Low barrier isomerization processes in radical cations

Jerzy Gebicki

Institute of Applied Radiation Chemistry, Technical University,
90-924 Lodz, Poland

Abstract: Methods of generation and characterization of radical cations in low temperature matrices are briefly presented. Advantages of steady-state and pulse radiolysis in the application to studies of low barrier isomerization processes in radical cations are described. Unimolecular radical cation transformations such as valence isomerization, conformational rotamerism and enolization studied by low temperature pulse radiolysis are reviewed.

GENERATION AND CHARACTERIZATION OF RADICAL CATIONS IN MATRICES

Organic radical cations are very important intermediates in a wide variety of chemical and biological processes. Because of the "unpaired" spin and charge, radical cations are very reactive and undergo reactions typical for either free radicals or cations. Unimolecular reactions of radical cations like geometric and valence isomerizations, rearrangement, cycloreversion and fragmentation are often significantly different than those of their parent precursors. Deficit of one electron leading to a reduced bond strength of key bonds manifests itself in unusual structures and reactivity of radical cations (1-14).

There are various methods available for the generation of radical cations such as electrolysis, chemical reactions, photolysis, radiolysis, electron or ion impact, and photocatalysis on semiconductor surfaces. Organic radical cations can be generated and detected in gas phase (mass spectrometry, ultraviolet photoelectron spectroscopy), in fluid solutions (fluorescence detected magnetic resonance - FDMR, chemically induced dynamic nuclear polarization - CIDNP, pulse radiolysis) or in low temperature matrices (optical spectroscopy, EPR). Low temperature studies in organic or noble gas matrices offer a number of interesting advantages in the characterization of the structure and reactivity of radical cations. First of all, in matrices radical cations can be produced *in situ* allowing for their systematic characterization. Unambiguous spectroscopic characterization is possible by UV-VIS-IR and EPR. Secondly, in rigid matrices the lifetime of molecular ions increases due to less effective diffusion-controlled recombination processes and inhibitory effects of the matrix on fragmentation reactions. Lowering the temperature also allows for monitoring unimolecular low barrier reactions on a much longer time-scale (15).

There are two major methods of generating of radical cations in rigid matrices: photolysis and radiolysis. A few different methods of photoionization such as vacuum-UV, argon resonance, neon-discharge and biphotonic UV-VIS resonance can be applied for the ionization of molecules embedded in rare gas matrices or during sample deposition (4,9,11).

The second method, which is complementary to photolysis and presently in wide use, is radiolysis. Photons of energy on the order of keV-MeV (*e.g.*, X- and γ-rays) interacting with matter eject highly

energetic electrons which ionize molecules of the system. Similar effects can be reached using high energy electron beams. Depending on if the target of investigation is radical cations or anions two different types of organic matrices can be used (1,5,16,17). To improve the radical ion yield the matrix should be able to act as a scavenger of counter-ions. Typically the matrices used for the generation of radical cations contain alkyl halides or freons as the electron scavengers. Electrons generated during very fast ionization processes are irreversibly trapped by organic halides. The positive charges formed on the solvent molecules are transferred to substrate molecules of lower ionization potential. Depending on the ionization potential of molecules which are the target of investigation different solvents may be used. For optical studies the most suitable are solvents which upon cooling form transparent glasses. These include a mixture of hydrocarbons (methylcyclohexane, isopentane, 3-methylpentane) and butyl chlorides, butyl chlorides themselves, a mixture of the freons CCl_3F and CF_2BrCF_2Br, or SF_6.

Additionally freons are excellent solvents for EPR measurements. Despite rather complex processes taking place during and after ionization this method of generation and observation of radical cations has gained significant success. A great concern related to the radiolytic method of generation of radical cations is the relatively high energy of irradiation. However, with a typical ratio of 10^3:1 solvent to solute molecules, which is sufficient to scavenge most of the positive charges generated during ionization, the majority of the ionization processes take place in the bulk solvent and do not affect solute molecules. In addition, dissipation of energy is expected to be much faster in organic polyatomic matrices than positive charge transfer and the formation of radical cations of interest (18). The main excess of energy is delivered to radical cations during the charge transfer process from matrix to substrate as a result of the difference in ionization potentials.

