LIGHT INDUCED PROCESSES IN ORGANIC MOLECULAR IONS

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Abstract – Of the many different chemical processes where organic mo-
lecular 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 pho-
tophysical 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 dis-
cussed in some detail.

INTRODUCTION

Electron transfer is a key step in a variety of chemical processes. If the re-
actants 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 photo-
electron ejection in the gas [5] or in condensed phase [6,7] as well as multi-
photon events [8] have been discussed in detail. Concerning analytical aspects
we find recent reviews emphasizing gas phase [9-12] or matrix isolation tech-
niques [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 photochemis-
try 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) cor-
responding 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^+ 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^+ 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^+.

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^+ within those orbitals (leading to so called Koopmans'-states) provided that the structures of M and M^+ do not differ too much. On the other hand, electron promotions into virtual orbitals (leading to so called Non-Koopmans'-states of M^+ 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^+ 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^+ for sorting out Koopmans'- and Non-Koopmans'-states of M^+ 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^+ 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^+ /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^+ 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^+ 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^+ 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^+ 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^+ 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^+ by recording time-resolved emission profiles. In addition, Photoelectron-Photoion Coincidence (PEPICO) measurements have provided quantum yields for deactivation of electronically excited M^+ 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^+ because their lowest excited D-state (Ã) often lies below ground-state decomposition thresholds /44/. Indeed, the three categories of emissive M^+ observed so far (acetylenic, polyenic and benzenoid compounds) all show low-lying Ã-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 $M^{\dot{+}}$ 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 $M^{\dot{+}}$, 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 $M^{\dot{+}}$ 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 ($M^{\dot{+}*}$). Taking 8-10 eV as typical values for ground state electron affinities (EA's) of $M^{\dot{+}}$ (i.e. IP's of M) and 2-4 eV as lowest excitation energies one arrives at EA ($M^{\dot{+}*}$)~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 $M^{\dot{+}}$ in the same medium see /29/ and /35/.

With respect to photochemistry, the major mechanism by which matrices often change the behavior of $M^{\dot{+}}$ 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 $(Ar)_n H^+$ 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 vicinty 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 $M^{\dot{+}}$

Gas phase processes

Although in gas-phase $M^{\dot{+}}$-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 $M^{\dot{+}}$ first has to be prepared from M which usually happens with more energy than needed to induce threshold ionization. Consequently, $M^{\dot{+}}$ 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 $M^{\dot{+}}$ 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 $M^{\ddagger}$ 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 $CH_2=C(Ph)(OH)^{\ddagger}$ or $^{+}O\equiv CCH_2CH_3$ 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 $M^{\ddagger}$ 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 finding 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 $M^{\ddagger}$ 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 $M^{\ddagger}$ to M resulting in the formation of secondary radical cations $X^{\ddagger}$ 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 $M^{\ddagger}$ 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 $M^{\ddagger}$ (acting as a photocatalyst) whereupon $X^{\ddagger}$ undergoes thermal reactions. Subsequent studies employed as anodically generated $M^{\ddagger}$ 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 $M^{\ddagger}$. While in direct anodic oxidation of X, $X^{\ddagger}$ is formed in a medium of high oxidizing power, the intermediacy of $M^{\ddagger}$ provides for a medium of low oxidizing power around $X^{\ddagger}$ and only in the vicinity of excited $M^{\ddagger}$ is high oxidizing power available.

Involvement of Quartet (Ω) states of $M^{\ddagger}$?

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 $M^{\ddagger}$ (D ground state) and X. Hence the question arises if the reacting state of $M^{\ddagger}$ may not be of long lived Q-nature. Unfortunately very little is known about Q-states of $M^{\ddagger}$, both experimentally and theoretically /44/. Since all excited Q-configurations involve electron promotion from the

doubly occupied to the virtual manifold of orbitals of $M^{\ddagger}$, 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 cros- sing (ISC) from higher-lying D-states of $M^{\ddagger}$) via back-ISC to the lower-lying D-manifold. Apart from this energetic reasoning, mixing between D- and Q- states of $M^{\ddagger}$ 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, how- ever, not possess this invariance and therefore dipolar interaction is ca- pable of mixing D- and Q-states /55/.

