e.g., molecules of biochemical interest, in cooperation with Professor A. A. Bothner-By (Pittsburgh). Attention is also being paid to small molecules to study the correspondence with $\Delta\chi$ determinations using microwave spectroscopy.[42]

EFNMR studies are at the moment focused on binary mixtures. The addition of a second component to the solution affects the alignment which thus provides information about intermolecular interactions.[43,44] In a recent study,[44] the change of the alignment upon dilution is interpreted in possible changes of the quadrupole

coupling constant, the asymmetry parameter, and the molecular geometry. At the moment, charge-transfer interactions between suitable donor and acceptor molecules are being studied. Furthermore, the feasibility to study zero-quantum transitions in proton spectra, to overcome the problems connected with the broad single-quantum lines, is being explored. Also pretransitional phenomena in the isotropic phase of liquid crystals, just above the transition temperature, are being successfully studied by EFNMR.

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Organic Radical Ions in Rigid Systems

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Radical ions are important chemical entities occurring in one-electron oxidation or reduction of closed-shell molecules. They are produced in chemical reactions as well as upon electrolysis, photolysis, and radiolysis.

Having an odd electron, radical ions are, in general, reactive, and their systematic generation and unambiguous spectroscopic characterization is not necessarily straightforward. This is particularly true for radical ions in fluid solutions. In rigid media, however, such species can be produced in situ by radiolysis or photolysis, and the observation of potentially reactive species can be carried out at leisure.

Tadamasa Shida, born in 1935, received his B.Sc. and Ph.D. from the University of Tokyo. From 1958 to 1974 he was a research fellow at the Institute of Physical and Chemical Research, Wako, Japan, where he worked mainly under Dr. Masashi Imamura. In 1974 he joined the faculty of Kyoto University, and he is now Professor of Chemistry. Professor Shida was a Fulbright research fellow to the University of Notre Dame (1964–1966), where he was associated with Professor William H. Hamill. He earned the Chemical Society of Japan Award for Young Chemists in 1970.

Edwin Haselbach was born in 1940 in Zurich, Switzerland. He received his university education from the Federal Institute of Technology (ETH) of Zurich where he completed a Ph.D. in physical–organic chemistry with Professor Edgar Heilbronner. After postdoctoral work with Professor Michael Dewar at the University of Texas at Austin (1967–1969), he returned to Switzerland where he became Professor of physical chemistry at the University of Basel. Since 1980 he is director of the Institute of Physical Chemistry of the University of Fribourg (Switzerland). He was recipient of the Association of Swiss Chemists Award in 1971 and the 1976 Werner Award of the Swiss Chemical Society.

Thomas Bally was born in 1948 in Geneva, Switzerland. After obtaining his Ph.D. at the University of Basel, he joined the group of Professor Satoru Masamune at MIT where he became acquainted with the technique of matrix isolation. In 1981 he returned to Switzerland and joined the institute of Professor Haselbach at the University of Fribourg where he is currently working on the spectroscopy and photochemistry of radical ions in matrices.

Generation of Radical Ions by Photolysis

Recent developments in cryogenic technology have led to the widespread use of matrix isolation spectroscopy.[1] In particular, vacuum-UV excitation of molecules embedded in rare gas matrices[2] or argon resonance photoionization during sample deposition[3] have enabled detailed vibronic analyses of elusive polyatomic radical cations. Interestingly, the spectra obtained in neon matrices at 4 K are comparable to those of the rotationally cooled gaseous ions.[2] Recent progress in the spectroscopy, photophysics, and photochemistry of ions and other transient species embedded in low-temperature rare-gas matrices has been reviewed by Bondybey.[2] Somewhat earlier optical studies of matrix-isolated charged species were reviewed by Andrews[3] and by Jacox,[4] emphasizing mostly IR spectroscopic results.

Finally, two recent innovations in this field should be mentioned. Firstly, Knight and Steadman[5] have launched the ESR study of simple radical cations such as $CO^+\cdot$, $NO_3^+\cdot$, and $H_2O^+\cdot$ generated by neon-discharge photolysis. Secondly, Andrews has begun to explore the technique of biphotonic UV/vis resonance photoionization in the presence of electron traps to generate relatively complex organic radical cations, such as those

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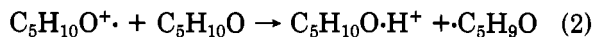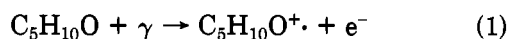
of naphthalene and biphenyl, in high yields.[6]

The research summarized above may be regarded as descended naturally from the classic work by G. N. Lewis.[7]

Generation of Radical Ions by Radiolysis

Radiolytic methods are perhaps less familiar, but they deserve attention because they complement photolysis and because of recent rapid progress in the optical and ESR spectroscopy of radical ions produced by such methods.