The pulse radiolytic method of generation of radical ions with short (ns or μs) pulses of high energy electron beams is widely used to observe processes like fragmentation, dimerization, complex formation in liquid phase or electron transfer processes both in liquid and solid phases. But only rarely it was used to answer some interesting kinetic questions concerning unimolecular rearrangement of radical cations (19-21). The major limitation of this method seems to involve an interference of the positive charge transfer. Although the detailed mechanism is not fully understood yet, it was found that the rate constant of charge transfer depends on many factors, most importantly, the concentration of solute molecules and the difference in ionization potentials between solvent and substrate. For typically used concentrations and matrices charge transfer is usually terminated in μs-ms. Fortunately, only processes with extremely low barriers ($E_a < 8$ kJ/mol) take place at low temperature in the μs time-scale where their observation could be obstructed by the hole transfer (15). Some examples of the application of the low temperature pulse radiolysis with optical detection in the UV-VIS-near IR region to the studies of low barrier unimolecular processes in radical cations conducted in the author's laboratory will be discussed in the section to follow.

LOW TEMPERATURE PULSE RADIOLYTIC STUDIES OF FAST ISOMERIZATION PROCESSES IN RADICAL CATIONS

Valence Isomerization

Radical cations generated from valence isomers of strained molecules attract significant attention. Conversion of ionized hexamethyl Dewar benzene (1) to hexamethylbenzene (2) and quadricyclane (3) to norbornadiene (4) can be viewed as a classical representation of radical cation chemistry. For a long time only the final products of isomerization processes, *i.e.*, hexamethylbenzene or norbornadiene radical cations have been detectable following the ionization of 1 or 3. Techniques such as mass spectrometry (22-24), steady-state radiolysis with optical detection (25-27), EPR detection (28) or electrolysis (29) were unable to detect the distinct radical cations of 1 and 3. Additionally, the results of many photosensitized reactions with different electron acceptors (30-34) or semiconductor photocatalyzed isomerizations (35-37) did not indicate any intermediates other than the radical cations of 2 and 4. These results immediately gave rise to the question as to whether there is a single minimum or two distinct minima on the isomerization energy surface. Photoelectron spectra of 1 and 2 (38) or 3 and 4 (39) supported by molecular orbital calculation (26,40,41) clearly indicate the

existence of two discrete radical states upon ionization of different precursors. The first indirect experimental confirmation of the existence of the radical cations of 1 and 3 was delivered by Roth *et al.* (41,42). CIDNP results indicate unpaired spin density localized on olefinic bonds for $4\cdot^+$ and in the cyclobutane ring of $3\cdot^+$ (13,42). In the case of $1\cdot^+$ Roth *et al.* (41) proposed two different minima on the radical cation surface: $^2B_2$ with unpaired spin localized mainly on the olefinic bonds and $^2A_1$ with spin localized on the bridgehead bond. These two discrete radical cations are generated by competing pathways and do not equilibrate rapidly. MO calculations indicate that the $^2B_2$ state is lower in energy. The CIDNP results suggest a radical cation lifetime of several nanoseconds which is needed to generate a nuclear spin polarization. However, nanosecond spectroscopic experiments by Peacock and Schuster (33) failed to reveal any evidence for radical cation other than $2\cdot^+$.

(1)

1·⁺   2·⁺

(2)