To our knowledge the question of Q-state involvement in a formally bimolecu- lar process as that between $M^{\ddagger}$ 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 ($M^{\ddagger}$--X) already before excitation of $M^{\ddagger}$ /54/.

Processes in solid matrices

Most of the available information on the chemical behaviour of photoexcited $M^{\ddagger}$ 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 sur- face of suitable type for the envisaged spectroscopic technique. Alternative- ly, 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-ener- gy radiation (gamma- /61/, X-rays /35/, hard UV light from a discharge lamp /14-16/) or biphotonic ionization /62/ leads to M → $M^{\ddagger}$, 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 de- tection technique).

During or after the ionizing step $M^{\ddagger}$ may undergo structural relaxation, re- arrangement 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 $M^{\ddagger}$ by selective irradiation with visible or UV light.

Before discussing individual examples we have to turn our attention to a ge- neral problem in solid-phase photochemistry. Cases of light-induced rearrange- ments of $M^{\ddagger}$ 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 sol- vent 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 $M^{\ddagger*}$ take place where the transition state or product does not take up more space than the starting ion /66/. The avai- lable evidence, though admittedly limited, indicates therefore that the pho- toinduced reactions of $M^{\ddagger}$ discussed below can be viewed as originating from excited electronic states $M^{\ddagger*}$ and are not "hot" ground state reactions occuring in a slightly softened matrix cage.

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

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 pro-
cess which is thought to involve elimination of a halogen atom to yield a car-
bonium 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 fur-
ther 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/ al-
kane$^+$ 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 thresh-
old energy of 1.9 eV (650 nm) /76/. Studies with isotopically labelled com-
pounds indicate that all carbon atoms of the primary n-alkane$^+$ end up with
nonzero probability in the neutral fragment alkane. Furthermore, photorear-
rangement 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 usu-
ally 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 photoisomeriza-
tions 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 absorp-
tions 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 unambiguouly /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. inter-
related by rotation around essential single bonds) and "isomers" (i.e. inter-
related 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 care-
ful inspection of the better resolved spectra in Ar which led to some changes
in the original assignements 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 dif-
ferences between the different hexatriene^{+}-"rotamers"; hence a definitive as-
signement 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 C_8H_{10}-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 octate-
traene^{+} 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/. Unfortunate-
ly, an unambiguous assignment is again impossible. By carefully avoiding irra-
diation 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 octa-
tetraene^{+} (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 dif-
ferent 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-cyclohexa-
diene^{+} to 1,3-cyclohexadiene^{+} /74,84/; 3-phenylpropene^{+} to 1-phenylpropene^{+}
/80/). Interestingly, 3-phenylpropene^{+} under these conditions (λ>290 nm) under-
goes concomitant reversible photocyclization to methyl-benzocyclobutene^{+} which
is in turn opened to 1-phenylpropene^{+} with λ = 400-600 nm. Prolongued photoly-
sis at λ>290 nm eventually results in conversion to indane^{+} in yet another cy-
clization process /80/. A similar type of mechanism is probably involved in
the photochemical ringopening of cyclopentene^{+} to 1,2-pentadiene^{+} observed in
CCl$_3$F /84/ (but not in CF$_3$CCl$_3$ /74/!).