Photons of the order of 1 MeV, such as γ rays from ^{60}Co, interact with matter constituted of elements from the first three rows of the periodic table mostly via the Compton effect. Thus highly energetic electrons are ejected, which in turn excite and ionize molecules of the system. Even though the chemical effects of ionizing radiation are very complex and not fully understood, there is a way of harnessing the energy for selective generation of radical ions of interest. One irradiates certain frozen solutions containing solutes whose radical ion is to be studied. A general description of this technique was given by Hamill.[8a] Here the essential features are recapitulated with emphasis on spectroscopic applications.[8b]
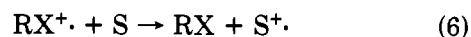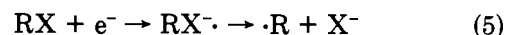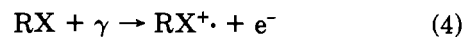
In the radiolytic method two types of polyatomic molecules are used as matrices. For the generation of radical anions, 2-methyltetrahydrofuran ($C_5H_{10}O$) is preferred (for optical monitoring) since (a) it forms a transparent glassy solid at 77 K and (b) upon γ-irradiation the following sequence of reactions takes place as the major processes:

$$C_5H_{10}O + \gamma \rightarrow C_5H_{10}O^+\cdot + e^- \qquad (1)$$

$$C_5H_{10}O^+\cdot + C_5H_{10}O \rightarrow C_5H_{10}O\cdot H^+ +\cdot C_5H_9O \quad (2)$$

$$e^- + S \rightarrow S^-\cdot \qquad (3)$$

Electrons ejected by reaction 1 travel through the bulk of the rigid solution until they find a solute molecule of sufficiently high electron affinity to yield the corresponding radical anion. Otherwise, the electrons eventually come to rest in the intermolecular vacancies of the matrix. The positive charge of the matrix molecule in reaction 1 moves intermolecularly to a very limited degree (perhaps a few molecules) and is trapped by ion–molecule reaction 2. ESR identification of a radical anion in a rigid glass depends upon one's ability to analyze the anisotropic powder spectrum, which can be a formidable task for a species of low molecular symmetry. Moreover, in the case of 2-methyltetrahydrofuran, the ESR signal for the radical $\cdot C_5H_9O$ produced by reaction 2 masks the signal due to the solute radical anion $S^-\cdot$. Polycrystalline matrices are preferred in this case, especially those of "rotator solids" like neopentane and tetramethylsilane, which frequently give rise to well-resolved spectra.[9]

The type of matrix molecules used for the generation of radical cations comprises alkyl halides such as CCl_4,[10]

the butyl chlorides, CCl_3F,[11] and the mixture of CCl_3F and CF_2BrCF_2Br.[12] The major processes that occur under irradiation, where the alkyl halide is denoted RX (X = halogen), can be summarized as

$$RX + \gamma \rightarrow RX^+\cdot + e^- \qquad (4)$$

$$RX + e^- \rightarrow RX^-\cdot \rightarrow \cdot R + X^- \qquad (5)$$

$$RX^+\cdot + S \rightarrow RX + S^+\cdot \qquad (6)$$

Although the detailed mechanism of the charge transfer in reaction 6 is not fully understood, it is found that most of the positive charges generated in reaction 4 eventually reach the solute molecules provided reaction 6 is thermodynamically feasible. Usually, a concentration of $10^3:1$ is sufficient to scavenge all the available positive charge from reaction 4. It should be pointed out that the positive charge transfer in reaction 6 is not due to the diffusion of matrix cations but is a charge-transfer process probably faster than the intermolecular vibrational period. X-rays can also be substituted for γ rays;[13] the spectral results thus obtained are identical with those in earlier experiments using γ rays. Since the above-mentioned Freons (especially $CFCl_3$) are of "solid rotator" type, ESR spectra taken for cations under these conditions are fairly well-resolved and isotropic due to motional averaging of the hyperfine and g anisotropy.