3·⁺   4·⁺
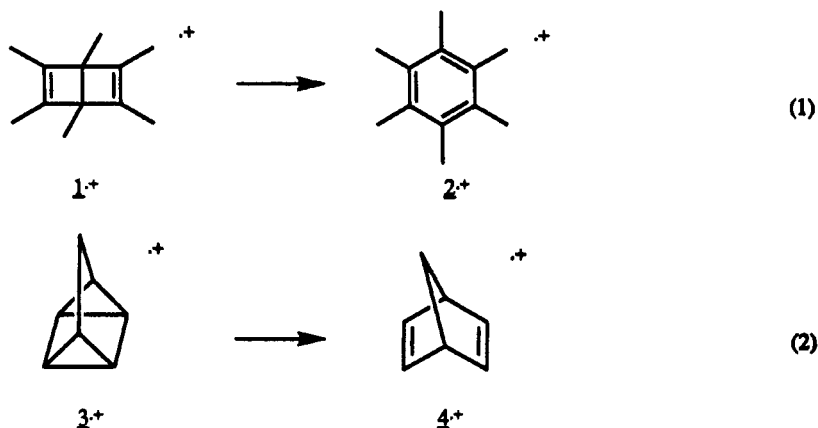
Indirect proof of the existence of the discrete radical cations of 1 and 3 was also implicated by Gebicki *et al.* (43,44) by means of low temperature pulse radiolysis. Efforts to monitor directly the absorptions of $1\cdot^+$ and $3\cdot^+$ were unsuccessful. However, only a limited spectral region was examined (350-700nm for $1\cdot^+$ and 400-1100nm for $3\cdot^+$). It was possible, however, to monitor a delayed formation of absorptions characteristic for $2\cdot^+$ and $4\cdot^+$ after pulse radiolytic ionization of 1 and 3 in low temperature matrices. Under similar experimental conditions the absorptions of $2\cdot^+$ and $4\cdot^+$ were seen immediately after ionization of 2 or 4. The observed delayed formation of $2\cdot^+$ and $4\cdot^+$ following ionization of 1 and 3 was assigned to isomerization processes (reactions (1) and (2)). It was possible to monitor reaction kinetics and to estimate activation parameters ($E_a=17.6$ kJ/mol for reaction (1) and $E_a=20.0$ kJ/mol for reaction (2)).

Recently, Williams *et al.* (45) have provided the first direct spectroscopic evidence for the isomerization of $3\cdot^+$ to $4\cdot^+$ by recording the EPR spectrum during continuous illumination of 4 which had been previously γ-irradiated. The photoproduct generated from $4\cdot^+$ was assigned to $3\cdot^+$ and the thermal recovery of $4\cdot^+$ from $3\cdot^+$ was monitored. The EPR spectrum of $3\cdot^+$ was obtained. Very recently $3\cdot^+$ was also characterized by EPR in zeolite matrices at 4K after electron beam irradiation (46).

Conformational Rotamerism

Delocalization of the positive charge is one of the basic problems in radical cation chemistry. Interactions leading to charge delocalization between heteroatoms like nitrogen and sulfur have attracted significant attention. Two major types of interaction "through-space" with the formation of a σ-three electron bond and "through-bond", play a dominant role (47-50). Radical cations generated from molecules bearing two or more nitrogen atoms were investigated from this point of view by photoelectron spectroscopy (49-53), EPR (3,54,55) and optical spectroscopy (53,56,57). Both through-space and through-bond interactions are strongly dependent on molecular structure and geometry (47-50). Recently Gebicki *et al.* (58) by means of low temperature pulse radiolysis investigated such interactions in terms of the conformational requirements necessary to obtain the most stable structures which are characterized by the strongest interaction between two nitrogen atoms

in the series of α,ω-diaminoalkanes (5-9), 1,4-dimethylpiperazine (10) and 1,4-diaza-bicyclo[2.2.2]octane (11).

The absorption spectra of the radical cations of diamines with three or less methylene groups separating the nitrogen atoms show only, a visible transition, in contrast to those with four and six methylene group, where only the UV-transition is seen. As the length of the polymethylene chain increases, the probability of achieving a favourable conformation for interaction decreases

$$CH_3 \diagdown N-(CH_2)_n-N \diagup CH_3$$
$$CH_3 \diagup \qquad\qquad \diagdown CH_3$$

n = 1 - 4, 6

5 - 9

CH₃—N⌐‾⌐N—CH₃   N⌐‾⌐N

10   11
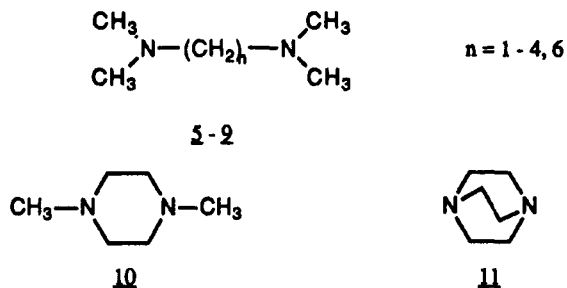
sharply especially in rigid matrices where conformational mobility can be quenched effectively. Hence, radical cations generated from diaminobutane (8) or diaminohexane (9) possess a charge localized on one nitrogen atom, similarly to the monoamine radical cations.