The mass spectroscopic observation of extensive H/D-scrambling in labelled
toluene^{+} and cycloheptatriene^{+} induced a study of these ions under stable con-
ditions in Ar matrices. It was concluded that these two $C_7H_8^{+}$ isomers as well
as norbornadiene^{+} and quadricyclane^{+} rearrange to a common structure upon pho-
tolysis 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 C_7H_8 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/ $C_7H_8^{+}$ 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-isotolu-
ene[†] along with 1- and 2-methylnaphtalene /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 thermoche-
mical and photophysical parameters of the involved molecular ions. Thermoche-
mical 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 spec-
trometer /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 H_2 to form phenan-
threne[†] /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:

$$C^† \; : \; \lambda_A \; = \; 750 \; nm \; (\varepsilon_A \; = \; 2630) \; , \; \lambda_B \; = \; 515 \; nm \; (\varepsilon_B \; = \; 10000)$$

$$T^† \; : \; \lambda_A \; = \; 763 \; nm \; (\varepsilon_A \; = \; 4950) \; , \; \lambda_B \; = \; 483 \; nm \; (\varepsilon_B \; = \; 33400)$$

A theoretical analysis /30/ shows that for both ions these A- and B-bands
correspond to electronic transitions from the ionic ground state D_0 to the
<u>third</u> (D_3) and <u>fifth</u> (D_5) 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 D_1, D_2, and
D_4 of C[†] and T[†] are either dipole forbidden or have very weak transition mo-
ments.

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 wavelenght of the incident light, rising steadily
when the first few vibrational quanta of D_3 are excited (A-band) to reach a
plateau in the region of the D_5 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 cor-
responding process C → T in the same /66/ or other low-temperature matrices
(Φ_F = 0.05 /98/).

The above observations can be rationalized on the basis of the following ar-
guments:

        a) The course of C[†] → T[†] is interpreted by using the energy diagram
depicted below /96/:
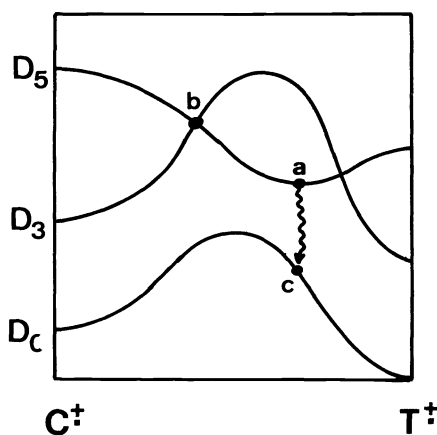
Population of D_5 ($C^{\ddagger}$) converts the ion to point a. Funneling to c results eventually in D_0 ($T^{\ddagger}$). Population of some excited vibrational quanta of D_3 ($C^{\ddagger}$) may also lead to passage onto the D_5-surface after crossing at point b.

      b) Given the disposition of point a with respect to point c as shown in the figure, the non-occurrence of $T^{\ddagger} \to C^{\ddagger}$ 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 $T \to C$ depends strongly on solvent viscosity whereas the reverse reaction is essentially unaffected by this parameter /98/.

      c) The higher quantum yield for $C^{\ddagger} \to T^{\ddagger}$ with respect to $C \to T$ 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 $C \rightleftarrows T$ 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/.

