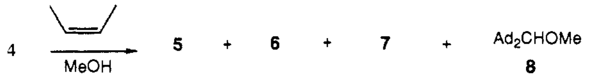
found from triplet reactions with hydrocarbons.[16] Similarly, sensitivity to oxygen is a well-known triplet trait.[15] Thus **4** becomes the first alkylcarbene to react as a triplet in solution. One may legitimately wonder why. Triplets are favored by wide central angles. Thus triplet methylene has an angle of 137° and the singlet only 103°.[9] Perhaps triplet **4** is exceptionally favored relative to the singlet state. In addition, singlet reactivity, which requires formation of two bonds will be disfavored relative to triplet reactivity which initially permits but one bond to form.[17] The wide angle of **4** and steric requirements of the adamantyl groups would surely favor a process requiring only one bond to form.

The singlet state of diphenylcarbene can be detected by characteristic reactions. This is also the case for **4**. Irradiation of diadamantyl diazomethane in *cis*-2-butene doped with methanol led to **5** and a product attributed to singlet **4**, diadamantylmethyl methyl ether, **8**. As little as 0.25% of the powerful singlet trap methanol led to a relative yield of 77% **8**. Diadamantylmethane (21%) and adducts (2%) were still formed. An analysis of the relative ratios of these products with varying concentrations of methanol leads to the tentative conclusion that **7** and **8** are products from the singlet carbene.



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Biomolecules in the Gas Phase.
1. Multiphoton-Ionization Mass Spectrometry of Native Chlorophylls

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We present here the results of a new technique by which it is possible to vaporize large, thermally unstable biomolecules, like native chlorophylls, into a molecular beam and subsequently study them by mass spectrometry. The chlorophylls have been obtained by methanolic extraction of the cyano-bacterium *Spirulina geitlerie*[1] and are investigated without further purification.

The laser vaporization in the first stage of our instrument is analyzed by multiphoton ionization (MPI) mass spectra obtained from the reflectron-time-of-flight mass spectrometer (RETOF-MS) in a second stage. This separation of the vaporizing and ionizing process is one special feature of our technique, yielding intense signals of pure intact molecular ions as opposed to all other previous vaporization techniques.[2] A second feature is the injection of the vaporized neutral molecules into a supersonic beam of a carrier gas which leads to intensive cooling of those molecules. This cooling provides small kinetic energy distributions and thus high mass resolutions in time-of-flight mass spectrometers. For conventional vaporization of ions from a solid surface, broad kinetic energy distributions are a fundamental problem for TOF mass spectrometers, even for energy-correcting RETOF mass spectrometers.

Most bimolecules have only a minimal vapor pressure or alternatively decompose if heated to attain an appreciable vapor pressure. Different approaches have been made to form supersonic beams with large molecules.[4] Recently two new adoptions have been published. One method[5] is a combination of the thermospray method[6] with the formation of a supersonic jet. The other method[7] uses laser desorption from a solid sample into the supersonic jet.

In our method a low-power CO_2 laser is focused on a probe tip, mounted just before the jet generating valve, thus, producing a mixture of the carrier gas and vaporized molecules. The supersonic beam is then introduced into the ion source of our RETOF instrument.[8] It should be noted that in our experimental setup only neutrals but no charged particles can enter the ion source. The MPI spectrum is produced with an eximer pumped frequency doubled dye laser running at a wavelength of 2750 Å. The mass spectrum is recorded with a transient recorder and is an average of 10 laser shots. The RETOF is running in a medium-resolution mode, even then yielding a resolution of 2900.

Intact chlorophylls have been previously investigated by several different methods.[9-12] In all these techniques vaporization and ionization are a combined process. Due to this simultaneous process the resulting mass spectra give not only the pure molecular ions but also quasi-molecular adduct ions formed either in the vaporization step or in the matrix on the sample holder. These so formed cluster ions often interfere in the peak pattern of the pure molecular ion, thus complicating the interpretation of the mass spectra. Sometimes molecular ions are not formed at all.

Multiphoton ionization has been proven to be a soft ionization method.[13] Depending on the laser power, it is possible to obtain all ranges of decomposition from only molecular ions to total fragmentation, thus giving all possible information with only one method. In Figure 1 the resulting mass spectrum is shown, demonstrating very clearly the softness of the MPI-process. This proves unequivocally not only that native chlorophyll *a* can be soft-ionized but more importantly that the intact chlorophyll *a* has survived the vaporization process and is present in a molecular beam. The ions in the high-mass region are extraordinary intense and very little fragmentation occurs. In this region three different compounds can be identified. The signal group at mass 892

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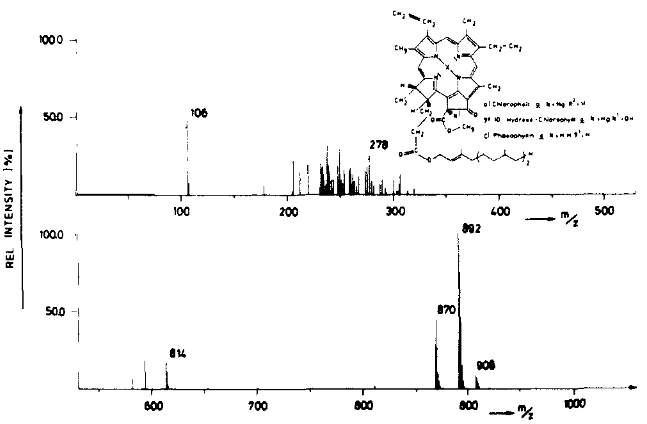

Figure 1. Laser desorption multiphoton-ionization mass spectrum of chlorophyll *a* from *Spirulina geitlerie*.

