The Matrix Isolation Technique and Its Application to Organic Chemistry

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1 Introduction

As the understanding of organic reaction mechanisms progressed, it was discovered that very many reactions proceed by way of short-lived intermediates. Such species as carbenium ions, carbanions, radicals, carbenes, nitrenes, and arynes are now familiar to all organic chemists; but these are only a few members of a large and continually growing class of recognized transient molecules. In many reactions, the existence of intermediates has been inferred from, for example, reaction rates, product distributions, the fates of isotopic labels, and medium effects. Only in relatively few have the intermediates proved isolable or sufficiently long-lived to be observable by ordinary spectroscopy.

However convincing inferences from rate data or products may be, the postulate of a reactive intermediate with a finite lifetime implies that it should be directly observable, and this is open to experimental test. Moreover, if information about the structure of an intermediate is sought, and not merely an answer to the question of its existence, then it becomes virtually essential to obtain spectra of the species concerned. Consequently, experimentalists have developed techniques that enable direct observations of transient species to be made. Most of these methods involve spectroscopy of one type or another, and each may be classified into one or other of the two following groups.

(*i*) *Rapid methods.* A number of methods exist in which the spectroscopic technique employed is fast enough to detect a transient species during its normal lifetime. Typical of these is flash photolysis. In this method, a substantial concentration of the transient is generated from a photosensitive precursor by an intense light-flash of short duration. The reaction is then monitored, commonly by u.v. or visible absorption spectroscopy. If a spectrograph is employed, a whole region of the spectrum may be examined at each flash. Alternatively, a spectrum of the transient may be built up point by point with multiple flashes. Obtaining vibrational spectra of complex molecules in this fashion, however, is scarcely realizable with current techniques. Flash photolysis and similar rapid methods do have some important advantages. In particular, they can yield data on the lifetimes of intermediates and can distinguish amongst intermediates which are formed sequentially or simultaneously.

(*ii*) *Slow methods.* An opposite approach is adopted with those techniques which we shall call slow methods. With these, a species that would normally have a short lifetime is generated in an environment conducive to its prolonged existence, thus permitting observation by ordinary spectroscopic means. The generation of stable carbenium ions in superacid media is one example of this type of method, and matrix isolation, the subject of this review, is another.

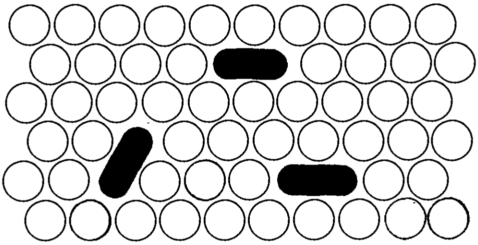

Figure 1 *Matrix Isolation. The inert, rigid host lattice (circles) isolates reactive species from each other and prevents reaction*

The principle of matrix isolation is illustrated in Figure 1. Reactive molecules are isolated within a rigid, inert host material, which inhibits diffusion of the reactive species in the matrix and thus prevents reaction. This basic idea has been utilized, though at first unwittingly, for nearly a century: the enhanced phosphorescence of certain organic molecules at low temperatures, first observed[1] in the 1880s and 1890s, relies, at least in part, on the suppression of diffusion of triplet quenchers such as molecular oxygen. Since about 1900, many studies have been made of species trapped in crystals, glasses, and ices.[2,3] The term 'matrix isolation' might justly be applied to all such studies, but recently the term has usually been confined to studies of species trapped in very inert hosts, typically the solidified noble gases or nitrogen, at extremely low temperatures (4—20 K). In this form, the technique was developed by Pimentel and first reported in 1954.[4]

Solid argon and nitrogen, taken as examples of matrix hosts, have three major advantages as materials for trapping intermediates. First they are very inert; so that even the most reactive species seldom react with them. Secondly, with careful preparation, optically clear matrices can be obtained, allowing good quality electronic spectra to be recorded. Thirdly, the host materials have no absorptions in the i.r. region between 200 and 10 000 cm^{-1}; so that complete i.r. spectra may also be recorded. This last property is crucial to the successful application of matrix isolation to organic molecules. Most matrix studies of reactive organic species have relied heavily on identifications made by interpreting the observed i.r. spectra.

The matrix isolation technique is now 25 years old and may be regarded as well-established. There are of course other reviews of various aspects of the

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[1] See ref. 2, Ch. 2.

[2] B. Meyer, 'Low Temperature Spectroscopy', Elsevier, New York, 1971.

[3] See, for example, O. L. Chapman, *Pure Appl. Chem.*, 1974, **40**, 511.

[4] E. Whittle, D. A. Dows, and G. C. Pimentel, *J. Chem. Phys.*, 1954, **22**, 1943.

subject,[5] including several complete books.[2,6] Nevertheless, the application of matrix isolation to any but the very simplest organic molecules is a relatively late development and other reviews have tended to concentrate on inorganic chemistry or more physical aspects of matrix isolation. In the 1970s this technique has been increasingly used in areas of general interest to organic chemists. It seems appropriate, therefore, to review its contribution to organic chemistry at this time. What follows is far from being an exhaustive catalogue of carbon-containing molecules that have been matrix-isolated. It is instead an attempt to illustrate the scope of matrix isolation as a tool for organic chemists, drawing upon those published results that, in the author's view, are the most complete or the most interesting.

2 Apparatus and Techniques

A. The Cold Cell and Preparation of Matrix Samples.—Figure 2 shows, in diagrammatic form, the essential features of a low-temperature cell suitable for matrix i.r. and u.v.–visible absorption studies. The main feature is a central window of CsBr or CsI which may be cooled to 4 K by means of a liquid-helium cryostat, or more conveniently to about 10 K by means of a commercially-available, closed-cycle helium refrigerator. Temperatures above the base temperature of the apparatus may be obtained by means of a small electric heater in thermal contact with the window. The central window is enclosed in a very-high-vacuum shroud, which has two external spectroscopic windows (CsBr or KBr), allowing the passage of both i.r. and u.v. beams for spectroscopy or photolysis. In addition, the vacuum shroud has an outlet port connected to a diffusion pump and one or more inlet ports for deposition of the sample on the cold window. Usually some provision is made to allow the central window to be rotated to face either the external windows or the inlet ports.

The cell depicted in Figure 2 can be designed so as to be small enough to fit comfortably into the sample compartments of most i.r. and u.v.–visible spectrometers. In a well-designed laboratory layout, the cell will be readily movable, during experiments, from one spectrometer to another and also to a location where photolysis may be carried out. With suitable modifications of design, cells may be adapted for use with e.s.r., Raman, or emission spectrometers, and the range of spectroscopic techniques used for matrix studies is growing continually.

[5] For example, (a) A. J. Downs and S. C. Peake, in 'Molecular Spectroscopy', ed. R. F. Barrow, D. A. Long, and D. J. Millen, (Specialist Periodical Reports), The Chemical Society, London, 1973, vol. 1, p. 523; (b) B. M. Chadwick, in 'Molecular Spectroscopy', ed. R. F. Barrow, D. A. Long, and D. J. Millen, (Specialist Periodical Reports), The Chemical Society, London, 1975, vol. 3, p. 281; (c) A. J. Barnes and H. E. Hallam, *Quart. Rev.*, 1969, **23**, 392; (d) J. J. Turner, *Angew. Chem. Internat. Edn.*, 1975, **14**, 304; (e) G. A. Ozin and A. Vander Voet, *Progr. Inorg. Chem.*, 1975, **19**, 105; (f) J. I. Goldanskii, *Ann. Rev. Phys. Chem.*, 1976, **27**, 85.

[6] (a) 'Vibrational Spectroscopy of Trapped Species', ed. H. E. Hallam, Wiley, London, 1973; (b) S. Cradock and A. J. Hinchcliffe, 'Matrix Isolation', Cambridge University Press, Cambridge, 1975.

