Photochemistry of Reactive Intermediates

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Introduction

Reactive intermediates are often not present long enough and/or in sufficiently high concentration to be detectable while they occur in the course of thermal or photochemical reactions. In order to find out about the spectroscopic or kinetic properties associated with a reactive intermediate of interest, one must therefore be able to generate it by an independent, often a photochemical, pathway. Thus, carbenes and nitrenes can often be generated very efficiently by photolysis of their formal N_2 adducts (diazirines, diazo compounds, azides), radicals and biradicals by photochemical extrusion of other suitable "leaving groups" (iodine atoms, NO radicals, CO, to name a few), and radical ions by photoinduced electron transfer. Thus, research on reactive intermediates is almost unthinkable without photochemistry.[1]

However, the title of this account is not " Reactive Intermediates by Photochemistry", but "Photochemistry *of* Reactive Intermediates", which is quite a different subject. In fact, generating reactive intemediates under conditions where they persist, e.g. in low temperature frozen solutions or noble gas matrices, opens the possibility to probe not only their spectroscopic properties at leisure, but also their possible *photochemical reactivity.*

In previous contributions to topical Chimia issues I had described other aspects of our program of resarch on reactive intermediates [2,3], in the present one I will illustrate the title subject using examples taken from our work on three different kinds of reactive intermediates (carbenes, nitrenes, radical cations).

Technical Aspects

As pointed out above, in order to study the photochemistry of reactive intermediates, these need to be stabilized, at least during the time it takes to effect a photochemical reaction and to probe the products. This is conveniently achieved by *matrix isolation*, nowadays a mature technique that is well documented in the scientific literature [4]. A speciality that we have developed in Fribourg is to generate *radical ions* in noble gas matrices (where molecules can be probed in transmission between 200 and 50'000 cm^{-1}) by exposing argon matrices containing the neutral precursors to X-irradiation [5]. It is important to realize that organic molecules are practically transparent to X-rays, whereas Ar has a large cross section for absorbing and scattering such radiation, a process which results in the creation of electron-hole pairs. A

small fraction of these pairs escape recombination and travel through the Ar matrix (presumably in the form of polarons), until the holes encounter species that have a lower oxidation potential than Ar (which is the case for most organic substrates) and the electrons are scavenged by a species that has a higher electron affinity than Ar (which, for example, most alkyl halides do). Thus, radical ions are *not* formed under the direct impact of X-rays (which, if absorbed, would probably knock any polyatomic molecule to pieces), but by charge transfer from $Ar^{\bullet+}$ or $Ar^{\bullet-}$. After thermalization, radical ions are for all practical purposes indefinitely stable at 10K, the temperature at which Ar matrices is usually held.

A second technical aspect concerns the photoreactions: normally, such processes are effected simply by exposing samples to the light of some commercial light source such as a Xe/Hg arc, perhaps passing the light through a UV cutoff filter. However, reactive intermediates, in particular radical ions, often absorb throughout the visible and sometimes even the NIR range, so indiscriminate irradiation often leads to a mixture of primary and secondary products which is then hard to disentangle. Therefore, whenever we study the photochemistry of reactive intermediates, we start by irradiating at the longest wavelength where we can discern an absorption. When this does not lead to the disappearance of that absorption, we carefully inch towards shorter wavelengths, using an array of interference and cutoff filters, until the system under investigation shows a change. Sometimes we even have to go as far as to use a monochromator to give us light of a desired wavelength (of course this only works if a photoconversion occurs with a high quantum yield). This strategy has allowed us to sort out rather complicated schemes of sequential and parallel photochemical reactions to which reactive intermediates may be subjected.

Photochemistry of Arylcarbenes

Arylcarbenes usually have triplet (T) ground states (but very low-lying singlet states that may even be in thermal equilibrium with the triplet at room temperature). In low-temperature matrices the bimolecular processes of the incipient singlet (S) carbenes that are responsible for their "chemical usefulness", as well as possible unimolecular decay processes, such as rearrangement to cycloheptatetraenes (see Scheme 1), are suppressed. Therefore, intersystem crossing (ISC) will dominate, and one can only observe triplet arylcarbenes in matrices [6].