Features of the Radiolytic Generation of Radical Ions

In comparing the radiolytic generation of radical ions in rigid organic systems with photoionization in rare-gas matrices, we note the following different, sometimes complementary, features.

(a) Due to the complexity of the site structure of polyatomic matrices used in radiolysis, the spectral resolution of $S^\pm\cdot$ in reactions 3 and 6 is lower than for spectra obtained for example in neon matrices.[14]

(b) Because reactions 1–6 occur with many solutes, the method can be applied quite generally for the production of any desired $S^\pm\cdot$ provided that the electron affinity of S is sufficiently high in reaction 3 and that the ionization potential of S is sufficiently low in reaction 6. Fortunately, the halogenated alkanes used for reactions 4–6 have a rather high ionization potentials. Recently, however, addition of organic electron scavengers to rare-gas matrices has also led to the generation of radical cations in high yield.[6,13]

(c) The concentration of radical ions generated by the radiolytic method in reactions 3 and 6 can be estimated by eq 7, where the so-called G value is defined as the

$$C \ (\text{mol/L}) = GItdN_L^{-1} \qquad (7)$$

number of resultant radical ions produced per 100 eV of energy deposited in the rigid solution,[15] I is the ra-

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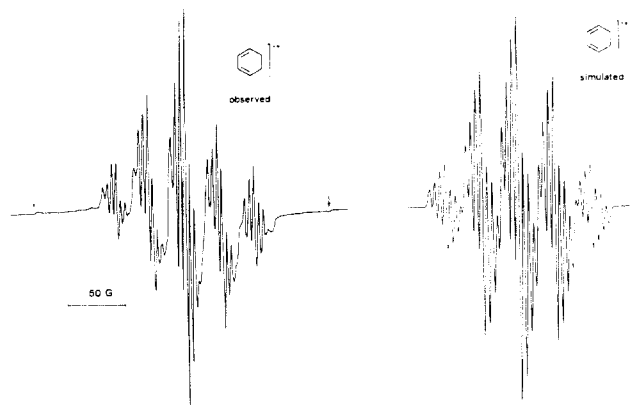
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Figure 1. Observed and simulated ESR spectra of the radical cation of 1,3-cyclohexadiene under ring puckering (effective C_{2v} symmetry).[17] Left: observed at 130 K. The arrows indicate the second and fifth peak of the manganese ions to calibrate the magnetic field. Right: simulation without taking into account the anisotropies.

diation dose rate (eV/g min), t is the irradiation time (min), d is the density (g/cm^3), and N_L is the Avogadro number. Typically, G is 2–3, so that if $I = 10^{17}$–10^{18} eV/g min (corresponding to 0.1–1 Mrad/h or 10^3–10^4 Gy/h), irradiation of 30 min produces radical ions to a concentration of 10^{-4}–10^{-3} M, which is sufficient for optical absorption and ESR measurements. Since the initial concentration of S is 10^{-2} M ($\sim 10^3$:1 mole ratio), the conversion from S to S$^{\pm}$· is 1–10%. Hence, if one knows the concentration of radical ions, the molar absorption coefficients can be roughly estimated.

(d) In the initial stage of irradiation, the ionization in reactions 1 and 4 proceeds in proportion to the irradiation time and the concentration of the resulting radical ion increases linearly. This is convenient for the amplification of weak absorption bands. Importantly, such prolonged irradiation does not deteriorate the system seriously, in contrast to photolysis where photoproducts often suffer subsequent photodecomposition.

(e) For ESR measurements of S$^{\pm}$· the paramagnetic byproducts in reactions 2 and 5 superimpose on the ESR spectrum of S$^{\pm}$·. This is a drawback of the radiolytic technique. However, it was found recently that matrices of CCl$_3$F or its mixture with CF$_2$BrCF$_2$Br provide an excellent medium for ESR measurements of radical cations generated through reaction 6.[11,16] As an example the ESR spectrum of 1,4-cyclohexadiene radical cation obtained in a CCl$_3$F matrix is presented in Figure 1.[17] The apparently negligible contribution of the background ESR signal due to the matrix radical in reaction 5 is due to the fact that the radical byproduct ·CFCl$_2$ is extremely dipolar broadened in the polycrystalline matrix because the anisotropy of the hyperfine coupling tensor of the fluorine atom in the radical is extremely large.[11]

