Asp 52 residue in the active site of hen's egg white lysozyme has been considered; but there is no clear evidence to support the formation of a covalent intermediate for this enzyme.[53] Intramolecular participation of a neighboring carboxylate anion has been shown to accelerate acetal hydrolysis in a few non-enzymatic systems by up to 10^3-fold[54,55] and probably represents nucleophilic participation, but it may arise simply from electrostatic stabilization of the transition state by the negative charge.

The results reported here show that there should be no barrier for the collapse of an intimate ion pair containing a carboxylate anion and a glycosyl oxocarbenium ion. Therefore, assistance to leaving group displacement by a carboxylate group at the active site of an enzyme should represent concerted nucleophilic substitution that gives an acylal intermediate. However, it is possible that steric constraints at the active site prevent close approach and formation of a full covalent bond between the carboxylate group and C_1 of the glycoside. In this situation nucleophilic assistance can facilitate leaving group departure but the immediate product is an unstable species that can be described as either a stabilized oxocarbenium ion or a strained acylal.[56]

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Photochemical Isomerization of Cyclobutene Radical Cation to 1,3-Butadiene Radical Cation. A "Nonelectrocyclic" Ring-Opening Reaction?

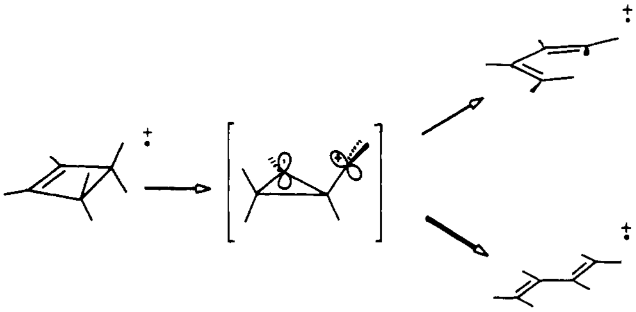
J. N. Aebischer,[†] T. Bally,[*,†] K. Roth,[†] E. Haselbach,[*,†] F. Gerson,[*,‡] and X.-Z. Qin[‡,§]

Contribution from the Institut de Chimie Physique de l'Université de Fribourg, Pérolles, CH-1700 Fribourg, Switzerland, and the Institut für Physikalische Chemie der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland. *Received January 9, 1989*

Abstract: The photochemical isomerization of cyclobutene radical cation (CB$^{\bullet+}$) to 1,3-butadiene radical cation (BD$^{\bullet+}$) is studied by optical as well as ESR/ENDOR spectroscopy in different cryogenic media. While in Ar matrices complete conversion of CB$^{\bullet+}$ to BD$^{\bullet+}$ occurs already upon radiolytic ionization, CB$^{\bullet+}$ remains intact in various frozen glasses. Both methods indicate that photolysis of CB$^{\bullet+}$ leads to *s-trans*-BD$^{\bullet+}$. Theoretical considerations show that a rapid *thermal s-cis-* to *s-trans*-BD$^{\bullet+}$ rearrangement can be excluded, while previous experience with longer polyene radical cations suggests that *s-cis*-BD$^{\bullet+}$ should be observable at some stage of the reaction, if it occurs as a *photochemical* intermediate. It is, therefore, concluded that the photochemical CB$^{\bullet+} \rightarrow$ BD$^{\bullet+}$ rearrangement must occur via a pathway leading *directly* to *s-trans*-BD$^{\bullet+}$, perhaps analogous to that previously postulated for the corresponding thermal isomerization. The applicability of orbital correlation diagrams to problems of electrocyclic reactions of M$^{\bullet+}$ is critically discussed.

