶ The pressure obtained by this method was found to agree with the Hastings gauge method to within $\pm 30\%$ maximum error.

The 1,3-butadiene was Matheson instrument grade and was admitted to the mass spectrometer either through a commercially available (Kratos Scientific Instruments) reagent gas inlet system or through a custom fabricated all-glass heated inlet system run at a temperature of 100 °C. This latter inlet system was used for 1,3-butadiene in the CS₂ experiments. No C₅H₁₂⁺ corresponding to the butadiene ion-molecule adduct could be detected in the 1,3-butadiene sample by using an electron impact source and the mass spectrometer tuned to its highest sensitivity. This was also true for 1,3-butadiene which had been exposed to the heated inlet system and the reagent gas inlet system for several hours. The CS₂ was Matheson, Coleman, and Bell reagent grade and was admitted through the reagent gas inlet system.

The rate constant for the reaction of the 1,3-butadiene cation radical plus neutral 1,3-butadiene was determined by using a Varian ICR-9

spectrometer modified for operation with an elongated cell similar to the type introduced by McIver.²⁷ The spectrometer was operated at a 5.38-kG magnetic field strength, 153.7-kHz excitation frequency, and a 15-eV ionization energy, as measured with a digital voltmeter. 1,3-Butadiene disappearance curves were recorded by monitoring m/z 54 abundance as ion detection delay time was increased from 0 to 100 ms under the control of a pulse programmer. 1,3-Butadiene pressure in the spectrometer was typically 1×10^{-6} torr and was measured by using an ion gauge which had been calibrated by using a Datametrics Model 1173 Barocel electronic manometer.

Fourier transform mass spectra were recorded by using a home-built mass spectrometer operated in the heterodyne mode.²⁸ The spectrometer was interfaced to a Nicolet Instrument FTMS 1000 computer system. Pressure measurements were recorded by using an ion gauge (uncorrected).

Reference Compounds. Those compounds that were purchased were used as received. The compounds that were synthesized were characterized by mass spectrometry (Kratos MS-50 triple analyzer), NMR spectroscopy (Varian EM-390 90-MHz spectrometer, Nicolet 360-MHz NMR spectrometer), and in some cases infrared spectroscopy (Perkin-Elmer 823 infrared spectrometer).

1,3,6-Octatriene (**1**) and 5-methyl-1,3,6-heptatriene (**3**) were obtained from the Alfred Bader Library of Rare Chemicals, Division of the Aldrich Chemical Co. 4-Vinylcyclohexene (**8**) and 1,5-cyclooctadiene (**12**) were obtained from the Aldrich Chemical Co. 1-Octen-4-yne (**2**), 1-ethyl-1,4-cyclohexadiene (**9**), 1,4-dimethylenecyclohexane (**10**), and 1,3-cyclooctadiene (**13**) were obtained from Wiley Organics of Columbus, OH.

3-Methylene-1,6-hexadiene (4). This compound was synthesized by using the method of Kawamura et al.²⁹ The NMR of the product was identical with that reported earlier. Mass spectrum (70 eV), m/z 108 (4.8%), 107 (5.5%), 106 (3.1%), 105 (6.1%), 93 (69.7%), 91 (38.2%), 80 (27.0%), 79 (100%), 78 (11.5%), 77 (40.4%), 67 (42.7%), 66 (7.6%), 65 (24.7%), 55 (7.4%), 54 (13.0%), 53 (18.0%), 52 (5.6%), 51 (9.0%), 41 (76.4%), 39 (42.7%).

cis- and trans-1,2-Divinylcyclobutane (5 and 6). These materials were synthesized by using the photodimerization method of Hammond et al.³⁰ The 90-MHz NMR spectra were identical with those reported in ref 30a. Mass spectrum for the cis isomer (70 eV), m/z 108 (0.2%), 107 (0.3%), 105 (0.1%), 103 (0.1%), 93 (6.4%), 91 (1.7%), 80 (11.5%), 79 (21.3%), 67 (11.1%), 66 (7.4%), 54 (100%), 53 (10.2%), 41 (9.6%), 39 (39.1%). Mass spectrum for the trans isomer (70 eV), m/z 108 (0.1%), 107 (0.4%), 105 (0.2%), 103 (0.1%), 93 (11.4%), 91 (2.4%), 80 (13.2%), 79 (27.4%), 67 (13.5%), 66 (7.5%), 54 (100%), 53 (7.8%), 41 (6.4%), 39 (25.6%).

