

LIGHT INDUCED PROCESSES IN ORGANIC MOLECULAR IONS

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Abstract - Of the many different chemical processes where organic molecular ions (in particular cations M^+) are known to engage in, most are thermally activated ones. Recently, however, a growing body of evidence has begun to emerge which indicates that M^+ also undergo a variety of photochemical transformations. They are quite distinct from those undergone by their parent neutrals (M) in that they can usually be induced with visible light and often follow different courses. This short review intends to summarize the present state of knowledge about M^+ -photoprocesses and highlights some pertinent photophysical parameters of M^+ used to rationalize these reactions. A general comparison between gas- and condensed phase results is made and the example of trans-stilbene⁺ and cis-stilbene⁺ interconversion which appears at present the best studied M^+ -photoreaction is discussed in some detail.

INTRODUCTION

Electron transfer is a key step in a variety of chemical processes. If the reactants are closed shell neutrals (M), radical ions (M^+ or M^-) are initially produced which subsequently engage in various transformations. Reviews dealing with the formation of such species via thermal /1/, electrochemical /1/ or photolytic /2-4/ processes are available. For the latter type, direct photoelectron ejection in the gas /5/ or in condensed phase /6,7/ as well as multiphoton events /8/ have been discussed in detail. Concerning analytical aspects we find recent reviews emphasizing gas phase /9-12/ or matrix isolation techniques /13-17/ for various types of spectroscopic investigations on radical ions. On the other hand the general chemical involvement of such species has frequently been highlighted /18-20/, and recent articles outline the current state of knowledge about their specific role in photosynthesis and vision /21/ radiation- /22/ and polymerization chemistry /23/ as well as chemiluminescence phenomena /24/. Finally, some accounts summing up recent work on negative ions should be mentioned /25,26/.

The above cited work shows clearly that open-shell organic ions play a crucial role in a variety of different chemical events, a fact which has only recently become fully apparent due to the advent of new instrumental techniques for production, detection and investigation of such species. One notes, however, that most of the chemical processes where M^+ and M^- are now known to engage in are thermally activated ones whereas only few reports shed light on the chemical behaviour of radical ions upon photoexcitation. It is the purpose of this paper to summarize the present state of knowledge about the photochemistry of radical ions. We shall concentrate on organic molecular cations M^+ which are dealt with in the majority of cases.

PHOTOPHYSICAL ASPECTS OF M^+

Absorption spectra

A thorough understanding of the photophysics of a molecule is a prerequisite for the understanding of its photochemistry. Here the first thing that strikes investigators working with such species M^+ (under stable conditions) is their color which sets them clearly apart from the (often colorless) corresponding neutrals. Apparently, the electronically excited doublet (D)-states of M^+ accessible through photon impact are generally lower lying than

the singlet (S)-states of the parent neutrals M. The theory underlying this phenomenon has been outlined a while ago /27/: In an orbital picture $S_0 \rightarrow S_1$ transitions in neutral molecules M involve electron promotion between the generally well separated bonding and virtual MO-levels, for example HOMO to LUMO in the lowest-energy transition. Although the latter two levels are usually more closely spaced in M^\ddagger the corresponding transitions are most often not the lowest energy ones because now a new type of electron promotion between various doubly occupied MO's and the singly occupied HOMO of M^\ddagger become available. Since the spacings within the bonding manifold of orbitals are usually smaller than the HOMO-LUMO gap, some of these electron promotions will give rise to optical transitions at lower wavelengths and are thus frequently responsible for the color of M^\ddagger .

Experimental insight into the energetic disposition of the bonding orbitals of M can be gained through UV-Photoelectron (UP) spectroscopy via Koopmans' theorem. Thus UP-spectra allow us to identify electronic transitions of M^\ddagger within those orbitals (leading to so called Koopmans'-states) provided that the structures of M and M^\ddagger do not differ too much. On the other hand, electron promotions into virtual orbitals (leading to so called Non-Koopmans'-states of M^\ddagger because they cannot be attained by simple electron ejection from M and hence do not show up in the UP-spectrum) give rise to optical transitions of M^\ddagger which can be seen in the Electronic Absorption (EA) spectrum provided they are dipole allowed.