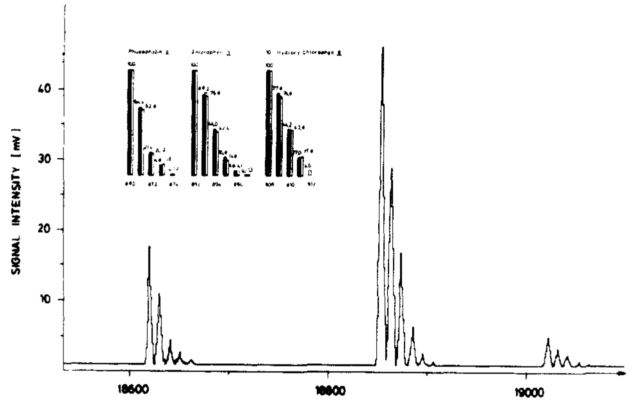

Figure 2. Raw data between data points 18532 and 19100, sampled with 10 ns per point. Insert upper left: comparison of calculated and measured peak pattern for the molecular ions from *Spirulina geitlerie*. Shaded area: calculated values.

belongs to the molecular ion of chlorophyll *a*, being also the base peak of the spectrum. The group at *m/z* 908 is assigned to the molecular ion of 10-hydroxychlorophyll *a*, which is an oxidation product formed during the extraction procedure.[14] The molecular ion of phaeophytin *a* is found at *m/z* 870. The replacement of the magnesium might occur either during the workup procedure or during the vaporization. The main fragmentation, the loss of the phytyl chain, leads to the signal at *m/z* 614. No cleavage reaction of the macrocycle nor loss of additional side groups of the macrocycle is observed.

Figure 2 shows the raw data of the high-mass region with the three different molecular ions. All isotopic peaks are clearly resolved and give the possibility to prove the identity of the molecular ions because of their isotopic distribution. The insert in Figure 2 shows the calculated isotopic distribution compared to the measured peak pattern of the molecular ions. The very good agreement between the two sets of data demonstrates again the softness of the vaporization process, showing that no hydrogen transfer or abstraction occurs during heating. This is unique for our method in contrast to all other vaporization methods.

This first results with this new method of vaporization in combination with multiphoton-ionization mass spectrometry point to new possibilities for the investigation of large thermally unstable molecules.

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Cation Radical Chain Cyclopropanation

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The pioneering discovery of the [2 + 1] olefin cyclodimerization reaction,[1] followed by the development of cation radical cycloadditions of dienes to triplet oxygen,[2] and the emergence of the cation radical Diels–Alder[3–5] reaction have now clearly established cycloaddition as an intrinsically preferred reaction mode of organic π cation radicals. Extended basis set ab initio SCF MO theoretical reaction path calculations[6,7] suggest that such reactions are activationless, with respect to potential energy in the gas phase, and experimental measurements confirm that even in solution the activation energy for the cycloaddition step is typically only 0–5 kcal at most[8] (compared to 62.5 and 32.4 kcal for the corresponding [2 + 2] and neutral Diels–Alder reactions.).[9,10] Despite such phenomenal rate enhancements, many of these reactions are quite reliably suprafacially stereospecific and typically exhibit enhanced stereoselectivities relative to corresponding neutral reactions.[5,11] Since cycloadditions play an especially powerful role in organic synthesis, further classes of hole-catalyzed/initiated cycloaddition reactions are being sought. The purpose of the present paper is to report the observation of facile, hole-catalyzed *cyclopropanation* of a variety of conjugated dienes, styrenes, and electron-rich alkenes using ethyl diazoacetate and a triarylaminium salt catalyst/initiator of appropriate oxidation potential.

Previous work has established the ability of aminium salts (and other hole catalyst/initiator systems) to generate small concentrations of chain-carrying cation radicals from ionizable substrates such as conjugated dienes, styrenes, and electron-rich alkenes. The cycloadditions of these cation radicals to neutral ethenic and dienic systems respectively engenders cyclobutanation and Diels–Alder cycloaddition. It was anticipated that addition of these same classes of chain-carrying cation radicals to diazo compounds would yield either pyrazolines, via 1,3-dipolar cycloaddition, or cyclopropanes, via cheleotropic carbene transfer with simultaneous or stepwise loss of dinitrogen. In fact, exclusive and efficient cyclopropanation has now been established.

Ethyl diazoacetate (**1**) was selected as the diazo component primarily because it was expected that the carbethoxy substituent would minimize competing ionization of the diazo component. This component was initially paired with several readily ionizable π components [*trans*-anethole (**2**), 1,1′-dicyclopentenyl (**3**), and 2,5-dimethyl-2,4-hexadiene (**4**); Scheme I].[12] In order to suppress the cyclodimerizations of **2–4**, reactions were carried out by using a 5:1 ratio of **1**/**2–4** (1.0 M in **1**) in dichloromethane solvent at 0 °C. The reactions were initiated by addition, over a 5-min period, of 10 mol % of tris(4-bromophenyl)aminimum hexachloroantimonate (**5**) relative to **2–4**, in ca. one-third of the solvent.

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[12] The oxidation potentials of **2** and **3** in acetonitrile vs. SCE are 1.11 and 1.30 V, respectively, compared to 1.05 V for tris(*p*-bromophenyl)amine.

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