

Review Commentary

Studies of reactive intermediates using matrix and gas-phase techniques

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ABSTRACT: In the direct investigation of reactive intermediates it is particularly valuable to use a combination of several spectroscopic techniques. This commentary highlights recent examples, using primarily flash vacuum thermolysis for the generation of the intermediates, and matrix IR spectroscopy in conjunction with gas-phase mass spectrometric methods for their identification. The examples include nitrile imines, nitrile ylides, nitrile sulfides and selenides, dinitrogen sulfide and several novel cumulenes ($X=C=C=Y$, $RN=C=C=X$). © 1998 John Wiley & Sons, Ltd.

KEYWORDS: 1,3-dipoles; cumulenes; infrared spectroscopy; mass spectrometry; flash vacuum thermolysis

INTRODUCTION

When writing a short commentary like this, it will be easy to offend numerous researchers whose work will not be mentioned; therefore, we immediately apologize for presenting a highly personal view of the very diverse area of research into reactive intermediates. We are focusing here on some intermediates partaking in important classes of organic chemical transformations, namely the nitrilium betaines (important in 1,3-dipolar cycloaddition reactions) and extended cumulenes (highly reactive ketene analogs). Although flavored by our personal interests, these examples illustrate what is currently achievable using a combination of (tandem) mass spectrometry and matrix isolation infrared spectroscopy.

DISCUSSION

Generation and identification of reactive intermediates

Many methods are available for the generation of the reactive species of interest. Some of the most common are thermolysis [flash vacuum thermolysis (FVT)], photolysis (static or time resolved) [laser flash photolysis (LFP)], microwave discharge, x-ray irradiation (ioniza-

tion) and bombardment with atoms, ions, nuclei, electrons, etc. In our group we are mainly concerned with FVT and matrix photolysis.

Although it is in principle a simple matter to generate reactive intermediates, the main task is to do so as selectively as possible and to identify the species formed securely. The selectivity depends on the choice of precursor. It can be advantageous to use one or more different precursors of the same intermediate. In FVT work, the success or otherwise depends on contact times, pressure, flight distance, etc. We use a short quartz tube (5–10 mm) installed in the high vacuum of the mass spectrometer or matrix isolation equipment, with only a few centimeters flight distance to the ion source or cold target, respectively.¹ It should be mentioned that the alternative technique of pulsed pyrolysis² offers a reduced contact time and the advantage of rapid cooling of the products in a free jet expansion; it often results in appreciably improved resolution in matrix isolation IR spectra, but also requires sufficient volatility of the sample to achieve a usable concentration of the compound seeded in argon, at an overall stagnation pressure of a few atmospheres. The work described in this paper was carried out using the FVT technique.

The reader is referred to more detailed texts and reviews for a comprehensive treatment of the matrix isolation technique and the spectroscopic methods used.³ Theoretical calculations [*ab initio* and density functional theory (DFT)] are becoming increasingly important as an adjunct to spectroscopy, so that it is now almost inconceivable to report the spectroscopic identification of a novel reactive species without theoretical support. The isolation of a derivative (trapping product, dimer,

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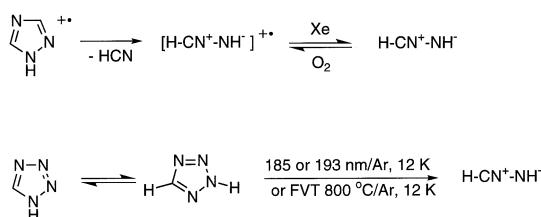
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etc.) remains a highly desirable means of chemical identification.

