Spontaneous Hydrogen Atom Transfer on Ionization: Characterization of Enol Radical Cations in Cryogenic Matrices

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1. Introduction

Organic radical cations are 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 transformations typical for both free radicals and/or cations. Unimolecular processes in radical cations such as valence isomerization, rearrangement, and fragmentation are often significantly different than those of their neutral precursors. The deficit of one electron leading to a reduced strength of key bonds

manifests itself in unusual structures and reactivities of radical cations.[1]

A special feature of radical cation chemistry is the possibility of hydrogen atom transfer which may occur spontaneously upon ionization if a cyclic transition state with five members can be formed. Mass spectrometric experiments showed that this occurs in many heteroatom-containing compounds leading to so-called distonic ions whose structure often does not correspond to that of a persistent neutral species, but which are nevertheless usually more stable than their conventional isomers.[2]

Distonic ions have also been investigated in condensed phase where they may occur as products of radiation or radical chemistry (cf. Section VI of ref 2c). However, apart from a few exceptional cases, the only distonic ions which form by spontanous intramolecular hydrogen atom transfer in solid media are those arising from aliphatic esters[3] where it is thought to occur by quantum mechanical tunneling.[3c] This Account is concerned with another class of compounds that show a similar behavior, namely *enones* (or related compounds) which are disposed for 1,5-hydrogen transfers via 6-membered ring transition states to yield dienols as shown here:
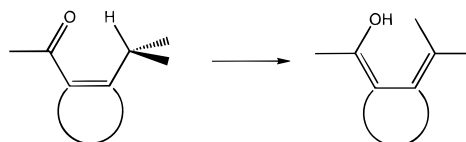
Keto−enol tautomerism in neutral molecules is well recognized in chemistry,[4] but simple enols are usually less

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Thomas Bally was born in Geneva, Switzerland, in 1948. He studied chemistry at the University of Basel, where he graduated in physical chemistry in 1978. After two postdoctoral years at MIT (with S. Masamune), he took up a position at the University of Fribourg, where he obtained his habilitation in 1988 and became a professor in 1991. His research focuses on the spectroscopic and chemical characterization of radical ions in solid matrices.

Ever since they met in 1987 at the laboratories of Josef Michl, then at Austin, TX, the research groups of the two authors have entertained close relations and engaged in a variety of joint projects.

[†] Technical University of Lodz.
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(1) (a) *Radical Ionic Systems*; Lund, A., Shiotoni, M., Eds.; Kluwer: Dordrecht, The Netherlands, 1991. (b) Shida, T. *Ann. Rev. Phys. Chem.* **1991**, *42*, 55. (c) Roth, H. D. *Top. Curr. Chem.* **1992**, *163*, 131. (d) Gerson, F. *Acc. Chem. Res.* **1994**, *27*, 63. (e) Gebicki, J. *Pure Appl. Chem.* **1995**, *67*, 55. (f) Dass. C. *Mass Spectrom. Rev.* **1990**, *9*, 1.
(2) (a) Schwarz, H. *Adv. Mass Spectrom.* **1985**, *10A*, 13. (b) Bouchoux, E. *Mass Spectrosc. Rev.* **1988**, *7*, 1, 203. (c) Hammerum, S. *Ibid.* **1988**, *7*, 123.
(3) (a) Iwasaki, M.; Muto, H.; Toriyama, K. Nunome, K. *Chem. Phys. Lett.* **1984**, *105*, 586, 592. (b) Sevilla, M. D.; Becker, D.; Sevilla, C. L.; Swarts, S. *J. Phys. Chem.* **1984**, *88*, 1701. (c) Rideout, J.; Symons, M. C. R.; *J. Chem. Soc., Perkin Trans. 2* **1986**, 625.
(4) (a) *The Chemistry of Enols*; Rappoport, Z., Ed.; Wiley: Chichester, U.K., 1990. (b) Toullec, J. In ref 4a, pp 323−398. (c) Turecek, F. In ref 4a, pp 95−146.

stable than their keto tautomers and exist only at very low concentration under equilibrium conditions.[4a] Conversely, gas-phase experiments and calculations showed that enol radical cations are usually more stable than their keto tautomers.[4b] A simple rationalization of the greater stability of keto tautomers in neutral molecules comes from comparison of bond energies, i.e. C−H, C−C, and C=O vs C=C, C−O, and O−H. However, as it takes much less energy to remove an electron from the π-orbital of the enol than from the n-orbital of the ketone, this can lead to a situation where the enol radical cation is favored energetically over its keto tautomer (Scheme 1).

Scheme 1
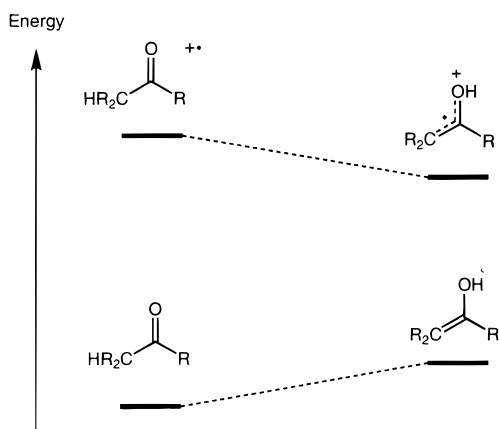
Compared to the considerable body of experimental data on enol radical cations in the gas phase,[4c] the reports on observations of such species in condensed phase, where the electronic and molecular structure can be probed, are more scarce. This is due to the fact that (a) simple enols as neutral precursors to their radical cations are difficult to prepare and to isolate due to the usually very rapid re-ketonization and (b) in solution, ketone radical cations appear to decay preferentially by intermolecular proton or hydrogen transfer or α-cleavage rather than by enolization. Thus, the only successful approach to genetae and identify enol radical cations in solution involved ionization of stable dimesityl substituted enols, an approach which allowed Schmittel *et al.*[5] to evaluate the relative stabilities of the neutral and the ionized keto and enol forms by a thermochemical cycle.

By working in cryogenic matrices, where the bimolecular reactions which prevail in solution are suppressed, we can extend these investigations to any enol which can be prepared photochemically and whose re-ketonization in the cation is endothermic. In addition, thermal barriers for pericyclic reactions such as hydrogen shifts are often lower in radical cations than in neutrals. Therefore enolization may even take place spontaneously on ionization of the corresponding keto forms.