Asmus *et al.* (59) have observed similar dependence of intramolecular interactions between sulfur atoms on the length of separating alkane chain in the radical cations of analogous. thio compounds -1,n-bis(alkylthio)alkanes ($RS(CH_2)_nSR$ for n = 2-10) in aqueous solution. If the number of methylene groups is less than five, the formation of intramolecular σ-three electron bonds dominates. The most stable structures are formed for n equal to three or four. For longer chain radical cations intermolecular interactions prevail.

The visible absorption observed for radical cations generated from cyclic (10) and bicyclic (11) diamines (58) points toward a structure with delocalized charge. The problem of charge delocalization in 11·⁺ was thoroughly studied by photoelectron spectroscopy considering a dominant through-bond interaction (52). Generally, dominant through-bond interactions are suggested in radical cations with nitrogen atoms linked by ethylene bridges (50). Absorption spectra themselves do not contain sufficient information for judging what type of interaction dominates. However, the striking feature of the diamine series with ethylene bridges is a shift of λ_{max} to lower wavelength as the number of ethylene bridges is increased. This is fully compatible with a picture based on dominant through-bond interactions. An increasing number of ethylene bridges leads to a stronger interaction between the nitrogen atoms as manifested by the shift of the observed transition to higher energy (58).

Low temperature pulse radiolysis studies indicate some significant changes both in the band shape (width and λ_{max}) and intensity of investigated absorption spectra. This effect is particularly pronounced for diaminopropane radical cation (7·⁺). At 90K the initial absorption is broad with maximum at 510nm. This absorption grows and shifts to lower frequency with time. At 77K the process is significantly slower with initial broad absorption at 540nm. At 30K a very broad absorption with maximum at 600nm is seen and any distinct changes of this spectrum in time are frozen. The observed process can be rationalized in terms of conformational motion leading to an enhanced interaction between the two nitrogen atoms of the diamine. At very low temperature this motion can be quenched as a result of intrinsic rotational barriers and/or rigidity of matrix. As one would expect, changes in the transient absorption spectra for other diamines are much less pronounced. For 11·⁺, where the bicyclic structure holds the two nitrogen atoms in almost a fixed configuration, no change at all with time is seen in the absorption spectra.

All of these conformational changes which lower the energy of radical cations and lead to structures suitable for charge delocalization should, in principle, follow first-order kinetics. This is the case if instead of classical one considers a dispersive first-order kinetics typical for the solid phase. By a comparison of the kinetic results for diamine radical cations with one, two and three separating methylene groups Gebicki *et al.* (60) have clearly demonstrated that the activation energy distribution

function becomes broader with increasing number of methylene groups. This effect is accompanied by a substantial increase in the mean value of activation energy. One can intuitively visualize this observation in the following way: Greater conformational flexibility of diamines with longer chains causes greater conformational disorder of diamines embedded in the glassy matrix. After ionization, any changes leading to the structures of favourable conformation for molecules with greater initial conformational disorder should be characterized by a broader activation energy distribution function. There is a close correlation between the kinetic behaviour of a conformationally driven reaction and the structure of the matrix site accommodating the reacting molecule.

Interesting examples of radical cations generated by low temperature steady-state and pulse radiolysis from 1,4,8,11-tetrathiocyclotetradecane (12) and derivatives bearing *gem*-dimethyl pairs at the 6- or at the 6- and 13-positions (13 and 14, respectively) were recently studied (61). Despite very different conformations for the neutral compounds 12-14, their radical cations ($12^{.+}$ - $14^{.+}$) possess
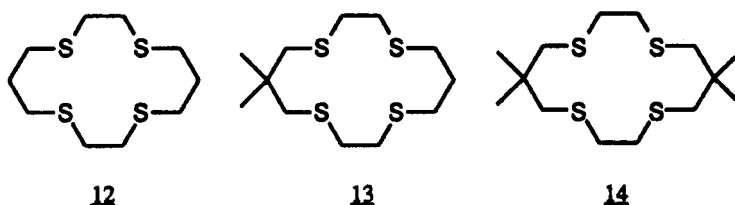
similarly located σ->σ^* transitions (about 450nm) for structures characterized by the strongest interactions between sulfur atoms. Delayed formation of characteristic absorptions for $13^{.+}$ and $14^{.+}$ indicates that the geometries of these radical cations differ substantially from the geometries of the neutral molecules. In the case of $14^{.+}$ an intermediate structure (λ_{max}= 600nm) was intercepted which rearranged to the most stable structure (λ_{max}= 450nm) both thermally and photochemically. Similar to the former case of diamine radical cations the kinetic data were also treated here by first-order dispersive kinetics.