Recently, pericyclic reactions of organic radical ions (M$^{\bullet+}$) have attracted considerable attention.[1,2] Prototypical of these are electrocyclic ring-opening reactions of cyclic polyene cations,[3] in particular that involving the "parent" systems, cyclobutene radical cation (CB$^{\bullet+}$) and 1,3-butadiene radical cation (BD$^{\bullet+}$)[2,3a,4,5a] or aryl-substituted derivatives thereof.[5b,6,7] In the gas phase, the CB$^{\bullet+} \rightarrow$ BD$^{\bullet+}$ isomerization proceeds with a very low activation barrier,[5] an observation that at first sight seems to contrast with the picture emerging from orbital or state correlation diagrams of the Woodward-Hoffmann type such as that for the title case depicted in Figure 1.[3a] These show that the reactant M$^{\bullet+}$ ground states always correlate with product N$^{\bullet+}$ *excited states* if synchronous concerted pathways (i.e., maintenance of a 2-fold axis or a mirror plane during the reaction) are followed. Furthermore, the ground states of the reactant cyclic precursor and the product open-chain polyene always transform differently with regard to the conserved symmetry element, and therefore, thermal M$^{\bullet+}$ electrocyclic processes are invariably *state symmetry forbidden* along concerted pathways involving synchronous con- or disrotation.[3a]

Scheme I



The fact that thermal M$^{\bullet+}$ electrocyclic reactions still proceed with considerable ease can be rationalized by comparing the

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[†] Institut de Chimie Physique de l'Université de Fribourg.

[‡] Institut für Physikalische Chemie der Universität Basel.

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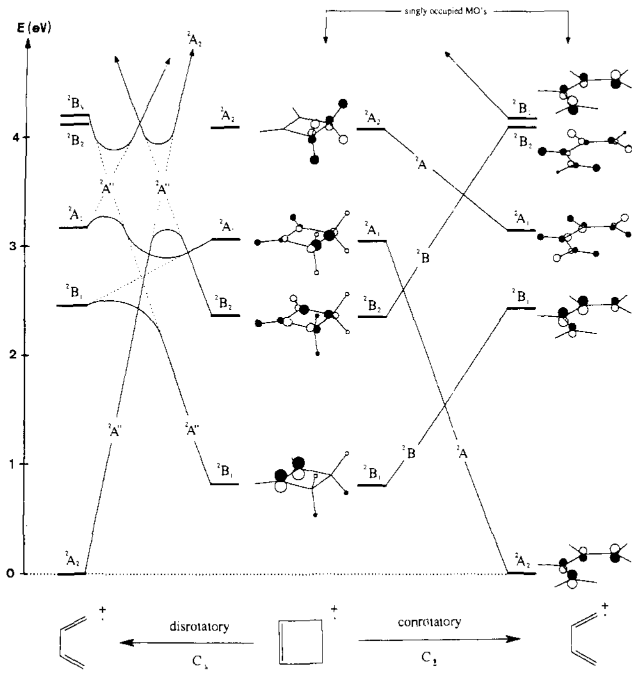

Figure 1. Correlation diagrams for the conrotatory and disrotatory ring opening of CB$^{\bullet+}$ to BD$^{\bullet+}$. Relative state energies are from the PE spectra of CB[22] and BD[30] and from $\Delta H_r(\mathrm{CB}^{\bullet+} \rightarrow \mathrm{BD}^{\bullet+}) = -0.89$ eV.[3a] MNDO wavefunctions are used to illustrate the nature of the singly occupied MO's in the different states.

energies of the excited states involved in the correlation diagrams to those in the neutral cases:[3a] There, the target states for "forbidden" reactions are of *doubly* excited nature, while in M$^{\bullet+}$ the reactant ground states correlate with *singly* excited states of the product. Depending on the presumed concerted reaction mode, these are either low-lying Koopmans (conrotatory ring opening of CB$^{\bullet+}$) or higher lying non-Koopmans states (disrotatory ring opening of CB$^{\bullet+}$; see Figure 1). It has been claimed[2,3] that one may actually predict the stereochemistry of M$^{\bullet+}$ electrocyclic reactions on the basis of this picture. The arguments were that the reaction mode leading to the lower lying of the two possible target excited states is the one that will be followed in practice, because the crossing point of the reactant and product ground-state surfaces lies at lower energy in this case.