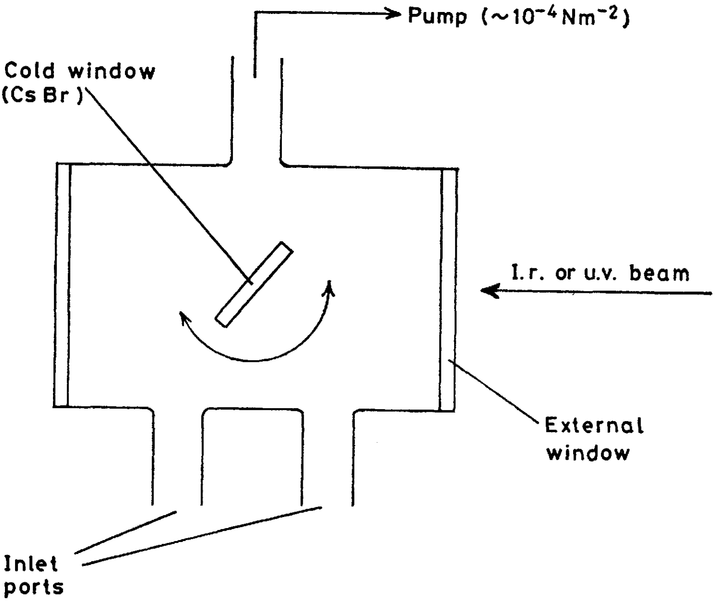

Figure 2 *Diagram of an i.r./u.v. cell for matrix isolation, showing the rotatable cold window enclosed in a glass or metal vacuum shroud*

Matrix samples of stable, volatile compounds are best made by first preparing a gas mixture of the compound and the matrix host. Host: guest matrix ratios (MR), measured manometrically, are typically 10^2—10^5. This gas mixture is then admitted, either as a slow stream or as small pulses, into the vacuum shroud, where it condenses as a solid on the cold window. When a compound is too involatile to be handled in this way, it may nevertheless be obtained in a matrix by direct sublimation from a heated tube connected to the vacuum shroud, with simultaneous deposition of the matrix host gas through another inlet port. In extreme cases, such as when metal atoms are required, a small furnace may be connected to an inlet port. When this sublimation technique is used, it is difficult to obtain a reliable estimate of the matrix ratio (MR). Quite large molecules, however, even porphins,[7] have been matrix-isolated in this manner.

In a review devoted primarily to chemistry in matrices, discussion of the apparatus must of necessity be confined to a few basics. The practical difficulties of cryostat design, refrigeration, and sample preparation, however, have been dealt with in detail by other authors.[2,6]

B. The Quality of Matrix Spectra.—Matrix studies of organic molecules have depended very largely on i.r. and, where appropriate, e.s.r. spectroscopy, to a

[7] J. J. Leonard and F. R. Longo, *J. Amer. Chem. Soc.*, 1973, **95**, 8506; *J. Phys. Chem.*, 1975, **79**, 62.

lesser extent on u.v.–visible spectroscopy, and, so far, almost negligibly on other forms of spectroscopy. It is generally recognized that electronic and e.s.r. spectra of matrix isolated species are not much perturbed from spectra of the same species in the gas phase, liquid solutions, or frozen organic glasses. The same cannot be true of i.r. spectra, though. Solution or neat liquid i.r. spectra often do not resemble very closely gas-phase i.r. spectra of the same compound, owing to loss of rotational fine structure and perturbations by molecular association in the liquid phase. Fortunately, non-polar matrix hosts such as Ar or N_2 do not usually perturb the positions or intensities of vibrational bands very much from gas-phase values. This fact may, of course, be demonstrated for volatile, stable molecules, but must be assumed for species capable of existing only within the matrix. Except for a few very small molecules, however, matrix isolation inhibits molecular rotation altogether. A matrix i.r. spectrum, therefore, is generally a series of sharp bands showing no rotational structure.

I.r. bands are often not so simple, however, in concentrated matrices, when molecular association becomes significant, or when matrix site-effects cause band-splitting. The former effect can be detected by varying the matrix ratio (MR); and the latter either by varying the matrix host material, which alters or eliminates the splitting of the bands, or by warming and re-cooling (annealing) the matrix, which may induce relaxation of the molecules in certain of the sites, thus changing the proportional intensities of the split bands.

The relative simplicity of matrix i.r. spectra and the sharpness of the bands are useful in two ways. Firstly, discrimination of individual species in mixtures is greatly facilitated; so much so that matrix isolation has been proposed as a method of quantitative analysis of gas mixtures.[8] Secondly, vibrational assignments and normal-co-ordinate analysis are easier than with gas-phase spectra. Recent applications of matrix isolation to the assignment of vibrational spectra include a methodical study of compounds containing the trifluoromethyl group,[9] assignments of nearly all 30 fundamental vibrations of fulvene,[10] a complete assignment for methyl nitrite,[11] and others.

An interesting feature of these studies is the observation of individual conformers. Thus for both methyl vinyl ketone [Scheme 1, (1a)$\rightleftharpoons$(1b)] and methyl propiolate [(2a)$\rightleftharpoons$(2b)] two conformers are observed in Ar matrices, and in each case interconversion of the conformers may be achieved by u.v. irradiation of the matrix.[12] Individual conformers have also been observed for but-1-ene,[13] acrylyl halides,[14] and alkyl thiols.[15]

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[8] M. M. Rochkind, *Analyt. Chem.*, 1967, **39**, 567; 1968, **40**, 762.

[9] (a) A. J. Barnes and J. Murto, *J.C.S. Faraday II*, 1972, **68**, 1642; (b) M. Perttilä, *Spectrochim. Acta*, 1976, **32A**, 1011; (c) J. Murto, A. Kivinen, K. Edelmann, and E. Hassinen, *Spectrochim. Acta*, 1975, **31A**, 479; (d) J. Korppi-Tommola, *Acta Chem. Scand.*, 1977, **31A**, 563, 568.

[10] P. J. Domaille, J. K. Kent, and M. F. O'Dwyer, *Austral. J. Chem.*, 1974, **27**, 2463.

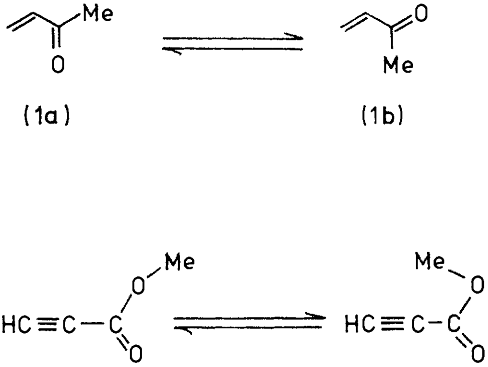
[11] J. F. Ogilvie, *J.C.S. Chem. Comm.*, 1973, 450.

[12] (a) A. Krantz, T. D. Golfarb, and C. Y. Lin, *J. Amer. Chem. Soc.*, 1972, **94**, 4022; (b) C. Y. Lin, A. Krantz, and T. D. Goldfarb, *J. Amer. Chem. Soc.*, 1972, **94**, 9282.

[13] A. J. Barnes and J. D. R. Howells, *J.C.S. Faraday II*, 1973, **69**, 532.

[14] (a) R. L. Redington and J. R. Kennedy, *Spectrochim. Acta*, 1974, **30A**, 2197; (b) R. L. Redington, *J. Chem. Phys.*, 1975, **62**, 4927.

[15] A. J. Barnes, H. E. Hallam, and J. D. R. Howells, *J.C.S. Faraday II*, 1972, **68**, 737.



(1a) (1b)

(2a) (2b)

Scheme 1

C. The Generation of Reactive Species.—Matrix isolation has undoubtedly been useful for spectroscopic studies of stable molecules and will continue to be so. Nevertheless, the technique is usually associated with, and was first developed for, the study of unstable species. In studies of this sort, the first problem is the generation of the unstable species in the matrix. Four general approaches are in common use.

(*i*) *Generation from stable precursors by irradiation.* The most frequently used method is u.v. irradiation of a photosensitive precursor either in the matrix or during deposition. Other forms of irradiation, for example i.r. lasers, proton beams, or γ-rays, find occasional application.

(*ii*) *External generation.* Unstable species may be generated in a gas flow by means of photolysis, pyrolysis, or a microwave discharge. Direct condensation of the reaction mixture on a cold window produces a matrix containing molecular fragments.

(*iii*) *Co-condensation of reactions.* Reactive species may in some cases be generated by condensing simultaneously two streams of gas, each containing one component of a reaction. A number of radicals have been isolated in matrices by co-condensation of alkyl halides with beams of alkali-metal atoms.

(*iv*) *Thermal reactions in the matrix.* Reactive species generated by one of the previous methods may react further, either with themselves or with other species present, to yield secondary products. Such reactions are achieved by warming the matrix sufficiently to allow diffusion.

Applications of each of these methods will be found in the remainder of this review. At this point, however, a summary of the general experimental approach to the identification of a reactive species is appropriate. In a typical experiment, irradiation of a precursor gives rise to a new set of absorptions (u.v., i.r., or e.s.r.). Subsequent manipulations, such as photolysis with a different wavelength or annealing the matrix, cause these absorptions to disappear again. Ideally a particular reactive species should be generated and made to vanish in several independent ways. It can then be claimed reasonably that absorptions which grow together and disappear together belong to the same species. Once the spectrum of the species has been identified, the identity of the species itself may be ascertained.