REFERENCES

1. A.J. Bard, A. Ledwith and H.J. Shine, *Adv. Phys. Org. Chem.* <u>13</u>, 155 (1976)
2. M. Gordon and M. Ware, *The Exciplex*, Academic Press, New York (1975).
3. P.G. Whitten, *Acc. Chem. Research* <u>13</u>, 83 (1980).
4. R.D. Connors, *Electron Transfer Reactions*, Butterworths, London (1980).
5. K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki and S. Iwata, *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules*, Japan Scientific Societies Press, Tokyo and Halstedt Press, New York (1981).
6. H. Gerischer, D.M. Kolb and J.K. Sass, *Adv. Phys.* <u>27</u>, 432 (1978).
7. D. Mauzerall and S.G. Ballard, *Ann. Rev. Phys. Chem.* <u>33</u>, 377 (1982).
8. D. M. Friedrich and W.M. McClain, *Ann. Rev. Phys. Chem.* <u>31</u>, 559 (1980).
9. R.J. Saykally and R.C. Woods, *Ann. Rev. Phys. Chem.* 32, <u>403</u> (1981).
10. *Molecular Ions: Geometric and Electronic Structure* (<u>NATO ASI Series</u> B <u>90</u>), J. Berkowitz and K.-O. Groeneveld (eds.), Plenum Press, New York (1983).
11. D. Klopstein, J.P. Maier and M. Liubomir, in: *Molecular Ions: Spectroscopy, Structure, and Chemistry*), T. Miller and V.E. Bondybey (eds.), North Holland, Amsterdam (1983).
12. *Ionic Processes in the Gas Phase*, M. A. Almoster-de Ferreira (ed.), Reidel, Dordrecht (1984).
13. E. Haselbach, T. Bally, R. Gschwind, U. Klemm and Z. Lanyiova, *Chimia* <u>33</u>, 405 (1978).
14. L. Andrews, *Ann. Rev. Phys. Chem.* <u>30</u>, 79 (1979). See also Ref. 41.
15. T.A. Miller and V.E. Bondybey, *Appl. Spectrosc. Rev.* <u>18</u>, 105 (1982); *Phil. Trans. Roy. Soc. London* <u>A307</u>, 617 (1982).
16. D.E. Milligan and M.E. Jacox in *Chemical Spectroscopy and Photochemistry in the Vacuum Ultraviolet*, C. Sandorfy, P.J. Ausloos and M.B. Robin (eds.) Reidel, Dordrecht (1974); M.E. Jacox, *Rev. Chem. Intermed.* <u>2</u>, 1 (1978).
17. T. Shida, E. Haselbach and T. Bally, *Acc. Chem. Research* <u>17</u>, 000 (1984).
18. L. Eberson, *Adv. Phys. Org. Chem.* <u>18</u>, 79 (1982).
19. R.S. Davidson, *Adv. Phys. Org. Chem.* <u>19</u>, 1 (1983).
20. M. Julliard and M. Chanon, *Chem. Rev.* <u>83</u>, 425 (1983).