1-Methylene-2-vinylcyclopentane (7). This compound was synthesized by using a variation of the catalytic dimerization of 1,3-butadiene first described by Kiji, Masui, and Furukawa.³¹ Bis(triethyl phosphine)-nickel(II) chloride (2.0 mmol 0.732 g, Alfa Ventron Corp.) was admitted to a 33-mL capacity sealable Pyrex tube fitted with a magnetic stirrer and an adapter with two air-tight septa. The apparatus was evacuated and filled with 1 atm of dry nitrogen, at which time 7.7 mL of benzene and 2.0 mmol of *n*-butyllithium (1.6 M in hexane, Aldrich) were added via syringe. This mixture was stirred at room temperature for 30 min, at which time 61.5 mmol of methanol (2.3 mL) was added to the stirring mixture via syringe. The greenish reaction mixture was cooled by using a dry ice-acetone slush, and 108 mmol of liquefied 1,3-butadiene (9.36 mL, Matheson) was added via a syringe. The reaction mixture was frozen, and the tube was then evacuated and sealed with a torch. The reaction mixture was allowed to warm slowly with stirring to room temperature, stirred in an oven at 70 °C for 43 h, and frozen by using liquid nitrogen, and then the tube was opened. No butadiene was observed to bubble out of solution as the reaction mixture warmed to room temperature. A short-path distillation was performed on the crude solution, and fractions collected from 88 to 124 °C were found to contain large quantities of 1-methylene-2-vinylcyclopentane (**7**). The product was purified by preparative gas chromatography (2 m, 5% didecylphthalate, 1.25% triethanolamine on Chromosorb B, column temperature 100 °C,

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flow rate 35 mL/min). IR (neat) cm^{-1} : 3076, 2988, 2960, 2860, 1825, 1775, 1651, 1644, 1464, 1446, 1430, 1418, 1409, 1217, 989, 905, 875. NMR (360 MHz, CDCl_3): δ 5.69 (ddd, 1, $^3J_{\text{trans}} = 17.1$, $^3J_{\text{cis}} = 10.1$, $^3J = 8.0$ Hz, =CH), 5.04-4.99 (complex, 2, decoupling at 2.90 ppm reveals ddd, $^3J_{\text{trans}} = 17.1$, $^3J_{\text{cis}} = 10.1$, $^2J = 2.0$ Hz, =CH₂), 4.93 (br s, 1, =CH₂), 4.79 (br s, 1, =CH₂), 2.90 (complex, 1, CH), 2.30 (complex, 2, CH₂), 2.00-1.30 (complex 4, CH₂). Mass spectrum (70 eV), m/z 108 (24.2%), 107 (7.6%), 105 (3.2%), 93 (100%), 91 (41.1%), 80 (22.4%), 79 (83.3%), 78 (14.6%), 77 (46.6%), 67 (22.8%), 66 (7.2%), 65 (12.9%), 54 (7.5%), 53 (14.0%), 52 (6.6%), 51 (11.6%), 41 (23.8%), 39 (34.0%). We thank K. Facchine for his assistance with the NMR spectroscopy of this compound.

3-Methylenecycloheptene (11). This compound was synthesized by using the method of Wittig and Schoellkopf³² with 3-cycloheptenone (Aldrich Chemical Co.) and (triphenylmethyl)phosphonium bromide (Aldrich Chemical Co.). The product was purified with gas chromatography (2 m, 5% didecylphthalate, 1.25% triethanolamine on Chromosorb B, column temperature of 100 °C, flow rate of 50 mL/min). IR spectrum (neat) cm^{-1} : 3073, 3010, 2920, 2855, 1770, 1640, 1595, 1450, 880, 844, 760. NMR (90 MHz, CDCl_3): δ 6.07 (d, 1, $^3H = 12.0$ Hz, =CH), 5.64 (dt, 1, $^3J = 12.0$, $^3J = 6.0$ Hz, =CH), 4.75 (br s, 2, =CH₂), 2.52-2.02 (complex, 4, CH₂), 1.83-1.54 (complex, 4, CH₂). Mass spectrum (70 eV), m/z 108 (49.7%), 107 (6.7%), 105 (3.0%), 93 (100%), 91 (45.4%), 80 (24.0%), 79 (56.1%), 78 (11.2%), 77 (46.2%), 67 (9.6%), 66 (5.9%), 65 (10.4%), 54 (3.5%), 53 (7.5%), 52 (4.7%), 51 (8.1%), 41 (14.4%), 39 (20.6%).