However, this line of thought fails to take into account that, unlike in the neutral case where the state symmetry does not change, the system *must lose all symmetry* at some point on the reaction path in order to be able to cross over adiabatically from the reactant to the product surface. It is, therefore, imperative in discussions of thermal M$^{\bullet+}$ electrocyclic reactions to consider alternative *nonsynchronous* reaction modes. Thus, recent calculations indicate that the lowest energy pathway for thermal CB$^{\bullet+}$ ring opening bears no resemblance to the commonly accepted reaction mode of the neutral species (i.e., concerted conrotatory twisting of the CH$_2$ groups) but involves primary contraction to a cyclopropylcarbinyl-type species which subsequently collapses readily to BD$^{\bullet+}$ formed preferentially in the s-trans conformation,[4] as shown in Scheme I. Interestingly, the conrotatory product stereochemistry predicted for the concerted electrocyclic mode is calculated to be retained also along this "nonelectrocyclic" pathway, which indicates that one should be cautious in drawing conclusions about the course of M$^{\bullet+}$ reactions from product analyses.[7]

In contrast, *photochemical* electrocyclic M$^{\bullet+}$ reactions are in principal not prohibited from following concerted synchronous pathways, since there is always a reactant M$^{\bullet+}$ excited state which connects adiabatically to the product ground states. We were, therefore, surprised to find in our recent study[8] that the ESR and ENDOR spectra of BD$^{\bullet+}$ observed upon photoisomerization of CB$^{\bullet+}$ in a CFCl$_3$ matrix were the same as those obtained by direct ionization of *s-trans*-BD (tBD). This finding indicates that BD$^{\bullet+}$ was formed exclusively in the s-trans conformation, which cannot arise as the primary product of a conventional electrocyclic ring-opening process. At that time, we could, however, not exclude the possibility that the tBD$^{\bullet+}$ arises as a secondary thermal or photochemical product from primarily formed *s-cis*-BD$^{\bullet+}$ (cBD$^{\bullet+}$). The results presented here suggest, however, that this is not the case and that we may be faced with a photochemical equivalent of the above-mentioned thermal nonelectrocyclic CB$^{\bullet+}$ → BD$^{\bullet+}$ isomerization.

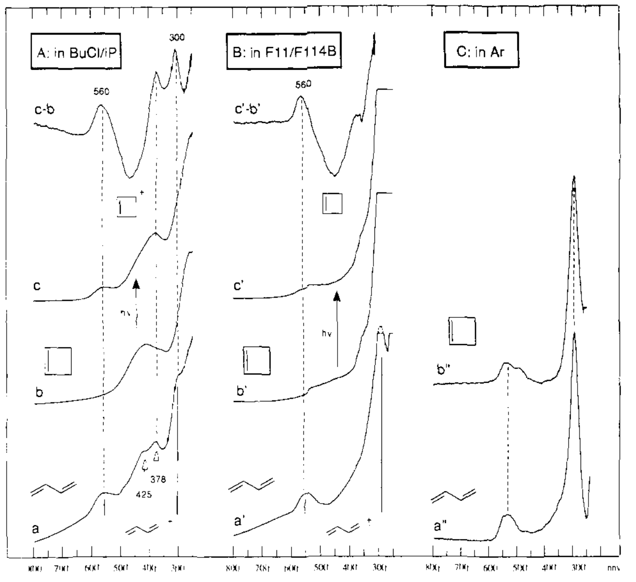

Figure 2. Spectra of ionized CB and BD and results of photochemical transformations of ionized CB in different rigid glasses. Spectra c are after ≈30-min photolysis at 450 nm (interference filter). The top traces represent digital difference spectra where bands pointing up belong to species arising in the course of the photolysis.

Experimental Section

The procedures employed for obtaining matrix-isolated radical ions in Ar have been described previously.[9] For the optical studies at 77 K, a home-built system of steel cuvettes which are adapted to a quartz Dewar vessel with Suprasil windows was used.[10] By fitting different windows onto the cuvettes, optical pathlengths between 0.5 and 3 mm could be realized. In order to pinpoint solvent-specific spectral manifestations, all optical experiments were done in two different solvent systems. The first was a 1:1 mixture of *n*-butyl chloride (Merck, for protein sequence analysis according to Edman, dried over 3-Å molecular sieves) and isopentane (Fluka, purum, distilled from Na and kept over 3-Å molecular sieves), abbreviated BuCl/iP.[11] The other medium was a 1:1 mixture of CFCl$_3$ (F11, Plüss-Staufer) and CF$_2$BrCF$_2$Br (F114B, Fluorochem Ldt.),[12] which was also dried over 3-Å molecular sieves. In the ESR studies, we employed also CF$_3$CCl$_3$ (Fluka, puriss.). Solutions (5×10^{-2} M) of 1,3-butadiene (Fluka, puriss.) or cyclobutene[13] in the above solvents were frozen to 77 K and exposed to ≈0.5 Mrad of ^{60}Co γ-radiation.