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We were reckoning that, after threshold photoexcitation, triplet phenylcarbene **1** might remain on the triplet surface long enough to undergo rearrangement to the elusive triplet cyclohepta-trienylidene carbene. However, it seems that at some point of this reaction, the system under-goes efficient ISC, because the only product we could observe from this photoreaction was the previously known nonplanar cycloheptatetraene **2**. Nevertheless, this experiment allowed us to fully characerize the electronic structure and the force field of the parent triplet phenyl-carbene **1** and cycloheptatraene **2** [7].
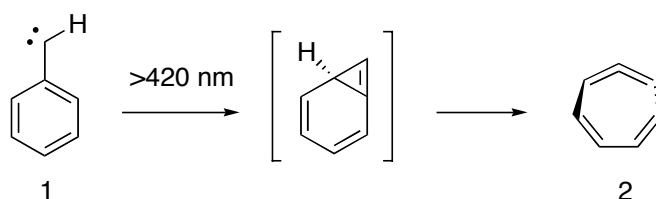
Scheme 1.

In another of our encounters with carbene chemistry, we were confronted with an enigmatic photorearrangement of triplet 2-naphthyl(carbomethoxy)carbene [3]**3** leading to a species with a broad absorption at 420 nm. We could indeed observe this spectral change in Ar matrices, but in addition, Zhendong Zhu found that the reaction could be reverted, both by irradiation at 450 nm and, more surprisingly, by letting a matrix stand overnight at 12 K. Altough, by virtue of this reversibility, we had full UV/Vis and IR spectra of the rearrangement product, this species resisted our attempts to provide a plausible assignment until Zhu came up with the somewhat iconoclastic proposition that it might be the singlet state of **3**, a proposition that initially met with much scepticism on the part of the "carbene community". In spite of that we eventually succeeded, with the help of our IR spectra (Fig 1B) and the ESR spectra in Ar matrices that were kindly provided by Prof. McMahon, to assemble sufficient convincing evidence that this assignment was accepted as the first example "spin isomerism", i.e. the interconversion between two (meta)stable spin states of the same pecies (see Scheme 2) [8].
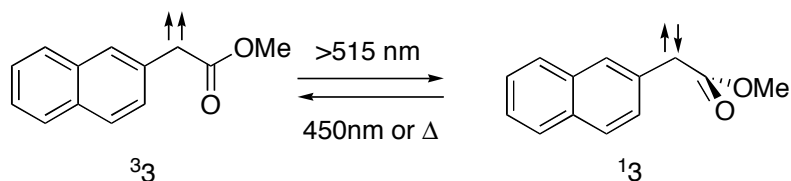
Scheme 2.

In appears that it was a lucky combination of circumstances that allowed us to make this discovery: Not only are the two spin states very close in energy [9], but on S/T interconversion the COOMe group assumes an orthogonal conformation which provides for a small barrier for the decay of the less stable singlet state to the triplet ground state [8].
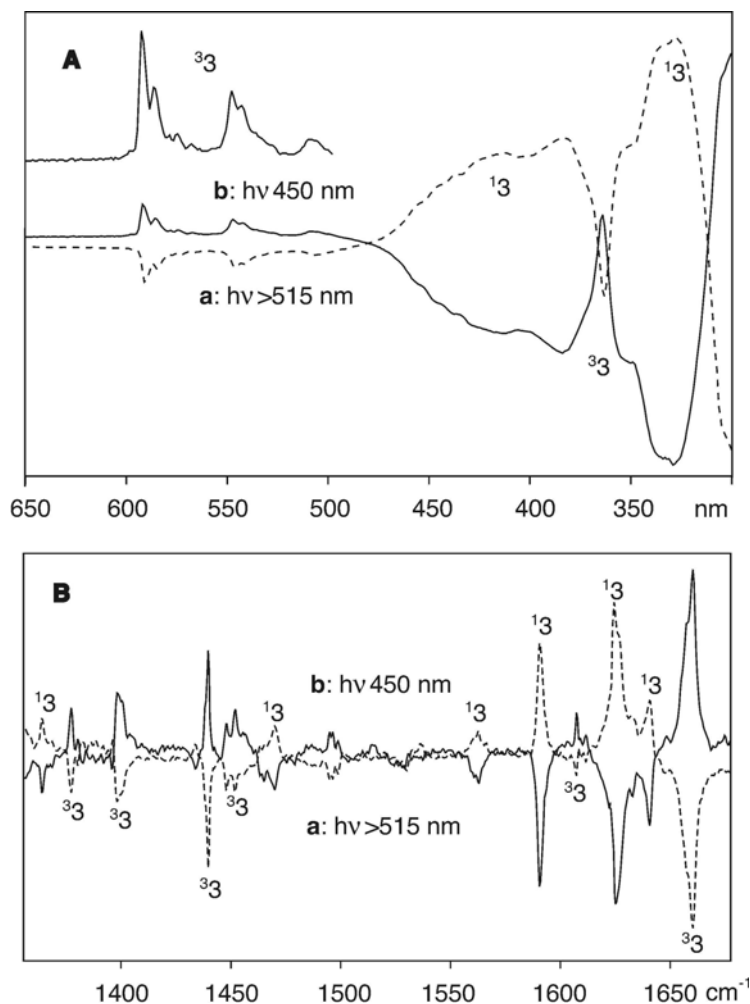