Enolization

Aromatic carbonyl compounds carrying an alkyl group in the *ortho*-position may undergo hydrogen atom transfer upon photoexcitation to form the corresponding *o*-quinoid enols (62,63). These are usually subject to rapid reketonization, as this is a thermodynamically favourable process involving a very small activation barrier. On the other hand, Gebicki *et al.* showed that upon radiolytic ionization various *ortho*-substituted aromatic compounds undergo spontaneous hydrogen atom transfer in low temperature matrices to yield radical cations with *o*-quinoid structures (64,65). It was shown that enolization is endothermic by 108-125 kJ/mol in the neutral molecules (15) but exothermic by 58-75 kJ/mol in the radical cations. The inverse stability of enol radical cations is schematically presented below:


R = H, CH₃, Ph
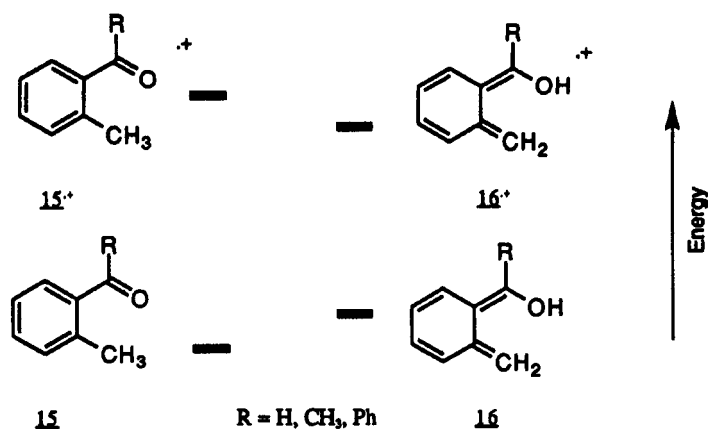
There are numerous gas phase experimental studies showing that the enolization of carbonyl radical cations is usually exothermic (66-68). A similar conclusion is also drawn from condensed phase experiments (68,69).

The UV-VIS and IR spectra of enol radical cations generated from o-carbonyl toluenes (15) by X- or γ-rays in frozen glasses or in argon matrices show a similar pattern of bands (64,65). All UV-VIS spectra can be interpreted in terms of electronic transitions of the four lowest excited states of the corresponding o-quinoid enol radical cations (70). The OH(OD) stretching frequencies in enol radical cations are significantly shifted to lower energy compared to the corresponding neutrals. This points toward weaker OH(OD) bonds in enol radical cations as these groups are adjacent to the electron deficient π system.

The kinetics of the enolization process and the formation of enol radical cations was studied by low temperature pulse radiolysis (64,65). Strong curvature of the Arrhenius plot and a substantial kinetic isotope effect (k_H/k_D) indicate participation of quantum-mechanical tunneling in the hydrogen (deuterium) atom transfer.

The occurrence of hydrogen atom transfer upon ionization appears to be dependent on conformational requirements. Acetylmesitylene (17), where the carbonyl group is held in a position perpendicular to the benzene ring, shows no enolization, whereas the corresponding formyl derivative, 2,4,6-trimethyl-benzaldehyde (19), does not suffer from this impediment (74).