Electronic absorption (EA) spectra were taken on a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrometer, while ESR and ENDOR spectra were obtained on a Bruker ESP 300 instrument. Semiempirical calculations were performed on a VAX 8350 computer with the AMPAC pro-

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[13] Prepared according to: Salaün, J.; Fadel, A. *Org. Synth.* **1986**, *64*, 50.

gram package which was modified to allow the calculation of excited $M^{\bullet+}$ configurations and aid their convergence as outlined previously.[14] Molecular orbitals were drawn by the MOPLOT program[15a] which was adapted to run on Olivetti M24 PC's.[15b]

Results and Discussion

(a) Spectra and Electronic Structure of the Ionized Hydrocarbons. Electronic Absorption Spectra. Figure 2 shows the spectra obtained after ionization of BD (a) or CB (b), respectively, in BuCl/iP (A) or F11/F114B (B) at 77 K as well as in solid Ar (C) at ≈20 K. The spectra of the two ionized valence isomers differ considerably in the three media, a finding that requires an explanation before going into a discussion of the photochemical results.

The literature records multiple attempts to measure the EA spectrum of $BD^{\bullet+}$. In several cases, the spectrum was perturbed by bands due either to the formation of the $(BD)_2^{\bullet+}$ dimer cation (λ_{max} = 425 nm)[16] and/or to what are presumed to be complexes with the solvent (λ_{max} = 378 nm in the case of BuCl/iP),[17] which actually led to original misassignments.[18] In 1975, the gas-phase photodissociation (PD) spectrum of $BD^{\bullet+}$ was published,[19] and shortly thereafter, Shida et al. presented the first correct EA spectrum of this ion in a Freon mixture[20] (λ_{max} = 560 and 300 nm; see Figure 2B,a′). Later, we remeasured the same spectrum in Ar[9] (reproduced in Figure 2C,a″) and discussed it on the basis of qualitative MO theory. Even in this highly inert medium, low concentrations of BD and electron scavenger must be employed to suppress the formation of bands which appear in the spectrum of the ionized substrate and cannot be attributed to $BD^{\bullet+}$. All three spectra at the bottom of Figure 2 show the characteristic features of $BD^{\bullet+}$ (i.e., excitation of the $^2A_2$ ground state to the two $^2B_1$ excited states at 560 and 300 nm, respectively[9,20]). In F11/F114B, we were unable to find conditions where both bands can be monitored simultaneously, while in BuCl/iP the above-mentioned bands due to $(BD)_2^{\bullet+}$ at 425 nm and the previously observed solvent complex at 378 nm are seen in addition to the characteristic pair of $BD^{\bullet+}$ absorptions (Figure 2A,a).

In the case of ionized $CB^{\bullet+}$, matters are unfortunately more complicated. In Ar, incipient $CB^{\bullet+}$ seems to be endowed with too much excess energy to survive intact[21] and apparently undergoes nearly complete conversion to $BD^{\bullet+}$ (the additional shoulder at ≈480 nm in Figure 2C,b″ is not due to $CB^{\bullet+}$ because it is not photosensitive; see below). The spectrum in BuCl/iP shows a rather intense band (λ_{max} = 420 nm) which can, however, not be due to free $CB^{\bullet+}$, because it is absent from the spectrum in F11/F114B. It may be due to a solvent complex of similar nature to that giving rise to the λ_{max} = 378 nm band in ionized BD. No absorption above 300 nm can be assigned to $CB^{\bullet+}$ from the spectra in Figure 2, and the question arises if $CB^{\bullet+}$ absorbs at all in this region.