The general strategy of comparing UP-spectra of M and EA-spectra of M^\ddagger for sorting out Koopmans'- and Non-Koopmans'-states of M^\ddagger has been outlined in /13/. Regarding our title topic, it should be retained that simple inspection of the UP-spectrum of M is often not sufficient for identifying the first electronically excited state of M^\ddagger whose properties (energy, symmetry) are obviously of paramount importance in their photochemistry. In fact, several cases have been identified where this state is of Non-Koopmans' nature and can only be detected in the EA-spectrum of M^\ddagger /28-31/. Other such cases were predicted by MO-calculations /27/.

Note, however, that a strict division between Koopmans'- and Non-Koopmans'-states of M^\ddagger becomes problematic when mixing between the two sets of corresponding configurations leads to a breakdown of the simple orbital picture as shown recently for paraquinodimethanes /32-34/ and linear polyenes /35/.

Extensive compilations of UP-spectra of M /5/ and EA-spectra of M^\ddagger in rigid media /36/ are (or will shortly become) available. Due to the low concentrations of charged species attainable in the gas phase, EA-spectra of M^\ddagger cannot be obtained under these conditions. However, indirect information of a similar type can be gained through detection of fragment ion abundances as a function of incident light energy, a technique called Photodissociation (PD) spectroscopy /37-39/. Such studies usually yield low resolution spectra similar in appearance to EA-spectra of M^\ddagger observed in inert rigid media (vide infra). PD-spectra have proven very useful in cases where the "true" optical spectra could not be obtained.

Emission spectra

Light emission of M^\ddagger was studied in the gas phase or in noble gas matrices either by dispersing the fluorescence or by scanning the excitation frequency while measuring total emission /11,40-43/. Since radical ions generally absorb at much lower energies than their closed shell parents, the first transitions often fall into a region accessible by pulsed lasers. This made it possible to determine lifetimes of excited D-states of M^\ddagger by recording time-resolved emission profiles. In addition, Photoelectron-Photoion Coincidence (PEPICO) measurements have provided quantum yields for deactivation of electronically excited M^\ddagger via different decay channels /39/. Altogether over one hundred fluorescing radical cations were found during the last years, whose gas phase excited state properties differ significantly from those of their parent neutrals: while the high first excited S-state energies of the latter often provide enough vibrational energy to induce isomerizations or fragmentations after internal conversion, such chemical deactivation channels are less accessible for certain classes of M^\ddagger because their lowest excited D-state (\tilde{A}) often lies below ground-state decomposition thresholds /44/. Indeed, the three categories of emissive M^\ddagger observed so far (acetylenic, polyenic and benzenoid compounds) all show low-lying \tilde{A} -states of predominant

Koopmans' nature which are not available to the neutrals. In spite of this, fluorescence quantum yields are generally smaller than one in the majority of known emissive M^{\ddagger} because the close proximity of the \tilde{A} -state and the ground state (\tilde{X}) provides for a dense manifold of vibronic \tilde{X} -levels around the \tilde{A} -state. Thus, nonradiative decay is facilitated under gas-phase experimental conditions within the accessible time scale. For the three mentioned categories of emissive M^{\ddagger} , radiative and nonradiative decay constants are roughly equal and lie around 10^{-6} to 10^{-8} s $^{-1}$, resulting in fluorescence quantum yields of 0.1 to 1 /43/.

General remarks about medium effects

In comparing photophysical data for M^{\ddagger} obtained for isolated species in the gas phase and in condensed phase, possible medium effects have to be considered. Solvation energies for a variety of ground-state organic ions in noble gas matrices were found to be in the 1-2 eV range /45/. As in the case of neutral molecules, spectral matrix shifts will occur unless the same solvation energies apply also for the excited states (which are intrinsically more polarizable than the ground states). In addition, guest-host charge-transfer interactions must be taken into account for charged species and these are likely to be energetically more favorable for excited radical cations ($M^{\ddagger*}$). Taking 8-10 eV as typical values for ground state electron affinities (EA's) of M^{\ddagger} (i.e. IP's of M) and 2-4 eV as lowest excitation energies one arrives at EA ($M^{\ddagger*}$) ~10-14 eV. This is well below the conduction band in a Ne matrix which lies about 1-2 eV below the gas phase IP (21.6 eV). Indeed, exceedingly small matrix perturbations are observed in solid Ne as opposed to Ar (IP=15.76 eV, conduction band 1-2 eV below) where significant shifts are found, presumably also as a consequence of the argon atom's higher polarizability. Even stronger deviations from gas phase behavior are expected and found for the commonly employed Freon glasses where in addition many cases of chemical (bond forming) interaction of solute ions with the medium were detected. A general discussion of these phenomena has been provided in /42/ while the specific example of naphthalene cation in different media is discussed in /13/. For a homologous series of M^{\ddagger} in the same medium see /29/ and /35/.