It will be apparent from the foregoing that conclusions drawn from single experiments need to be regarded circumspectly. Much painstaking work is usually necessary to establish the identity of an intermediate on the basis of matrix spectra alone. Indeed, even careful work has occasionally, if only temporarily, come to grief.

3 Neutral Organic Molecular Fragments in Matrices

A. Radicals.—The earliest matrix studies of organic radicals concentrated on the smallest molecules. The methyl radical was first generated in argon matrices by the reaction of CH_3I or CH_3Br with simultaneously condensed lithium atoms.[16] I.r. bands at 730 and 1383 cm^{-1} were observed and attributed to the ν_2 and ν_4 vibrations of planar CH_3. Upon warming the matrix, these absorptions disappeared while those of ethane appeared [equation (1)]. Matrix-isolated methyl radicals were also produced by vacuum-u.v. photolysis of CH_4,[17] and by the gas-phase pyrolysis of CH_3I and $(CH_3)_2Hg$.[18] This work showed that the previously observed band at 730 cm^{-1} was strongly perturbed by neighbouring lithium halide molecules and gave for the frequencies of properly isolated CH_3: ν_2 617, ν_3 3162, and ν_4 1396 cm^{-1}.

$$CH_3I + Li \xrightarrow{\text{Ar, 15 K}} \cdot CH_3 \xrightarrow{\Delta} CH_3CH_3 \qquad (1)$$

Besides the methyl radical itself, the various mono-, di-, and tri-halogenomethyl radicals have been the subjects of numerous studies. For example, CF_3 has been generated by vacuum-u.v. photolysis of CF_3Br and by other means;[19] CCl_3 by co-deposition of CCl_4 or CCl_3Br and Li atoms[20] or pyrolysis of $Hg(CCl_3)_2$;[21] and CBr_3 and CI_3 by co-deposition of CBr_4 or CI_4 and Li atoms.[22,23] Normal-co-ordinate analyses and e.s.r. measurements indicate that CH_3 is planar (D_{3h}), whereas CF_3 and CCl_3 are pyramidal (C_{3v}). CBr_3 and CI_3

[16] W. L. S. Andrews and G. C. Pimentel, *J. Chem. Phys.*, 1966, **44**, 2527; 1967, **47**, 3637.

[17] D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, 1967, **47**, 5146.

[18] A. Snelson, *J. Phys. Chem.*, 1970, **74**, 537.

[19] (a) D. E. Milligan, M. E. Jacox, and J. J. Comeford, *J. Chem. Phys.*, 1966, **44**, 4058; (b) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, 1968, **48**, 2265.

[20] (a) L. Andrews, *J. Phys. Chem.*, 1967, **71**, 2761; 1968, **48**, 972; *Tetrahedron Letters*, 1968, 1423; (b) M. E. Jacox and D. E. Milligan, *J. Chem. Phys.*, 1971, **54**, 3935.

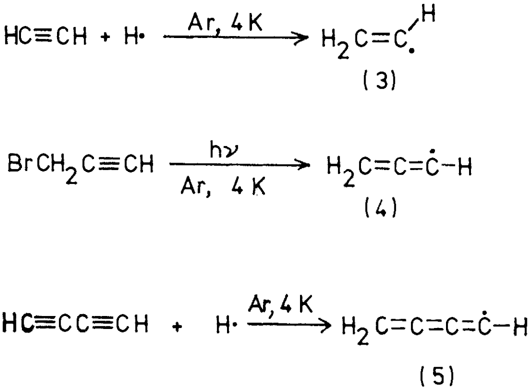
[21] G. Maass, A. K. Maltsev, and J. L. Margrave, *J. Inorg. Nuclear Chem.*, 1973, **35**, 1945.

[22] (a) L. Andrews and T. G. Carver, *J. Chem. Phys.*, 1968, **49**, 896; (b) E. E. Rogers, S. Abramowitz, M. E. Jacox, and D. E. Milligan, *J. Chem. Phys.*, 1970, **52**, 2198.

[23] D. W. Smith and L. Andrews, *J. Phys. Chem.*, 1972, **76**, 2718.

appear to be planar, the latter molecule having a high value of the C–I force constant, indicative of significant (*p*–*p*)π and (*p*–*d*)π bonding.

In matrix studies of more complex radicals, e.s.r. spectroscopy has been the most favoured technique. E.s.r. spectra have been obtained of n-propyl,[24] n-butyl,[24,25] trifluoroethyl,[26] and benzoylmethyl[27] radicals in argon matrices at 4 K, the usual method of generation being photolysis of the corresponding alkyl iodide. Kasai[28] has also observed and discussed the matrix e.s.r. spectra of the unsaturated radicals (3), (4), and (5) (Scheme 2). Radicals (3) and (5) were generated by matrix reaction of hydrogen atoms, from photolysis of HI, with the corresponding alkynes, and (4) by photolysis of prop-2-ynyl bromide. In contrast to (4) and (5), which are linear, the vinyl radical (3) is bent. The experimental spin densities of all three species agreed well with INDO molecular orbital calculations.



Scheme 2

2-Hydroxyphenyl (6) and 2-methoxyphenyl (7) radicals have been generated in Ar matrices by photolysis of the corresponding iodides (Scheme 3).[29] The e.s.r. spectra indicated that both species are σ radicals. When a matrix containing (7) was allowed to warm to 14 K, hydrogen abstraction occurred and (8) was formed. On further photolysis, however, (7) gave phenyl radicals, presumably *via* (8). In the same paper[29] was reported the e.s.r. spectrum of matrix-isolated cyclopentadienyl radical, C_5H_5. At 4 K, this species does not have five-fold symmetry, but is Jahn–Teller distorted.

[24] C. A. McDowell and K. Shimokoshi, *J. Chem. Phys.*, 1974, **60**, 1619.

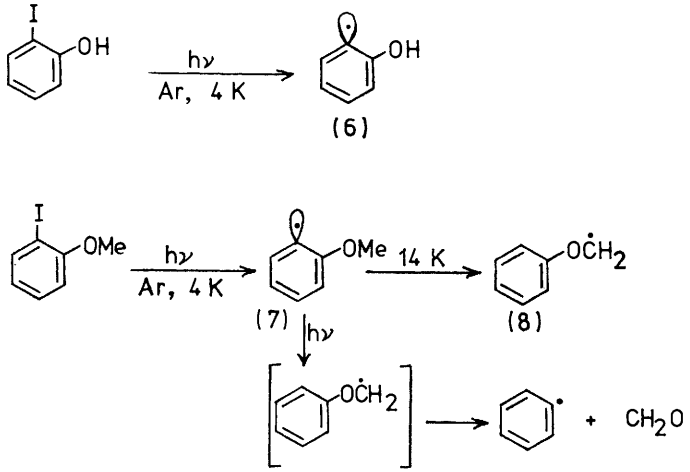
[25] F. J. Adrian, V. A. Bowers, and E. L. Cochran, *J. Chem. Phys.*, 1975, **63**, 919.

[26] M. Jinguji, K. C. Lin, C. A. McDowell, and P. Raghunathan, *J. Chem. Phys.*, 1976, **65**, 3910.

[27] P. H. Kasai, D. McLeod, Jr., and H. C. McBay, *J. Amer. Chem. Soc.*, 1974, **96**, 6864.

[28] P. H. Kasai, *J. Amer. Chem. Soc.*, 1972, **94**, 5950.

[29] P. H. Kasai and D. McLeod, Jr., *J. Amer. Chem. Soc.*, 1974, **96**, 2338.



Scheme 3

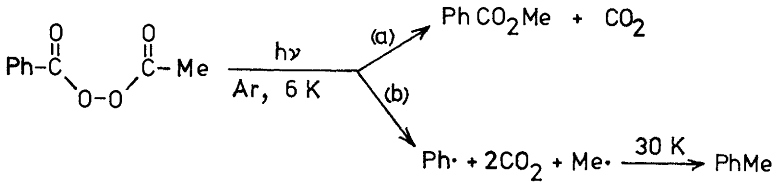
Several recent reviews of solid-state e.s.r. studies[30] include sections on matrix spectra.

