

# Studies of Unusual Simple Molecules by Neutralization-Reionization Mass Spectrometry

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Reactive or unstable molecules are key intermediates in many important reactions, but can be difficult to prepare for experimental studies. Species with missing ( $\text{:CH-OH}$ ) or extra ( $\text{H}_3$ ) substituents can often be formed conveniently in the gas phase by neutralizing a beam of a more stable ionic counterpart ( $\text{CH=O}^+\text{H}$ ,  $\text{H}_3^+$ ). Reionization of the neutral after  $\sim 10^{-6}$  seconds tests its stability, whereas its unimolecular chemistry can be probed by preparing it with different amounts of internal energy. The resulting neutral products are reionized and mass analyzed. Isomers are then characterized by ion dissociation and a third mass-analysis step. Many unusual molecules have been characterized with this technique, which can also be used to probe complex unimolecular chemistry, such as that of cyclobutadiene and ethylene oxide.

THE TANTALIZING CHEMISTRY OF HIGHLY REACTIVE, short-lived neutral species (1), including hypervalent molecules (such as  $\text{H}_3$ ), zwitterions and ylides ( $\text{^-CH}_2\text{Cl}^+\text{H}$ ), carbenes ( $\text{:CH-OH}$ ), diradicals ( $\text{CH}_2\text{CH}_2\text{O}$ ), enols ( $\text{CH}_2=\text{CHOH}$ ), and antiaromatic molecules (cyclobutadiene), has been obscured by the experimental problems brought on by these same fascinating characteristics. Such species are key intermediates in flames and explosions (2), interstellar space (3), the upper atmosphere (4), and other photochemical systems (5), as well as in molecular clusters (2, 6) and industrial synthesis and refining (1, 7). For many such species our main knowledge of their chemistry has come from spectroscopic measurements of species formed in energetic reactions (such as electric discharges) or trapped at very low temperatures, as well as from theoretical calculations.

Neutralization-reionization mass spectrometry (NRMS) has several advantages as an experimental method for such studies. Used originally for the study of di- and triatomic species such as  $\text{H}_3$  (8), it has been applied more recently (9-13) to a variety of larger species. In NRMS a fast ( $\sim 10^5$  m/s) beam of the neutral species can often be conveniently produced in vacuum (minimizing bimolecular reactions) by neutralization after mass analysis (MS-I) of the counterpart cation or anion (Fig. 1); one of these ions may have sufficient stability ( $\sim 10^{-5}$ -s lifetime) even if the corresponding neutral is unstable. To examine the neutral's chemistry, the time scale before reionization occurs (a microsecond) provides a crucial test of its stability. Furthermore (10, 14-18), the unimolecular dissociation

and isomerization reactions of the neutral can be probed by forming it with a specified average internal energy (11) or by adding energy by collision (10, 16-19); the dissociation products are characterized by reionization and mass analysis (MS-II), with further isomeric identification of these separated product ions by collisionally activated dissociation (20) and mass analysis (MS-III).

To illustrate the advantage of forming or characterizing neutrals using their counterpart ions, the familiar hydronium ion  $\text{H}_3\text{O}^+$  is highly stable, making it a convenient precursor for the preparation of  $\text{H}_3\text{O}$ , which is "hypervalent" compared with  $\text{H}_2\text{O}$  because of its extra hydrogen (11). Similarly, the anion of hydroxycarbene,  $\text{:CH-OH}$ , is stable, whereas the anion of its common isomer formaldehyde,  $\text{H}_2\text{C=O}$ , is not (although both its neutral and cation are stable), so that reionization clearly distinguishes these isomers (21). For such reasons NRMS is particularly useful for the structural characterization of ions (10, 16, 22, 23); in addition, such tandem mass spectrometry methods (MS/MS or  $\text{MS}^n$ ) have many exciting analytical applications (24). Reactively generated radicals have also been studied by several other mass spectrometric methods (18, 25).

