Highly reactive molecules: Examples for the interplay between theory and experiment

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Abstract - Matrix isolation in combination with quantum chemical calculations is the method of choice for the study of highly reactive molecules. Different methods (A - F) can be applied for the generation of the target molecules. Irradiation in a halogen-doped xenon matrix may be a fundamentally new method which can be important in those cases in which previous methods cannot be applied.

Cyclobutadiene **1**, cyclopropenylidene **2** and trimethylenemethane **3** are the parent molecules of three completely different families of conjugated hydrocarbons. Cyclobutadiene **1** is the first member of the series of cyclic conjugated hydrocarbons (Kekulé compounds); cyclopropenylidene **2**, of cyclic conjugated carbenes; trimethylenemethane **3**, of the non- Kekulé hydrocarbons.
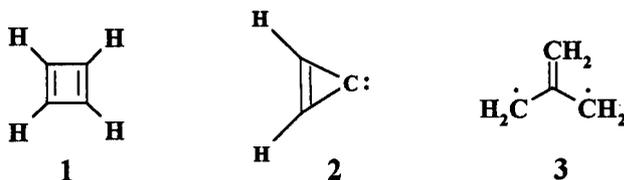
During our studies of cyclobutadiene **1** some years ago (1), we wondered whether matrix-isolation IR spectroscopy might be also a good tool for the study of cyclopropenylidene **2** and trimethylenemethane **3**. This is indeed the case, as shown in this paper. Our efforts to isolate and identify **2** and **3** resulted in the development of new techniques to generate the target molecules. At the same time this report demonstrates the importance of the interplay between theory and experiment in elucidating the structure and specific properties of the matrix-isolated species.

Cyclopropenylidenes

We were able to prepare cyclopropenylidene for the first time by high-vacuum flash pyrolysis (method A) of the polycyclic precursor **4** and to isolate it in an argon matrix (2). The identification was based on the excellent agreement of the experimental and calculated (3) IR frequencies. A better candidate for the preparation of **2** is perester **5** (4). The best route is the thermal HCl elimination from 3-chlorocyclopropene **6** (5,6)
Cyclopropenylidene **2,S**, which has a singlet ground state, can be photoisomerized in the matrix (method B) into triplet propargylene **7,T** (4) which on further irradiation yields singlet vinylidenecarbene **8,S**.
Originally propargylene **7,T** was identified by its electron spin resonance (ESR) spectrum by Skell (7). Surprisingly the experimental IR spectrum of **7,T** (8) did not show the expected triple bond stretching

vibration around 2000 cm^{-1}. Instead an absorbtion at 1620 cm^{-1} could be detected. This pointed out that triplet propargylene is a C_3H_2 isomer with unusual bonding (8). It was anticipated that 7 eventually has to be treated as a quasilinear molecule (8). Newer calculations (9) indicate that a C_2 structure (as shown in formula 7,T) with two identical CC bonds is an energy minimum and gives an acceptable agreement between the calculated and experimental spectrum.
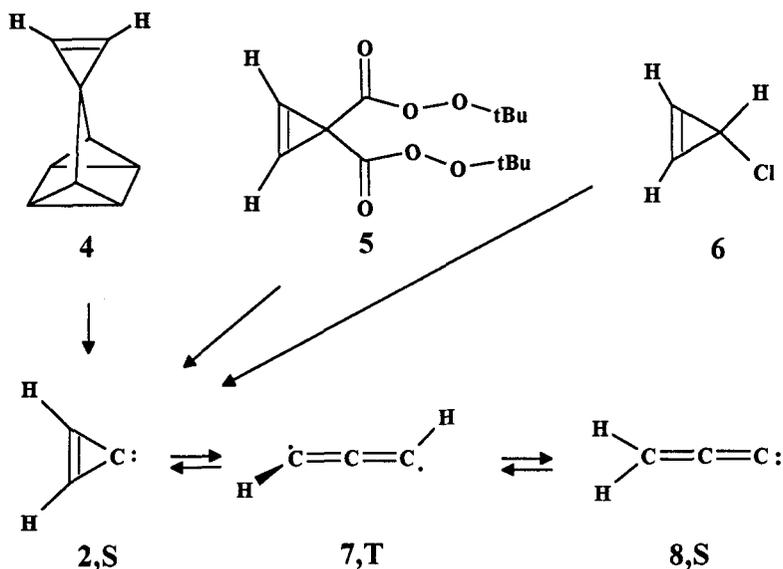
It is known that a halogen atom at the carbenic center stabilizes the singlet state by π-electron donation. So it might be expected that halogen-substituted propargylenes could have a singlet rather than a triplet ground state and they should show "normal" (acetylene-type) IR spectra.
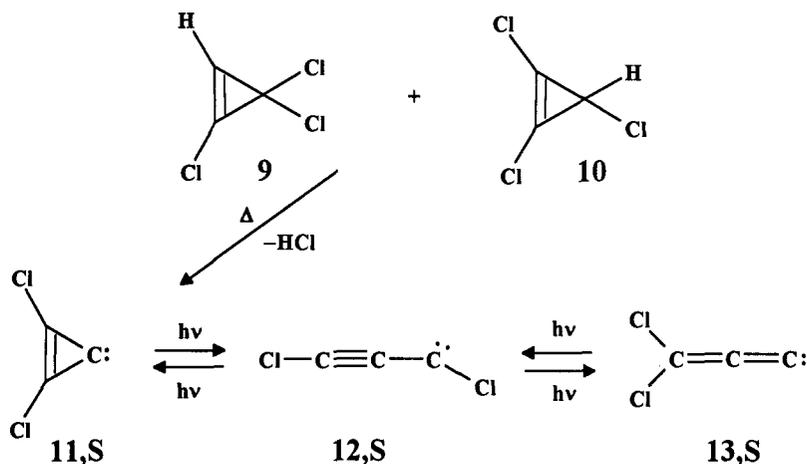
To test this prediction, matrix-isolated mono- and dichlorocyclopropenylidene were generated by high-vacuum flash pyrolysis of the corresponding bi- and trichlorocyclopropenes. By subsequent photolysis they have been isomerized to the corresponding vinylidenecarbenes and propargylenes (5). All these carbenes, for example 11, 12 and 13, (found by pyrolysis of 9 / 10) have singlet electronic ground states.