21. R.E. Blankenship and W.W. Parson, *Ann. Rev. Biochem.* <u>47</u>, 635 (1978); H. Gerischer and J.J. Katz (eds.) *Light-induced Charge Separation in Biology and Chemistry*, Verlag Chemie, Weinheim (1979).
22. A. Hummel, *Adv. Radiat. Chem.* <u>4</u>, 1 (1974).
23. S.P. Pappas, *UV-Curing: Science and Technology*, Technology Marketing Corp. Norwalk, Conneticut (1978).
24. G.B. Schuster and S.P. Schmidt, *Adv. Phys. Org. Chem.* <u>18</u>, 187 (1983).
25. R.R. Cordermann and W.C. Lineberger, *Ann. Rev. Phys. Chem.* <u>30</u>, 347 (1979).
26. M.A. Fox, *Chem. Rev.* <u>79</u>, 253 (1979).
27. P. Čarsky and R. Zahradnik, *Acc. Chem. Research* <u>9</u>, 407 (1976); *Top. Curr. Chem.* <u>43</u>, 1 (1973).
28. R. Forster, R. Gschwind, E. Haselbach, U. Klemm and J. Wirz, *Nouv. J. Chim* <u>4</u>, 365 (1980).
29. E. Haselbach, U. Klemm, U. Buser, R. Gschwind, M. Jungen, E. Kloster-Jensen, J.P. Maier, O. Marthaler, H. Christen and P. Baertschi, *Helv. Chim Acta* <u>64</u>, 823 (1981).
30. E. Haselbach, U. Klemm, R. Gschwind, T. Bally, L. Chassot and S. Nitsche, *Helv. Chim. Acta* <u>65</u>, 2464 (1982).
31. T. Bally, L. Neuhaus, S. Nitsche, E. Haselbach, J. Janssen and W. Lüttke, *Helv. Chim. Acta* <u>66</u>, 1288 (1983).
32. T. Koenig and S. Southworth, *J. Am. Chem. Soc.* <u>99</u>, 2807 (1977).
33. R.W. Bigelow, *Chem. Phys.* <u>80</u>, 45 (1983); *Chem. Phys. Letters* <u>100</u>, 445 (1983).
34. R. Schultz, A. Schweig and W. Zittlau, *J. Am. Chem. Soc.* <u>105</u>, 2980 (1983).
35. T. Bally, S. Nitsche, K. Roth and E. Haselbach, *J. Am. Chem. Soc.* <u>106</u>, 000 (1984).
36. T. Shida, Catalogue of M^+ and M^- EA-spectra in solid matrices, to be published by North Holland, Amsterdam (1984).
37. R.C. Dunbar in *Molecular Ions, Spectroscopy, Structure and Chemistry*, T.A. Miller and V.E. Bondybey (eds.), North Holland, Amsterdam (1983).
38. R.C. Dunbar in *Ionic Processes in the gas phase*, M.A. Almoster-Ferreira (ed.), Reidel, Dordrecht (1984).
39. T. Baer in *Ionic Processes in the gas phase*, M.A. Almoster-Ferreira (ed.), Reidel, Dordrecht (1984).
40. T.A. Miller, *Ann. Rev. Phys. Chem.* <u>33</u>, 257 (1982).
41. L. Andrews in *Molecular Ions, Spectroscopy, Structure and Chemistry*, T.A. Miller and V.E. Bondybey (eds.), North Holland, Amsterdam (1983).