Fig 1. UV-Vis (A) and IR (B) spectral changes for the reversible interconversion of the singlet and triplet states of 2-(carbomethoxy)naphthyl nitrene **3**.

Photochemistry of Arylnitrenes

Nitrenes are iso-π-electronic to the corresponding carbenes (one C-H bond being formally replaced by a lone pair on the nitrogen atom). Arylnitrenes also have triplet ground states, but the singlet-triplet gap is usually much bigger (ca 18 kcal/mol in phenylnitrene), and intersystem crossing is slower than in comparable arylcarbenes [10]. On the other hand the barriers for expansion of arylnitrenes to azacycloheptatetraenes (or dehydroazepines) are lower

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than those for the corresponding arylcarbene rearrangements [11]. As dehydroazepines polymerize readily, arylnitrenes were long regarded as chemically useless, until it was discovered that ortho-bisubstituted arylnitrenes resist rearrangement enough that bimolecular reactions of singlet arylnitrenes can be exploited, for example in photoaffinity labelling [12] or in imaging applications [13].

o-Bisubstitution does not only raise the barrier for the attack of the nitrene's N-atom on the aryl ring, but also that for the subsequent opening of the bicyclic compound to form the dehydroazepine [11]. This opens the possibility to observe all three species, and we have succeeded to achieve that in the case of 2,5-difluorophenylnitrene **4**. We found that the three reactive intermediates which are in equilibrium at room temperature, i.e. the nitrene **4**, azirine **5**, and dehydroazepine **6** (see Scheme 3), can be interconverted by selective photolyses and characterized by their full UV/Vis and IR spectra [14].
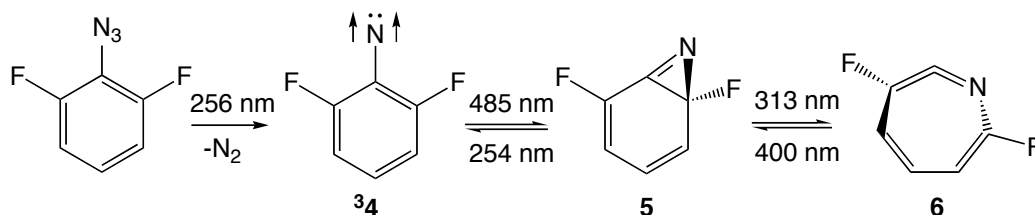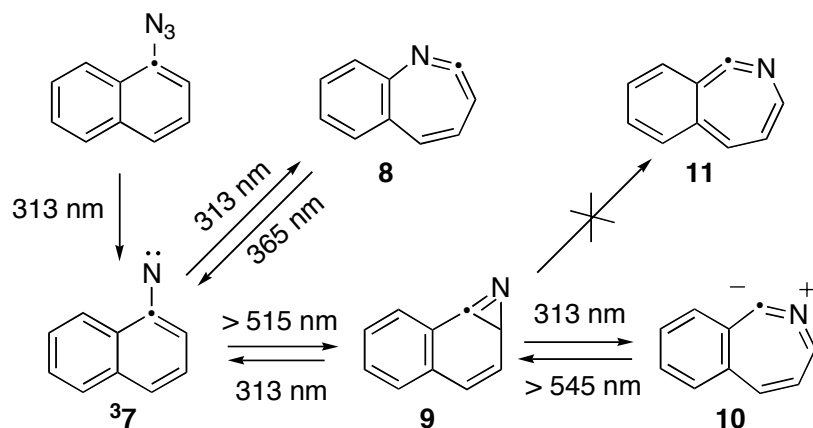

Scheme 3.