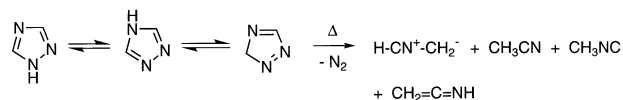
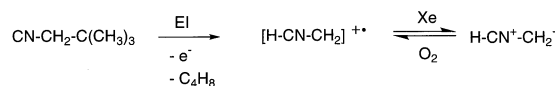
Just as it can be hazardous to rely on a single precursor, it can be dangerous to rely on just one type of spectroscopy for the identification of a reactive intermediate. In our laboratories we tend to use a highly successful combination of matrix infrared and gas-phase mass spectrometric methods, whenever possible together with chemical trapping experiments and theoretical calculations of spectra, energies and structures. In particular, the use of modern tandem mass spectrometric methods such as collisional activation (CA), MSⁿ and neutralization–reionization (NR) gives valuable and detailed information and permits very precise monitoring of FVT reactions. Such combinations of techniques are virtually indispensable when studying reactions with cascades of different reactive intermediates. Where relevant, matrix UV–visible, ESR and photoelectron spectroscopy (PES) are also employed.

1,3-Dipoles

Nitrile imines, R—C≡N⁺—N[−]—R', are well known reactive intermediates in cycloaddition chemistry, normally requiring matrix isolation for their direct IR and UV spectroscopic identification. The gas-phase mass and photoelectron spectra have also been reported.⁴ However, by using proper (large) substituents, nitrile imines can become isolable at ordinary temperatures. This work has been reviewed recently.⁵ Similarly, nitrile ylides, R'—C≡N⁺—C[−]R₂, are usually reactive intermediates, amenable to low-temperature spectroscopy,⁶ but stable derivatives can be obtained by using steric and electronic stabilization.⁷ Recently, the unsubstituted formonitrile imine has been observed by both neutralization–reionization mass spectrometry⁸ and matrix IR spectroscopy,⁹ using different precursors for the two observational methods (Scheme 1). The matrix photochemical conversion of formonitrile imine to diazomethane, carbodiimide, cyanamide, and the nitrene complex H—N^{••}—C≡N has been described.⁹ High-level *ab initio* calculations indicate that an allenic (bent and non-planar) structure is preferred for nitrile imine.¹⁰ This has been confirmed by x-ray structure analysis of several substituted derivatives⁵ and by low-temperature NMR spectroscopy in solution. The bent and non-planar



Scheme 1.



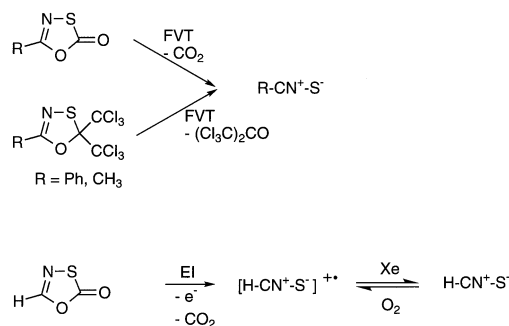
Scheme 2.

structure renders the nitrile imine chiral, as manifested in an enantioselective cycloaddition reaction in solution.¹¹ The relative energies of the various CH₂N₂ isomers have also been evaluated by thorough *ab initio* calculations.^{5,10,12}

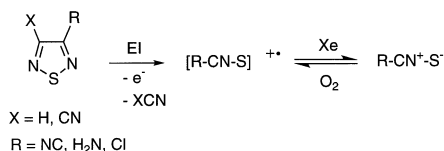
The unsubstituted formonitrile ylide, H—C≡N⁺—CH₂[−], has likewise been detected by the NRMS technique and by matrix IR spectroscopy (Scheme 2).¹³ In the latter case it is best generated by nitrogen elimination from the thermodynamically least stable 3*H* tautomer of 1,2,4-triazole, which is itself generated by FVT of the triazole. The interrelationships of formonitrile ylide, vinylnitrene, azirine, ketenimine, acetonitrile and isocyanomethane have been discussed.^{13b}

