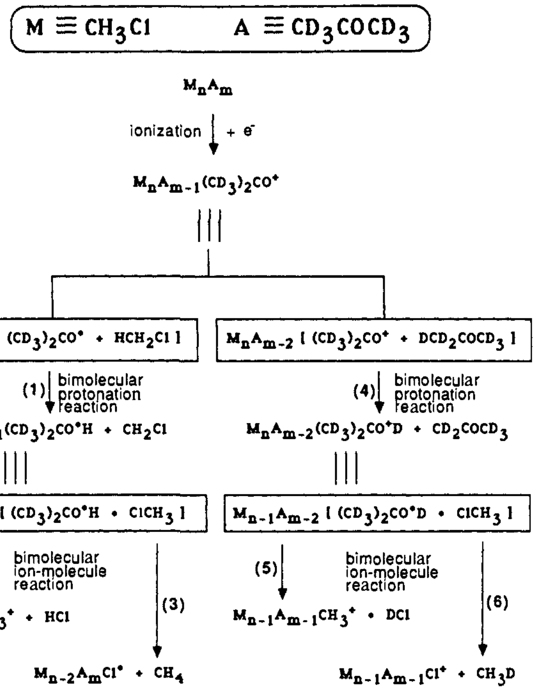

Figure 2. Overall reaction mechanism, accounting for all observed mass peaks of Figure 1b. Symbols ≡ and ||| denote equivalence of empirical formulas. Formulas in boxes serve as heuristic aids.

On the basis of the ionization potentials of the monomers (the IP of A being 1.7 eV less than that of M), we assume that it is an acetone molecule in the hetero cluster which is ionized (either directly or by very rapid intracluster charge transfer from an initially ionized CH_3Cl) and proceeds to react. Then there are two possible protonation reactions, (1) or (4) [either of which can be followed by further reactions,[14-19] i.e., (2) and (3) or (5) and (6)]. Which of these is the predominant protonation mechanism?

This question can be answered using hetero clusters of methyl chloride and perdeuterioacetone (Figure 1b). Defining a "reaction yield" as the ratio of the ion intensity of "product" peak to "reactant" peak,[20] we can compare processes 1 and 4, i.e., $MA_{n-1}^+ \rightarrow A_{n-1}H^+ + CH_2Cl$ with $A_n^+ \rightarrow A_{n-1}D^+ + CD_3COCD_2$ (see Table I).

We note that these reactions would yield identical ion products if CH_3COCH_3 were used, thus the utility of isotope labeling. The preferential protonation reaction is thus the attack of an acetone cation on a CH_3Cl solvent molecule within the cluster (preference enhanced with increasing cluster size[21]).

This propensity for H abstraction from CH_3Cl rather than acetone does not follow simply from the overall thermochemistry[18] but may be the result of the acetone dimer (trimer) ion being more stable than the corresponding hetero dimer (trimer) ion.

We have extended this work to other M_nA_m systems (M = CH_3X with X ≡ F, Cl, and I and A = H_2O, CH_3OH, CH_3OCH_3, and CO), to be reported later.

Our observations of intramolecular ion–molecule reactions with neat[6,7] and hetero–cluster ions of increasing size have shown the profound effect that even a few solvent molecules have on the course of a reaction. Such intramolecular cluster ion reactions provide a bridge between bimolecular gas-phase reaction dynamics and solution kinetics.

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(14) As previously observed with neat CH_3Cl clusters,[7] the protonated cluster ion can undergo further rearrangement to eject HCl or CH_4. Such a fast, sequential ion–molecule reaction also occurs with the hetero clusters of methyl halides. In accord with ref 13, in our hetero system no ions are observed corresponding to the dehydration reaction $A_{m-1}H^+ \rightarrow A_{n-2}CH_3CCH_2^+ + H_2O$. Yet this ion product is prevalent in gas-phase ion–molecule reactions.[15] An explanation involving collisional deactivation of the excited precursor $A_{m-1}H^+$ has been proposed.[16]

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(18) In the gas phase, the analogous processes are, respectively, acetone ion (A^+) attacking CH_3Cl (1) and A^+ attacking acetone, both yielding AH^+ (4). Reaction 1 is exothermic by ca. 2.8 kcal mol^{-1}, reaction 4 by ca. 5.4 kcal mol^{-1} (based upon tabulated proton affinities).[10,19] (However, their relative rates are not known.)

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(20) Our work on CH_3F clusters[7] suggests that little or no "solvent evaporation" occurs for the cluster ions in the course of the protonation reaction. We assume this to be the case here also.

(21) Since the present data are limited to $m/z \leq 200$, Table I is limited to $n = 3$.