With respect to photochemistry, the major mechanism by which matrices often change the behavior of M^{\ddagger} relative to the gas phase is the "cage effect" /16/. The rigid surrounding may impose a steric constraint for (energetically favorable) rearrangement processes or inhibit fragmentations by preventing diffusion of the fragments from the excitation site. Furthermore, one or both of the initially formed fragments may retain a considerable amount of excess energy which in the case of noble gas matrices is only haltingly transferred to the low-energy lattice vibrations /46/. Thus, even fragments with a reasonable potential energy barrier to recombination will for a short time have enough energy at their disposition to surmount it.

Exceptions to these rules are fragment atoms which - depending on their size and the matrix material - may escape more or less freely from the excitation site /16/. For neutral precursors typical examples are hydrogen atoms (from photolysis of hydrides). On the other hand, fragments may become stabilized by interaction with the matrix material, for example $(Ar)_nH^{\ddagger}$ in the case of protons in argon matrices /47/. Finally, one of the fragments may be a highly inert closed shell molecule which may even persist in the vicinity of a secondary radical ion (see for example H_2 or CH_4 -elimination from alkane cations discussed below). Note, however, that "inertness" has to be assessed relative to the cofragment: for example CH_2N_2 does not yield methylene upon photolysis in matrices due to immediate recombination with N_2 /48/.

LIGHT-INDUCED REACTIONS OF M^{\ddagger}

Gas phase processes

Although in gas-phase M^{\ddagger} -chemistry fragmentations, rearrangements and bimolecular reactions are all thought to play an important role, detailed mechanistic insight has not yet been obtained for many of these processes /37,38,49/. In laboratory investigations M^{\ddagger} first has to be prepared from M which usually happens with more energy than needed to induce threshold ionization. Consequently, M^{\ddagger} retains some excess energy whose exact amount at the time of subsequent photolysis is in most cases unknown and depends strongly on the experimental conditions. Specifically, collisions of M^{\ddagger} with other molecules

prior to detection or photolysis may remove some of this excess energy or may lead to initial rearrangements. Thus, benzyl chloride absorbs red light (594 nm) which induces dissociation. At higher pressures it rearranges, however, to a blue-absorbing species (458 nm) which also fragments /37,33/. Cases were found where even IR-photons sufficed to provide the small amount of incremental energy required to induce chemical reactions in M^{\dagger} containing already a large amount of excess energy. On the other hand, energy redistribution within electronically excited gas phase ions may not be fast enough to occur before dissociation - in contrast to the predictions of RRKM theory. For example ethyl chloride[†] dissociates either into ethyl cation and $Cl\cdot$ or ethylene[†] and HCl , the branching ratio being strongly dependent on the incident photon energy /37,38/. Similar behavior is found in butyrophenone which loses either $CH_2=C(Ph)(OH)^{\dagger}$ or $^+O=CCH_2CH_3$ on impact of 440 nm or 310 nm radiation, respectively. It appears as though two different electronic states of the reactant are involved /50,51/.

Interesting rearrangement-dissociation processes were found in the following ICR experiments. *p*-bromotoluene[†] has a threshold for dissociation into tolyl[†] and $Br\cdot$ of 2.81 eV (440 nm). Nevertheless, $C_7H_7^+$ -fragments are formed in irradiation with $\lambda > 600$ nm and the absence of any pressure dependence for the quantum yield of fragmentation indicates that a one-photon process is involved. Hence, rearrangement to a more stable $C_7H_7^+$ -isomer (e.g. benzyl[†] or tropylium[†]) must take place concurrently with dissociation. In contrast, *p*-iodotoluene[†] fragments in a two-photon process below its one-photon dissociation threshold and it can be speculated that the first photon induces rearrangement to an isomer which then dissociates with the second photon.