Of the remaining nitrilium betaines, the nitrile oxides, R—C≡N⁺—O[−], are sometimes stable, albeit highly reactive, compounds (the mesityl derivative being isolable),¹⁴ but many have the character of reactive intermediates.¹⁵ They can often be generated by FVT of the dimers, furoxans, or α -chlorooximes. The thoroughly investigated cyanogen oxide, NCCNO, is an example.¹⁵ The parent compound, fulminic acid, HCNO, is most conveniently prepared by FVT of 3-methyl- or -aryl-4-oximinisoxazol-5(4*H*)-one.¹⁶

The nitrile sulfides, R—C≡N⁺—S[−] are short-lived intermediates, often detected by low-temperature UV but seldom by matrix IR spectroscopy.^{17,18} PhCNS and MeCNS, generated by FVT of the appropriate oxathiazolones and 5,5-bis(trichloromethyl)oxathiazoles (Scheme 3), have been identified by both mass spectrometry (NRMS) and matrix IR spectroscopy and differentiated from the isothiocyanate (RNCS) and thiocyanate (RSCN) isomers.¹⁹ The simplest nitrile sulfide, H—



Scheme 3.



Scheme 4.

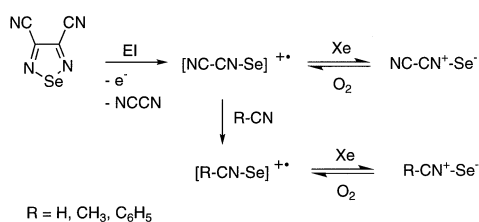
$\text{C}\equiv\text{N}^+-\text{S}^-$ (Scheme 3) was also identified by NRMS, but so far it has not been detected securely by any other spectroscopic method. A variety of new nitrile sulfides, RCNS ($\text{R} = \text{NC, H}_2\text{N, halogen}$) have been generated from 4,5-disubstituted 1,2,5-thiadiazoles and identified by CA and NR mass spectrometry (Scheme 4).²⁰ Recently, a new method of generating nitrile sulfides in the gas phase, viz. sulfuration of nitriles using CS_3^+ cation radicals in a mass spectrometer has been reported.^{20,21}



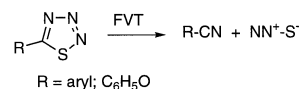
The CA and NR mass spectra of these species, including the unsubstituted HCNS, are identical with those obtained using the more conventional methods described in Schemes 3 and 4.

Nitrile selenides, $\text{R}-\text{C}\equiv\text{N}^+-\text{Se}^-$, can be generated in the same manner as nitrile sulfides from selenadiazoles (Scheme 5) and identified by the CA and NR mass spectra.²² There is also evidence for matrix isolation/IR spectroscopy of the phenyl derivative in particular (PhCNSe, 2200 cm^{-1} ; N_2 , 20 K).²³ Most interestingly, selenium atom transfer to other nitriles is possible, and HCNSe, CH_3CNSe and PhCNSe were generated in this manner and identified by their CAMS and NRMS fragmentation patterns.²²

The diazonium analogs of the nitrilium betaines are the azides, diazo compounds, nitrous oxide (N_2O) and dinitrogen sulfide (N_2S). The first three are essentially stable compounds whereas N_2S is a highly unstable intermediate. Nevertheless, it can be generated very efficiently by FVT of several 1,2,3,4-thiadiazoles, along with the requisite nitrile or cyanate ($\text{R}-\text{O}-\text{CN}$) (Scheme 6). This linear NNS molecule has been thoroughly characterized by means of its matrix and gas-phase IR spectra,²⁴⁻²⁶ its mass spectrum²⁴ and its photoelectron spectrum.²⁷ It decomposes in the gas phase to S_2 and N_2 .^{18,24,27} Advanced *ab initio* calculations of its structure and spectra have been reported.^{25,28} N_2S has



Scheme 5.

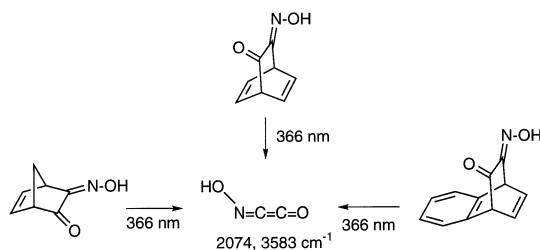


Scheme 6.