42. V.E. Bondybey and T.A. Miller in *Molecular Ions, Spectroscopy, Structure and Chemistry*, T.A. Miller and V.E. Bondybey (eds.), North Holland, Amsterdam (1983).
43. J.P. Maier, D. Klapstein, S. Leutwyler, L. Misev and F. Thommen in *Ionic Processes in the Gas Phase*, M.A. Almoster-Ferreira (ed.), Reidel, Dordrecht (1984).
44. S. Leach, G. Dujardin and G. Tajeb, *J. Chim. Phys.* <u>77</u>, 705 (1980).
45. A. Gedanken, B. Raz and J. Jortner, *J. Chem. Phys.* <u>58</u>, 1178 (1973).
46. V.E. Bondybey, *Adv. Chem. Phys.* <u>47 (2)</u>, 521 (1981); H. Dubost, *NATO ASI Ser. C* <u>76</u>, 129 (1981) and references cited in these two publications. For examples of quick vibrational relaxation to ground-state M^+ see, however: V.E. Bondybey and C.E. Brus, *J. Chem. Phys.* <u>64</u>, 3724 (1976).
47. V.E. Bondybey and G.E. Pimentel, *J. Chem. Phys.* <u>56</u>, 3832 (1972); M.E. Jacox and D.E. Milligan, *J. Molec. Spectrosc.* <u>46</u>, 460 (1973); C.A. Wight, B.S. Ault and L. Andrews, *J. Chem. Phys.* <u>65</u>, 1244 (1976).
48. C.B. Moore and G. Pimentel, *J. Chem. Phys.* <u>41</u>, 3504 (1964).
49. R.J. Dunbar in *Ion Photodissociations*, P. Ausloos (ed.), Plenum Press, New York (1979).
50. L.N. Morgenthaler and J.R. Eyler, *J. Chem. Phys.* <u>71</u>, 1486 (1979).
51. R. Godden and J.I. Brauman, *J. Am. Chem. Soc.* <u>104</u>, 1483 (1982).
52. U. Swanholm and V.D. Parker, *J. Am. Chem. Soc.* <u>94</u>, 5507 (1972).
53. J.-C. Moutet and G. Reverdy, *J. Chem. Soc. Chem. Commun.* 654 (1982).
54. J.-C. Moutet and G. Reverdy, *Nouv. J. Chim.* <u>7</u>, 105 (1983).
55. G. Kothe, S.S. Kim and S.I. Weissman, *Chem. Phys. Lett.* <u>71</u>, 445 (1980).
56. G. Reverdy, private discussion with one of the authors (E.H.)
57. T. Shida and W.H. Hamill, *J. Chem. Phys.* <u>44</u>, 2375, 4372 (1966).
58. T. Shida and T. Kato, *Chem. Phys. Lett.* <u>68</u>, 106 (1979); L.D. Snow, J.T. Wang and F. Williams, *J. Am. Chem. Soc.* <u>102</u>, 2062 (1982); M.C.R. Symons and B.W. Wren, *J. Chem. Soc. Chem. Commun.* 817 (1982).
59. B. Hurni and R.E. Buehler, *Radiat. Phys. Chem.* <u>15</u>, 231 (1980); K. Toriyma, K. Nunome and M. Iwasaki, *J. Chem. Phys.* <u>85</u>, 2149 (1981); *J. Chem. Soc. Chem. Commun.* 202, 320 (1983).