In contrast to the unsubstituted triplet propargylene, the experimental IR spectrum of dichloro derivative **12,S** has a structure with a "fixed" CC triple and CC single bond, again in accordance with the calculated spectrum.
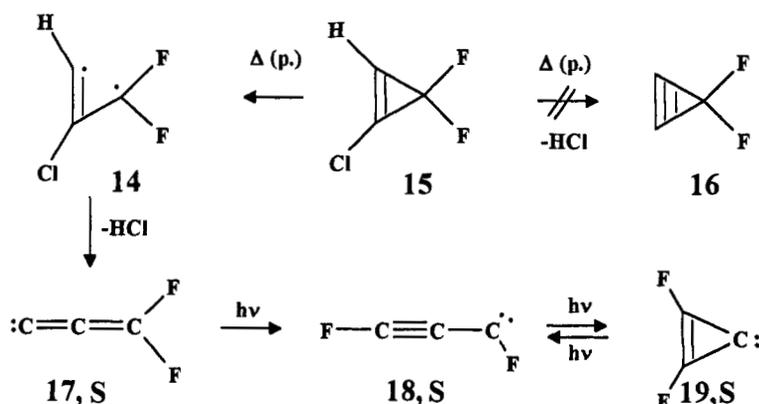
The difluoro derivatives **17**, **18** and **19** have also been calculated (10) to have singlet ground states. Cyclopropene **15** is not the ideal candidate for a HCl elimination, since this reaction should lead to the highly strained cyclopropyne **16**. Therefore it is no surprise that the "classical" pyrolysis (method A) of **15** gives only traces of vinylidenecarbene **17** (probably via diradical **14**). A reasonable amount of **17** could only be generated by underlined pulsed flash pyrolysis (method C) of **15** (11). On photolysis **17** is isomerized to propargylene **18** and finally to difluorocyclopropenylidene **19**. The identification of **17**, **18** and **19** could easily be achieved by comparison of the calculated (10) with the experimental (11) IR spectra.

Silacyclopropenylidene, Silacyclopropyne

Pulsed flash pyrolysis in combination with matrix isolation (method C) can also be used for the isolation of the sila analogues of **2**, **7** and **8**. According to calculations (12) 1-silacyclopropenylidene **24** is expected to be the most stable C_2H_2Si isomer (13). Indeed, when gaseous mixtures of disilane **21** and argon were subjected to pulsed flash pyrolysis and the products condensed onto the matrix window at 10 K, apart from the bands for trimethylsilane **23** those of another compound could be detected (14). This substance has been identified as **24**, even though the structure of reactant **21** suggests formation of ethynylsilylene **25**. This isomer **25** is formed upon irradiation (313 nm) of matrix-isolated **24**. The broad UV/Vis absorption of **25** also allows the photoisomerisation of **25** into **26** (14).
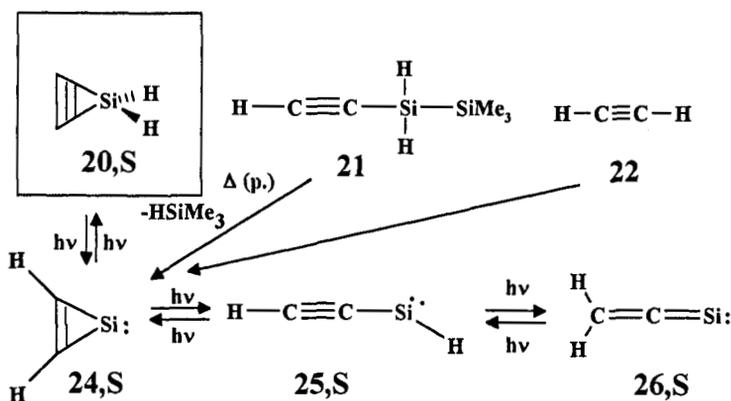
If **24** is irradiated with light of wavelength λ = 254 nm besides **25** another C_2H_2Si isomer is formed (14). Most surprisingly this new compound turned out to be 1-silacyclopropyne **20** (14,15). Because of some inconsistencies in the comparison between the calculated and experimental IR spectrum the final proof for the structure of **20** was only possible by the study of the ^{13}C isotopomer of **20** (15).