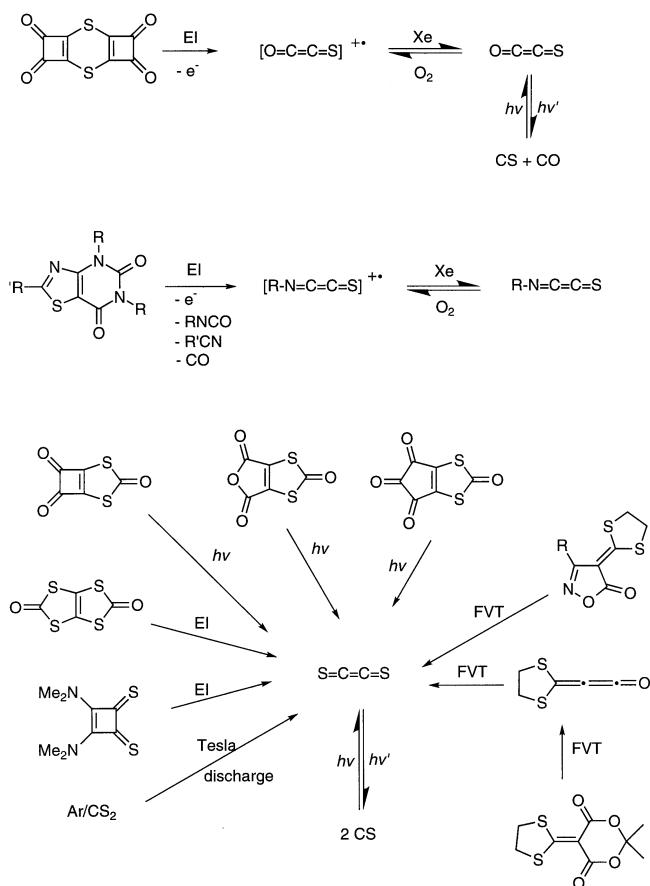
also been produced, together with NS, NS_2 (two isomers) and N SSS by microwave discharge of an argon–nitrogen–sulfur vapor mixture,²⁹ and it has been suggested as a decomposition product, together with NCS^- , of the thiatriazolethione anion in a flowing afterglow experiment.³⁰ Dinitrogen selenide is unknown, and it can be expected to be a rather ephemeral molecule.

Cumulenes

In this section we will be concerned primarily with the oxides of carbon and their analogs, $\text{X}=\text{C}_n=\text{Y}$ (X and $\text{Y} = \text{O, S, NR}$). In general, heterocumulenes with an odd number of cumulated atoms are more stable than the even-numbered ones. Thus, $\text{O}=\text{C}=\text{C}=\text{O}$ remains unknown, although its cation can be generated in a mass spectrometer.³¹ Similarly, the cation radicals of the monoimines, $\text{RN}=\text{C}=\text{C}=\text{O}^+$ ($\text{R} = \text{H}$ or CH_3) can be generated in the mass spectrometer but do not survive a neutralization experiment.³² However, the monoxime, $\text{HO}-\text{N}=\text{C}=\text{C}=\text{O}$, has been generated by matrix photolysis of several precursors (Scheme 7) and observed by IR spectroscopy (CCO stretch at 2074 cm^{-1}).³³ Photolysis at 290 nm caused fragmentation to CO and (mainly) isocyanic acid, HNC. Interestingly, an isomer of this monoxime, nitrosoketene, $\text{ON}-\text{CH}=\text{C}=\text{O}$, is reportedly formed on thermolysis of hydroximino-Meldrum's acid,³⁴ and its gas-phase IR (2146 cm^{-1} ; w) and chemical ionization ($[\text{M} + 1]^+ = 72\text{ u}$) mass spectrometric observation has recently been asserted, along with a lifetime of *ca* 4 h at 90°C and 10^{-4} Torr (1 Torr = 133.3 Pa).³⁵ Our own extensive experiments make us sceptical about this identification: although an ion with the correct composition (C_2HNO_2 , m/z 71) is observed in the electron ionization mass spectrum of hydroximino-Meldrum's acid, there is no evidence that the corresponding neutral species is formed on FVT, and all attempts at FVT/matrix



Scheme 7.