Optical Studies of Radical Ions Produced Radiolytically

The number of high-resolution emission and excitation spectra of radical cations of polyatomic molecules in photolyzed rare-gas matrices is increasing rapidly.[2] Until very recently only emissive cations were studied,

although attempts to observe absorption spectra by way of a waveguide technique were reported in 1980.[18]

The organic cations studied by emission spectroscopy in photolyzed rare-gas matrices are divided roughly into the two categories of halobenzenes and acetylenic derivatives including those carrying a cyano group. On the other hand, the repertoire dealt with in radiolytic studies has always been much more varied. Although the spectral resolution in radiolyzed polyatomic matrices is poorer, as mentioned above, the wide range of spectroscopic information on radical ions obtained in this fashion constitutes in its own right a significant contribution to the understanding of reactive intermediates in chemistry.[19] Moreover, authentic spectral patterns are implemental in the interpretation of newly observed transient species produced in flash-photolyzed and pulse-radiolyzed fluid systems. As discussed below, the radiolytic method also allows study of chemical reactions of radical ions such as valence isomerizations, dimerizations, ion–molecule reactions, and fragmentations, under fairly well-controlled conditions.

Electronic Structures. Since the radical ions are produced in frozen solvents, we will first have to discuss the question of solvatochromic shifts in order to be able to compare their spectra with theoretical predictions and with spectra obtained for gaseous ions, such as photoelectron and photodissociation spectra. It turns out that the solvent shift is, in general, $\lesssim 0.1$ eV as is evidenced by the close agreement between the spectra of the hexatriene cation in the Freon matrix[20] and in the gas phase.[21] Similar proximity between the absorption spectra in the matrix[22] and the photodissociation spectra[23] is noted also for the cations of alkanes. Nevertheless, individual matrices yield slightly different solvent shifts as a result of their different polarity.[24] Furthermore, in a given matrix the solvent-induced red shift decreases with increasing size of the radical cation as exemplified by the series of polyacetylenes t-Bu-$(C\equiv C)_n$-t-Bu$^+$; where shifts of 1500, 1000, and 500 cm^{-1} for $n = 3$, 4, and 5, respectively, were found.[25] Obviously, increasing the space for hole delocalization decreases interaction of the radical ions with the medium.

Now that the solvent shift is known to be practically insignificant for the solvent systems commonly employed, the spectral data obtained for radical ions can be used for discussion of their electronic structure. Čársky and Zahradník, among others, made analyses some time ago.[26,27] A Longuet-Higgins/Pople type calculation with π-space CI gives a fair agreement between the observed and calculated spectra of planar conjugated systems.[28] A problem of interest arose from

(16) T. Kato and T. Shida, *J. Am. Chem. Chem.*, **101**, 6869, (1979).
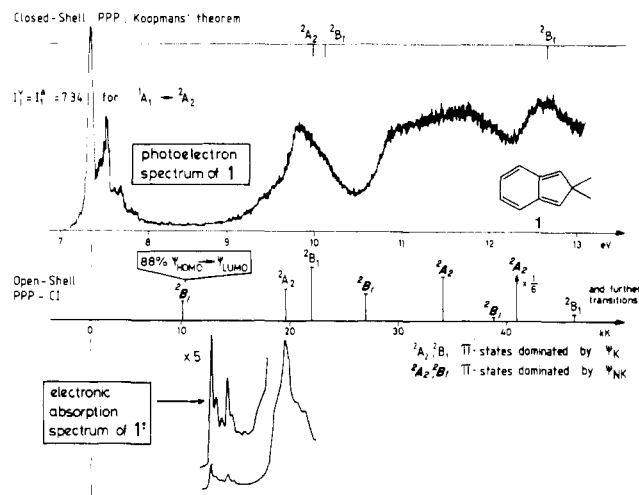(17) T. Shida, Y. Egawa, H. Kubodera, and T. Kato, *J. Chem. Phys.*, **73**, 5963 (1980).