The observation of radicals by i.r. or u.v. spectroscopy rather than e.s.r. suffers from the disadvantage of low sensitivity, but has the very important advantage that non-radical products may also be detected. Pacansky[31] has reported several i.r. studies of the formation of alkyl and phenyl radicals by photolysis of diacyl peroxides in matrices. For example, photolysis of acetyl benzoyl peroxide in Ar at 6 K has been observed to go by two fragmentation processes. One was elimination of CO_2 to give methyl benzoate [Scheme 4, path (a)], the other was elimination of two molecules of CO_2 to give phenyl and methyl radicals [path (b)]. The radicals survived in the matrix cage without recombination, because they were separated from each other by the CO_2 molecules. Warming the matrix to 30 K softened it sufficiently to allow the CO_2 molecules to diffuse away, and then the i.r. spectra of the two radicals were seen to disappear and that of toluene arose. Thus radical recombination, not surprisingly, requires little or no activation energy.

The same is apparently true also for radical disproportionation. Photolysis of dipropanoyl peroxide in Ar at 6 K yielded ethyl radicals and CO_2, and on

[30] (a) J. E. Bennett and K. D. J. Root, in 'Electron Spin Resonance,' ed. R. O. C. Norman, (Specialist Periodical Reports), The Chemical Society, London, 1973, vol. 1, p. 118; (b) T. J. Kemp, in 'Electron Spin Resonance', ed. R. O. C. Norman, (Specialist Periodical Reports), The Chemical Society, London, 1976, vol. 3, p. 221, and in vol. 4 (ed. P. B. Ayscough), p. 163 (1977).

[31] (a) J. Pacansky and J. Bargon, *J. Amer. Chem. Soc.*, 1975, **97**, 6896; (b) J. Pacansky, G. P. Gardini, and J. Bargon, *J. Amer. Chem. Soc.*, 1976, **98**, 2665; *Ber. Bunsengesellschaft Phys. Chem.*, 1978, **82**, 19; (c) J. Pacansky, D. E. Horne, G. P. Gardini, and J. Bargon, *J. Phys. Chem.*, 1977, **81**, 2149.

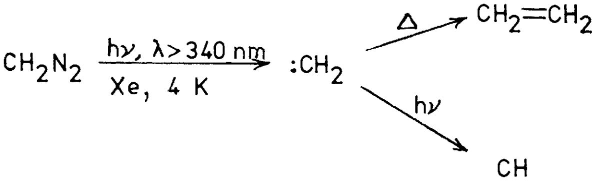


Scheme 4

warming to 30 K, n-butane from radical recombination and ethane and ethene from disproportionation were formed [equation (2)].

$$\mathrm{Et{\cdot}CO{\cdot}OO{\cdot}CO{\cdot}Et} \xrightarrow[\mathrm{Ar,\ 6K}]{h\nu} \mathrm{Et\cdot} + 2\mathrm{CO_2} + \mathrm{Et\cdot} \xrightarrow{30\ \mathrm{K}} \mathrm{C_4H_{10}} + \mathrm{C_2H_6} + \mathrm{C_2H_4} \qquad (2)$$

B. Carbenes.—The simplest carbene, methylene, has been the subject of many theoretical and experimental studies, including matrix work. The e.s.r. spectrum of CH_2 was obtained, when diazirine was photolysed in Xe matrices.[32] An H–C–H bond angle of 137.7° was estimated. The i.r. spectrum of matrix-isolated CH_2 has, however, proved elusive. The photolysis of diazomethane in N_2 at 20 K gave an unstable substance, which produced ethene after diffusion had been permitted.[33] The unstable ethene precursor had u.v. absorptions at 305–330, 397, and 418 nm, but no corresponding i.r. absorptions were observed. Further irradiation of the intermediate gave the species CH (Scheme 5).[34]



Scheme 5

Low-temperature e.s.r. spectra of a number of triplet carbenes, generated by photolysis of diazo-compounds, have been reported by Wasserman and co-workers.[35] I.r. matrix studies of carbenes from diazo precursors, on the other hand, have met with mixed success. Matrix photolysis of diazoacetaldehyde gave

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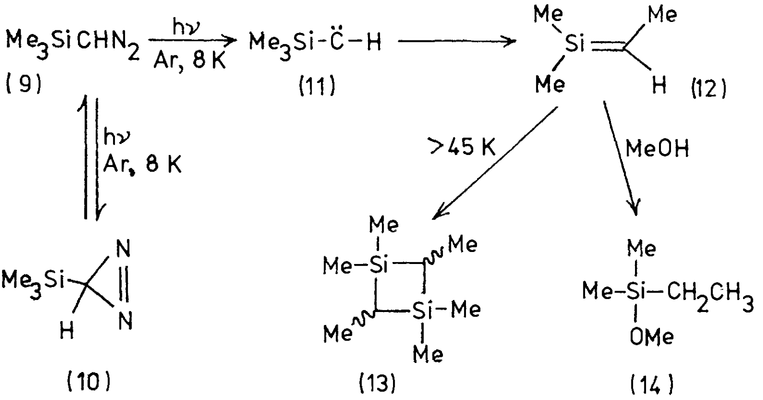
[32] (a) R. A. Bernheim, H. W. Bernard, P. S. Wang, L. S. Wood, and P. S. Skell, *J. Chem. Phys.*, 1970, **53**, 1280; 1971, **54**, 3223; (b) E. Wasserman, V. J. Kuck, R. S. Hutton, E. D. Anderson, and W. A. Yager, *J. Chem. Phys.*, 1971, **54**, 4120; (c) R. A. Bernheim, S. H. Chien, *J. Chem. Phys.*, 1976, **65**, 2023.

[33] T. D. Goldfarb and G. C. Pimentel, *J. Amer. Chem. Soc.*, 1960, **82**, 1865.

[34] G. W. Robinson and M. McCarty, Jr., *J. Amer. Chem. Soc.*, 1960, **82**, 1859.

[35] E. Wasserman, L. Barash, A. M. Trozzolo, R. W. Murray, and W. A. Yager, *J. Amer. Chem. Soc.*, 1964, **86**, 2304.

a quantitative yield of keten, and ethyl diazoacetate gave ethoxyketen.[36] In neither case was an intermediate carbene or oxiren detected spectroscopically, but the yield of ethoxyketen was reduced in reactive matrices (CH_4, C_2H_6, or C_2H_4), suggesting the intermediacy of the carbene, $:CHCO_2Et$. Photolysis of trimethylsilyldiazomethane[37] [compound (9), Scheme 6] in Ar at 8 K resulted in interconversion of (9) and the diazirine (10). At the same time an e.s.r. signal was observed, and this was attributed to the triplet carbene (11). The i.r. spectrum of (11) was not detected, however. Instead, an i.r. spectrum arose that was attributed to the silaethylene (12), although the $\nu_{Si=C}$ vibration was not assigned. Warming the matrix gave the *cis*- and *trans*-isomers of the dimer (13), while in the presence of methanol, (14) was formed.



Scheme 6

In other cases, carbenes have been detected by i.r. spectroscopy. For example, $:CHCN$ was generated from diazocyanomethane[38] and its i.r. spectrum obtained, and both i.r. and u.v. absorption spectra were recorded for cyclopentadienylidene (15) from diazocyclopentadiene[39] (Scheme 7). The carbene (15) dimerized to fulvalene (16) when allowed to diffuse in the matrix at 20—35 K, and if CO were present in the matrix, (15) gave the keten (17).

Besides photolysis, two other methods have been used to generate a variety of simple carbenes in matrices. The first is reaction of carbon atoms with halogens or hydrogen halides, exemplified in equation (3). Photolysis of cyanogen azide in matrices containing HCl gave carbon atoms which reacted with HCl, yielding

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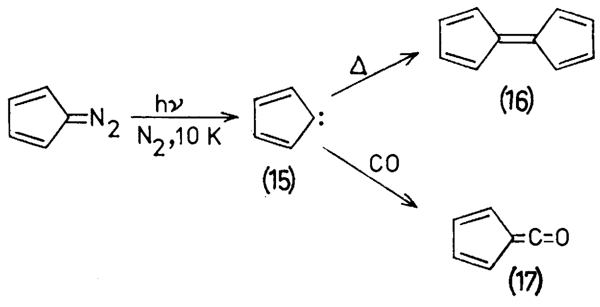
[36] A. Krantz, *J.C.S. Chem. Comm.*, 1973, 670.

[37] (a) O. L. Chapman, C.-C. Chang, J. Kolc, M. E. Jung, J. A. Lowe, T. J. Barton, and M. L. Tumey, *J. Amer. Chem. Soc.*, 1976, **98**, 7844; (b) M. R. Chedekel, M. Skoglund, R. L. Kreeger, and H. Schechter, *J. Amer. Chem. Soc.*, 1976, **98**, 7846.