Electron-Transfer-Induced Dimerization of Spiro[2.4]heptadiene. A Facile Radical Cation Diels–Alder Reaction

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The oxidative dimerization of diolefins resulting in cycloadducts of the [4 + 2] type (cation radical Diels–Alder reaction) has been the focus of much interest recently.[1-8] However, only limited experimental evidence is available concerning the key step of the dimerization, i.e., the addition of the radical cation to the parent olefin. Is this addition stepwise or concerted? Does the radical cation serve as the "diene" component ([3 + 2] cycloaddition) or as dienophile ([4 + 1] cycloaddition)? The observed retention of dienophile stereochemistry supports a concerted mechanism,[2] whereas the existence of a singly linked doubly allylic radical cation derived from *endo*-dicyclopentadiene[9] might be viewed as evidence for a stepwise mechanism. No experimental evidence differentiates the [3 + 2] from the [4 + 1] cycloaddition type, but orbital symmetry arguments favor the latter type.[4,5] In this paper we describe a system which provides evidence for a nonconcerted component in the cycloaddition/cycloreversion.

We have been interested in radical cations derived from cyclopropane derivatives.[10,11] The radical cation of spiro[2.4]heptadiene (M) appeared to be an interesting target. It can be generated as a short-lived intermediate by photoinduced electron transfer to strong electron acceptors.[9,11-15] During the elec-

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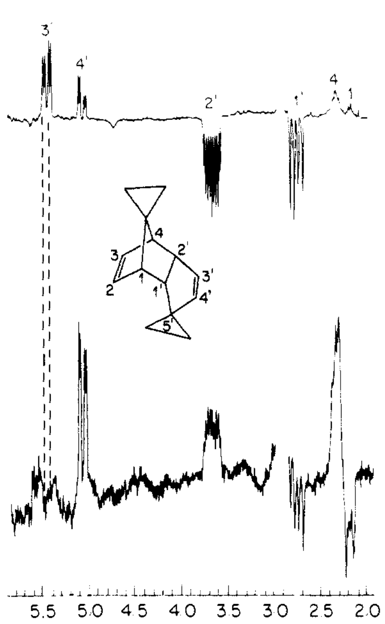


Figure 1. ^1H NMR spectra (90 MHz) observed 100 μs after excitation of chloranil solutions (0.02 M) with the frequency-tripled output (355 nm) of a Nd/YAG laser. (Top) Acetone-d_6 solution containing 0.01 M bis(spiroheptadiene); 16 laser pulses. (Bottom) Acetone-d_6 solution containing 0.1 M spiroheptadiene; 4 × 16 laser pulses.

tron-transfer reaction, M shows strongly enhanced absorption (A) for the α-protons and weaker absorption for the β-protons, indicating a radical cation of the butadiene type. The cyclopropane protons show only weak emission (E), documenting the absence of appreciable interaction between the cyclopropane orbitals and the butadiene fragment. The reaction of M also produces CIDNP effects for the [4 + 2] dimer (D), suggesting a rapid cycloaddition of the radical cation to the neutral diolefin. Protons $H_{3'}$ and $H_{4'}$ show respectively strong and moderate A, whereas $H_{1'}$ and $H_{2'}$ show E as do the cyclopropane protons of this fragment. This pattern suggests a radical cation with high spin density at $C_{3'}$ and $C_{5'}$ and somewhat lower spin density at $C_{4'}$, establishing the existence of a doubly linked ($D^{\bullet+}$) dimer radical cation. Spin and charge are localized in the vinylcyclopropane moiety, i.e., in the spiroheptene fragment originating as the dienophilic monomer.

The identical dimer polarization, though considerably stronger, is observed during the electron-transfer reaction of D with chloranil, implicating the same radical cation. The M polarization generated in the reaction of D is noticeably different from that observed in the reaction of M. Its pattern suggests that it originates in $D^{\bullet+}$, indicating rapid cycloreversion. It is tempting to interpret these results as evidence for a concerted [4 + 1] cycloaddition with $M^{\bullet+}$ as dienophile.

However, this conclusion is not strictly justified, since the CIDNP effects are observed under continuous irradiation for a reaction proceeding with significant conversion. Under these conditions, a fraction of rapidly formed dimer (D) may serve as a competitive quencher and cause the characteristic strong polarization typical for this reaction. These effects may mask any polarization induced in $M^{\bullet+}$ and transferred to D via $S^{\bullet+}$ or $D^{\bullet+}$. This potential problem can be minimized by a change in experimental conditions to pulsed laser excitation. The typical advantage of time-resolved CIDNP spectroscopy lies in the ability to "isolate" CIDNP effects due to "early" pair recombination (100 ns–10 μs).[16-18] However, in the system discussed here it is more significant that this experiment minimizes the conversion of M to D, preventing D from entering the reaction cycle as a competing electron donor. Accordingly, the polarization generated in $M^{\bullet+}$ and transferred to D can be evaluated with a minimum of interference.