From the MO's in Figure 1, it can be gathered that the first palpable absorption of $CB^{\bullet+}$ should occur for the $^2B_1 \rightarrow {}^2A_2$ excitation (the first one *not* involving a $\sigma \rightarrow \pi$ electron promotion associated with a very small transition moment). From the $I_v{}^4 - I_a{}^1$ energy difference in the PE spectrum of CB[22] (3.25 eV), this band is expected to be around 380 nm with the FC maximum perhaps displaced to slightly lower energies, due to the $CB^{\bullet+}$/CB equilibrium geometry difference. The next excited state from the PE spectrum lies almost 6 eV above the $CB^{\bullet+}$ ground state[22] and is hence well outside our present observation range. The same is true of the $^2A_2$ $\pi \rightarrow \pi^*$ excited state of $CB^{\bullet+}$ (which does not show up in the PE spectrum due to its non-Koopmans nature): its position must be higher in energy relative to the ground state than the $\pi \rightarrow \pi^*$ excited state of the diene cation, $BD^{\bullet+}$,[9] i.e., at >4.2 eV (λ_{max} < 300 nm).

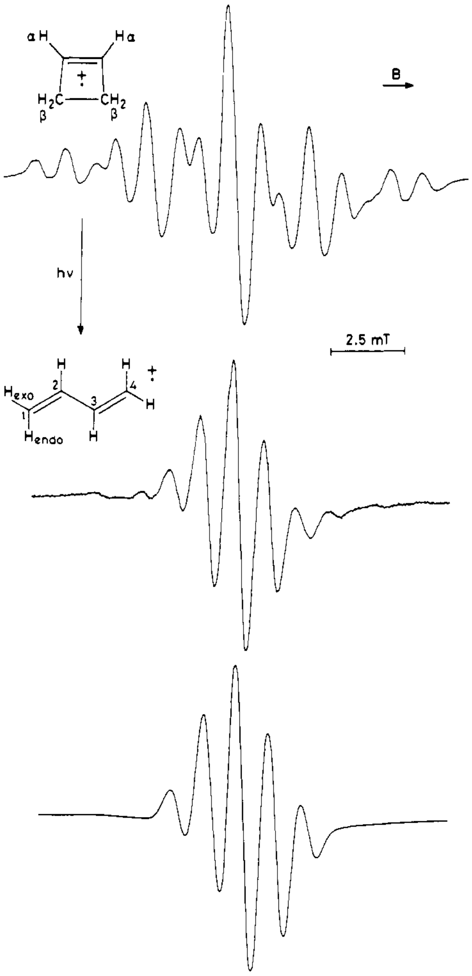

Figure 3. ESR spectra of radical cations in a CF_3CCl_3 matrix at 135 K. Top: Spectrum of $CB^{\bullet+}$. Center: Spectrum of $BD^{\bullet+}$ observed after 10-min photolysis of $CB^{\bullet+}$ at 610 nm (the weak signals outside the four-proton quintet arise presumably from unrearranged $CB^{\bullet+}$). Bottom: Spectrum of $tBD^{\bullet+}$ obtained upon ionization of tBD by γ-rays.

Table I. Isotropic Coupling Constants (mT) for the Radical Cations of CB and tBD

	$CB^{\bullet+}$			$tBD^{\bullet+}$	
	$CFCl_3$[a]	CF_3CCl_3		$CFCl_3$[b]	CF_3CCl_3
α:	1.11 (2 H)	1.05 (2 H)	1,4:	1.12 (2 H_{exo})	1.11 (2 H_{exo})
β:	2.80 (4 H)	2.80 (2 H)		1.05 (2 H_{endo})	1.06 (2 H_{endo})
		2.73 (2 H)	2,3:	0.28 (2 H)	0.19 (2 H)

[a] Reference 8. [b] Reference 23.

ESR/ENDOR Spectra. In order to confirm the generality of the $CB^{\bullet+} \rightarrow BD^{\bullet+}$ transformation, we have repeated the previous ESR/ENDOR experiments,[8] using CF_3CCl_3 instead of $CFCl_3$ as a matrix. Although the spectra of the radical cations in CF_3CCl_3 (Figure 3) are qualitatively similar to those in $CFCl_3$,[8,23] some differences are noteworthy:

(a) The ESR spectrum of $CB^{\bullet+}$ in CF_3CCl_3, which consists of a four-proton quintet (ca. 2.8-mT) split into two-proton triplets (ca. 1.1 mT) is better resolved than in $CFCl_3$.[8] Moreover, the previously unavailable ^1H ENDOR spectrum could now be ob-

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[14] Haselbach, E.; Bally, T.; Lanyiova, Z.; Baertschi, P. *Helv. Chim. Acta* **1979**, *62*, 583.