In the early 1990s we initiated a research program to investigate such compounds by synergetic application of the methods available in the Lodz and Fribourg laboratories. Thereby it turned out that the phenomenon of ionization-induced hydrogen transfer is of much wider scope than we had initially anticipated. This interesting phenomenon and its role in the reactivity of ionic systems will be addressed in this Account. Particular attention will be paid to the spectroscopic and kinetic characterization of ionized tautomers in cryogenic matrices.

2. Studies of Radical Cations in Cryogenic Matrices

Low-temperature studies in organic glasses or noble gas matrices offer a number of interesting advantages in the characterization of the structure and the reactivity of radical cations. First, in rigid matrices, radical cations can be produced in situ which allows for their systematic spectroscopic characterization by optical and magnetic resonance methods.[6] Second, the lifetime of molecular ions increases greatly due to suppression of diffusion-controlled recombination processes and to the inhibitory effect of the matrix on fragmentation reactions which prevail especially in the gas phase. Lowering the temperature also allows monitoring of fast unimolecular reactions on a much longer time scale.[1e]

The two major methods for generating radical cations in rigid matrices are photolysis and radiolysis. Thus, direct *photoionization* can be effected by monophotonic VUV (discharge lamps) or biphotonic UV/vis irradiation (lasers) during sample deposition or (if the matrix is transparent to that light) after matrix isolation.[7] Complementary to photolysis, and presently in wide use, is *radiolysis* where high-energy photons on the order of kiloelectonvolts to megaelectronvolts (e.g., X- and γ-rays) interacting with matter eject highly energetic electrons which ionize (mostly solvent) molecules of the system and generate the radical ions of interest via secondary processes. Similar effects can be achieved using high-energy electron or proton beams. If the target of investigation are radical cations or anions two specific types of organic matrices are used.[8]

To improve the radical ion yield, the matrix should be able to act as a scavenger of counterions. Therefore, the matrices used for the generation of radical cations typically contain alkyl halides which irreversibly trap the electrons generated during the fast ionization process. The positive charges formed on the solvent molecules are then transferred to solute molecules of lower ionization potential. Depending on the ionization potential of molecules which are the target of investigation, different solvents may be used. Those forming transparent glasses upon cooling are suitable for optical studies. They include a mixture of hydrocarbons (methylcyclohexane, isopentane, 3-methylpentane) and alkyl chlorides, Freons (a mixture of CCl_3F and CF_2BrCF_2Br for optical studies),[6,8] or argon doped with CH_2Cl_2.[6]

A common concern related to the radiolytic generation of radical cations is the relatively high energy of irradiation. However, with a typical ratio of 1000:1 solvent to solute molecules, the overwhelming majority of the ion-

(5) (a) Schmittel, M. *Top. Curr. Chem.* **1994**, *169*, 183. (b) Schmittel, M.; Gescheidt, E.; Röck, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1961.

(6) Bally, T. In ref 1a, pp 3−54.

(7) *Molecular Ions: Spectroscopy, Structure and Chemistry*; Miller, T. A., Bondybey, V. E., Eds.; North-Holland: Amsterdam, 1983; Chapters 5 and 6.

(8) (a) Shida, T.; Haselbach, E.; Bally, T. *Acc. Chem. Res.* **1984**, *17*, 180. (b) Iwamura, H.; Eaton, D. F. *Pure Appl. Chem.* **1991**, *63*, 1003. (c) Shida, T.; *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, 1988.
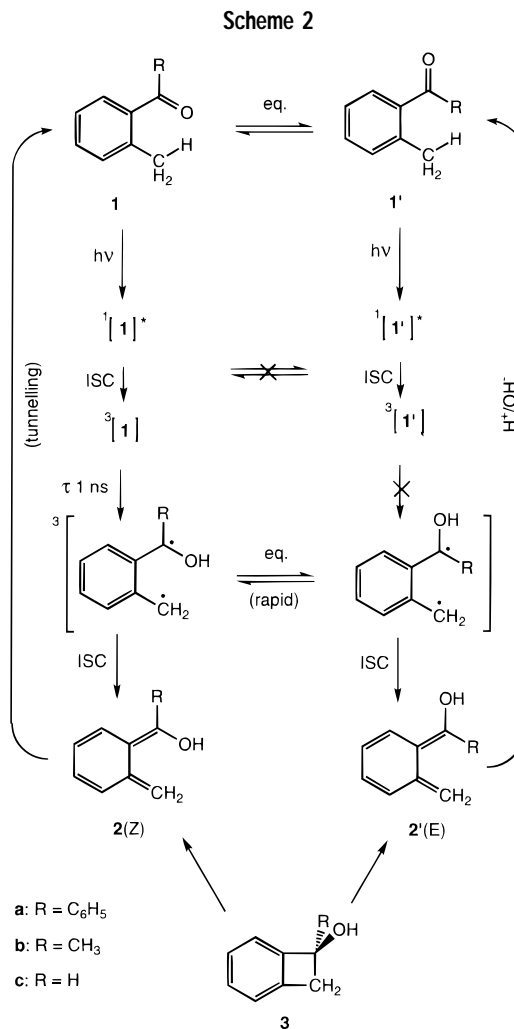
ization processes take place in the bulk solvent and do not directly affect solute molecules. In addition, dissipation of energy is expected to be much faster in organic polyatomic matrices than charge migration and the formation of radical cations of interest.[9] However, some excess energy is imparted onto radical cations during the charge transfer process from matrix to solute as a result of the difference in ionization potentials, and this excess energy may drive rearrangement or fragmentation of the primary radical cations, especially if the medium is unsuitable to dissipate energy rapidly, as is the case for argon matrices.

The method of generation of radical ions with short (nanosecond or microseconds) pulses of high-energy electron beams is widely used to observe processes such as fragmentation, dimerization, or complex formation in liquid phase. However, it was only rarely employed to probe unimolecular rearrangements of radical cations.[10] Recently we have established that low-temperature pulse radiolysis with optical detection in the UV−vis/near-IR region can be a powerful technique in the studies of low-barrier unimolecular processes in radical cations, such as valence isomerization[11] and conformational isomerization.[12] This technique can be viewed as complementary to time-resolved ESR[13a] or FDMR[13b] spectroscopy which are not generally applicable.