[38] A. Dendramis, J. F. Harrison, and G. E. Leroi, *Ber. Bunsengesellschaft Phys. Chem.*, 1978, **82**, 7.

[39] M. S. Baird, I. R Dunkin, and M. Poliakoff, *J.C.S. Chem. Comm.*, 1974, 904.



Scheme 7

$$N_3CN + HCl \xrightarrow[-2N_2]{h\nu} H\ddot{C}Cl \xrightarrow{HCl} CH_2Cl_2 \qquad (3)$$

chlorocarbene, for which both i.r. and electronic spectra were obtained.[40] Further, thermal reaction of CHCl with HCl gave CH_2Cl_2. Neither process required significant activation energy. Other halogenocarbenes, *e.g.* CCl_2, CF_2, and HCF, have been observed in analogous reactions.[41] Matrix reaction of atomic carbon with CO gave the carbene species CCO, the spectra of which (i.r., u.v., and e.s.r.) indicated a linear structure.[42] The second method is reaction of atomic lithium with tetrahalogenomethanes during matrix deposition.[22a,43] Carbenes are obtained, in addition to trihalogenomethyl radicals and other species [e.g. equation (4)]. Force field calculations have indicated that there is very little π-bonding in CBr_2 and similar species.

$$Li + CBr_4 \xrightarrow{Ar, 15\,K} \cdot CBr_3 \xrightarrow{Li} :CBr_2 \xrightarrow{\Delta} C_2Br_4 \qquad (4)$$

C. Nitrenes.—The case with matrix-isolated nitrenes is almost the complete reverse of the case with carbenes. Electronic and i.r. spectra of the parent nitrene, NH (ν_{NH} 3122 cm^{-1}), have been reported for several studies of the photolysis of HN_3 in a variety of matrices, and the dimerization of NH to form di-imide has

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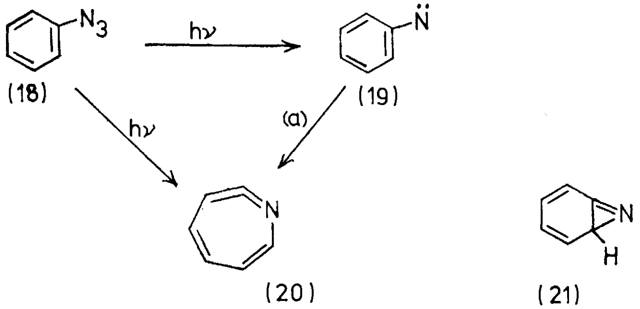
[40] M. E. Jacox and D. E. Milligan, *J. Chem. Phys.*, 1967, **47**, 1626.

[41] (a) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, 1967, **47**, 703, 2265; (b) M. E. Jacox and D. E. Milligan, *J. Chem. Phys.*, 1969, **50**, 3252.

[42] (a) M. E. Jacox, D. E. Milligan, N. G. Moll, and W. E. Thompson, *J. Chem. Phys.*, 1965, **43**, 3734; (b) G. R. Smith and W. Weltner, Jr., *J. Chem. Phys.*, 1975, **62**, 4592.

[43] (a) L. Andrews, *J. Chem. Phys.*, 1968, **48**, 979; (b) D. A. Hatzenbühler, L. Andrews, and F. A. Carey, *J. Amer. Chem. Soc.*, 1975, **97**, 189; (c) D. E. Tevault and L. Andrews, *J. Amer. Chem. Soc.*, 1975, **97**, 1707.

been observed.[44] In contrast, organic nitrenes have been generated in matrices in concentrations sufficient to allow their observation by e.s.r.,[45] but they have escaped detection by means of their i.r. or u.v. absorptions. The difficulty of preparing matrix-isolated nitrenes in substantial concentrations seems to be related to the ease with which nitrenes rearrange. Thus matrix photolysis of CH_3N_3 gave $CH_2{=}NH$, possibly *via* the nitrene CH_3N;[46] $(CH_3)_3SiN_3$[47] and $(CH_3)_3CN_3$[48] also gave imines; and methyl azidoformate gave CH_3ONCO, CH_2O, and HNCO.[49] Perhaps the most interesting results have come from studies of the photolysis of phenyl azide [compound (18), Scheme 8]. Despite claims that phenyl nitrene (19) may be observed during flash photolysis[50] of (18) or in organic glasses,[51] matrix i.r. studies[52] have led to the discovery of a new species with a strong absorption at 1895 cm^{-1}. The frequency of this band is such as might be expected for a bent ketenimine, and was accordingly assigned to the azacycloheptatetraene (20). It has been known for some time that the major intermediate in the solution photolysis of phenyl azide shows little of the expected reactivity towards saturated hydrocarbons or alkenes and that, in the presence of secondary amines for example, ring-expanded compounds, in this case 2-dialkylamino-3*H*-azepines, are produced.[53] It had usually been supposed that the formation of the bicyclic azirine (21) could account for this reactivity pattern, but (20) now seems the more plausible candidate. When matrix photolysis of phenyl azide was followed by e.s.r. rather than i.r. spectroscopy, triplet phenyl nitrene was detected. So far there appears to be no resolution, however, of the question whether (20) is formed from (18) *via* (19). [Scheme 8, path (a)] or whether (19) and (20) lie on different reaction paths.



Scheme 8

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[44] (a) D. A. Dows, E. Whittle, and G. C. Pimentel, *J. Chem. Phys.*, 1955, **23**, 1475; (b) M. McCarty, Jr., and G. W. Robinson, *J. Amer. Chem. Soc.*, 1959, **81**, 4472; (c) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, 1964, **41**, 2838; (d) K. Rosengren and G. C. Pimentel, *J. Chem. Phys.*, 1965, **43**, 507.

[45] E. Wasserman, *Progr. Phys. Org. Chem.*, 1971, **8**, 319.

[46] D. E. Milligan, *J. Chem. Phys.*, 1961, **35**, 1491.

[47] R. N. Perutz, *J.C.S. Chem. Comm.*, 1978, 762.

[48] I. R. Dunkin and P. C P. Thomson, unpublished results.

[49] R. E. Wilde, T. K. K. Srinivasan, and W. Lwowski, *J. Amer. Chem. Soc.*, 1971, **93**, 860.

[50] P. A. Lehman and R. S. Berry, *J. Amer. Chem. Soc.*, 1973, **95**, 8614.

[51] A. Reiser, H. Wagner, and G. Bowes, *Tetrahedron Letters*, 1966, 2635.

[52] O. L. Chapman and J.- P. Le Roux, *J. Amer. Chem. Soc.*, 1978, **100**, 282.

[53] B. A. DeGraff, D. W. Gillespie, and R. J. Sundberg, *J. Amer. Chem. Soc.*, 1974, **96**, 7491.

4 Unstable Organic Molecules in Matrices

A. Cyclobutadiene.—The structure of cyclobutadiene has been debated for a long time. Theoretical predictions indicate two possible structures: (i) a square (D_{4h}) triplet, or (ii) a rectangular (D_{2h}) singlet. Most calculations have favoured the latter as the ground state. The crucial question about cyclobutadiene is, therefore, whether it is square or rectangular. Straightforward symmetry arguments predict only four i.r.-active vibrational fundamentals for the square molecule* and seven for the rectangle.

In 1972–3, three groups of workers[54] reported matrix studies of the photolysis of α-pyrone [compound (22), Scheme 9]. Irradiation of (22) in Ar at 8 K with Pyrex-filtered u.v. light led to rapid reversible formation of the ring-opened keten (23). All four conformers of the keten (23a—d) were observed. Initially a non-equilibrium mixture was produced, presumably with (23a) predominating, but on warming the matrix to 35 K, equilibrium was approached, presumably now with (23d) predominating. Prolonged irradiation of the matrix gave the bicyclic β-lactone (24), which on further photolysis lost CO_2 to give cyclobutadiene (25). Four i.r. bands, at 3040, 1240, 650, and 570 cm^{-1}, were attributed to (25). On the basis of these experiments and the failure to observe a triplet e.s.r. signal, it was tentatively concluded, in conflict with most predictions, that cyclobutadiene had a square singlet structure. More elaborate studies with deuteriated α-pyrones seemed to confirm this conclusion.[55]

The assignment of a square singlet structure to (25) was obviously of great interest, but was based solely on negative evidence (the observation of four and not seven i.r. bands, and the absence of an e.s.r. signal). A MINDO/3 study of the singlet–triplet interconversion of cyclobutadiene suggested that this process might be very slow at low temperatures and that the matrix-isolated species might therefore be a metastable square triplet.[56] The possibility remained, however, that the molecule really had rectangular geometry and that only four i.r. bands were observed because the others were either weak or obscured by the absorptions of the other species in the matrix.