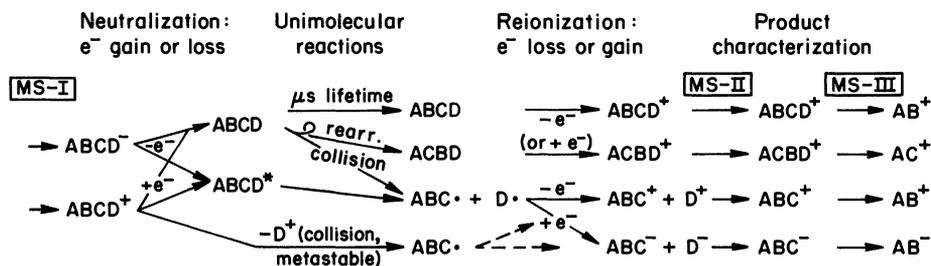
Neutralization of gaseous ionic beams has been used experimentally for years to provide basic information on atoms and simple molecules (8). For neutralization techniques (26) my research group has been heavily indebted to my colleague R. Porter and his students who, for example, have demonstrated the unusual stability of  $\text{H}_3$   $2p^2A_2'$  state) and other hypervalent species such as  $\text{D}_3\text{O}$  and  $\text{ND}_4$  (11). For the examination of larger species, reionization has provided valuable additional information (9, 10, 27), with the extensive contributions of Holmes and Terlouw (12) and, later, those of Schwarz and Harrison (13), deserving special mention. The recent use of MS/MS/MS for structural characterization of the reionized species (14-18) appears to provide a substantial expansion of the chemical information available from NRMS.

## NRMS Instrumentation

Most of this research has been done with magnetic sector instruments containing multiple sectors, such as the Cornell instrument shown in Fig. 2 (9, 14). Ions can be prepared by neutral ionization, ion dissociation, or ion-molecule reactions, accelerated (for example, with a 10-kV field), and separated under double-focusing conditions [first electrostatic analyzer (ESA) and magnet] to eliminate even isobaric impurities (same nominal mass but different elemental formula). The selected ions are neutralized (for example, with metal vapor) (11, 26) in the first collision chamber (Cls-I), and any remaining ions are deflected electrostatically (Dfl-I). The resulting fast neutral beam is made to undergo unimolecular reactions (such as rearrangement or dissociation) either by collision-

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**Fig. 1.** NRMS schematic. Mass-selected anions or cations from MS-I are neutralized to either the ground state or to excited neutrals. After  $10^{-6}$  s these have survived unchanged, rearranged, or dissociated; a fast neutral can also be prepared by dissociation of a precursor ion. Reionization produces either fast cations or anions, with mass analysis in MS-II indicating dissociations that have occurred for both the neutral and the reionized species. Isomer identification of an MS-II-selected ion beam can then be effected by collisionally activated dissociation and MS-III mass analysis.



al activation in Cls-II with a target gas (such as helium, with Dfl-II deflecting any ions formed), or by neutralization with a target of lower ionization energy than the neutral (the lower energy required for ionization is reflected in a higher internal energy in the resulting neutral) (11, 14–18, 23). Neutrals can also be prepared (Fig. 1) by ion dissociation to produce a product ion and a neutral (9, 12, 28), but this method can be compromised by competing ion dissociations that produce contaminant neutrals.

Reionization is then effected in Cls-III (27); removal of one or more (19) electrons to form cation products is done with a target such as  $O_2$  or  $NO$ , whereas addition of an electron to form anionic products allows targets such as mercury vapor, benzene, or xenon to be used (21, 29, 30). High- or low-resolution mass analysis (MS-II) of these products is effected by ESA-II and magnet-II together or by ESA-II alone, respectively. Isomeric characterization of the ESA-II separated ions can then be effected by their collisionally activated dissociation (20, 24) in Cls-IV followed by mass separation (MS-III) with magnet-II (14–18). Cross sections for neutralization and reionization can also be useful structural characteristics of these species; for accurate reionization cross sections, the neutral beam flux can be determined by an in-line channeltron multiplier inserted in place of Cls-III (10, 14, 31). A personal computer system controls the instrumentation and averages multiple scans for signal-to-noise improvement (32).

## Hypervalent Species

Transition states in some of the simplest chemical reactions involve hypervalent species, such as  $H_3$  (8, 33) from the reaction  $H + H_2$ . Neutralization of a fast beam of the stable ion  $H_3^+$ , with subsequent reionization, shows that two forms of  $H_3$  have lifetimes of at least microseconds. One represents high electronic (Rydberg) states, in which an outer electron moves around an  $H_3^+$  core (8). The other is the ground rotational level of the  $2p^2A_2'$  electronic state (11, 34), confirmed by its absorption spectrum measured by photo-assisted fragmentation (35). Other such metastable hypervalent species include  $He_2$ ,  $Ne_2$ , and  $Ar_2$  (36), as well as  $NeH$  (ground state, although  $HeH$ ,  $ArH$ ,  $KrH$ ,  $XeH$ , and  $N_2H$  are unstable) (37).