3. *o*-Alkyl Phenyl Ketones: the Prototypical Systems

3.1. Background. Aromatic rings carrying an alkyl group adjacent to a carbonyl function (**1**) are predisposed for 1,5-hydrogen transfer to form *o*-quinoid enols (**2**), if the former can be sufficiently energized.

It has been known for some time that such enolizations can occur photochemically for compounds **1,** and the mechanism of the reaction (see above Scheme) has been largely elucidated.[14] Thus it was found that, once formed, the *E*-isomers of the photoenols **2** are quite long-lived in dry aprotic solvents, whereas the *Z*-isomers decay to their precursors **1** in the nanosecond time range, presumably by way of quantum mechanical tunneling. An alternate way of formation of compounds **2** is by thermal electro-cyclic ring opening of isomeric benzocyclobutenols **3**, a

(9) Bos, J.; Schmidt, J.; Mai, H.; Decker, V.; Halbing, M. *Radiat. Phys. Chem.* **1989**, *34*, 361.

(10) (a) Mehnert, R. In ref 1a, pp 231−285. (b) Trifunac, A. D.; Werst, D. W. In ref 1a, pp 195−229. (c) Werst, D. W.; Trifunac, A. D. *J. Phys. Chem.* **1991**, *95*, 3466.

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(12) (a) Gebicki, J.; Marcinek, A.; Stradowski, C. *J. Phys. Org. Chem.* **1990**, *3*, 606. (b) Marcinek, A.; Gebicki, J.; Plonka, A. *Ibid.* **1990**, *3*, 757. (c) Rogowski, J.; Adamus, J.; Gebicki, J.; Nelsen, S. F. *J. Chem. Soc., Perkin Trans. 2*, **1994**, 779. (d) Marcinek, A.; Rogowski, J.; Adamus, J.; Gebicki, J.; Platz, M. S. *J. Phys. Chem.* **1996**, *100*, 13539.

(13) (a) Ishiguro, K.; Khudyakov, I. V.; McGarry, P. F.; Turro, N. J.; Roth, H. D. *J. Am. Chem. Soc.* **1994**, *116*, 6933. (b) Trifunac, A. D.; Werst, D. W.; Herges, R.; Neumann, H.; Prinzbach, H.; Etzkorn, M. *Ibid.* **1996**, *118*, 9444.

(14) (a) Sammes, P. G. *Tetrahedron*, **1976**, *32*, 405. (b) Haag, R; Wirz, J.; Wagner, P. J. *Helv. Chim. Acta* **1977**, *60*, 2595. (c) Scaiano, J. C. *Acc. Chem. Res.* **1982**, *15*, 252. (d) Wagner, P. J. *Acc. Chem. Res.* **1989**, *22*, 83. (e) Weedon, A. C. In ref 2, pp 591−638.

Scheme 2

a: R = C_6H_5
b: R = CH_3
c: R = H

feature which we have also exploited in our investigations of the corresponding radical cations described below.

3.2. Formation of Enol Radical Cations. As mentioned in the previous section, the thermochemical order of stabilities of keto and enol forms is often reversed upon ionizaton. Enolization of **1** requires some 25−30 kcal/mol, a good part of which is engendred by the loss of the benzene ring's resonance energy. As radical cations of aromatic compounds do not profit from this form of special stabilization,[15] enolization of **1**[·+] should be as exothermic as that of simple ketone radical cations (cf. above). Indeed, exploratory quantum chemical calculations of various kinds all predicted that the process **1**[·+]→ **2**[·+] is exothermic by 15−20 kcal/mol. Therefore we chose compounds of type **1** for our initial explorations of ionization-induced tautomeriations.

The first pulse-radiolytic experiments on *o*-methyl-benzophenone (**1a**)[16] revealed a transient electronic absorption (EA) spectrum which changed with time from the spectrum obtained just after the electron pulse showing

(15) This can be seen readily if one compares the hydrogenation enthalpy of benzene giving 1,3-cyclohexadiene (+5.6 kcal/mol) to that of the corresponding radical cation (−17.4 kcal/mol). The difference between the two numbers is close to the ca. 20 kcal/mol which is customarily associated with the extra resonance energy of benzene, which is lost on removing an electron from the 6π cyclic system.

(16) Gebicki, J.; Marcinek, A.; Michalak, J.; Rogowski, J.; Bally, T.; Tang, W. *J. Mol. Struct.* **1992**, *275*, 249.
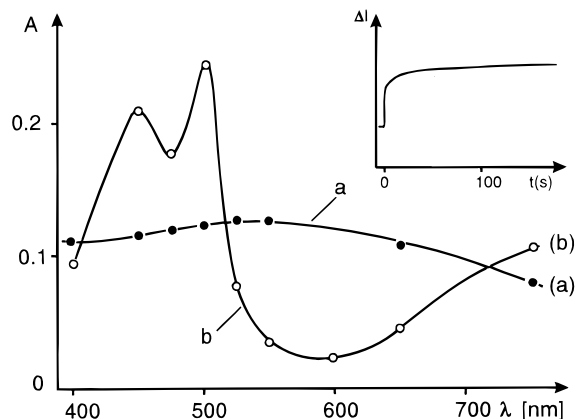
FIGURE 1. Transient absorption spectra generated by electron pulse radiolysis from *o*-methylbenzophenone (1a) in the methylcyclohexane—*n*-butyl chloride glass at 70 K (a) 0.25 s and (b) 23 s after the electron pulse. Inset: scope trace at 500 nm.

very nondescript weak absorption (Figure 1a) to a spectrum with bands at 400−500 and 700−800 nm obtained within seconds after the pulse at 70 K (Figure 1b), a pattern which is a telltale signature of *o*-quinoid radical cations. Similar spectra were observed for *o*-methylacetophenone (**1b**)[17] and *o*-methylbenzaldehyde (**1c**).[18] Although the pulse-radiolytic experiments permitted kinetic analyses which proved to be quite revealing (see below), they did not contain sufficient information to serve as unambiguous structural proof.

Therefore we turned to steady-state experiments by embedding the neutral precursors in argon matrices where they can be ionized by X irradiation and where products can be probed in the IR as well as in the UV−vis spectral region. Figure 2 shows the spectra we obtained in this fashion.[16] Whereas benzophenone gave a weak, broad NIR band peaking at ≈1100 nm on ionization, **1a** showed the same spectral pattern as observed previously by pulse radiolysis, thus confirming that the same species was generated in both experiments.