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Figure 2. UV photoelectron spectrum of 1 and electronic absorption spectrum of 1[+]. The energy scale for the electronic spectrum has its origin at I_1^a of the PE spectrum. At the top of the figure PPP π-orbital energies are indicated; above the electronic spectrum the state energies and oscillator strengths for 1[+] from an open-shell PPP-CI calculation are displayed. Note that the first optical transition of 1[+] is predicted and occurs in a region where the PE spectrum is "empty"; hence it must be due to a transition to a "non-Koopmans'" state.[33]

the availability of spectral data of both radical cations and anions for alternant hydrocarbons, in that a slight but systematic difference between the two sets of spectra was observed.[8,29] This implies a breakdown of the pairing theorem. The problem may deserve further theoretical analysis beyond the π-electron approximation. Recently, the optical spectrum of a radical ion was utilized to probe the much argued character of the Rh–Rh bond in some dirhodium compounds.[30]

Comparison with Photoelectron Spectra. As a natural consequence of Koopmans' theorem, the energy difference between the first and the remaining photoelectron (PE) peaks should correlate with the electronic transitions in radical cations, provided that the excited states of the cations are so-called "Koopmans'" states, that is, states dominated by a single-hole configuration. This correlation was discussed already by Dixon for H_2S^+· a decade ago[31] and later exemplified for a number of cations of aromatic hydrocarbons.[32] However, some cases are found where states dominated by the HOMO → LUMO excited configuration (so-called "non-Koopmans'" states) appear at $\lambda > 300$ nm in the optical absorption spectrum of the cation.[24,25,33-35] For the orthoquinoid system 1 in Figure 2, it was found that already the *first* excited doublet state of the cation (D₁) is of this nature since no optical transition is expected in this energy range on the basis of the PE spectrum.

A simple relationship between the energy of such "non-Koopmans'" doublet states in the cation (D) and the corresponding HOMO → LUMO excited singlet (S)

Figure 3. UV photoelectron spectrum of 2, electronic absorption spectra of 2 and 2[+]·, and phosphorescence spectrum of 2 (all condensed phase spectra at 77 K except where indicated). Note that the second ion band must correspond to the HOMO–LUMO transition even though it exactly coincides with the fifth PE band, because the transition to the corresponding "Koopmans'" state is dipole forbidden.[34] Relevant vertical energies are highlighted with bold arrows.

and triplet (T) states in the neutral precursor has been derived: $E_D = (E_S E_T)^{1/2}$, provided all three excitations involve a one-electron promotion between the same "paired" MO's in an alternant system.[33,34] An example where these conditions are fulfilled is displayed in Figure 3 for 2. In 2[+]·, E_D is predicted from the above equation at $(2.06 \times 3.92)^{1/2} = 2.84$ eV, while the second electronic absorption band of the ion, corresponding to the HOMO → LUMO transition, occurs at 2.74 eV, in good agreement with theory.

We note that the collection of photoelectron spectra by Kimura et al.[36] serves as an excellent source of data to be used in identifying "Koopmans'" transitions in radical cations.

Identification of Transient Optical Spectra. Once the authenticity of a radical ion spectrum is established, these data can be used for the identification of transient species produced by photon- and electron-pulse excitation in fluid systems. For a laser flash photolyzed system of *p*-chloranil/naphthalene at room temperature, charge separation takes place to produce the cation of naphthalene and the anion of the quinone, as verified by optical absorption spectroscopy and conductivity measurements.[37] The formation of the radical cation of vinylcarbazole in a photoinduced polymerization was also confirmed by referring to the matrix spectrum.[38] In their extensive studies using picosecond laser photolysis, Mataga and co-workers consulted the spectra of radiolytically produced radical ions to identify transient species.[39,40]

Also, in pulse radiolysis the authentic matrix spectra often serve as a reference for the confirmation of a transient. An example is provided by the agreement

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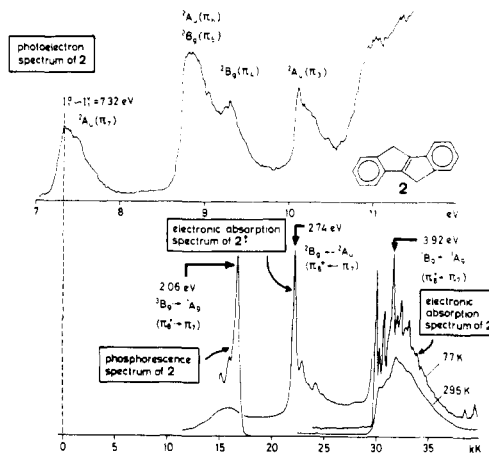
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Scheme I
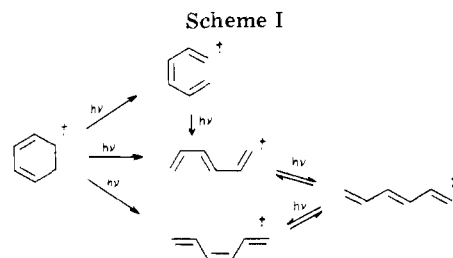
of the spectra of alkane cations produced in pulse radiolysis[41] with those obtained by the matrix photolysis technique.[22] Takamuku et al. combined both techniques for the identification of the radical anions of dimethyl truxinates and *trans*-methyl cinnamate.[42]