Even the negative evidence became suspect when Masamune and co-workers[57] generated cyclobutadiene in Ar matrices by photolysis of the tetracyclic compound (26) (Scheme 10). I.r. bands at 3040, 1240, and 570 cm^{-1} were observed as before, but the band at 650 cm^{-1}, previously attributed to

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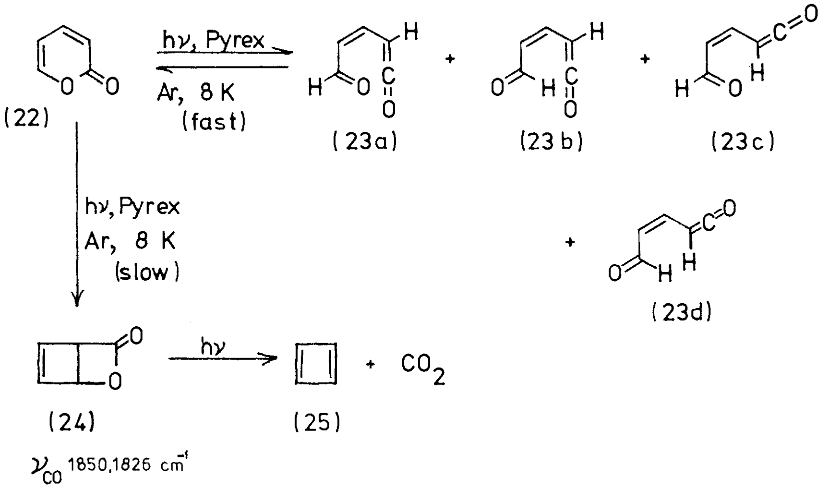
*The perhaps surprisingly small number of predicted i.r. bands for the square molecule is due to the relatively high symmetry of the species. This gives rise to several degenerate vibrations and also to several vibrations which maintain the centre of symmetry of the molecule and are therefore i.r. inactive.

[54] (a) C. Y. Lin and A. Krantz, *J.C.S. Chem. Comm.*, 1972, 1111, 1316; (b) O. L. Chapman, C. L. McIntosh, and J. Pacansky, *J. Amer. Chem. Soc.*, 1973, **95**, 244, 614; (c) R. G. S. Pong and J. S. Shirk, *J. Amer. Chem. Soc.*, 1973, **95**, 248.

[55] (a) O. L. Chapman, D. De la Cruz, R. Roth, and J. Pacansky, *J. Amer. Chem. Soc.*, 1973, **95**, 1337; (b) A. Krantz, C. Y. Lin, and M. D. Newton, *J. Amer. Chem. Soc.*, 1973, **95**, 2744.

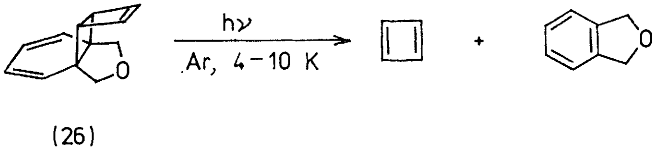
[56] (a) M. J. S. Dewar and H. W. Kollmar, *J. Amer. Chem. Soc.*, 1975, **97**, 2933; (b) M. J. S. Dewar and A. Komornicki, *J. Amer. Chem. Soc.*, 1977, **99**, 6174.

[57] S. Masamune, Y. Sugihara, K. Morio, and J. E. Bertie, *Canad. J. Chem.*, 1976, **54**, 2679.



Scheme 9

cyclobutadiene, was absent. This band was now assigned to CO_2 molecules in which the bending vibration (normally at 667 cm^{-1}) was perturbed by cyclobutadiene molecules in the same matrix cage. Confirmation of this assignment came also from matrix photolysis of ^{13}C-labelled α-pyrone.[58] At this stage, only three i.r. bands could be assigned to cyclobutadiene; so that the assumption that all the i.r. bands had been observed in the original work, with the implication of square geometry, was now untenable. Very recently,[59] Masamune and co-workers have reported a matrix study of cyclobutadiene and perdeuteriocyclobutadiene in which thay have identified four i.r. bands of (25) at frequencies below 1700 cm^{-1}, in addition to the ν_{C-H} band at 3040 cm^{-1}. This would seem to dispose of the hypothesis that cyclobutadiene has D_{4h} symmetry in the ground state. It is most likely rectangular.



Scheme 10

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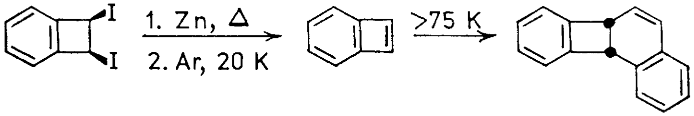
[58] R. G. S. Pong, B.- S. Huang, J. Laureni, and A. Krantz, *J. Amer. Chem. Soc.*, 1977, **99**, 4153.

[59] S. Masamune, F. A. Sonto-Bachiller, T. Machiguchi, and J. E. Bertie, *J. Amer. Chem. Soc.*, 1978, **100**, 4889.

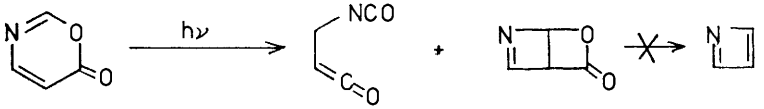
Benzocyclobutadiene [compound (28), Scheme 11] has been isolated in a matrix by passing the *cis*-di-iodide (27) in a stream of argon over hot zinc and condensing the resultant gas stream at 20 K.[60] Benzocyclobutadiene (28) was detected by its u.v. and i.r. absorptions. Warming the matrix above 75 K yielded the dimer (29).



(27) (28) (29)

Scheme 11

An attempt to isolate azocyclobutadiene (33) from aza-α-pyrone (30) failed (Scheme 12).[61] Irradiation of (30) yielded the isocyanatoketen (31) and the aza-β-lactone (32), but further photolysis produced only HCN, CO_2, and acetylene.

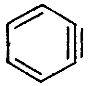


(30) (31) (32) (33)

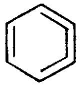
ν_{CCO} 2140 cm^{-1} ν_{CO} 1878, 1840 cm^{-1}

Scheme 12

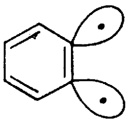
B. Benzyne.—The nature of the bonding in benzynes has been discussed ever since the existence of these intermediates was first postulated.[62] One of the main points at issue is whether benzyne is best described as a cycloalkyne (34), a cyclic cumulene (35), or a biradical (36). Matrix studies conducted by Chapman and co-workers have been directed towards answering this question.[63,64]



(34)



(35)



(36)

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[60] O. L. Chapman, C. -C. Chang, and N. R. Rosenquist, *J. Amer. Chem. Soc.*, 1976, **98**, 261.

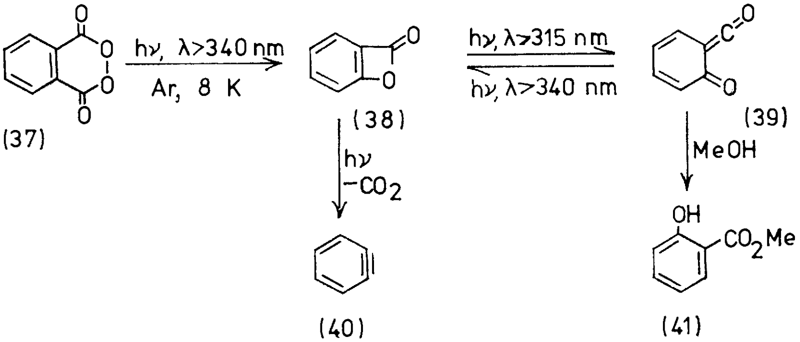
[61] A. Krantz and B. Hoppe, *J. Amer. Chem. Soc.*, 1975, **97**, 6590.

[62] R. W. Hoffmann, 'Dehydrobenzene and Cycloalkynes', Academic Press, New York, 1967.

[63] (a) O. L. Chapman, C. L. McIntosh, J. Pacansky, G. V. Calder, and G. Orr, *J. Amer. Chem. Soc.*, 1973, **95**, 4061; (b) O. L. Chapman, K. Mattes, C. L. McIntosh, J. Pacansky, G. V. Calder, and G. Orr, *J. Amer. Chem. Soc.*, 1973, **95**, 6134.

[64] O. L. Chapman, C. -C. Chang, J. Kolc, N. R. Rosenquist, and H. Tomioka, *J. Amer. Chem. Soc.*, 1975, **97**, 6586.