We should note at this point that the EA spectra depicted in Figures 1 and 2 are in qualitative accord with expectations for **2a•+**, which may be regarded as a substituted *o*-quinodimethane radical cation (**4•+**). The

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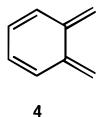
latter shows a weak band at 860 nm and a pair of stronger ones peaking at 525 and 440 nm,[19] which compare well with those at 770, 500, and 445 nm in Figures 1 and 2. This, and the fact that the observed shifts between **4•+** and **2a•+** are in accord with the predictions from PPP-CI calculations, lends support to our assignment of this spectrum to **2a•+**.[16,17]

More conclusively, ionization of **1a** resulted in the formation of a group of strong new IR bands around 3450

(17) Marcinek, A.; Michalak, J.; Rogowski, J.; Tang, W.; Bally, T.; Gebicki, J. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1353.
(18) Tang, W.; Bally, T. Unpublished results.
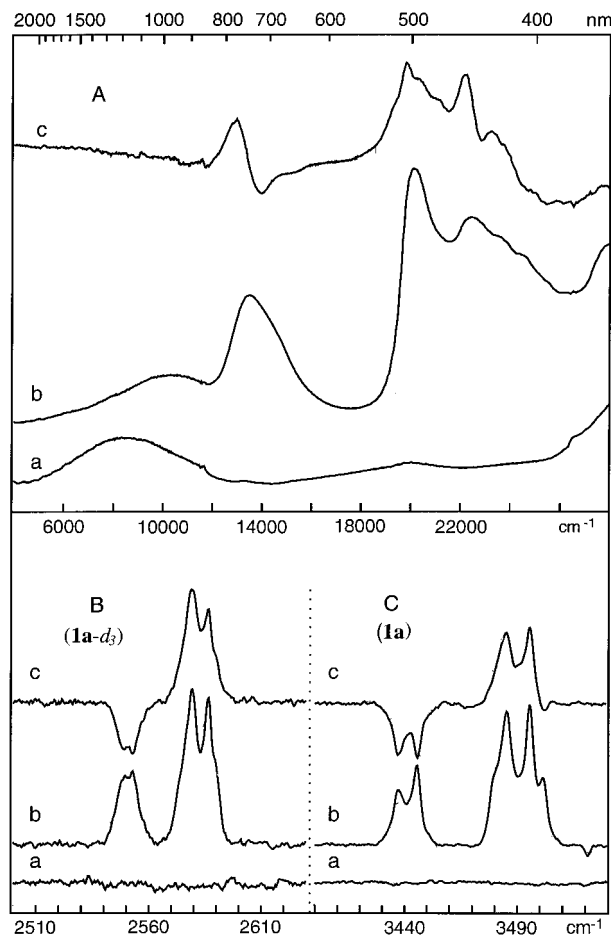(19) Kesper, K.; Münzel, N.; Pietzuch, W.; Specht, H.; Schweig, A. *J. Mol. Struct. (THEOCHEM)* **1989**, *200*, 375.

FIGURE 2. UV−vis/near-IR (A) and IR (B, C) spectra of ionized benzophenone (traces a) and of radical cations 2a•+ generated by ionization of *o*-methylbenzophenone (1a) (traces b) by X-ray irradiation in argon matrices. Trace c illustrates the changes in the spectra on 500 nm photolysis of the samples shown in trace b. Panel B is the IR part for ionized *o*-methylbenzophenone-*methyl-d₃* (2a-*d₃*).

cm⁻¹, in contrast to benzophenone which showed no changes in this spectral region on X-irradiation. On replacement of the methyl group of **1a** by CD₃ (**1a-*d₃***) this group of bands shifted to ∼2600 cm⁻¹, which proved that they are due to O−H (O−D) stretches and that therefore enolization to **2a•+** had actually occurred. Interestingly, the intensities in both the EA and IR bands were significantly lower in the deuterated compound which provided a first hint that tunneling might be involved in the process of enolization (cf. next section). Also, we note the pronounced splittings in the IR bands, a point to which we will return in the section 3.4.

Finally, an important detail which becomes evident from the argon matrix EA spectra is that a broad NIR band is also present after ionization of **1a**. We believe that this is due to residual **1a•+** formed in the anti conformation which is ill disposed to undergo spontaneous hydrogen shift. Unfortunately we could detect no IR bands which we could unambiguously attribute to **1a•+**, so that this conjecture remained somewhat speculative.

Indirect evidence for the formation of enol radical cations was also obtained from studies of hydrogen isotope exchange reactions in *o*-alkyl phenyl ketones
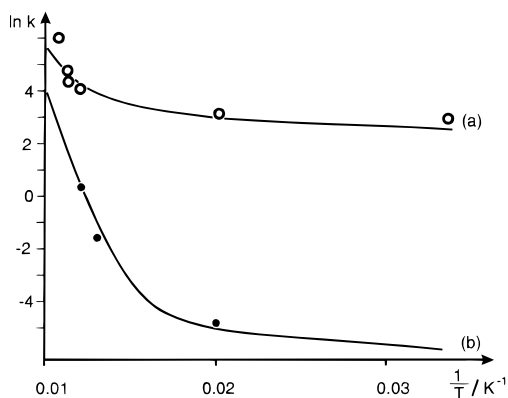
FIGURE 3. Rate constants of the enolization process in radical cations of (a) *o*-methylacetophenone (**1b**) and (b) *o*-methyloacetophenone-methyl-*d₃* (**1b**-*d₃*) presented in the Arrhenius coordinates.

mediated by illuminated semiconductor powders, where they were proposed as reactive intermediates.[20]

3.3. Kinetic Studies. Armed with the insight from the argon matrix studies, we returned to the time-resolved experiments which allowed us to probe the kinetics of the enolization process (which in the case of **1a** takes place within seconds after the electron pulse; see Figure 1, inset). Before going into this, we should, however, recall that the kinetics of isomerizations in solid glasses often show considerable deviation from first-order rate laws. This is due to the fact that different matrix sites may impose different constraints on the probed reaction which results in a *distribution* of activation energies instead of a single, well-defined one. A suitable way to handle such situations of so-called *dispersive kinetics* is to introduce a time-dependent rate constant:

$$k(t) = B \cdot t^{\alpha-1}$$

where $0 < \alpha \leq 1$ measures the dispersion in activation energies.[21]

The Arrhenius plots we obtained in this way for the enolization of **1a**[.+] and **1b**[.+] were, however, strongly curved and indicated that the rates become nearly independent of temperature below 50 K[16,17] (see Figure 3). In **1a**[.+]-*d₃*, enolization was too slow to be monitored, but in related **1b**[.+]-*d₃*, we could determine a kinetic isotope effect k_H/k_D which vared between 40 (at 83 K) and 3340 (at 50 K).[17] The enolization in **1b**[.+]-*d₃* was too slow to deduce the rate constant below 50 K, where it is expected to become temperature independent by analogy with **1b**[.+].