Reactions of Radical Ions

So far only spectroscopic applications have been discussed. However, the data are also useful to get insight into some structural reorganizations of radical ions.

(a) Structural Relaxations. Such changes are by definition nonactivated processes for the isolated systems, but matrices impose a rigid cagelike environment which may prevent extensive relaxation of the solute after ionization. However, thermal- or light-induced softening of the matrix removes this constraint. Pertinent examples involve the radical ions of benzenoid π-systems connected by essential single bonds,[43] stilbenes,[43] and perfluorobutadiene,[45] which exhibit an increased tendency toward planarity with respect to the neutral precursors.

The radical cation of highly symmetric [3]radialene
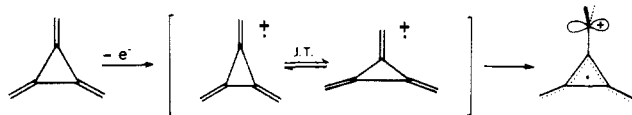
is expected to suffer a Jahn–Teller distortion[44] leading to a deformation at least down to C_{2v} symmetry. Experimentally there is, however, good evidence that the cation is subject to further structural relaxation[46] as shown above.

(b) Isomerizations. Simple rotational changes such as cis → trans isomerizations of polyaryl type molecules have been demonstrated for the radical ions of stilbenes and related compounds.[43,47] Photoinduced isomerization between the radical cations of 1,3-cyclohexadiene and 1,3,5-hexatriene has been studied to reveal the reactions given in Scheme I.[20] All the conformers have been optically characterized. Similar photoisomerizations are also observed in 1,3,5,7-octatetraene radical cation produced by direct ionization of the parent neutral or ring opening of 1,3,5-cyclooctatriene radical cation.[13b] Likewise photolysis of the radical cation of

cyclobutene with visible light leads to butadiene radical cation.[24]

The valence isomerization between quadricyclane and norbornadiene has attracted much attention as a chemical energy storage system. It is found that the potential barrier between the radical cations of quadricyclane and norbornadiene is much lower than in the neutral molecules so that the former cation isomerizes to the latter even in the rigid matrix at 77 K.[48] Under
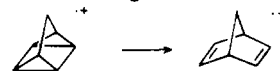
the same conditions the radical cation of hexamethyl-(Dewar benzene) isomerizes to that of hexamethylbenzene.[24] Such a lowering is in agreement with
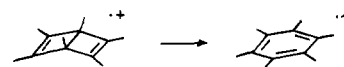
MINDO/3 type calculations[48] and is also expected on the basis of general theoretical arguments concerning barriers to rearrangement in radical ions.[49] Recent experiments conducted in fluid phase support this conclusion.[50]

(c) Complex Formation. The enigmatic near-IR absorption first observed for the γ-irradiated benzene/CCl_4 system[10] was later interpreted by Badger and Brocklehurst in terms of a sandwich type intermolecular complex between a benzene molecule and its radical cation, which they termed "dimer cation".[51] They found that a 1:1 mixture of 1-chlorobutane and isopentane gives a conveniently soft matrix to study controlled diffusion of the two components. Later, it was found that the aggregation of the molecule and its cation is a rather frequent occurrence in a softened matrix.[52] However, a careful observation of the spectral changes revealed that the process of aggregation can be rather complicated,[53] at least in the Freon matrices employed.

In comparison to dimer cations, there are relatively few reports of dimer anion formation, although it has been observed in the case of acetonitrile radical anion.[54]

ESR Studies of Radical Ions Produced Radiolytically

As mentioned, the ESR spectroscopic information obtained in matrices is often not as detailed as that in solutions or single crystals. The line width of a single ESR line usually amounts to a few Gauss due to the random orientation of individual radical ions. That obliterates the hyperfine structure if it occurs over a relatively narrow magnetic field region.