Processes in fluid media

Here, only few studies can be cited at present. Ten years ago it was recognized that the low-lying excited D-states of M^{\dagger} may allow chemical transformations which are excluded for the (higher lying) excited S-states of the parent neutrals *M* when those lie above a fragmentation threshold /52/. Thus, tetraphenylhydrazine absorbs light at 300 nm to dissociate into diphenylnitrene, no benzidine rearrangement being observed. However, the corresponding radical cation upon excitation at 465 nm yields the corresponding benzidine[†] as a primary photorearrangement product which subsequently undergoes disproportionation with the starting hydrazine[†] to give finally the benzidine dication. When reporting these findings the authors hailed "a new area of photochemistry [which] appeared to be opened" /52/. The above cited work appears to be the only account of true photochemistry of M^{\dagger} in fluid phase, i.e. dealing with the breaking of old and the formation of new bonds upon photolysis. In our view the more recent work /53,54/ described below is photophysical in nature as the primary step is photoreduction of M^{\dagger} to *M* resulting in the formation of secondary radical cations X^{\dagger} which subsequently engage in thermal reactions. Nevertheless, the chemical importance of these processes warrants their inclusion in this overview. Anodic oxidation of *M* = *N,N'*-tetraphenyl-1,4-diaminobenzene yields its radical cation M^{\dagger} which upon photolysis with light above 360 nm in the presence of *X* = benzyl alcohol gives benzaldehyde /53/. The crucial step in this and similar reactions is electron transfer from the substrate *X* to excited M^{\dagger} (acting as a photocatalyst) whereupon X^{\dagger} undergoes thermal reactions. Subsequent studies employed as anodically generated M^{\dagger} to be photoexcited (and then reduced by *X* = 1,1-diphenylethylene) derivatives of di- and triphenylamines, benzidines, 1,4-diaminobenzenes and phenothiazines /54/. The results indicate that this strategy provides a means of controlled oxidation of *X*, controlled in particular with respect to the oxidizing power of excited M^{\dagger} . While in direct anodic oxidation of *X*, X^{\dagger} is formed in a medium of high oxidizing power, the intermediacy of M^{\dagger} provides for a medium of low oxidizing power around X^{\dagger} and only in the vicinity of excited M^{\dagger} is high oxidizing power available.

Involvement of Quartet (Q) states of M^{\dagger} ?

Excited electronic states of triplet (T) multiplicity play an important role in the photochemistry of closed-shell organic singlet (S) species. Specifically, their long lifetime enables them to engage in bimolecular reactions. The previous chapter dealt with bimolecular electron transfer processes between excited M^{\dagger} (D ground state) and *X*. Hence the question arises if the reacting state of M^{\dagger} may not be of long lived Q-nature. Unfortunately very little is known about Q-states of M^{\dagger} , both experimentally and theoretically /44/. Since all excited Q-configurations involve electron promotion from the

doubly occupied to the virtual manifold of orbitals of M^+ , there are for the same molecular structure two excited D-configurations (HOMO-1→HOMO and HOMO→LUMO excited) beneath the lowest Q-type one. This situation will certainly pertain also for the corresponding states in the majority of cases, contrary to that for S states and their higher multiplicity T-counterparts. It favors rapid intramolecular deactivation of Q-states (formed via intersystem crossing (ISC) from higher-lying D-states of M^+) via back-ISC to the lower-lying D-manifold. Apart from this energetic reasoning, mixing between D- and Q-states of M^+ will further facilitate this mode of deactivation. In a two-electron system the dipolar interaction cannot mix S- and T-states due to its invariance to permutation of spin variables. Three-electron systems do, however, not possess this invariance and therefore dipolar interaction is capable of mixing D- and Q-states /55/. To our knowledge the question of Q-state involvement in a formally bimolecular process as that between M^+ and X above has not been discussed explicitly in the literature although it was considered in private discussions /56/ in the context of the work described above /54/. In print it was concluded that presumably a weak association exists between the two reaction partners ($M^+ \cdots X$) already before excitation of M^+ /54/.