The simplest hypervalent organic species,  $CH_5$ , is found not to be stable (lifetime  $< 10^{-8}$  s) when formed from fast  $CH_5^+$  (and  $CD_5^+$ ) ions by Na or K neutralization (11), in agreement with theory (38). However, Zn neutralization forms long-lived ( $> 10^{-6}$  s)  $CH_5$  and  $CD_5$  that apparently represent high Rydberg levels (39). The analogous  $NH_4$ ,  $H_3O$ , and  $H_2F$  species are also unstable in their ground states, but show an unusual isotope effect in that their perdeuterio analogs produce abundant reionized species; this same effect is observed in clusters such as  $NH_4(NH_3)_n$  and  $CH_3NH_3(NH_3)_n$  (11, 40). Dramatically different isotope effects are found, however, for  $C_2H_5OD_2$ , which is stable, whereas  $C_2H_5OH_2$  and  $C_2D_5OD_2$  are not (41), and for  $H_2Cl$ , an intermediate in the

long-studied  $H_2 + Cl_2$  reaction (42). The relative abundances indicated by reionization for the  $D_2Cl$ ,  $H_2Cl$ , and  $HDCl$  species surviving for  $10^{-6}$  s are 1, 3, and 30, respectively; a possible explanation for this double isotope effect is the reaction sequence  $HCl^+ + HCl \rightarrow H-Cl^+-H^* \rightarrow H-H^+-Cl \rightarrow H-H-Cl$  (43).

## Carbenes and Radicals

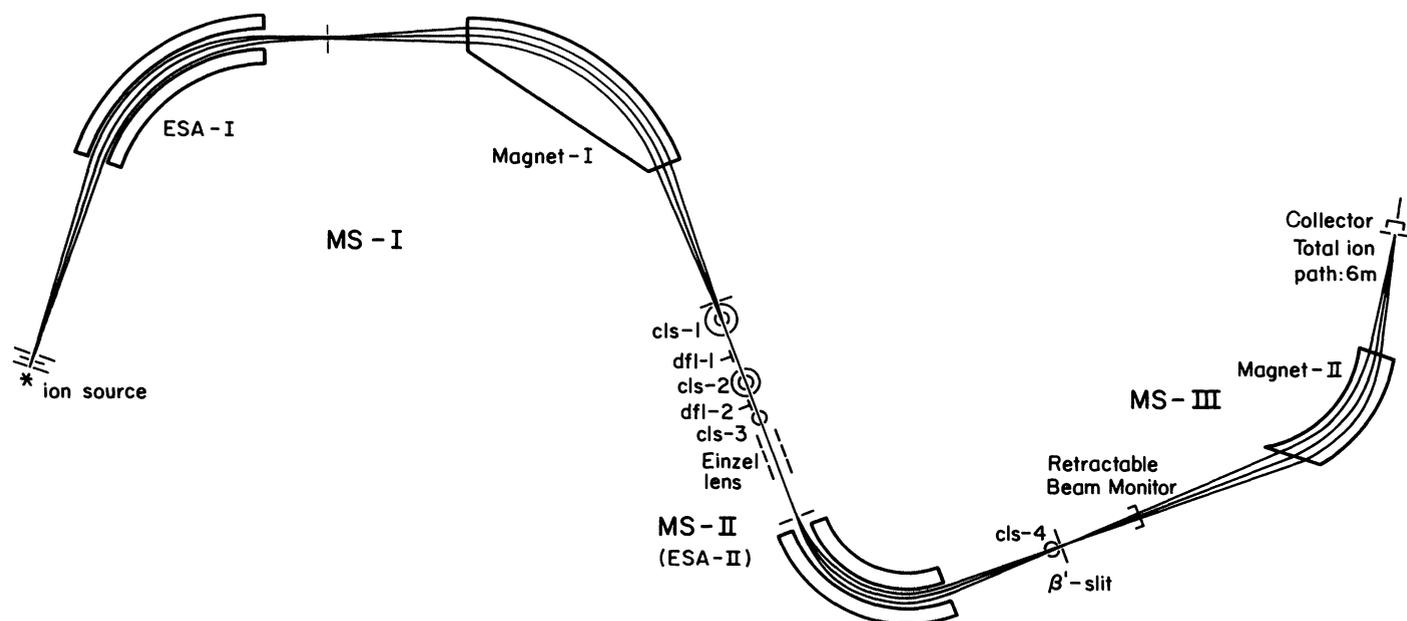
Hydroxycarbene ( $:CH-OH$ ), one of the simplest such species, should be long lived (1). However, the first experimental verification came in neutralizing a beam of  $^1CH=O^+H$  ions, formed from  $CH_3OH^+$ , followed  $10^{-6}$  s later by reionization of the resulting neutral beam to anions with a mass-to-charge ratio ( $m/z$ ) of 30 (C,  $H_2$ , O) (21). Such carbenes should have positive electron affinities (44), whereas the isomeric formaldehyde ( $H_2C=O$ ) gives no molecular anion in its NR spectrum. Other carbenes characterized from their NR spectra include  $:C(CH_3)OH$  (45),  $:CH-OCH_3$  (17) (both discussed further below),  $H_2C=C:$  (46; NR spectra of  $HC\equiv CH$ , 47, 48), and  $:CF-OH$  (49). For carbon clusters, theory predicts both linear and cyclic forms of  $C_4$  as stable isomers (6); preliminary NRMS evidence finds significant differences in the reionization spectra of  $C_4$  neutrals from hexachlorobutadiene and hexachlorocyclopentadiene (31).