Nevertheless, the available evidence indictates participation of quantum-mechanical tunneling in the enolization of **1b**[.+]. Indeed, the Arrhenius plots for the **1b**[.+] → **2b**[.+] process could be fitted reasonably well by introducing a temperature-dependent tunneling correction factor based on the crude assumption of a parabolic thermal barrier.[22] The activation energy of 16.8 kJ/mol and the barrier width of 1.44 Å carry some uncertainty, but both

Scheme 3
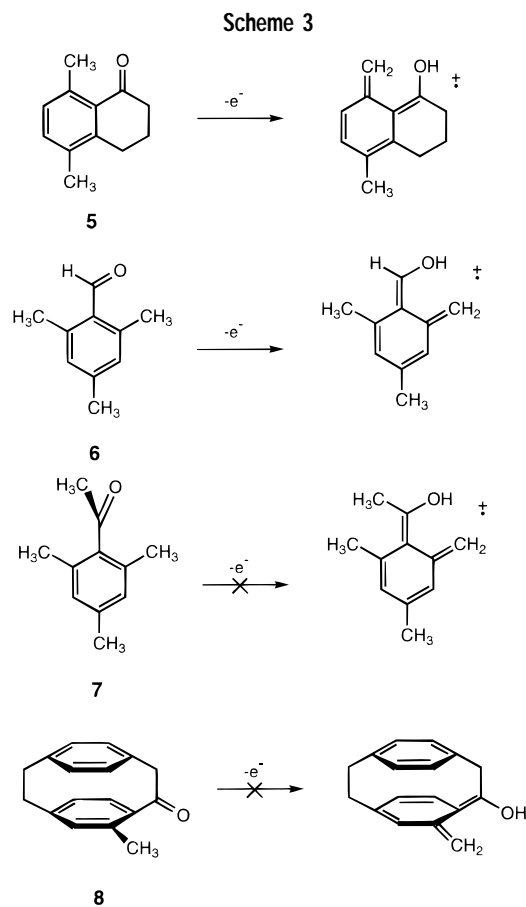
values seem to be quite reasonable. Participation of quantum mechanical tunneling was earlier suggested for other tautomerizations of radical cations in condensed phase,[3c] and the re-ketonization of the corresponding neutral photoenols is also thought to occur largely by tunneling.[23]

3.4. Conformational Questions. We mentioned above that spontaneous enolization can probably occur only from the syn conformation of the starting ketones, especially if it should proceed by tunneling. To probe the conformational requirements of the process we prepared derivatives with different fixed conformations (see Scheme 3). Thus, in the bicyclic tetralone derivative **5**, the methyl group is held in the favorable syn position. Enolization is indeed observed, in both the protio and the deuterio compound.[17]

When *two o*-methyl groups are present, there is no anti conformation. 2,4,6-Trimethylbenzaldehyde (**6**) indeed undergoes smooth enolization on ionizaton.[24] However, if the aldehyde is replaced by a keto group (**7**), enolization is completely suppressed because now a perpendicular conformation is enforced. A similar situation prevails in a cyclophane derivative **8**,[25] but here, twisting of the exocyclic double bond in the enol could also play a role. Taken together, these experiments indicate that enolization can only occur from a periplanar syn conformation of ketones.

These results suggest that enol cations. e.g. **2**[.+], arise initially as *Z*-isomers with the OH group syn to the

(20) (a) Michalak, J.; Jonska, A.; Tang, W.; Gebicki, J. *Polish J. Chem.* **1993**, *67*, 1505. (b) Michalak, J. W.; Gebicki, J. *J. Chem. Soc., Perkin Trans 2*, **1993**, 2249.

(21) See, e.g.: Plonka, A. In *Time-Dependent Reactivity of Species in Condensed Media*; Lecture Notes in Chemistry, Vol. 40; Springer: Heidelberg, Germany, 1986.

(22) See: Caldin, E. F. *Chem. Rev.* **1969**, *69*, 135.

(23) Grellmann, K. H.; Weller, H.; Tauer, E. *Chem. Phys. Lett.* **1983**, *95*, 195.

(24) Michalak, J.; Bally, T.; Gebicki, J. *Pol. J. Chem.* **1993**, *67*, 1403.

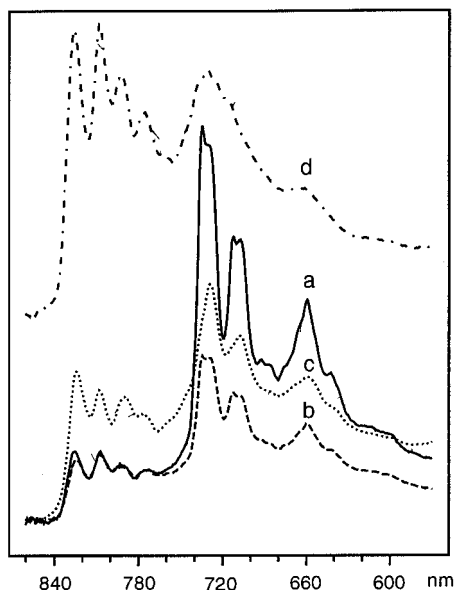(25) Michalak, J.; Bally, T. Unpublished results.

FIGURE 4. First absorption band of radical cations **2c**·⁺ generated by X-irradiation in argon matrices of (a) *o*-methylbenzaldehyde (**1c**), (b) **1c** exposed to 290 nm photolysis (→ partial conversion to enol **2c**), and (c) methylbenzocyclobutenone (**3c**). Spectrum d was recorded after 700 nm photolysis of the sample giving spectrum a.

exocyclic methylene group. However, the splittings in the IR peaks of the O−H/O−D stretches in argon matrices indicated the presence of different conformers after ionization. In addition we found that, on photolysis with visible light, the EA and IR spectra of radical cations undergo subtle but reproducible changes. These are exemplified for **2a**·⁺ in Figure 2 (cf. difference spectra c). Clearly, photolysis leads to an increase in one population ($\nu_{OH} = 3480-3500$, $\nu_{OD} = 2570-2590$ cm⁻¹) at the expense of another ($\nu_{OH} = 3430-3450$, $\nu_{OD} = 2540-2560$ cm⁻¹).