Processes in solid matrices

Most of the available information on the chemical behaviour of photoexcited M^+ stems from work in solid matrices at low temperatures /14,17,40-42/. In "true" matrix isolation, a mixture of the vapour of M with a large excess of noble gas and eventually some electron scavenger is deposited on a cold surface of suitable type for the envisaged spectroscopic technique. Alternatively, solid media can be formed by rapidly freezing solutions of M containing or made up of an electron scavenging solvent such as butyl chloride /57/, CCl_3F /58/, $CF_2Cl-CCl_2F$ /59/ or a mixture of freons /60/. Impact of high-energy radiation (gamma- /61/, X-rays /35/, hard UV light from a discharge lamp /14-16/) or biphotonic ionization /62/ leads to $M \rightarrow M^+$, the outgoing electron being trapped by dissociative electron capture on the halide (in the case of the emission studies in noble gas matrices mentioned earlier, addition of electron scavenger proved unnecessary due to the high sensitivity of the detection technique).

During or after the ionizing step M^+ may undergo structural relaxation, rearrangement or even fragmentation /63/. It is therefore always necessary to assess to what extent the precursor structure is retained before proceeding to study the photochemical behavior of M^+ by selective irradiation with visible or UV light.

Before discussing individual examples we have to turn our attention to a general problem in solid-phase photochemistry. Cases of light-induced rearrangements of M^+ requiring profound changes in shape or volume of the matrix cavity raised the question to what extent excess vibrational energy available after internal conversion from the electronically excited state can serve to locally soften or even melt the matrix /64/. A detailed recent study addressed this problem by trying to detect progressive shifts in fluorescence maxima as a function of incident photon energy, possibly indicative of progressive solvent rearrangement with increasing amount of excess vibrational energy. Such shifts were, however, only detected in solvents forming H-bridges, where the excess energy is apparently funneled preferentially into specifically bonded neighbouring solvent molecules /65/. Furthermore there is evidence that in Freon matrices only such reactions of M^{+*} take place where the transition state or product does not take up more space than the starting ion /66/. The available evidence, though admittedly limited, indicates therefore that the photoinduced reactions of M^+ discussed below can be viewed as originating from excited electronic states M^{+*} and are not "hot" ground state reactions occurring in a slightly softened matrix cage.

Another general remark concerns matrix chemistry of radical ions: most M^+ eventually undergo bleaching, i.e. neutralization upon photolysis. This feature is so general that it was originally employed as a diagnostic tool to distinguish M^+ absorption from those of radicals or closed shell ions which usually prove to be photostable /57/. It seems that M^{+*} is endowed with a greater thermodynamic driving force for recombination with an electron trapped in the matrix due to the increased electron affinity of M^{+*} relative to M^+ . Fortunately, conditions can usually be found where this photoneutralization is sufficiently inefficient to allow the study of other photoreactions without excessive loss of M^+ .

Only few photodissociations of M^+ have been observed so far. The best studied examples are halomethane cations ($CH_nX_{4-n}^+$, $X=F, Cl, Br$ or combinations thereof) which generally undergo facile photodecomposition with visible light by a process which is thought to involve elimination of a halogen atom to yield a carbonium ion /67/. Even though elimination of H-atoms which are known to diffuse freely through Ar matrices would seem to be a feasible process it was never observed, presumably because C-X bonds are weaker than C-H bonds in M^+ , too. For CCl_4 a rather complex photofragmentation mechanism was put forward which implied that the Jahn-Teller distorted molecular cation would first dissociate into a complex $(CCl_2--Cl_2)^+$ of ion-dipole nature /68/ which would undergo further photodecomposition into CCl_3^+ and $Cl\cdot$ /69/.