Many diradicals can cyclize intramolecularly, a further complication to their experimental characterization (1). NRMS evidence has recently shown that the ring-opened isomers of oxirane,  $^1CH_2OCH_2^+$  and  $^1CH_2CH_2O^+$ , can be formed as long-lived species, distinguishable from other  $C_2H_4O$  neutral isomers (17). For example, of these three isomers only  $^1CH_2CH_2O^+$  can be reionized to a stable molecular anion, consistent with its terminal oxygen atom.

Many radical species have now been studied by NRMS. A 1987 review (10) lists studies on  $^1CH_3$ ,  $^1C_2H_5$ ,  $^1C_3H_7$ ,  $^1C_4H_9$ ,  $^1C_7H_9$ ,  $^1CH_2NH_2$ ,  $^1CH_2OH$ ,  $^1CH_3O$ ,  $^1CH_2F$ ,  $^1CH_2Cl$ ,  $^1CH(CH_3)OH$ ,  $^1CH_2CH_2OH$ ,  $^1CH(CH_3)NH_2$ ,  $^1CH_2CH_2NH_2$ ,  $^1CH_2CH_2CH_2CH_2OH$ ,  $^1HCO$ ,  $^1DCO$ ,  $^1CH_3CO$ ,  $^1(CD_3)_2COD$ ,  $^1COOH$ , and  $^1COOD$ . Additional reports describe  $^1C_2H_3$  (48),  $^1CD_3OCD_2$  (50),  $^1C_2H_5O$ ,  $^1HCO_3$  (30),  $^1H_2NO$ ,  $^1NHOH$  (51),  $^1HSO_3$  (intermediate in the atmospheric oxidation of  $SO_2$ ) (52),  $^1CH_3SO$ ,  $^1CH_2SOH$  (intermediates in the biological and atmospheric oxidation of sulfur compounds) (18), and  $^1SF_5$  (30).