Whereas 1-silacyclopropenylidene **24** - the same is true for cyclopropenylidene **2,5** - can be described by a Lewis structure with a delocalized three-center π-bond orbital, 1-silacyclopropyne **20** is characterized by a localized π-bond orbital and an almost non-bonding CC-σ orbital (15). The formal triple bond drawn in formula **20** *in reality does not exist*. Silacyclopropyne is probably the most strained ring compound ever prepared (the calculated ring strain energy is roughly 100 kcal /mol, i. e. 33 kcal /mol per ring bond).

In conclusion of this chapter it should be mentioned, that 1-silacyclopropenylidene **24** is also formed when atomic silicon - generated by thermal evaporation - is treated with acetylene in an argon matrix (method D) (16). On the other hand 1-silacyclopropene, also a long sought-after compound, can be synthesized by pyrolysis of 1,1,1-trimethyl-2-vinyldisilane (triple bond in **21** replaced by a vinylgroup) (17).

Trimethylenemethane

Compound **3** was first prepared by Dowd (18) upon photolysis of 4-methylenedihydropyrazole **27** and later of 3-methylencyclobutanone **28** in an organic matrix at liquid nitrogen temperature. Its existence was proved by ESR spectroscopy (18). Our previous attempts (19) to isolate **3** in an argon matrix gave the following results: Irradiation of **27** in argon at 10K gave a well resolved ESR spectrum of **3**, but in the IR spectrum only the bands of methylenecyclopropane were recognizable.
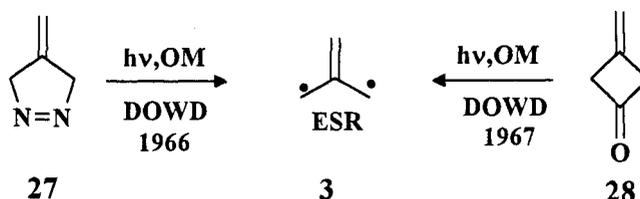
Despite these diappointing results we recently reopened our investigations, and our efforts have been rewarded (20). To make a long story short: We found that methylenecyclopropane **29** opens to trimethylenemethane **3** upon irradiation in a halogen-doped xenon matrix at 10 K (method E), but not in an argon matrix (20,21). The identification of trimethylenemethane **3** formed is based primarily on the comparison of the measured with the calculated (20-22) IR spectrum.
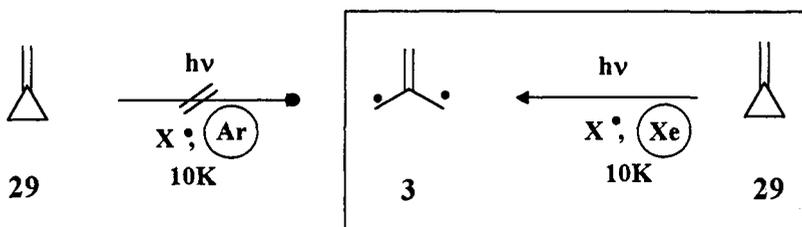
How does one explain the photoexcitation of **29**, a compound that does not absorb in the UV range? We assume that the halogen atoms (I⁺, Br⁺ or Cl⁺) form exciplexes **30** with xenon when irradiated. These exciplexes represent a delocalized hole in the xenon valence band (23). They can either relax to the more

stable exciplexes **31** (23) or can be trapped to the localized charge-transfer complexes **32**. The energy stored in the charge separation of the cation radical and halogen anion is released instantaniously on neutralization and is sufficient for the bond cleavage in the substrate molecule. For neutral **29** the barrier to overcome is 47 kcal / mol (24), for the radical cation of **29** the calculated barrier is 15.7 kcal / mol (25).

The same procedure (method E) also works in the case of cyclopropane (26) and cyclobutane (27). Again ring opening (**33** → **34** → **35** or **36** → **37** → **38** + **39**) is observed upon irradiation in a halogen-doped xenon matrix.

Cyclobutane can not only be cleaved (mainly into ethene **38** and 1-butene **39**) in the presence of a bromine atom via an exciplex of type **32**, but also upon irradiation with a KrF-laser ($\lambda = 248$ nm) at 10 K in absence of the halogen (method F) . The excitation of the non-doped xenon matrix with 248 nm-light demands a two photon process in order to form the "free" exciton Xe_n^*, which now functions as the energy carrier.

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