Very recently the first molecular photoeliminations were reported for alkane $^+$ which play a pivotal role in radiation chemistry /70/. It had been known for some time that alkane $^+$ are strongly colored /71/, showing absorption maxima in the visible to NIR region which can readily be photobleached /61,72/, but it was only after the discovery of a suitable matrix material for ESR studies /58/ that detailed investigation of the structure of these species and their photoproducts became feasible. Thus, branched /73/ and monocyclic /79/ alkane $^+$ in freon glasses were found to lose CH_4 or H_2 upon visible irradiation whereas for linear n-alkanes $[C_nH_{2n+2}]^+$ a general fragmentation route in CCl_3CF_3 leads to 2-butene $^+$ and a secondary alkane $C_{n-4}H_{2n-6}$ /75/ at a threshold energy of 1.9 eV (650 nm) /76/. Studies with isotopically labelled compounds indicate that all carbon atoms of the primary n-alkane $^+$ end up with nonzero probability in the neutral fragment alkane. Furthermore, photorearrangement of linear to branched alkane $^+$ was detected below the decomposition threshold which indicates that the fragmentations mechanism may be rather complex /77/. Note also that photochemical /73-77/ as well as thermal /78/ fragmentations of alkane $^+$ in matrices seem to be very strongly affected by the medium /72,76,78/ such that results obtained in a particular matrix cannot be generalized.

By virtue of the cage effect discussed above, photofragmentations do not usually represent the most readily accessible chemical deactivation pathway in solid matrices. Therefore, the majority of reported M^+ photoreactions concern photoisomerizations of various types which shall be discussed below. The fact that M^+ rearrangements can usually also be induced by visible light has aroused interest in the solar energy research community and certain hopes are focussed on the possibility of harnessing sunlight via such photoisomerizations of M^+ .

The first photoreaction of M^+ in a solid matrix was reported almost 20 years ago in a pioneering paper describing the clean isomerization of cis-stilbene $^+$ to trans-stilbene $^+$ on illumination with visible light /57/. This process has recently received considerable attention and is now probably the best studied photoreaction of any M^+ . It will be reviewed in detail at the end of this chapter in a separate paragraph.

In 1973 it was found that the initially broad and featureless spectrum of cyclooctatetraene cation (COT^+) in a freon matrix at 77K could be converted by selective illumination in several steps into a set of very sharp absorptions whose origin remained, however, unexplained /79/. These measurements were recently repeated in Ar matrices but the identity of the product ion(s) could again not be assessed unambiguously /80/.

A significant advance in this field was signaled by the first systematic study on the photochemistry of an organic radical cation in 1977. It concerned the electrocyclic ring-opening of 1,3-cyclohexadiene $^+$ to 1,3,5-hexatriene $^+$ in a freon matrix at 77K by impact of green light /81/. Through a judicious choice of optical filter combinations it was possible to selectively photolyze four different polyene $^+$ structures whose individual spectra were obtained by successive subtraction of consecutive spectra. Note that when dealing with polyene $^+$ the distinction between essential single and double bonds becomes meaningless because all bonds have partial double bond character. Hence, structures interrelated by low-energy rotations (typically 4 kcal/mole) around the essential single bonds in the neutrals end up in much deeper potential troughs after ionization and the distinctive terms "conformers" (i.e. interrelated by rotation around essential single bonds) and "isomers" (i.e. interrelated by rotation around essential double bonds) should perhaps be replaced for the ions by a common term such as "rotamers" /82/. In any event, it seems

justified to use the term "photoisomerization" for the light-induced inter-conversion of different open-chain hexatriene⁺ structures.

Recent work in Ar matrices at 20K /35,83/ by and large confirmed the cited earlier results /81/. Additional information was, however, obtained by careful inspection of the better resolved spectra in Ar which led to some changes in the original assignments of subtractively obtained spectra to individual hexatriene⁺- "rotamers". In particular, cis- and trans-hexatriene⁺ were found to show very similar spectra with the main peaks separated by only 5 nm /83/. Unfortunately there are no theoretical methods presently available which could be consulted to give reliable predictions of the rather subtle spectral differences between the different hexatriene⁺- "rotamers"; hence a definitive assignment will have to await a more comprehensive study.

Similarly to hexatriene⁺, butadiene⁺ and octatetraene⁺ can be generated with visible light from the corresponding monocyclic precursor ions cyclobutene⁺ and 1,3,5-cyclooctatriene⁺, respectively, in Ar at 20K /35,83/. The former electrocyclic process was observed earlier in an alkyl chloride matrix at 77K /13/ as well as in the gas phase /85/. It has been discussed in terms of state correlation diagrams /86/ but unfortunately no experimental evidence regarding the stereochemical course (conrotatory or disrotatory) of this reaction has emerged so far.