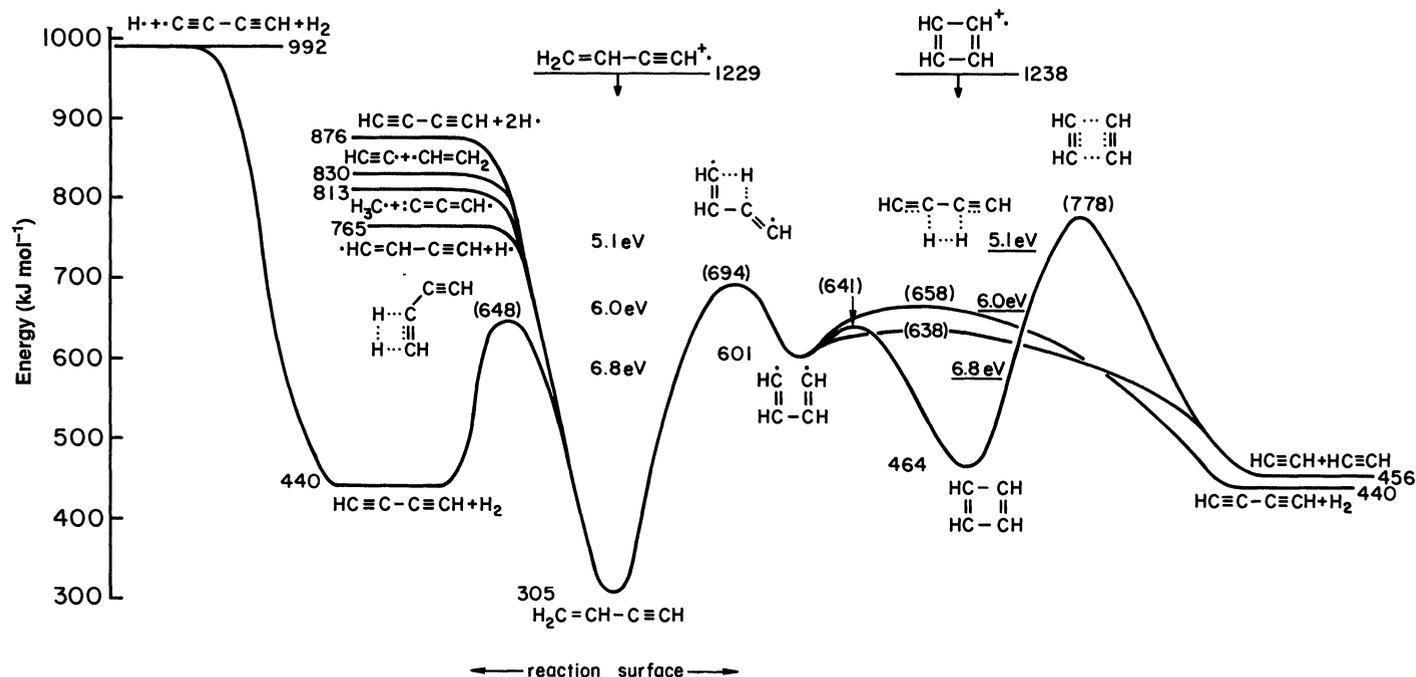
## Unusual Simple Molecules

Long-lived even-electron neutrals such as HNC (identified first from interstellar spectroscopy), the enols  $CH_2=CHOH$  and  $CH_2=C(OH)CH_3$ , the ylides  $H_2CYH$  ( $Y=NH_2, OH, F, Cl$ ), the zwitterions  $^-CH_2CH_2O^+H_2$  and  $^-CH_2CH_2N^+H_3$ , the acetylenes  $XC\equiv CY$  ( $X=^-H, ^-OH, ^-NH_2$ ;  $Y=^-OH, ^-NH_2$ ), and the free acids  $HOCOOH$  and  $H_2NCOOH$  were discussed in the earlier



**Fig. 2.** The Cornell NMRS instrument. Double-focusing selection of ions using the first electrostatic and magnetic analyzers (MS-I) gives a precursor ion beam that can be neutralized in Cls-I. Any remaining ions are deflected in Dfl-I. Neutrals can be collisionally activated in Cls-II, with any ions

produced deflected in Dfl-II. Neutral products can be reionized in Cls-III and mass analyzed in the second electrostatic analyzer, with isomeric characterization by dissociation in Cls-IV and mass analysis in magnet-II.



**Fig. 3.** Energy surface for neutral vinyl acetylene and cyclobutadiene. [Adapted from (16) with permission © American Chemical Society]

NRMS review (10). There has been controversy (53) over the claimed (19) stability of  $\text{H}_2\text{CCHH}$ , the ylide isomer of  $\text{H}_3\text{CCl}$ ; however, a recent MS/MS/MS experiment in my laboratory has shown that much of the reionized molecular species retains the  $\text{H}_2\text{CCHH}^+$  structure (15).