Under these conditions the reaction of D still produces polarization, supporting the involvement of $D^{\bullet+}$ (Figure 1, top). However, the reaction of M gives rise to a dramatically changed polarization pattern (Figure 1, bottom), providing evidence for a different dimer radical cation. The A signals observed for $H_{4'}$, $H_{2'}$, and H_4 indicate positive spin densities on the corresponding carbon atoms, whereas the E signals observed for $H_{1'}$ and H_1 indicate positive spin densities on adjacent carbon atoms, $C_{2'}$ and/or $C_{4'}$, and C_2 and/or C_4. The nature of this intermediate is most clearly indicated by the A signals of H_4 and $H_{2'}$, which are characteristic for the singly linked radical cation $S^{\bullet+}$.

The spectra clearly support the involvement of a second dimer radical cation, $S^{\bullet+}$, following the generation of $M^{\bullet+}$, by electron-transfer quenching of the acceptor triplet state (eq 1). The

$$^3A^* + M \rightarrow A^{\bullet-} + M^{\bullet+} \quad (1)$$

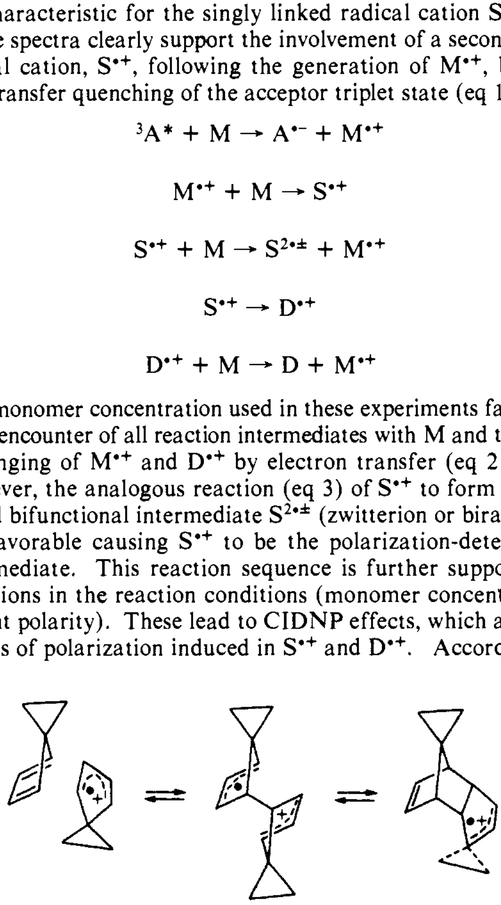
$$M^{\bullet+} + M \rightarrow S^{\bullet+} \quad (2)$$

$$S^{\bullet+} + M \rightarrow S^{2\bullet\pm} + M^{\bullet+} \quad (3)$$

$$S^{\bullet+} \rightarrow D^{\bullet+} \quad (4)$$

$$D^{\bullet+} + M \rightarrow D + M^{\bullet+} \quad (5)$$

high monomer concentration used in these experiments favors the rapid encounter of all reaction intermediates with M and the rapid scavenging of $M^{\bullet+}$ and $D^{\bullet+}$ by electron transfer (eq 2 and 5). However, the analogous reaction (eq 3) of $S^{\bullet+}$ to form a singly linked bifunctional intermediate $S^{2\bullet\pm}$ (zwitterion or biradical) is less favorable causing $S^{\bullet+}$ to be the polarization-determining intermediate. This reaction sequence is further supported by variations in the reaction conditions (monomer concentrations, solvent polarity). These lead to CIDNP effects, which are composites of polarization induced in $S^{\bullet+}$ and $D^{\bullet+}$. Accordingly, a nonconcerted contribution to the radical cation Diels–Alder reaction of spiroheptadiene is clearly established, although a competing concerted mechanism cannot be eliminated. The difference between a truly stepwise and a nonsynchronous concerted reaction is subtle. However, our results unambiguously require the existence of the stepwise mechanism with $S^{\bullet+}$ as an intermediate and cannot be explained by a nonsynchronous concerted process.



$S^{\bullet+}$ $D^{\bullet+}$

The existence of a singly linked bis(spiroheptadiene) radical cation reported here suggests a somewhat greater mechanistic variety for radical cation cycloadditions than previously considered. The notion of mechanistic variety is also supported by the rapid intramolecular [3 + 2] cycloaddition of the molecular ion of 9-methylenebicyclo[4.2.1]nona-2.4.7-triene at low temperatures[19] and by the existence of other singly linked dimer radical cations as intermediates in the electron-transfer-induced dimer cleavage or dimerization in solution[20] and in the gas phase.[21]

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