The C₈H₁₀-hydrocarbon ions revealed some additional photochemistry. Thus, 1,3,5-cyclooctatriene⁺ which shows a weak but sharp absorption at 500 nm in Ar can be photolyzed to give a very photosensitive transient absorbing weakly at 550 nm. This in turn can be irradiated to give several octatetraene cations /83,87/. The set of possible "rotamers" is of course much larger for octatetraene⁺ than for hexatriene⁺ (20 vs. 6) and indeed, the spectra of more than ten different species with main absorptions between 450 and 500 nm could be obtained subtractively with selective bleaching experiments /83/. Unfortunately, an unambiguous assignment is again impossible. By carefully avoiding irradiation below 450 nm one succeeds in bleaching everything but a very intense band system with a 350 cm⁻¹ progression which was ascribed to all-trans octatetraene⁺ (it is also the most intense band if one prepares this ion from the matrix-isolated neutral parent /35/).

Interestingly, careful photolysis with very narrow bandwidth light reveals that even this band system comprises at least six components each of which shows the same 350 cm⁻¹ progression but is linearly displaced by about 50 cm⁻¹ relative to its nearest spectral neighbour. Since there is no reason why different octatetraene⁺ rotamers should show identical vibrational progressions in their electronic absorption bands a site effect is presumably responsible for this observation which will be reported in more detail /83/.

A rather general type of M⁺ photoreactions seems to be the shifting of double bonds as exemplified by the conversion of 1-butene⁺ to 2-butene⁺ with visible light /84/. The preferred course for this reactions is, in general, double bond shifting into conjugation with other double bonds (e.g. 1,4-cyclohexadiene⁺ to 1,3-cyclohexadiene⁺ /74,84/; 3-phenylpropene⁺ to 1-phenylpropene⁺ /80/). Interestingly, 3-phenylpropene⁺ under these conditions ($\lambda > 290$ nm) undergoes concomitant reversible photocyclization to methyl-benzocyclobutene⁺ which is in turn opened to 1-phenylpropene⁺ with $\lambda = 400-600$ nm. Prolongued photolysis at $\lambda > 290$ nm eventually results in conversion to indane⁺ in yet another cyclization process /80/. A similar type of mechanism is probably involved in the photochemical ringopening of cyclopentene⁺ to 1,2-pentadiene⁺ observed in CCl₃F /84/ (but not in CF₃CCl₃ /74/!).

The mass spectroscopic observation of extensive H/D-scrambling in labelled toluene⁺ and cycloheptatriene⁺ induced a study of these ions under stable conditions in Ar matrices. It was concluded that these two C₇H₈⁺ isomers as well as norbornadiene⁺ and quadricyclane⁺ rearrange to a common structure upon photolysis or even during the ionization step /88,89/. The optical spectrum of this species was assigned to 1-methylene-2,4-cyclohexadiene⁺ ("o-isotoluene⁺"), a rather elusive species on the neutral C₇H₈ hypersurface. The same ion was formed by photoinduced McLafferty rearrangement from n-butylbenzene⁺ /88/ or 1-phenyl-2-butene⁺ /80,89/. Similar behavior was also observed for various alkylated /90/ and chlorinated /91/ C₇H₈⁺ derivatives and most recently the study was extended to benzannelated derivatives of cycloheptatriene where for

the first time evidence for the intermediacy of a norcardiene⁺ was obtained which underwent subsequent photolysis to yield the corresponding o-isotoluene⁺ along with 1- and 2-methylnaphthalene /92/.

We shall conclude this chapter with a more detailed description of the above mentioned isomerization of cis-stilbene⁺ (C⁺) to trans-stilbene⁺ (T⁺). This process appears to be the only one at present where a serious attempt was made to rationalize the experimental observations on the basis of thermochemical and photophysical parameters of the involved molecular ions. Thermochemical considerations show that C⁺ is less stable than T⁺ /13/. On the other hand, experiments in solution indicated that both ions are separated by an activation barrier and are therefore distinct species /93/. However, only T⁺ is observed if either C or T are ionized by electron impact in the mass spectrometer /94/ which indicates that "milder" methods such as field ionization or charge transfer may be required to form C⁺ with retention of structure (i.e. without excess energy) in the gas phase. In the same experiment, C⁺ was, however, obtained by excitation of T⁺ with visible light. Subsequent ring-closure of C⁺ results in dihydrophenanthrene⁺ which loses H₂ to form phenanthrene⁺ /94/.