The problem of underlying ESR signals due to matrix radicals in reaction 5 can, however, be mitigated by

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using fluorine-containing matrices, as mentioned before. After it was established that the Freon mixture of CCl_3F/CF_2BrCF_2Br is useful for the study of radical cations whose hyperfine splittings are large,[16] it was found that a single component matrix of CCl_3F is even better to minimize the contribution of the background signal due to the byproduct $\cdot CCl_2F$.[11] Furthermore, resolution is generally good with this matrix due to the "solid rotator" effect. A number of radical cations have been newly characterized in this matrix by ESR.

The electronic structure of aza aromatic hydrocarbons has been studied with respect to the relative ordering of the electronic states of π- and σ-nature. For example, in a series of diazanaphthalenes, photoelectron spectroscopy predicts that the radical cations of 1,2-diaza-substituted naphthalenes have a σ ground state, whereas the others have mostly a π ground state. This prediction can be tested by producing the radical cations of each class and assessing the spin-density distribution. In the σ-cations the hyperfine interaction with the nitrogen atom should be pronounced. Indeed, the ESR spectra of the 1,2-diaza-substituted naphthalenes are very different in appearance from those of the other isomers, unambiguously substantiating the PES assignment.[16]

A straightforward example of Jahn–Teller distortion was demonstrated for the radical cation of allene.[55] The experimental finding of the distortion from D_{2d} to D_2 symmetry is in accord with a theoretical prediction 10 years earlier.[56]

ESR studies on the electronic structure of the alkane cations were initiated by Symons who used CBr_4 and other haloalkanes as matrices to detect the radical cation of hexamethylethane.[57] Their result was confirmed by Williams et al.[58] and by ourselves[59] using the better resolving Freon matrices. All these results indicate clearly that the conformation of the radical cation of hexamethylethane is rigid at 77 K with six protons lying in parallel with the central C–C bond.

A remarkable improvement in the study of alkane radical cations was made by Iwasaki and co-workers[60-63] after the suggestion from our study on some cycloalkane radical cations.[64] Iwasaki et al. found that SF_6 is also a useful matrix for the production of radical cations whose parent molecules have an ionization potential higher than that of the Freon CCl_3F, which is about 11.7 eV. This matrix has enabled them to detect the radical cation of ethane which is subject to a Jahn–Teller distortion.[44,62] The static Jahn–Teller distortion of cyclopropane[65] as well as benzene[66] was shown clearly

Figure 4. Observed ESR spectral change upon photoillumination.[17] Upper: the spectrum for the radical cation of butene-1. Lower: the same sample after illumination with visible light. Simulation indicates that this spectrum is now identical with that of the radical cation of butene-2.

by virtue of their technique of irradiation and measurement at about 4 K; other symmetric hydrocarbons were also studied.[22,67-69] Ring puckering of the radical cation of tetrahydrofuran was analyzed as a function of temperature.[70]

As mentioned before, some radical cations are subject to photoisomerization which can be followed by ESR spectroscopic changes. For example, upon illumination the radical cation of 1-butene, which absorbs over the entire visible range, isomerizes to the radical cation of 2-butene (Figure 4).

As for the reactions of alkane cations, two types have been found. One is the deprotonation to yield neutral radicals and the other is molecular elimination of H_2

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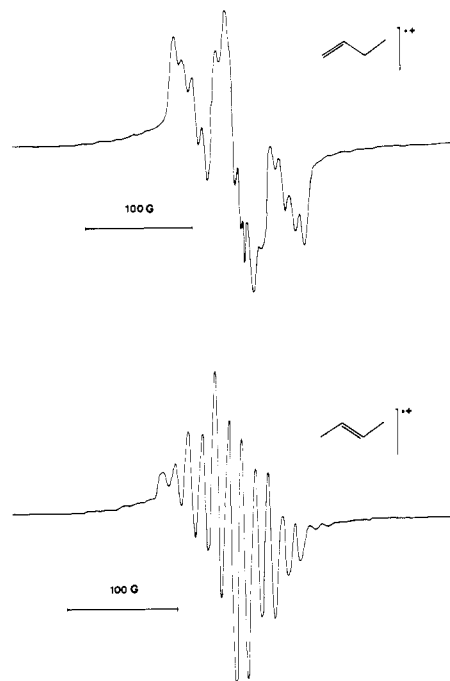(66) M. Iwasaki, K. Toriyama, and K. Nunome, *J. Chem. Soc., Chem. Commun.*, 320 (1983).