Attempts to form long-lived oxirene, the cyclic isomer of  $\text{HC}\equiv\text{COH}$  and  $\text{CH}_2=\text{C}=\text{O}$  (54), and  $\text{O}=\text{C}=\text{C}=\text{O}$  (55), by NRMS have not been successful. For the analogous polycarbon disulfides,  $\text{S}=\text{C}_n=\text{S}$ , the even-numbered  $n$  analogs have escaped experimental verification in solution; Schwarz and co-workers have recently characterized (56) by NRMS those of  $n = 2$  [a possible intermediate

in forming  $(\text{CS})_n$  "laser snow" from  $\text{CS}_2$ ] (57) and 4, as well as  $\text{O}=\text{C}=\text{C}=\text{S}$  (55). Other simple molecules found to be long lived in this way include  $\text{CO}_3$  (cyclic or linear) (30); two isomers of  $\text{CS}_3$  (58);  $\text{HOSO}(\text{H})$  (59);  $\text{HNCO}$ ,  $\text{HCNO}$  (the subjects of the first isomerism controversy) (60), and  $\text{CNOH}$  (61);  $\text{H}_2\text{C}=\text{N}(\text{OH})\text{O}$  (*aci*-nitromethane, the assumed initial product from  $\text{CH}_2\text{NO}_2 + \text{H}^+$ ),  $\text{H}_3\text{CNO}_2$ , and  $\text{H}_3\text{CONO}$  (62); methylenoxirane, cyclopropanone, and diradical isomers (63); cyclohexa-2,4-dienone (to which hexa-1,3,5-trienal was found to isomerize spontaneously) (64); and metal-cyclopentadienyl (65),  $\text{HCN}-\text{Cu}(0)$ , and  $\text{HNC}-\text{Cu}(0)$  (66) complexes.

The elusive antiaromatic compound cyclobutadiene and its  $C_4H_4$  isomer methylenecyclopropene have been characterized by NRMS (16), preparing their precursor  $C_4H_4^+$  ions from ionization of their corresponding Diels-Alder adducts with a suitable naphthalene derivative (67). These and the  $C_4H_4$  isomers  $HC\equiv CCH=CH_2$  and  $H_2C=C=C=CH_2$  can be distinguished by reionization to either cations or anions (16); the use of NRMS for further chemical characterization of  $C_4H_4$  is discussed below.

## Unimolecular Chemistry from NRMS

Neutralization of a stable ion followed by reionization to the same structure is used in the above examples as compelling evidence for the stability of the corresponding neutral on the NRMS experimental time scale (usually microseconds). If more than one isomer is possible, the structure as well as the mass of the neutral must be determined. For example, the collisionally activated dissociation (CAD) of the  $H_2CCIH$  neutral ("NCR spectrum") yielding HCl (19) and the CAD of its reionized  $H_2CCIH^+$  ("NR/CAD spectrum") to yield more  $H_2C^+$  than  $H_3C^+$  (15) (whereas the opposite is found for  $H_3CCl$ ) both provide compelling evidence for the stability of this ylide on a microsecond time scale.

We have recently shown that these complementary NCR and NR/CAD capabilities (Fig. 1) can provide much more extensive information concerning the unimolecular chemistry of such elusive neutrals by examining their reactivity as a function of internal energy. Two methods, albeit crude, are used for changing the neutral's average internal energy. An excited neutral (ABCD\*, Fig. 1) can be formed by using a target of lower ionization energy (IE) than that of the neutral. Alternatively, the fast neutral formed in its ground state (ABCD) by using a target of high ionization energy can be subjected to separate collisions with a target such as helium (to minimize reionization), with the number of effective collisions dependent on the target pressure (68); however, the nanosecond time scales between such multiple collisions can be sufficient for rearrangement to take place before dissociation thresholds are exceeded (23).