$$\underset{\textbf{17}^{\cdot+}}{\text{(mesityl methyl ketone radical cation)}} \quad \xrightarrow{\;\;\;\not\to\;\;\;} \quad \underset{\textbf{18}^{\cdot+}}{\text{(enol radical cation)}} \qquad (3)$$

$$\underset{\textbf{19}^{\cdot+}}{\text{(2,4,6-trimethylbenzaldehyde radical cation)}} \quad \xrightarrow{\;\;\;\;\;\;} \quad \underset{\textbf{20}^{\cdot+}}{\text{(enol radical cation)}} \qquad (4)$$
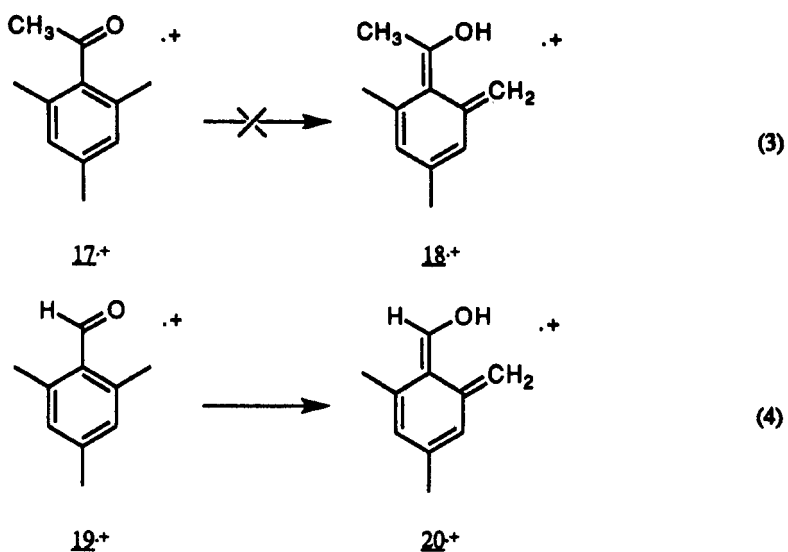
Spontaneous hydrogen atom transfer and formation of stable enol radical cations is not limited to aromatic carbonyl compounds carrying o-alkyl substituents. The migrating hydrogen can also originate from a hydroxy (64) or formyl group and a nitro or nitroso group can act as acceptor (72).

The reactivity of enol radical cations generated photocatalytically on semiconductor surfaces was recently investigated by Gebicki $et\ al.$ who applied hydrogen isotope exchange as a model reaction (73,74). This reaction can be successfully applied to test reactivity of both neutral photoenols and enol radical cations (75,76).

Concluding Remarks

Radiolytic generation of radical cations combined with optical detection is powerful technique that enjoys widespread use. A variety of radical cations of unusual structure and reactivity have been evaluated by means of this method. However, the application of complementary time-resolved techniques like pulse radiolysis is essential to determine activation barriers and to elucidate interesting mechanistic details of radical cation interconversions.