R=C₆H₅ : **2a** ; R=CH₃ : **2b** ; R=H : **2c**
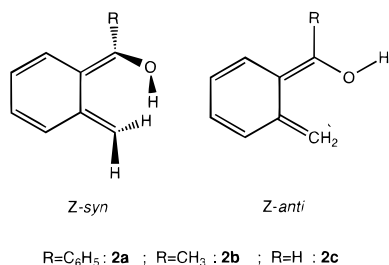
If **2**·⁺ arises primarily as the *Z*-isomer, then we can distinguish between two different conformations of the OH group. Due to conjugation of the oxygen p-type lone pair with the charge-deficient π-system, the barrier for rotation around the C−O bond in enol cations **2**·⁺ is much increased from that in neutral **2**, so that these different OH conformers (hereafter called "rotamers") do not readily interconvert. Furthermore, the syn rotamer must be strongly nonplanar, which would explain the rather substantial shifts in ν_{OH}/ν_{OD} and leads us to propose that the two groups of IR peaks are due to the syn and anti rotamers of (*Z*)-**2a** which may be interconverted on illumination.

This simple picture was found to require some extension when we found that the parent compound of the series, *o*-methylbenzaldehyde **1c** gives at least *three*

populations of enol cations **2c**·⁺ on ionzation.[18] We also would like to use this example to show the possibility of generating enol cations **2**·⁺ from independent sources, for example, from the photochemically preformed neutral enols **2** or from the isomeric benzocyclobutenols **3** which were found to undergo spontaneous ring opening on ionization.[26] In Figure 4 we show, with the example of the first EA band of **2c**·⁺, that quite distinct EA and IR spectra are obtained from precursors **1c**, **2c**, and **3c**, respectively.

X-irradiation of **1c** before (a) or after 290 nm photolysis (which converts it partially to enol **2c**, spectrum b) or of **3c** (c) leads to different proportions of two distinct populations, one of which absorbs above 750 nm and the other one between 600 and 750 nm. Photolysis of any of the above samples through a 700 nm interference filter leads to a further increase of the >750 nm band system at the expense of the <750 nm one (d), but photolysis at lower wavelengths reverts this process.

These results can be explained if we assume that ring opening of ionized **3c** leads predominantly to the sterically less hindered *E*-isomers of **2c**·⁺ which are also formed preferentially from the neutral enol (*E*)-**2c** (the only one which persists long enough to experience ionization after formation from **1c**). Conversely, those molecules of **1c** which are in the syn conformation enolize spontaneously to form (*Z*)-**2c**·⁺, whereas *anti*-**1c**·⁺ presumably remains in the keto form on ionization. The substantial shifts between the two groups of optical bands may be due to (*Z*)-**2c**·⁺ being present mostly in the (incipient) nonplanar conformation.

Interestingly, we found also that the >720 nm component of the **2c**·⁺ spectrum consists of *two* overlapping band systems which can be reversibly interconverted by selective narrow-band photolyses whereas the band peaking at 720 nm shows no indication of this.[18] We conclude that enol radical cations **2**·⁺ are generally formed in several conformations which can sometimes be interconverted by selective photolyses.

3.5. Photochemical Re-ketonizaton. In all of the above-described systems, enolization in the radical cations is an irreversible process in that none of them showed any loss of the intensity of the O−H/O−D stretching bands in the IR or the optical absorptions characteristic of **2**·⁺ on photolysis, except under the most drastic conditions which lead to decomposition of the molecules. However, we recently found an exception to this rule which proved to be quite informative because we were able to follow the **1**·⁺ → **2**·⁺ process in an argon matrix: When 4,7-dimethylindanone (**9**) is ionized by X-irradiation in this matrix, the spectroscopic signatures of the corresponding enol cations **10**·⁺ arise unmistakably.[27]

Subsequent illumination of the sample at 500 nm leads to the bleaching of these features. This process is reversible, very efficiently by photolysis at 640 nm, and over several hours by standing in the dark at 10−20 K. We are

(26) Bally, T.; Michalak, J. *J. Photochem. Photobiol. A: Chem.* **1992**, *69*, 185.

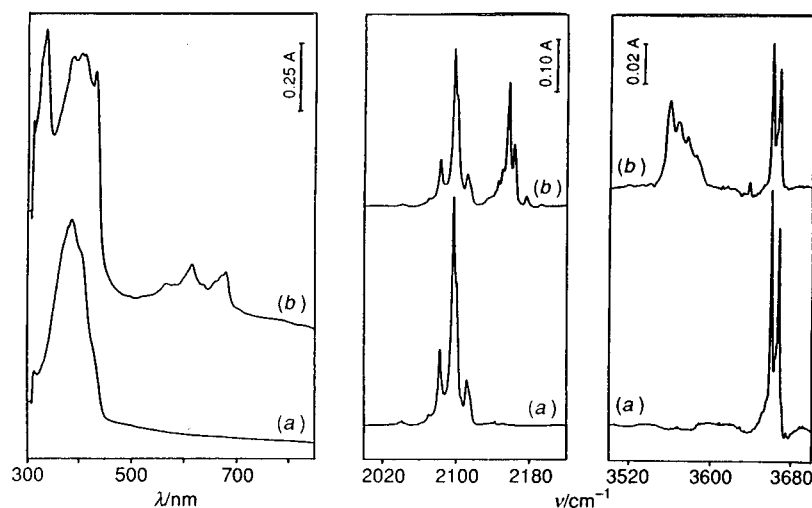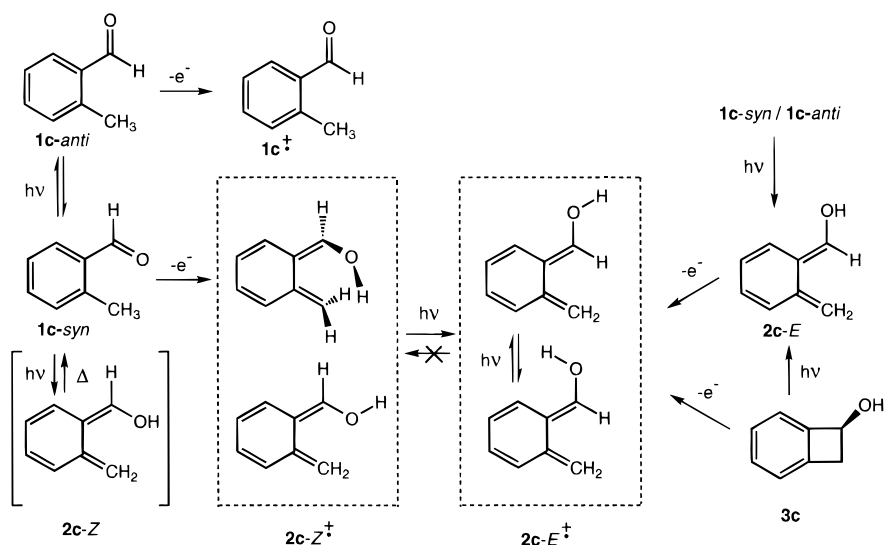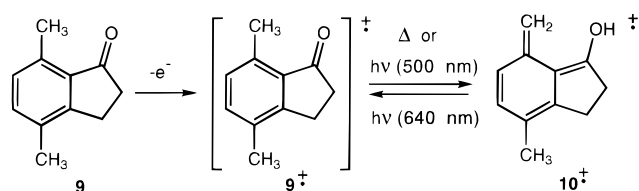(27) Huben, K.; Zhu, Z.; Bally, T.; Filipiak, T.; Gebicki, J. To be published.