An energy profile of the unimolecular chemistry of cyclobutadiene and its  $C_4H_4$  isomer vinylacetylene derived in this way and from available thermochemical data and theoretical predictions (17, 69) is shown in Fig. 3. The internal energy levels indicated as 5.1,

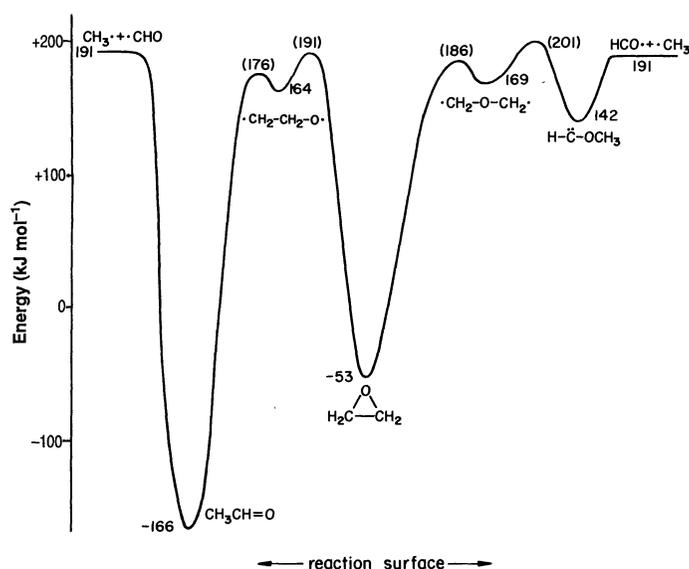


Fig. 4. Energy surface for neutral  $C_2H_4O$  isomers.

6.0, and 6.8 eV represent neutralization of the corresponding  $C_4H_4^+$  precursors with targets of these IEs, presumably producing vinyl acetylene with average energies of  $\sim 268$ , 345, and 432  $\text{kJ mol}^{-1}$ , respectively, and cyclobutadiene with  $\sim 118$ , 195, and 282  $\text{kJ mol}^{-1}$ , respectively. The lowest energies gave NR spectra closely similar to those from Hg (IE = 10.4 eV), so these energies must be below those of the dissociation barriers. At the highest energies, both neutrals gave similar NR spectra showing no reionized  $C_4H_4^+$ , consistent with energies above both their lowest dissociation and isomerization barriers. The 345 and 190  $\text{kJ mol}^{-1}$  energies caused 26% and 49% dissociation of vinyl acetylene and cyclobutadiene, respectively, reflecting the higher stability of the former, and yielding 19% and 58%  $C_2H_2$ , 33% and 19%  $C_4H_2$ , and 27% and 10%  $C_4H_3$ . CAD of the ground-state vinyl acetylene and cyclobutadiene under the same collision conditions gave, respectively, 14% and 59%  $C_2H_2$ , 38% and 19%  $C_4H_2$ , and 28% and 8%  $C_4H_3$ .

Oxirane (ethylene oxide) is an important chemical commodity whose dissociation has been extensively studied over many years (70). Elucidation of the initial unimolecular reactions has been seriously hampered, however, by the extent to which the resulting radical products must be characterized from products of subsequent bimolecular reactions. For this problem (Fig. 4), NRMS (17, 45) can be used to prepare and identify the reactive  $C_2H_4O$  isomers  $\cdot CH_2OCH_2$ ,  $\cdot CH_2CH_2O$ ,  $\cdot CH-OCH_3$ ,  $\cdot C(OH)CH_3$ , and  $C=CHOH$ , as well as oxirane and acetaldehyde ( $CH_3CH=O$ ). Excited forms of all of these isomers dissociate to produce the same major products,  $CH_3\cdot$  and  $\cdot CHO$ , indicating that the stable  $CH_3CH=O$  is a common intermediate (although  $\cdot CH-OCH_3$  is also possible). Key evidence comes from inducing isomerization in each possible intermediate; excited  $\cdot CH_2CH_2O$  and  $\cdot C(OH)CH_3$  yield mainly  $CH_3CH=O$ ,  $\cdot CH_2OCH_2$  yields mainly oxirane, while  $\cdot CH-OCH_3$  shows only dissociation. The relative energy barriers inferred from these data are shown in Fig. 4, with absolute values estimated from thermochemical and theoretical data (69, 70).

A similar recent study has predicted the energy surface for  $CH_3SOH$ ,  $\cdot CH_2^+SHOH$ ,  $CH_3SO\cdot$ , and  $\cdot CH_2SOH$ . Sulfenic acids are key intermediates in double-bond introduction using sulfoxide pyrolysis and in the biological and photochemical decomposition of  $CH_3SH$  and  $CH_3SSCH_3$  (71). The NRMS technique should thus provide new insights for many basic chemical reactions involving intermediates that are highly reactive or unstable or both (72).

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