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Bicyclo[4.2.0]oct-7-ene (14). This sample was prepared from 1,3-cyclooctadiene by using the method of Liu.³³ The product was purified by gas chromatography (2 m, 5% SE30, column temperature of 100 °C, flow rate of 50 mL/min). NMR (90 MHz, CDCl_3): δ 6.03 (s, 2, =CH), 2.95-2.78 (m, 2, CH), 1.85-1.30 (complex, 8, CH₂). Mass spectrum (70 eV), m/z 108 (1.7%), 107 (3.0%), 105 (1.3%), 93 (52.4%), 91 (19.8%), 80 (51.5%), 79 (100%), 78 (9.8%), 77 (30.2%), 67 (59.8%), 66 (20.1%), 65 (13.3%), 54 (14.9%), 53 (7.0%), 52 (4.7%), 51 (7.8%), 41 (27.6%), 39 (25.0%).

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Registry No. 1, 929-20-4; 2, 24612-83-7; 3, 925-52-0; 4, 16626-48-5; 5, 16177-46-1; 6, 6553-48-6; 7, 6196-78-7; 9, 19841-74-8; 10, 4982-20-1; 11, 34564-56-2; 12, 111-78-4; 13, 1700-10-3; 14, 616-10-4; 1,3-butadiene, 106-99-0; 1,3-butadiene cation radical, 34488-62-5; 4-vinylcyclohexene cation radical, 91798-27-5; 4-vinylcyclohexene, 100-40-3; 5-methyl-1,3,6-heptatriene, 925-52-0; 5-methyl-1,3,6-heptatriene cation radical, 92142-91-1; bis(triethylphosphine)nickel(II) chloride, 17523-24-9; *n*-butyllithium, 109-72-8; 3-cycloheptenone, 1121-64-8; triphenylmethylphosphonium bromide, 1779-49-3.

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Reaction of the Vinyl Methyl Ether Cation Radical and 1,3-Butadiene: A Two-Step Cycloaddition

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Abstract: The structure of the intermediate formed in the ion-molecule reaction of 1,3-butadiene and vinyl methyl ether has been determined by stabilizing the intermediate in a high-pressure chemical ionization source, isolating the intermediate by using the first stage of mass analysis of a tandem mass spectrometer, and finally acquiring its mass spectrum by using collision-activated decomposition (CAD) spectroscopy and the second stage of mass analysis. The structure of the intermediate is demonstrated to be acyclic by comparing its CAD spectrum with CAD spectra of several isomeric $\text{C}_7\text{H}_{12}\text{O}$ reference compounds. This conclusion is in contrast to previous low-pressure ion cyclotron resonance (ICR) and present Fourier transform mass spectrometry (FTMS) experiments, which are interpreted in terms of a cycloaddition. These two interpretations are reconciled by invoking a two-step reaction mechanism in which an acyclic intermediate is initially formed. This intermediate ultimately cyclizes, unless it is intercepted by stabilizing collisions.

Organic cation radicals and their reactions have become important subjects for study in analytical and organic chemistry. Recent research in mass spectrometry and in synthetic organic chemistry has been focused on cycloaddition reactions involving a cation radical reactant. Solution-phase cation radical cycloaddition reactions have been reported recently,¹ and gas-phase cation radical cycloadditions involving *o*-xylylene,² fulvene,³ and 1,3-butadiene^{4,5} have been demonstrated also. The cation radical Diels-Alder reaction has also been studied by using theoretical

methods, and conflicting interpretations have been drawn. The results of one study point to a nonsynchronous, concerted mechanism^{6a} whereas those of another are interpreted in terms of a two-step process.^{6b}

van Doorn and co-workers⁴ in 1978 reported investigations of gas-phase ion-molecule reactions in ionized mixtures of 1,3-butadiene and vinyl methyl ether. The results of ion cyclotron resonance (ICR) and collision-activated decomposition (CAD) experiments were interpreted in terms of a methoxy-substituted, six-membered cyclic adduct (4-methoxycyclohexene). A Diels-Alder mechanism was suggested,⁴ but no evidence was presented to distinguish between a concerted and a two-step process. A stable (1,3-butadiene plus vinyl methyl ether) cation radical adduct could not be observed in that work because the low pressures ($\leq 2 \times$

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