REFERENCES

1. W. H. Hamill, *Radical Ions*, p. 321, E. T. Kaiser and L. Kevan (eds.), Wiley-Interscience, New York (1968).
2. K.-D. Asmus, *Acc. Chem. Res.* **12**, 436 (1979).
3. M. C. R. Symons, *Pure Appl. Chem.* **53**, 223 (1981).
4. T. A. Miller and V. E. Bondybey (eds.), *Molecular Ions: Spectroscopy Structure and Chemistry*, North-Holland, Amsterdam (1983).
5. T. Shida, E. Haselbach and T. Bally, *Acc. Chem. Res.* **17**, 180 (1984).
6. M. C. R. Symons, *Chem. Soc. Rev.* **13**, 393 (1984).
7. H. D. Roth, *Acc. Chem. Res.* **20**, 343 (1987).
8. M. Shiotani, *Magn. Reson. Rev.* **12**, 333 (1987).
9. L. Andrews and M. Moskovits (eds.), *Chemistry and Physics of Matrix-isolated Species*, North-Holland, Amsterdam (1989).
10. M. E. Jacox and W. E. Thompson, *Res. Chem. Intermed.* **12**, 33 (1989).
11. A. Lund and M. Shiotani (eds.), *Radical Ionic Systems*, Kluwer Academic, Dordrecht (1991).
12. T. Shida, *Annu. Rev. Phys. Chem.* **42**, 55 (1991).
13. H. D. Roth, *Top. Curr. Chem.* **163**, 131 (1992).
14. F. Gerson, *Acc. Chem. Res.* **27**, 63 (1994).
15. J. Gebicki, A. Marcinek and J. Rogowski, *Radiat. Phys. Chem.* **39**, 41 (1992).
16. H. Iwamura and D. F. Eaton, *Pure Appl. Chem.* **63**, 1003 (1991).
17. T. Shida, *Electronic Absorption Spectra of Radical Ions*, Elsevier, Amsterdam (1988).
18. J. Bos, J. Schmidt, H. Mai, V. Decker and M. Halbig, *Radiat. Phys. Chem.* **34**, 361 (1989).
19. R. Mehnert, *Radical Ionic Systems*, p. 231, A. Lund and M. Shiotani (eds.), Kluwer Academic, Dordrecht (1991).
20. A. D. Trifunac and D. W. Werst, *Radical Ionic Systems*, p. 195, A. Lund and M. Shiotani (eds.) Kluwer Academic, Dordrecht (1991).
21. D. W. Werst and A. D. Trifunac, *J. Phys. Chem.* **95**, 3466 (1991).
22. Z. Dolejsek, V. Hanus and H. Prinzbach, *Angew Chem.* **74**, 902 (1962).
23. M. Rabrenovic, A. G. Brenton and T. Ast, *Org. Mass Spectrom.* **18**, 587 (1983).
24. D. Kuck, *Mass Spectrom. Rev.* **9**, 187 (1990).
25. E. Haselbach, T. Bally, R. Gschwind, U. Klemm and Z. Lanyiova, *Chimia* **33**, 405 (1979).
26. E. Haselbach, T. Bally, Z. Lanyiova and P. Baertschi, *Helv. Chim. Acta* **62**, 583 (1979).
27. B. J. Kelsall and L. Andrews, *J. Am. Chem. Soc.* **105**, 1413 (1983).
28. K. Nunome, K. Toriyama and M. Iwasaki, *Tetrahedron* **42**, 6315 (1986).
29. K. Yasufuku, K. Takahashi and C. Kutal, *Tetrahedron Lett.* **25**, 4893 (1984).
30. T. R. Evans, R. W. Wake and M. M. Sifain, *Tetrahedron Lett.* 701 (1973).
31. G. Jones II and S.-H. Chiang, *J. Am. Chem. Soc.* **101**, 7421 (1979).
32. G. Jones II and W. G. Becker, *J. Am. Chem. Soc.* **103**, 4630 (1981).
33. G. Jones II, S.-H. Chiang, W. G. Becker and J. A. Welch, *J. Phys. Chem.* **86**, 2805 (1982).
34. N. J. Peacock and G. B. Schuster, *J. Am. Chem. Soc.* **105**, 3632 (1983).
35. H. Al-Ekabi and P. de Mayo, *J. Phys. Chem.* **90**, 4075 (1986).
36. A. M. Draper and P. de Mayo, *Tetrahedron Lett.* **27**, 6157 (1986).
37. H. Ikezawa and C. Kutal, *J. Org Chem.* **52**, 3299 (1987).
38. G. Bieri, E. Heilbronner, T. Kobayashi, M. J. Goldstein, R. S. Leight and M. S. Lipton, *Helv. Chim. Acta* **59**, 2657 (1976).
39. E. Heilbronner and E. Martin, *Helv. Chim. Acta* **55**, 1490 (1972).
40. K. Raghavachari, R. C. Haddon and H. D. Roth, *J. Am. Chem. Soc.* **105**, 3110 (1983).
41. H. D. Roth, M. L. M. Schilling and K. Raghavachari, *J. Am. Chem. Soc.* **106**, 253 (1984).