If *naphthylnitrenes* undergo the above type of rearrangement, this may entrail the loss of an aromatic ring which would be expected to affect the thermochemistry. We thus set out to explore the photochemistry of naphtylnitrenes and thereby made an interesting discovery: instead of forming, from the appropriate azirines which can easily be generated, the high-energy *o*-quinoid dehydroazepines (which, if formed, would in any event decay back to the percursor azirines in practically barrierless processes, as predicted by calculations), these systems undergo a bond-shift isomerization to form novel ylidic compounds, as exemplified below for the case of 1-naphthylnitrene, **7**

The UV/Vis and IR-spectra obtained on 313 nm bleaching of 1-naphthylazide are too complex to be analyzed in terms of a single product. Careful photolyses allow, however, to selectively affect different constituents of this mixture and to identify eventually the triplet nitrene, [3]**7**, the azirine, **9**, and the aromatic dehydroazepine **8** (see Scheme 4). However, the spectra of

the last of the expected constituents of the mixture, the *o*-quinoid dehydroazepine **11**, could not be brought into agreement with those calculated by quantum chemical methods. This forced us to consider alternative hypotheses for this species, the spectra of which we had in our hands.

Scheme 4.

It then happened that students in three reserach groups (Alexander Maltsev in our group, Meng-Lin Tsao in the group of Prof. Platz at Ohio State University and Arvid Kuhn in that of Prof. Wentrup at the University of Queensland in Australia) independently discovered that the missing dehydroazepine **11** existed in the form of a more stable ylidic structure **10** which restores the aromaticity in the benzene ring. The existence of such species had been postulated earlier by calculations, but the careful photochemical work of Alexander Maltsev allowed it to isolate and unambiguously characterize these novel species for the first time. Eventually the three groups teamed up to publish these findings [15].

We have also recently explored the "internal trapping" of phenylnitrenes by nucleophiles or by biradicaloid pathways, a study that involved a lot of photochemistry [16].

Photochemistry of Radical Cations

Radical cations often show rich electronic absorption spectra that extend throughout the visible, and sometimes even into the near IR-range, which offers the opportunity for inducing photochemical reactions by selective irradiations. In this way we have studied several photo-induced ring-opening reactions of radical cations containing three-[17-21] or four-membered rings [22-25], phototautomerizations of ionized ketones and enols [26-28], and rotamer inter-

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conversions in polyene radical cations [29-31]. I will use two examples to illustrate the photo-chemistry of radical cations:

Photolysis of the radical cations of perinaphthocyclopropanes **11•+** leads directly to phenal-ene radical cations **13•+** (see Scheme 5), irrespective of whether R=H or CH$_3$, i.e. the primary 1,3 perinaphthadiyl radical cations **12•+**, if they are formed at all, decay spontaneously (in fact, calculations indicate that, in the case of R=CH$_3$, the phenalene radical cation is formed by initial *lateral* cleavage of the cyclopropane ring, followed by rearrangment to **13•+**. Un-fortunately we were not able to distinguish the two isomeric forms of **13b•+** by optical spec-troscopy).
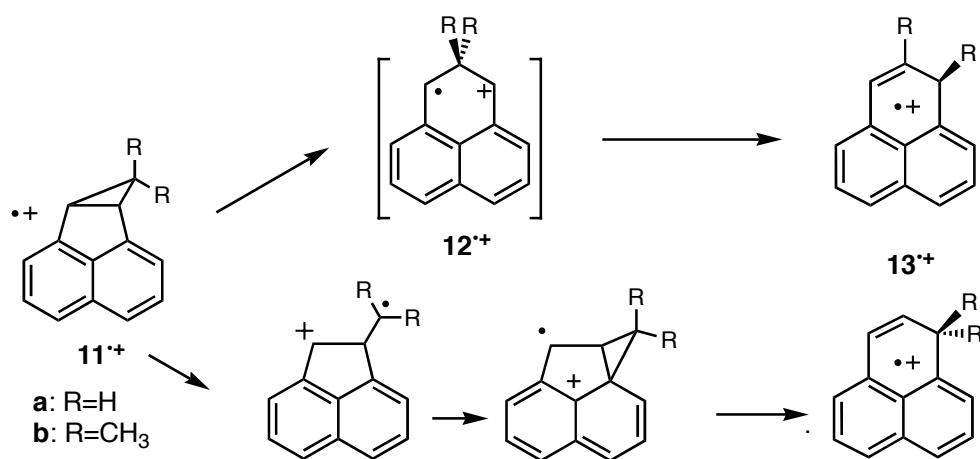
Scheme 5