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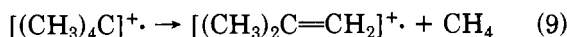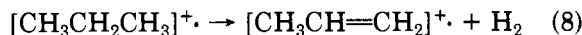(79) M. C. R. Symons, A. Hasegawa, and P. Maj, *Chem. Phys. Lett.*, **89**, 254 (1982).

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or CH_4 to form the radical cation of an olefin, as in eq 8 and 9.[62]

$$[CH_3CH_2CH_3]^{+\cdot} \rightarrow [CH_3CH{=}CH_2]^{+\cdot} + H_2 \quad (8)$$

$$[(CH_3)_4C]^{+\cdot} \rightarrow [(CH_3)_2C{=}CH_2]^{+\cdot} + CH_4 \quad (9)$$

We cite numerous recent publications on radical cations produced by the methods described above.[71-92]

We also note that the radiolytic method is now being applied for the study of biologically significant systems such as porphyrins.[93-96] Radical cations doubtlessly

play a key role in the photosynthetic process. Recognition of that role requires authentic spectral information.

Concluding Remarks

In this Account the technique of the radiolytic production of radical ions in rigid organic media is explained in some detail and the usefulness of the spectroscopic data obtainable in this way is demonstrated. It is shown that the photolytic and radiolytic generation of ions are complementary in that the former technique gives very detailed spectral information while the latter is more generally applicable. The CCl_3F matrix is shown to be a seminal medium for the ESR study of various radical cations.

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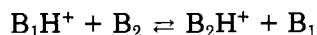# Structurally Complex Organic Ions: Thermochemistry and Noncovalent Interactions

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Protonated organic compounds play important roles in natural and technological systems. In many cases, the organic ions possess complex structures including such features as multiple functional groups, steric crowding, large size, and extensive conjugated π-electron systems. The effects of these features on the intrinsic, solvent-free thermochemical properties and interactions of the ions will be reviewed in this Account.

Mass spectrometric techniques developed in the last two decades can be used to obtain the thermochemistry of ions in the gas phase where solvent interactions are absent. Thus, gas-phase measurements can be applied to the proton-transfer equilbria between two gas-phase bases B_1 and B_2:

$$B_1H^+ + B_2 \rightleftharpoons B_2H^+ + B_1$$

These measurements yield the intrinsic solvent-free

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relative basicities ($\Delta G^\circ_{\text{proton transfer}}$) and relative proton affinities ($\Delta H^\circ_{\text{protron transfer}}$) of organic molecules. Further, mass spectrometric measurements can also elucidate the details of ion–solvent interactions. Thus, we can measure in the gas phase the enthalpies and entropies of equilibria leading to the formation of the n-fold solvated cluster ions $BH^+{\cdot}nS$ and of dimer ions $B_1H^+{\cdot}B_2$:

$$BH^+{\cdot}(n-1)S + S \rightleftharpoons BH^+{\cdot}nS \quad (n = 1{-}6)$$

$$B_1H^+ + B_2 \rightleftharpoons B_1H^+{\cdot}B_2$$
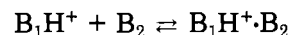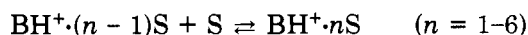
Gas-phase ion–molecule equilibria are usually measured by ion cyclotron resonance (ICR), flowing afterglow and pulsed high-pressure mass spectrometry (PHPMS). We use the latter technique, where, typically, reagents flow to the ion source as minor additives (0.01–10%) in a protonating (CH_4, i-C_4H_{10}, H_2O) or ionizing (C_6H_6, CS_2, N_2) gas. Solids can be introduced directly by a heated probe and the partial pressure measured by using ion–molecule kinetics; this makes the techniques applicable to refractory compounds such as polycyclic aromatics and nucleic bases. The total source pressure ranges from 0.1 to 2 torr, and the temperature is variable from 80 to 700 K. Ionic reactions are initiated by an electron pulse, and the change in ion signal intensities in the course of ion–molecule reactions