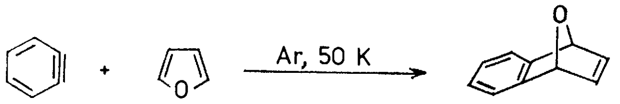
Irradiation of matrix-isolated phthaloyl peroxide [compound (37), Scheme 13] gave a mixture of benzpropiolactone (38) and its monocyclic valence tautomer (39). These two molecules could be interconverted photochemically by a suitable choice of wavelength. Thus, irradiation with $\lambda > 340$ nm favoured formation of (38), and irradiation with $\lambda > 315$ nm favoured (39). If the experiment were performed with a matrix containing some methanol, (39) gave methyl salicylate (41) upon annealing. Further irradiation of benzpropiolactone (38) resulted in loss of CO_2 and formation of benzyne (40).



Scheme 13

In the first set of experiments, eight i.r. bands in the region 1700—400 cm^{-1} were assigned to benzyne. Laing and Berry[65] used these data for force field calculations on various possible benzyne structures. They concluded that benzyne could be described satisfactorily only by a cycloalkyne structure (34), and predicted the existence of additional i.r. bands at 2450 and 2083 cm^{-1}. At almost exactly the same time, a band at 2085 cm^{-1} was observed experimentally,[64] corresponding well with the predicted 2083 cm^{-1} vibration. So far the band at 2450 cm^{-1} has not been detected.

The Diels–Alder reactivity of benzyne persists even down to very low temperatures.[63b] When benzyne was generated in a matrix containing furan, the Diels–Alder adduct was produced on warming to 50 K [equation (5)].



(5)

So far, no reports have appeared of matrix-isolated 1,3- or 1,4-dehydrobenzene. An analogue of the latter, however, 9,10-dehydroanthracene (43), has been generated from the corresponding bis-keten (42).[66] It seems to behave like a radical, and its u.v. spectrum, which is similar to that of anthracene, has been claimed to

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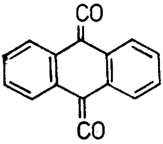
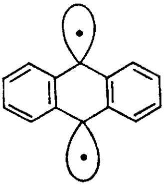
[65] J. W. Laing and R. S. Berry, *J. Amer. Chem. Soc.*, 1976, **98**, 660.

[66] O. L. Chapman, C. -C. Chang, and J. Kolc, *J. Amer. Chem. Soc.*, 1976, **98**, 5703.

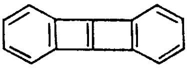
indicate a tricyclic structure (43) rather than, for example, the tetracyclic structure (44).



(42)

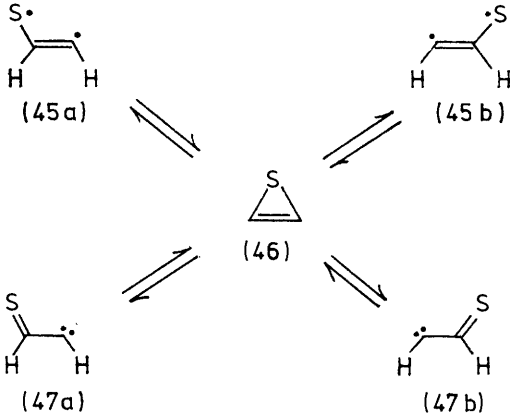


(43)



(44)

C. Thiiren.—Thiiren (46) may be considered as bearing the same relationship to thiophen as cyclobutadiene does to benzene. In other words, it is the next lower thia-annulene, and as such is expected to be rather unstable possibly even representing an energy maximum in the degenerate rearrangements of the triplet biradicals (45a $\rightleftharpoons$ 45b) or the thioketocarbenes (47a $\rightleftharpoons$ 47b) (Scheme 14). Two questions about thiiren may be asked, therefore:
(i) does it exist on any reaction pathway, and (ii) if so, is it a genuine intermediate capable of existing for a finite time? Krantz and co-workers have made a very detailed matrix i.r. study of one reaction in which thiiren was expected as an intermediate.



Scheme 14

Matrix photolysis of 1,2,3-thiadiazole (48; R = H) gave a mixture of thioketen (50; R = H) and ethynyl mercaptan (51; R = H) (Scheme 15).[67] When the same experiment was performed with either of the deuterio-compounds (48; R = D)

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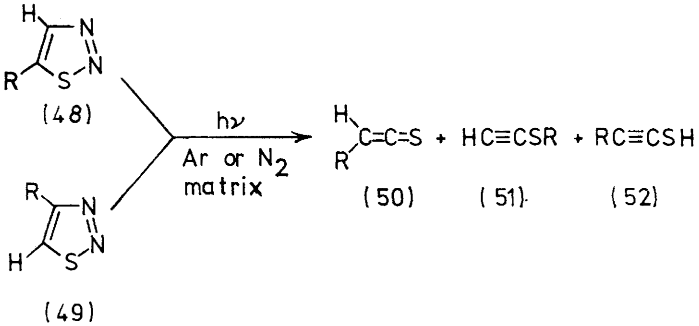
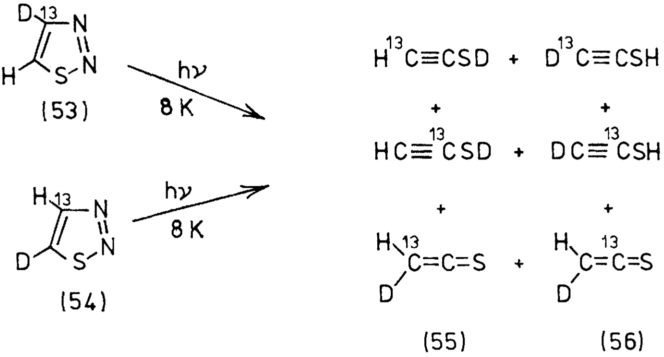
[67] A. Krantz and J. Laureni, *J. Amer. Chem. Soc.*, 1974, **96**, 6768; 1975, **97**, 6106; 1976, **98**, 641.

and (49; R = D), the same mixture of (50; R = D) and both possible monodeuterio-mercaptans, (51 and 52; R = D) was obtained in each case. The deuterium scrambling in the mercaptan suggested the intermediacy of a symmetrical species, presumably thiiren.



Scheme 15

Subsequently,[68] thiiren was actually detected after careful matrix photolysis of (48; R = H), and six i.r. bands (at 3207, 3169, 3166, 1663, 912, and 563 cm^{-1}) were assigned to this molecule. A combination of deuterium- and ^{13}C-labelling, however, showed that the photodecomposition of 1,2,3-thiadiazole is not completely straightforward.[69] Photolysis (Scheme 16) of the doubly labelled thiadiazoles (53) and (54) led to all four possible monodeuterio mono-^{13}C ethynyl mercaptans and to the two thioketens (55) and (56), with (55) predominating in both cases. Thus, the hydrogen atom bound to carbon in the mercaptan is not necessarily the same hydrogen that was bound to this carbon atom in the starting-material. Moreover, in order to account for the preponderance of thioketen (55), it has been suggested that two reaction pathways are followed: one *via* thiiren and the other *via* the biradical ·CH = CHS·.



Scheme 16

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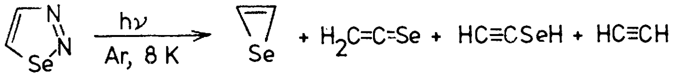
[68] A. Krantz and J. Laureni, *J. Amer. Chem. Soc.*, 1977, **99**, 4842.
[69] J. Laureni, A. Krantz, and R. A. Hajdu, *J. Amer. Chem. Soc.*, 1976, **98**, 7872.

In an analogous matrix reaction,[69] seleniren (57), selenoketen (58), ethynyl selenol (59), and acetylene were detected as photoproducts of 1,2,3-selenadiazole [equation (6)].



(57) (58) (59) (6)

5 Organic Ions in Matrices

Since with present techniques it is necessary to volatilize any compound which it is intended to trap in a matrix, and because of the low vapour pressure of most ionic compounds, studies of organic ionic species in matrices have been very few. They have been confined to methods in which ions are generated from uncharged precursors either in the matrix or during deposition.

Andrews[70] has shown that the matrix reaction between methyl radicals and lithium atoms gives methyl-lithium. A force field calculation on this species, based on the observed i.r. spectrum (with isotopic substitution), indicates a low H–C–Li bending force constant, and this suggests a significant amount of ionic character in the C–Li bond. Similar reactions[71] between lithium atoms and trihalogenomethyl radicals (CX_3; X = Cl or Br, and CXY_2; X,Y = Cl or Br) led to the formation of $LiCX_3$ and $LiCXY_2$ species, in which, again, the halogenomethyl groups showed a significant anionic character.