However, if formed from the doubly bridged compound **14** the corresponding 1,3-perinaph-thadiyl radical cation **15•+** is stable, and it can in turn be converted to the radical cation of the cross-conjugated polyene, 2,7-dihydro-2,2,7,7-tetramethylpyrene, **16•+** (which was generated independently from neutral **16**) [18].

This example demonstrates the importance of selective photolysis: on irradiation of **14•+** through a simple UV-cutoff filter, the spectrum of **15•+** never appears, because ist ring-open-ing to **16•+** occurs with a much higher quantum yield than ist formation from **14•+**. **15•+** can only be formed and observed under conditions of irradiation where it does not absorb.
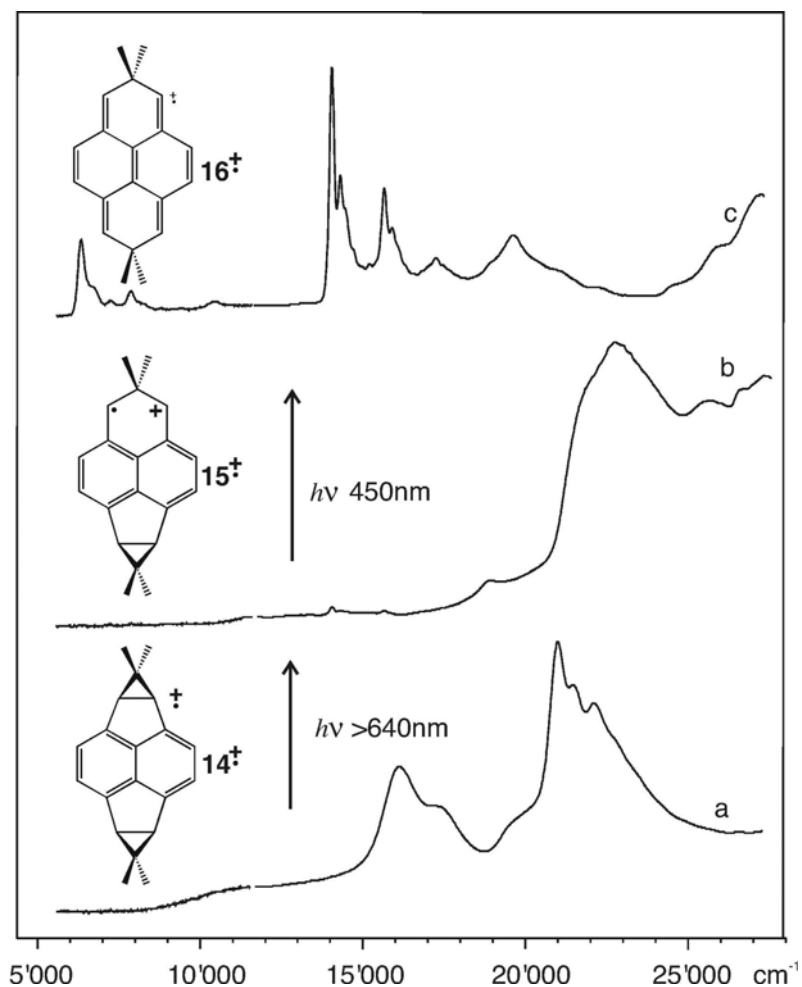
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Fig 2. Changes in the electronic absorption spectra on generation of the radical cation of naphthalene derivative **14** and its subsequent conversion to diradical cation **16•+** and the radical cation of the cross-conjugated dihydropyrene **17**