60. A. Grimison and G.A. Simpson, *J. Phys. Chem.* <u>72</u>, 1776 (1968).
61. W.H. Hamill in *Radical Ions*, E.T. Kaiser and L. Kevan (eds.), Wiley-Inter-science, New York (1968).
62. B.J. Kelsall and L. Andrews, *J. Chem. Phys.* <u>76</u>, 5005 (1982).
63. This is especially true if the method of resonance photoionization during sample deposition is used. For pertinent examples see References 67,69,80 and 88-92 below.
64. T. Shida, *J. Chem. Phys.* <u>82</u>, 991 (1978).
65. P. Suppan, D. Bardy and E. Haselbach, *J. Photochem.*, submitted for publication.
66. M. Rakhmatov, V.A. Sazhnikov and M.V. Alfimov, *Khim. Vysok. Energii* (english translation) <u>16</u>, 254 (1982).
67. F.T. Prochaska and L. Andrews, *J. Phys. Chem.* <u>82</u>, 1731 (1978); <u>83</u>, 368 (1979); *J. Am. Chem. Soc.* <u>100</u>, 2102 (1978); *J. Chem. Phys.* <u>68</u>, 5568, 5577 (1978); L. Andrews, F.T. Prochaska and B. Ault, *J. Am. Chem. Soc.* <u>101</u>, 9 (1979); B.J. Kelsall and L. Andrews, *J. Molec. Spectrosc.* <u>97</u>, 362 (1983).
68. H. Schwarz, *Nachr. Chem. Techn. Lab.* <u>31</u>, 451 (1983).
69. R.O. Allen, J.M. Grzybowsky and L. Andrews, *J. Phys. Chem.* <u>79</u>, 898 (1975); L. Andrews, J.M. Grzybowsky and R.O. Allen, *J. Phys. Chem.* <u>79</u>, 904 (1975); F.T. Prochaska and L. Andrews, *J. Chem. Phys.* <u>67</u>, 1091 (1977).
70. *Radiation Chemistry of Hydrocarbons*, G. Földiäk (ed.), North Holland, Am-sterdam (1981).
71. R. Dunbar, *Anal. Chem.* <u>48</u>, 723 (1976).
72. M. Strobbe and J. Ceulemans, *Spectrosc. Lett.* <u>15</u>, 201 (1982); *J. Mol. Struct.* <u>80</u>, 71 (1982); For a comprehensive recent study of alkane$^+$ spectra see: T. Shida and Y. Takemura, *Radiat. Phys. Chem.* <u>21</u>, 157 (1983).
73. K. Nunome, K. Toriyma and M. Iwasaki, *Chem. Phys. Lett.* <u>105</u>, 414 (1984).
74. M. Tabata and A. Lund, *Chem. Phys.* <u>75</u>, 379 (1983).
75. M. Tabata and A. Lund, *Radiat. Phys. Chem.* <u>22</u>, 000 (1984).
76. G. Dolivo and A. Lund, *J. Chem. Phys.*, submitted for publication.
77. G. Dolivo, T. Gäumann, A. Lund and A. Ruf, *Spectroscopy: an International Journal*, submitted for publication; G. Dolivo, T. Gäumann and A. Ruf, ma-nuscript in preparation (to be submitted to *J. Chem. Phys.*).
78. M. Iwasaki, K. Toriyama and K. Nunome, *Radiat. Phys. Chem.* <u>21</u>, 147 (1983) and references cited therein.
79. T. Shida and S. Iwata, *J. Am. Chem. Soc.* <u>95</u>, 3473 (1973).
80. L. Andrews, J.A. Harvey, B.J. Kelsall and D.C. Duffy, *J. Am. Chem. Soc.* <u>103</u>, 6415 (1981).
81. T. Shida, T. Kato and Y. Nosaka, *J. Phys. Chem.* <u>81</u>, 1095 (1977).
82. For further elaboration on this point for the related cases of vinylalco-hol and vinylamine, see B. Albrecht, M. Allan, E. Haselbach, L. Neuhaus and P.-A. Carrupt, *Helv. Chim. Acta* <u>67</u>, 216 (1984).
83. T. Bally, K. Roth, S. Nitsche and E. Haselbach, to be published.
84. T. Shida, Y. Egawa, H. Kubodera and T. Kato, *J. Chem. Phys.* <u>73</u>, 5963 (1980).
85. M.L. Gross and D.H. Russell, *J. Am. Chem. Soc.* <u>101</u>, 2082 (1979).
86. E. Haselbach, T. Bally and Z. Lanyiova, *Helv. Chim. Acta* <u>62</u>, 577 (1979).
87. The same sequence of reactions was observed before in a freon matrix. T. Shida, personal communication.
88. L. Andrews and B.W. Keelan, *J. Am. Chem. Soc.* <u>102</u>, 5732 (1980).
89. B.J. Kelsall and L. Andrews, *J. Am. Chem. Soc.* <u>105</u>, 1413 (1983).
90. L. Andrews, B.J. Kelsall and G.J. McGarvey, *J. Phys. Chem.* <u>87</u>, 1788 (1983).
91. L. Andrews, B.J. Kelsall, C.P. Payne, O.R. Rodig and H. Schwarz, *J. Phys. Chem.* <u>86</u>, 3714 (1983).
92. B.J. Kelsall, L. Andrews and C. Trindle *J. Phys. Chem.* <u>87</u>, 4898 (1983).
93. L.T. Spada and C.S. Foote, *J. Am. Chem. Soc.* <u>102</u>, 391 (1980).
94. R. Gooden and J.I. Brauman, *J. Am. Chem. Soc.* <u>104</u>, 1483 (1982).
95. H. Suzuki, K. Koyano, T. Shida and A. Kira, *Bull. Chem. Soc. Japan* <u>55</u>, 3690 (1982).
96. H. Suzuki, K. Ogawa, T. Shida and A. Kira, *Bull. Chem. Soc. Japan* <u>56</u>, 66 (1983).
97. V.A. Sazhnikov, M. Rakhmatov and M.V. Alfimov, *Dokl. Akad. Nauk SSSR* <u>241</u>, 1378; *Chem. Phys. Lett.* <u>71</u>, 33 (1980).
98. S. Malkin and E. Fischer, *J. Phys. Chem.* <u>68</u>, 1153 (1964); G. Fischer, K.A. Muskat and E. Fischer, *J. Chem. Soc.* B 1156 (1968); D. Gegiou, K.A. Muskat and E. Fischer, *J. Am. Chem. Soc.* <u>90</u>, 12 (1968).