Scheme 4

FIGURE 5. Changes in the UV—vis and IR spectra of matrix isolated *o*-phthalaldehyde (a) on photolysis at 313 nm and (b) on X-irradiation.

Scheme 5

currently exploring this process by studying the corresponding deuterated derivative, but it appears from the temperature independence of the thermal enolization rate that, once again, tunneling is involved.
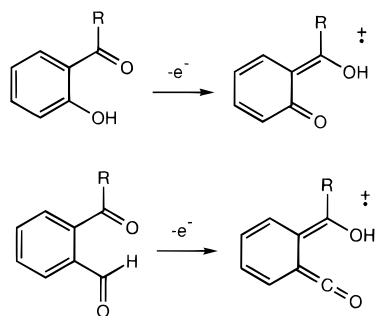
The reason why we could never observe a similar process in related systems is probably that a certain CH—O distance is required to keep the ketone cation from collapsing rapidly to the enol cation, which may also be the reason why we never observed photoreketonization of **2**$^{\bullet+}$. Indanone radical cation **9**$^{\bullet+}$ and its enol **10**$^{\bullet+}$ appear to offer just the right combination of features to permit re-ketonization and relatively slow enolization to be observed. We are currently also examining to what extent the relative disposition of σ- and π-states of the ketone radical cations affect the rate of enolization.
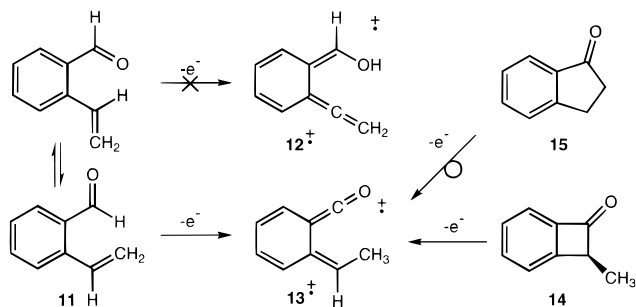
4. Related Carbonyl Compounds

In the course of our studies we found that ionization-induced hydrogen transfer to a carbonyl group is not limited to alkyl derivatives but that other potentially hydrogen-donating groups can also engage in such reactions. In particular, the hydrogen atom can originate from a hydroxy[16] or another formyl group,[28] thus giving rise to *o*-quinoid ketones or ketenes, respectively. As an example, we show in Figure 5 the spectral changes observed on photolyis and ionization, respectively, of *o*-phthalalde-hyde: in both cases, the typical 380 nm UV band and the 2100 cm^{-1} IR peaks of the *o*-quinoid ketene arise in addition to a pair of vinylic OH stretches at 3670 cm^{-1} due to two C—OH rotamers present in similar quantity. After X-irradiation we see additionally the 600—700 nm absorptions of the quinoketene cation and the associated IR bands. These are shifted to higher energies for the ketene stretch (in accord with the antibonding nature of the HOMO from which an electron is removed) and to lower energies for the OH stretch, indicating a weakening of the OH bond on ionization, presumably due to polarization of the σ electrons by the charged π system.

(28) Michalak, J.; Gebicki, J.; Bally, T. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1321.

Scheme 6
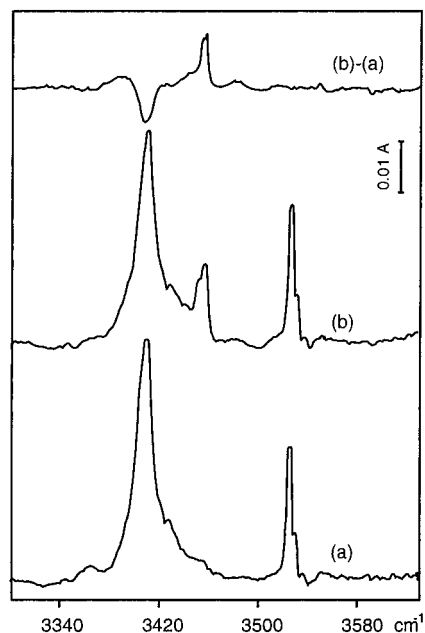

FIGURE 6. Changes in the IR spectrum (OH stretching vibration region) (a) upon X-irradiation of *o*-nitrotoluene 16 in an argon matrix and (b) upon subsequent photolysis at 900 nm. Difference spectrum (b − a) indicates the changes induced by 900 nm photolysis.