42. H. D. Roth, M. L. M. Schilling and G. Jones II, *J. Am. Chem. Soc.* **103**, 1246 (1981).
43. J. Gebicki, A. Marcinek and J. Mayer, *J. Am. Chem. Soc.* **111**, 3098 (1989).
44. J. L. Gebicki, J. Gebicki and J. Mayer, *Radiat. Phys. Chem.* **30**, 165 (1987).
45. G.-F. Chen, R. S. Pappas and F. Williams, *J. Am. Chem. Soc.* **114**, 8314 (1992).
46. K. R. Cromack, D. W. Werst, M. V. Barnabas and A. D. Trifunac, *Chem. Phys. Lett.* **218**, 485 (1994).
47. R. Hoffman, A. Imamura and W. J. Hehre, *J. Am. Chem. Soc.* **90**, 1499 (1968).
48. R. Hoffman, *Acc. Chem. Res.* **4**, 975 (1971).
49. S. F. Nelsen and J. M. Buschek, *J. Am. Chem. Soc.* **96**, 7930 (1974).
50. R. W. Alder, R. J. Arrowsmith, A. Casson, R. B. Sessions, E. Heilbronner, B. Kovac, H. Huber and M. Taagepera, *J. Am. Chem. Soc.* **103**, 6137 (1981).
51. P. Bischof, J. A. Hashmall, E. Heilbronner and V. Hornung, *Tetrahedron Lett.* 4025 (1969).
52. E. Heilbronner and K. A. Muszkat, *J. Am. Chem. Soc.* **92**, 3818 (1970).
53. T. Shida, Y. Nosaka and T. Kato, *J. Phys. Chem.* **82**, 695 (1978).
54. G. W. Eastland, R. Rao and M. C. R. Symons, *J. Chem. Soc., Perkin Trans.* 2 1551 (1984).
55. J. P. Dinnocenzo and T. E. Banach, *J. Am. Chem. Soc.* **110**, 971 (1988).
56. S. F. Nelsen, E. Haselbach, R. Gschwind, R. Klemm and Z. Lanyiova, *J. Am. Chem. Soc.* **100**, 4367 (1978).
57. R. W. Alder, M. Bonifacic and K.-D. Asmus, *J. Chem. Soc., Perkin Trans.* 2 277 (1986).
58. J. Gebicki, A. Marcinek and C. Stradowski, *J. Phys. Org. Chem.* **3**, 606 (1990).
59. E. Anklam, K.-D. Asmus and H. Mohan, *J. Phys. Org. Chem.* **3**, 17 (1990).
60. A. Marcinek, J. Gebicki and A. Plonka, *J. Phys. Org. Chem.* **3**, 757 (1990).
61. J. Rogowski, J. Adamus, J. Gebicki and S. F. Nelsen, *J. Chem. Soc., Perkin Trans.* 2 779 (1994)
62. J. C. Scaiano, *Acc. Chem. Res.* **15**, 252 (1982).
63. P. J. Wagner, *Acc. Chem. Res.* **22**, 83 (1989).
64. J. Gebicki, A. Marcinek, J. Michalak, J. Rogowski, T. Bally and W. Tang, *J. Mol. Struct.* **275**, 249 (1992).
65. A. Marcinek, J. Michalak, J. Rogowski, W. Tang, T. Bally and J. Gebicki, *J. Chem. Soc., Perkin Trans.* 2 1353 (1992).
66. H. Schwarz, *Adv. Mass Spectrom.* **10A**, 13 (1985).
67. F. Turecek, *The Chemistry of Enols,* p. 95, Z. Rappaport (ed.), Wiley, New York (1990).
68. S. Hammerum, *Mass Spectrom. Rev.* **7**, 123 (1988).
69. M. Schmittel and U. Baumann, *Angew. Chem. Int. Ed. Eng.* **29**, 541 (1990).
70. K. Kesper, N. Munzel, W. Pietzuch, H. Specht and A. Schweig, *J. Mol. Struct. (Teochem)* **200**, 375 (1989).
71. J. Michalak, T. Bally and J. Gebicki, *Pol. J. Chem.* **67**, 1403 (1993).
72. J. Michalak, J. Gebicki and T. Bally, *J. Chem. Soc., Perkin Trans.* 2 1321 (1993).
73. J. Michalak, A. Jonska, W. Tang and J. Gebicki, *Pol. J. Chem.* **67**, 1505 (1993).
74. J. Michalak and J. Gebicki, *J. Chem. Soc., Perkin Trans.* 2 2249 (1993).
75. J. Gebicki, W. Reimschussel and B. Zurawinska, *J. Phys. Org. Chem.* **3**, 38 (1990).
76. J. Michalak, M. Wolszczak and J. Gebicki, *J. Phys. Org. Chem.* **6**, 465 (1993).