Scheme 8.

isolation/IR spectroscopy of nitrosoketene from this precursor were either negative or produced at best very weak signals in the ketene region.³⁶

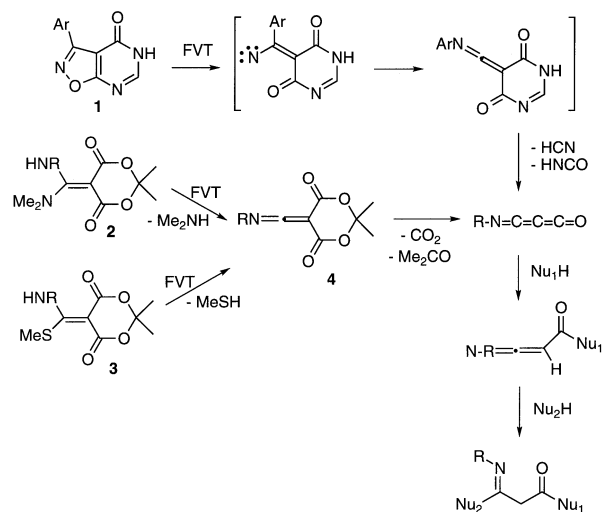
The monothione^{37a} O=C=C=S and the iminoethenethiones^{37b} RN=C=C=S (R = CH₃ or H) have been identified in the gas phase by NRMS (Scheme 8). HN=C=C=S isomerizes to thioformyl cyanide, HCS—CN, on FVT.^{37b} The matrix synthesis of O=C=C=S by photochemical combination of CO and CS ($\lambda = 254$ nm; reversed at 313 nm; Ar, 10 K) was reported recently.^{37c} *Ab initio* calculations and the isotopic shift observed in the IR spectrum when using ¹³C-labeled CO indicate a linear triplet ground state molecule (Scheme 8).

Ethenedithione, S=C=C=S, has been generated from a variety of precursors using FVT, matrix photolysis and mass spectrometric fragmentation methods (Scheme 8)^{38–40} and by a Tesla coil discharge of an Ar-CS₂ mixture (generating CS and C₃S₂ predominantly).⁴¹ SCCS has been thoroughly identified by NRMS and by argon matrix IR and UV spectroscopy.^{38–41} Extensive theoretical calculations indicate that the molecule has a singlet ground state (but not far below the triplet)⁴² although a triplet ground state was first predicted.⁴³ Attempts to observe an ESR spectrum of the triplet have been unsuccessful.³⁹ SCCS survives generation by FVT at

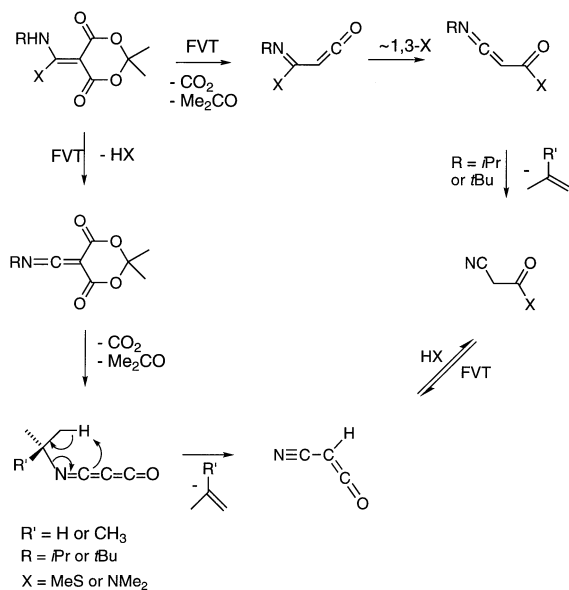
temperatures as high as 1000 °C as long as a high vacuum and short contact times (millisecond range) are used.⁴⁰ When the collision number is increased by using a pressure higher than 0.01 Torr, the molecule vanishes, and CS is formed in its place.⁴⁰ Accordingly, a gas-phase IR spectrum has so far not been obtainable. The isolated, neat SCCS is extremely reactive, polymerizing on warming above 60 K.^{39,40} SCCS is reversibly cleaved to two CS molecules on photolysis in the matrix (dissociation at >320 nm; association at 254 nm).^{39–41}