Scheme 7

Scheme 8

On the other hand, our recent attempt to use a vinyl group as a hydrogen donor to a formyl group led to an unexpected result in that the latter turned out to be the better hydrogen *acceptor*. Thus, ionization of *o*-vinylbenzaldehyde (11) did not yield the expected *o*-quinoid allene cation 12$^{•+}$. Instead it gave the quinoketene cation 13$^{•+}$, as we were able to prove by generating 13$^{•+}$ independently from methylcyclobutenone 14.[29] However, in this case, the parent cation 11$^{•+}$ does not decay completely by hydrogen transfer. It could be identified and photoconverted selectively to 13$^{•+}$. Interestingly, indanone 15 proved to be an independent source of 13$^{•+}$ in that it suffers ring opening (and subsequent H-migration) on ionization.

5. Phenyl Nitro and Nitroso Compounds

In analogy to the above-described *o*-alkyl phenyl ketones hydrogen atom migration also occurs upon ionization of *o*-alkyl phenyl nitro compounds, where instead of the carbonyl group the nitro group plays the acceptor role. For example, ionization of *o*-nitrotoluene 16 by X-irradiation in argon matrices results in the formation of two rotamers of the tautomerized *aci*-nitro cation 17$^{•+}$, which can be interconverted by subsequent irradiation with visible light (Figure 6).[30] Neutral 17, characterized in solution as a short-lived intermediate, could not be stabilized in argon matrices due to efficient H back-transfer.

The nonionic products generated from 16 upon X-irradiation, observed at 3520−3530 cm^{-1} in argon matrices, tentatively assigned to *o*-nitrosobenzyl alcohol (18) and *N*-hydroxybenzisoxazoline (19), which can be formed by neutralization of 17$^{•+}$ via unstable neutral *aci*-nitro
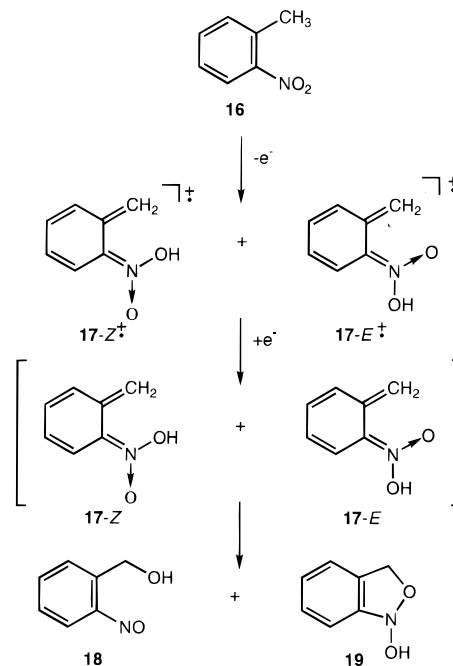
tautomers 17, which apparently rearrange to 18 and 19 (Scheme 8). Thus, the chemical transformations initiated by ionization can also result in generation of other neutral species. These reactions seem to be more efficient in cases where neutral tautomers are well stabilized.

A formyl hydrogen can also be transferred to a nitro group upon ionization as demonstrated for *o*-nitrobenzaldehyde (20).[28] A similar reaction was observed for *o*-nitrosobenzaldehyde (22), where the NO group played the acceptor role, thus yielding the oxime tautomer of radical cation 23$^{•+}$.[28] In both cases some nonionic products were also detected.

(29) Huben, K.; Zhu, Z.; Bally, T.; Gebicki, J. *J. Am. Chem. Soc.* **1997**, *119*, 2825.
(30) Michalak, J.; Bally, T.; Gebicki, J. *Radiat. Phys. Chem.* **1995**, *45*, 749

Scheme 9

Scheme 10

$R_1 = H$, CH_3 or NH_2 and $R_2 = CH_3$ or benzyl
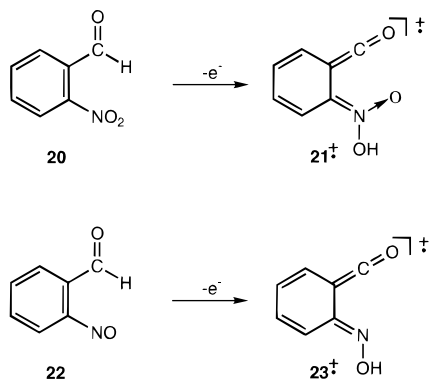
6. Outlook

In the systems discussed above, tautomers of radical cations were formed by 1,5-hydrogen migration. In many cases the neutral forms of these tautomers could be independently generated and structurally characterized. A direct comparison of optical and infrared spectral features of the neutral and the ionized enols was then possible. Kinetic measurements for hydrogen and deuterium transfer pointed toward participation of quantum mechanical tunneling in the tautomerization. The examples discussed in this Account suggest that ionization-induced enolization of enones and related compounds is a reaction of wide scope and that it may also occur in cases where the neutral enols cannot be observed.

Encouraged by the success of the above-described studies, we recently decided to expand this project to include other important electron-transfer systems where the incipient radical cations may undergo spontaneous tautomerization. An evident target is the conversion of NADH to NAD$^+$, where radical cations were implied in a multistep electron−proton−electron transfer mechanism. Exploratory calculations on model NADH analogues **24**
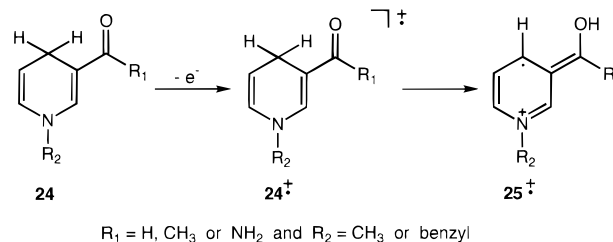
indicated that H transfer from C-4 to the carbonyl group is indeed exothermic for radical cations, in contrast to the same process in the neutrals. However, the expected 1,4-H transfer in radical cations **24** leading to **25** could not be observed, presumably because the activation barrier is too high.[31] It seems that such a barrier could be substantially reduced if the reaction would involve participation of solvent molecules[32] or in complexes with metals, a possibility which we are presently exploring.

Thus, thermodynamically favored hydrogen atom migration in radical cations can also be considered in mechanistic discussions of electron-transfer systems of practical importance such as photocatalysis on semiconductor surfaces, enzyme catalysis, and others.

(31) Gebicki, J.; Marcinek, A.; Adamus, J.; Paneth, P.; Rogowski, J. *J. Am. Chem. Soc.* **1996**, *118*, 691.
(32) Gauld, J. W.; Audier, H.; Fossey, J.; Radom, L. *J. Am. Chem. Soc.* **1996**, *118*, 6299.