The radical cation of perinaphthocyclobutane **17•+** (Scheme 6) also proved to be photolabile and undergo ring opening to a 1,4-perinaphtadiyl radical cation **18•+** (which we could generate independently from the corresponding azo precursors). On higher-energy photolysis, cleavage of the second σ-bond occurred and the radical cation of 1,8-divinylnaphthalene. **19•+**. was formed. Again, intermediate **18•+** cannot be seen under full visible irradiation [22].

Scheme 6.

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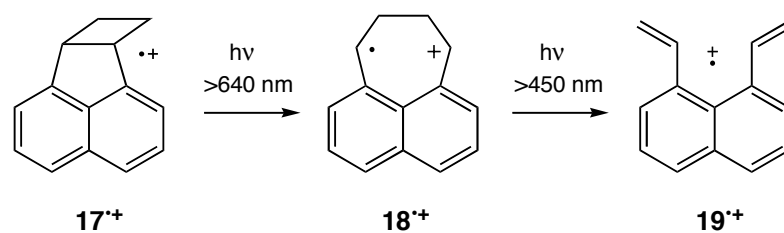
The last example comes from our work on electron-transfer-induced tautomerizations [26], and this example taught us to watch out for subtle electronic factors in organic radical cations.

On ionization, *dimethylindanone* **20** spontaneously undergoes partial tautomerization to the more stable *o*-quinoid enol **21**$^{•+}$ (see Scheme 7) which distinguishes itself by a well-resolved absorption band around 700 nm. On irradiation of this band (λ>640 nm), **21**$^{•+}$ is bleached and **20**$^{•+}$ is reformed, as shown very clearly by the IR-spectra. On irradiation at 490 nm, or on standing overnight at 12 K, the spectrum of **21**$^{•+}$ can be fully recovered. Replacing the two methyl groups in **20** by CD_3-groups has no influence on the photochemical behaviour of the system, but the spectrum of the ketone radical cation is indefinitely stable at 12 K (or even at 25 K), which suggests that tunnelling is involved in the tautomerization.
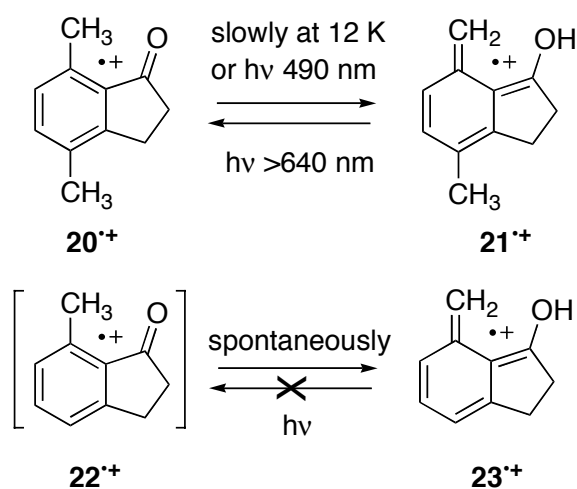
Scheme 7.