The groups of Maier and Schwarz in particular have generated a large number of other carbon oxides, sulfides and oxysulfides and investigated them by argon matrix IR and mass spectrometry (NRMS), respectively.^{44,45} Thus, all the species C_nO ($n = 1–4$), C_nO₂ ($n = 1$ and $3–5$), C_nOS ($n = 1–5$), C_nS₂ ($n = 1–5$) and C_nS ($n = 1–4$) are now known, and C₇O₂ and C₆O have also been made.⁴⁶ Particularly noteworthy is the stability of C₅O₂ (O=C=C=C=C=O) in solution at room temperature, the sulfur analog, C₅S₂, is stable in solution below –30 °C.⁴⁴

Our group has been engaged in detailed studies of the characterization and chemistry of the iminopropadienones, RN=C=C=C=O, in recent years. Although these compounds can be regarded as derivatives of carbon suboxide, C₃O₂, they are for the most part less stable. The bisimine and thione derivatives, RN=C=C=C=X (X = NR' or S) are even more elusive, having the character of reactive intermediates.^{47,48} The iminopropadienones are generated by FVT of suitably substituted isoxazolopyrimidinones (**1**) (for aryl-NC₃O) or Meldrum's acid derivatives (for aryl- and alkyl-NC₃O) (Scheme 9), whereby the dimethylaminomethylene-Meldrum's acid precursors (**2**) are preferred as they tend to give the highest yields. These fragmentation reactions have been monitored by NRMS and matrix IR methods, permitting the observation of the ketenimine intermediates **4**.⁴⁹ The fragmentation of **1** and **2** are very efficient



Scheme 9.



Scheme 10.

processes, giving high and synthetically useful yields of the iminopropadienones. The methylthio (**3**) and methoxy analogs also generate RNC_3O , but now in competition with the formation of imidoalkenes and oxoketenimines, themselves detectable by MS and/or IR spectroscopy (Scheme 10).⁵⁰ The RNC_3O cumulenes are characterized by intense absorptions around 2240 cm^{-1} , accompanied by very weak absorptions near 2140 cm^{-1} .^{49c} The aryl derivatives are stable enough for investigation of their chemical reactions at temperatures between -60°C and ambient. They undergo nucleophilic addition reactions preferentially, first to the 'ketene' carbon atom and then, more slowly, to the 'ketenimine' carbon atom. Recently, the mesityl derivative has been isolated at room temperature, and its chemistry is under active investigation in our group.⁵¹

In contrast, the alkyl derivatives RNC_3O are unstable. $\text{CH}_3\text{NC}_3\text{O}$ has been investigated by matrix isolation IR spectroscopy, mass spectrometry and nucleophilic trapping reactions.^{49ab,51,52} The isopropyl and *tert*-butyl derivatives can be detected by matrix IR and mass spectrometry but undergo a very facile retro-ene-type fragmentation resulting in an efficient synthesis of cyanoketene, itself a highly reactive molecule (Scheme 10).⁵³ All the species shown in Scheme 10 are detectable. The reactions described here, involving cascades of different ketene, ketenimine and cumulene intermediates, could hardly have been elucidated securely using just one spectroscopic method and thus illustrate the convergent use of IR and MS techniques.

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