In alkyl chloride or freon matrices both C⁺ and T⁺ can be obtained from their neutral precursors by γ -irradiation as shown in the pioneering study cited earlier /57/ and confirmed more recently /13,95-97/. Both ions show similar optical spectra with two band systems A and B in the visible range:

$$C^+ : \lambda_A = 750 \text{ nm } (\epsilon_A = 2630) , \lambda_B = 515 \text{ nm } (\epsilon_B = 10000)$$

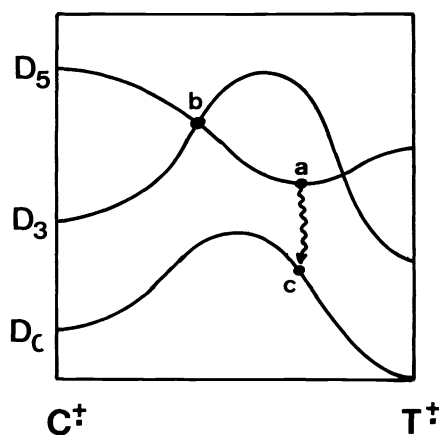
$$T^+ : \lambda_A = 763 \text{ nm } (\epsilon_A = 4950) , \lambda_B = 483 \text{ nm } (\epsilon_B = 33400)$$

A theoretical analysis /30/ shows that for both ions these A- and B-bands correspond to electronic transitions from the ionic ground state D₀ to the third (D₃) and fifth (D₅) excited state, respectively, the former being of Koopmans' nature, the latter corresponding to the HOMO-LUMO transition. The electronic transitions leading to the Koopmans' excited states D₁, D₂, and D₄ of C⁺ and T⁺ are either dipole forbidden or have very weak transition moments.

Returning to matrix photochemistry we note that C⁺ isomerizes cleanly to T⁺ but the reverse process is not observed. The quantum yield for C⁺ → T⁺ is strongly dependent on the wavelength of the incident light, rising steadily when the first few vibrational quanta of D₃ are excited (A-band) to reach a plateau in the region of the D₅ state (B-band). The maximum quantum yield of 0.6 (reached at the peak of the B-band /97/) is much higher than for the corresponding process C → T in the same /66/ or other low-temperature matrices ($\phi_F = 0.05$ /98/).

The above observations can be rationalized on the basis of the following arguments:

a) The course of C⁺ → T⁺ is interpreted by using the energy diagram depicted below /96/:



Population of $D_5(C^{\ddagger})$ converts the ion to point a. Funneling to c results eventually in $D_0(T^{\ddagger})$. Population of some excited vibrational quanta of $D_3(C^{\ddagger})$ may also lead to passage onto the D_5 -surface after crossing at point b.

b) Given the disposition of point a with respect to point c as shown in the figure, the non-occurrence of $T^{\ddagger} \rightarrow C^{\ddagger}$ in matrices can be explained. In addition, arguments based on the "cage effect" may be advanced: the smaller volume of T^{\ddagger} makes its conversion to C^{\ddagger} difficult in a rigid matrix. Note in this context that the efficiency of the process $T \rightarrow C$ depends strongly on solvent viscosity whereas the reverse reaction is essentially unaffected by this parameter /98/.

c) The higher quantum yield for $C^{\ddagger} \rightarrow T^{\ddagger}$ with respect to $C \rightarrow T$ may be related to the fact that the central double bond in the ions is clearly weaker than in the neutrals given that the HOMO partial bond order for the C=C linkage in stilbene is particularly large. Observation from other diarylethylene ‡ systems support the above conclusions /95-97/.

Let us, however, finally point out that the states D_1 , D_2 , and D_4 do not show up in the above analysis although it must be assumed that internal conversion to one or the other of these states after initial population of D_3 or D_5 is certainly also a very fast process. This problem does not arise in the discussion of the $C \rightleftharpoons T$ interconversion as here only the lowest S_1 and T_1 states play a role. It appears that much work remains to be done to elucidate the exact mechanism of this and other M^{\ddagger} -photoreactions until our understanding of these processes reaches a level comparable to that presently achieved for photoexcited neutral closed shell species /6/.

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