To our surprise we found that, on ionization of *methylindanone* **22**, there was no trace of the keto radical cation, **22**$^{•+}$, in the spectra, and that the corresponding enol radical cation, **23**$^{•+}$, was entirely photostable. However, deuteration of the methyl group in **22** fully restituted the phototautomerism observed in **20**$^{•+}$/**21**$^{•+}$. Apparently the rate of tunnelling is several orders of magnitude higher in **22**$^{•+}$ than it is in **20**$^{•+}$ so that the the former immediately decays to **23**$^{•+}$ (possibly **22**$^{•+}$ could be generated by flash photolysis and observed by time-resolved spectroscopy, but cannot be readily done in matrix isolated samples) [28].
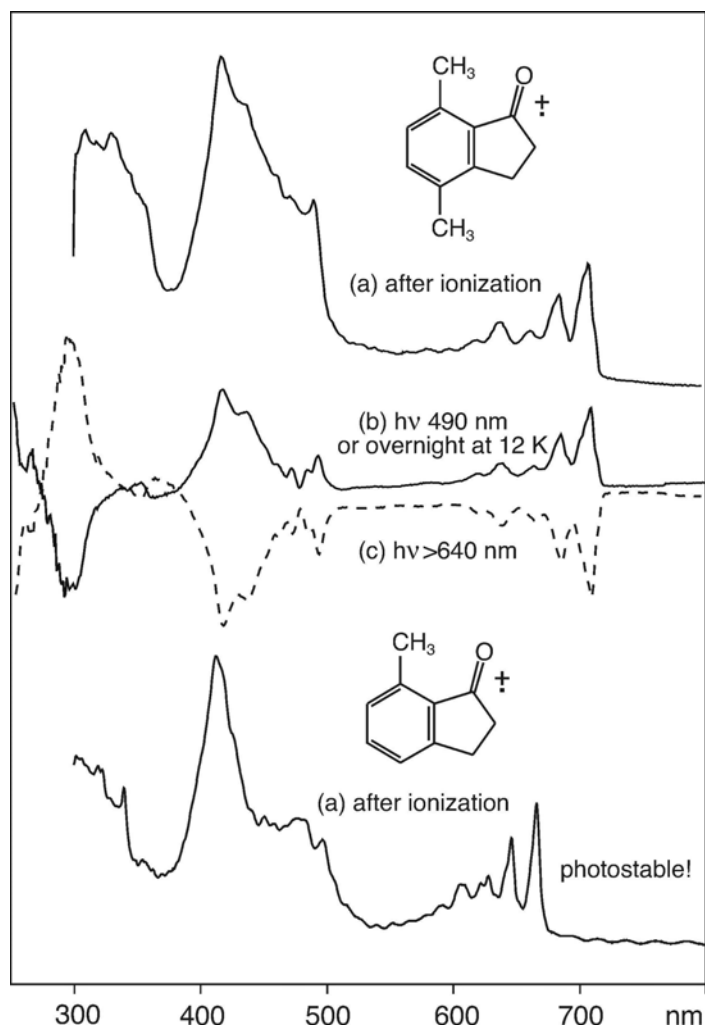
Fig. 3 (a) Changes in the UV/Vis spectra on ionization of methyl- or dimethylindanone (**22** or **20**, respectively) which results in its partial conversion to the corrsponding enol radical cations (see Scheme 7); (b) and (c) reversible interconversion of **20•⁺** and **21•⁺** by selective photolysis or, in the case of the reaction leading to the enol radical cation, thermally at 12K (see text).

These results raised the question of why and how a remote methyl group can so strongly influence the tautomerization kinetics of the radical cation of methylindanone. Indeed calculations showed that the additional methyl group in **20•⁺** raises the barrier for enolization by ca. 6.5 kcal/mol, enough to explain our observations.

The reason for this lies in the electronic structure of aromatic ketone radical cations: Enolization can only occur from a state where an electron is missing from an oxygen lone pair (which is then poised to abstract a hydrogen atom from a vicinal alkyl group), whereas states where the electron is missing from the π-system are unreactive with regard to H-abstraction.

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In **22**$^{\bullet+}$ these two states are nearly degenerate, whereas in **20**$^{\bullet+}$ the ground state arises from ionization of a π-MO while the σ-radical state lies 6.5 kcal/mol higher in energy. Once this reactive state has been reached, the enolization kinetics of **20**$^{\bullet+}$ and **22**$^{\bullet+}$ are nearly identical. Thus, the difference in reactivity of these two very similar compounds are a result of the stabilization of the unreactive π-radical state by the additional methyl group [28].

This example shows that it is worthwhile to pay close attention to proximate electronic states in radical cations, because the photochemical and thermal reactivity of radical cations can be very different in different electronic states.

Conclusion

This account gives a flavor of the interesting photochemistry that different reactive intermediates reveal under conditions where they are sufficiently stable to undergo light-induced reactions, and that this photochemistry is worthwhile to explore, not only for ist academic interest, but also in view of the fate of reactive intermediates in various applications.

Acknowledgments

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