A second approach adopted by Andrews, which has succeeded in producing some unusual positive ions, is the proton bombardment of neutral precursors during matrix deposition. In a typical experiment,[72] carbon tetrachloride at high dilution in Ar was deposited at 15 K with simultaneous 2.0 keV proton-beam irradiation. The observed i.r. spectrum had bands belonging to the known neutral species, CCl_3 and CCl_2, and also others which were attributed to the cations: CCl_4^+, CCl_3^+, CCl_2^+, Cl_4^+, and Cl_3^+. Cationic species could be identified as such, because the i.r. bands belonging to them disappeared when the cations were neutralized by electrons from a heated filament. A comparable proton radiolysis study[73] of $CHCl_3$ and $CHBr_3$ led to the detection of $CHCl_2^+$ and $CHBr_2^+$.

A fairly general method for the production of matrix-isolated radical anions has been developed by Kasai.[74–76] This depends on the fact that irradiation ($\lambda > 550$ nm) of a matrix containing sodium atoms and a suitable electron acceptor can result in an electron transfer process. The radical anions may be

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[70] L. Andrews, *J. Chem. Phys.*, 1967, **47**, 4834.

[71] L. Andrews and T. G. Carver, *J. Phys. Chem.*, 1968, **72**, 1743.

[72] L. Andrews, J. M. Grzybowski, and R O. Allen, *J. Phys. Chem.*, 1975, **79**, 904.

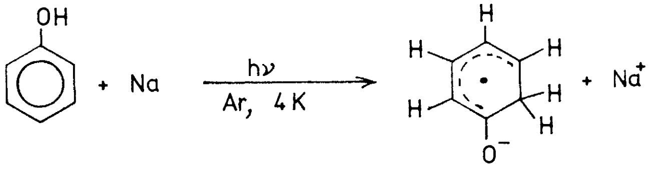
[73] B. S. Ault and L. Andrews, *J. Chem. Phys.*, 1975, **63**, 1411.

[74] P. H. Kasai, *Accounts Chem. Res.*, 1971, **4**, 329.

[75] P. H. Kasai and D. McLeod, Jr., *J. Amer. Chem. Soc.*, 1972, **94**, 6872.

[76] P. H. Kasai and D. McLeod, Jr., *J. Amer. Chem. Soc.*, 1973, **95**, 27.

observed by e.s.r. spectroscopy; so that low concentrations may be tolerated. Thus, irradiation of sodium atoms and phenol in Ar matrices [equation (7)] gave the radical anion (60), the e.s.r. spectrum of which indicated the ketonic structure



(7)

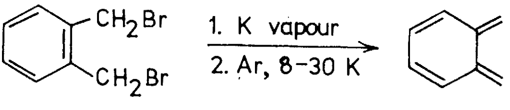
(60)

shown.[75] In the same vein, Kasai and McLeod have observed radical anions derived from pyrrole, pyrazole, imidazole, and indole.[76]

6 Conclusion

The matrix-isolation technique was developed to bestow longevity on otherwise ephemeral species. It is often asked if argon at 10 K sufficiently resembles, say, ethanol at room temperature for matrix results to have any bearing on reaction mechanisms in more usual conditions. The chemistry reviewed in these pages seems to merit an affirmative answer. That being so, we can look forward to continued application of matrix isolation as a means of identifying and gaining information about intermediates that would otherwise remain hypothetical.

One recent tendency has been to use a wider variety of spectroscopic and other techniques in conjunction with matrix isolation. Tseng and Michl, for example, isolated *o*-xylylene (62) in Ar matrices after reaction of (61) with Na or K vapour [equation (8)].[77] Compound (62) was detected by its i.r. Raman, u.v. absorption, fluorescence, and fluorescence excitation spectra. Matrix experiments



(8)

(61) (62)

involving Mössbauer spectroscopy,[78] magnetic circular dichroism,[79] flash photolysis,[80] and high pressures[81] have also been reported. Turner and coworkers have demonstrated, with certain transition-metal compounds, that

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[77] K. L. Tseng and J. Michl, *J. Amer. Chem. Soc.*, 1977, **99**, 4840

[78] See for example, (a) A. Boos and A. T. Howe, *J.C.S. Faraday II*, 1975, **71**, 28; (b) P. A. Montano, P. H. Barrett, and H. Micklitz, *Ber. Bunsengesellschaft Phys. Chem.*, 1978, **82**, 37.

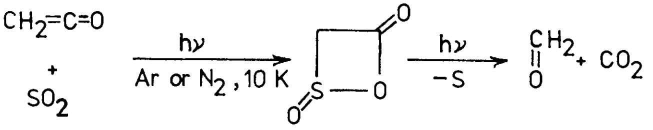
[79] See for example, T. J. Barton, R. Grinter, and A. J. Thomson, *Ber. Bunsengesellschaft Phys. Chem.*, 1978, **82**, 131.

[80] See for example, L. J. Schoen, *J. Chem. Phys.*, 1966, **45**, 2773.

[81] H. J. Jodl, *Ber. Bunsengesellschaft Phys. Chem.*, 1978, **82**, 71.

matrix photolysis with plane-polarized light and subsequent analysis with polarized spectrometers can yield information about the symmetries of electronic and vibrational transitions and about the motions of molecules during photoreactions.[82] These and other developments will bring more and more mechanistic problems within the range of experiment. There is still, however, an outstanding need for more general methods of isolating ions at low temperatures.

Matrix isolation has sometimes created its own chemistry. A recent example is the photoaddition of keten and sulphur dioxide.[83] U.v. irradiation of keten in N_2 or Ar matrices containing SO_2 gave the novel adduct (63) [equation (9)], which on further irradiation, broke down to CO_2 and formaldehyde, the latter arising presumably *via* sulphine, CH_2SO. Although compounds of similar structure to (63) had been suggested in other reactions, the process depicted in equation (9) seems to be peculiar to matrix photolysis. Irradiation of gas-phase mixtures of keten and SO_2 did not lead to the formation of CO_2.[83b]



(63)

(9)

Perhaps it will be some time before matrix isolation becomes a routine technique and not one practised only by matrix specialists. Nevertheless, reports of the uses of matrix isolation other than in the identification of novel species have become more common. The thermal decompositions of certain organomercury compounds[84] and organic halides[85] have been studied by trapping the preliminary products, species such as halogenocarbenes and halogeno-radicals, in Ar matrices. The i.r. spectra of these products are well known; so that matrix i.r. analysis was a convenient method for determining the course of reaction. Matrix isolation has been used in the study of molecular beam encounter complexes,[86] and in relation to interstellar chemistry;[87] while cryostats have even been sent aloft in balloons to collect samples of stratospheric air for subsequent (ground

[82] (a) J. K. Burdett, R. N. Perutz, M. Poliakoff, and J. J. Turner, *J.C.S. Chem. Comm.*, 1975, 157; (b) J. K. Burdett, J. M. Gryzbowski, M. Poliakoff, and J. J. Turner, *J. Amer. Chem. Soc.*, 1976, **98**, 5728.

[83] (a) I. R. Dunkin and J. G. MacDonald, *J.C.S. Chem. Comm.*, 1978, 1020; (b) I. R. Dunkin and J. G. MacDonald, unpublished results.

[84] A. K. Maltsev, O. M. Nefedov, R. H. Hauge, J. L. Margrave, and D. Seyferth, *J. Phys. Chem.*, 1971, **75**, 3984.

[85] O. M. Nefedov, A. K. Maltsev, and V. A. Svyatkin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1976, **25**, 1792.

[86] J. V. Martinez de Pinillos and W. Weltner, Jr., *Ber. Bunsengesellschaft Phys. Chem.*, 1974, **78**, 196.

[87] W. Weltner, Jr., *Ber. Bunsengesellschaft, Phys. Chem.*, 1978, **82**, 80.

level) e.s.r. investigation of atmospheric radicals.[88] It would be too bold to predict where matrix isolation will go from here.

I am greatly indebted to Professor J. J. Turner, Dr. M. Poliakoff, and Dr. J. K. Burdett, who first introduced me to the matrix technique and imbued me with enthusiasm for this area of research.

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[88] D. Mihelcic, D. H. Ehhalt, J. Klomfass, G. F. Kulessa, U. Schmidt, and M. Trainer, *Ber. Bunsengesellschaft. Phys. Chem.*, 1978, **82**, 16.