[15] Haselbach, E.; Schmelzer, A. *Helv. Chim. Acta* **1971**, *54*, 1299. Albrecht, B. Ph.D. Dissertation, University of Fribourg, Fribourg, Switzerland, 1989.

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[19] Dunbar, R. C. *Chem. Phys. Lett.* **1975**, *32*, 508.

[20] Shida, T. *Kagaku no Ryoiki* **1976**, *30*, 31. See also: Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, 1988.

[21] From $I(Ar) - I_a{}^1(CB)^{22}$ = 6.33 eV, the ultimate hole transfer step $Ar^{\bullet+} + CB \rightarrow CB^{\bullet+} + Ar$ liberates some 150 kcal/mol, which is apparently not dissipated rapidly enough to prevent $CB^{\bullet+} \rightarrow BD^{\bullet+}$ rearrangement.

[22] Wiberg, K. B.; Ellison, G. B.; Wendoloski, J. J.; Brundle, C. R.; Kuebler, N. A. *J. Am. Chem. Soc.* **1976**, *98*, 7179.

[23] Gerson, F.; Qin, X.-Z. *Helv. Chim. Acta* **1988**, *71*, 1065.

served (see Appendix). Surprisingly, separate signals for *two* pairs of methylene β-protons having slightly different coupling constants (Table I) appear next to the ENDOR signals due to the pair of olefinic α-protons. This finding indicates a distortion of the carbon framework of CB$^{\bullet+}$ from planarity.

(b) The ESR spectrum of BD$^{\bullet+}$ in CF_3CCl_3, like that in $CFCl_3$,[23] consists of a four-proton quintet (ca. 1.1 mT), and the corresponding ENDOR signals likewise arise from three pairs of protons (Table I). However, the latter spectra reveal that the couplings to the 2,3-protons are reduced from 0.28 mT in $CFCl_3$[23] to 0.19 mT in CF_3CCl_3 (Table I). Since the ESR and ENDOR spectra of BD$^{\bullet+}$ in the same solvent are identical, irrespective of the starting material (i.e., CB or tBD; see the following section), this difference must be caused by the change of the host medium. Matrix dependence of coupling constants for olefinic radical cations in Freon glasses is not unprecedented[24] and may be rationalized in terms of the slight differences in geometry imposed by the rigid environments.[25]

(b) Photochemical Experiments. While the Ar matrix EA spectra did not change upon photolysis (except for eventual bleaching of the ions), the corresponding experiments in the frozen glasses led to the changes documented by the top two pairs of spectra in parts A and B of Figure 2. Although these changes appear to be rather dissimilar in the two media, inspection of the upper-most *difference* spectra reveals that this is not the case: In both solvents, the BD$^{\bullet+}$ bands at 560 and 300 nm (not readily visible in F11/F114B) arise at the expense of a broad band centered at 465 (in BuCl/iP) or 450 nm (in F11/F114B). In addition, the spectrum in BuCl/iP shows an upward peak that coincides with the 378-nm band in the spectrum of ionized BD in the same medium and that was assigned to a complex between BD$^{\bullet+}$ and the solvent. Apparently CB$^{\bullet+}$ does seem to have a proprietary absorption in the blue-spectral region, peaking at a slightly different wavelength in the two solvent systems. As discussed above, this band is probably due to a_2(pseudo-π) $\rightarrow$ $b_1(\pi)$ electron promotion.

The finding that the EA bands arising from photolysis of CB$^{\bullet+}$ at 450 nm are the same as those obtained upon ionization of tBD is corroborated by ESR/ENDOR studies of the radical cation in CF_3CCl_3. As in the previous case of $CFCl_3$,[8] the spectra observed after photolysis of CB$^{\bullet+}$ are virtually identical with those of a γ-irradiated tBD in the same matrix (Figure 3).

Four explanations may be proposed to account for the above results: (1) the photochemical CB$^{\bullet+}$ $\rightarrow$ BD$^{\bullet+}$ ring opening leads to cBD$^{\bullet+}$ but the EA spectra of tBD$^{\bullet+}$ and cBD$^{\bullet+}$ are indistinguishable; (2) cBD$^{\bullet+}$ is instantly converted to tBD$^{\bullet+}$ by a secondary photolysis; (3) tBD$^{\bullet+}$ arises as a secondary thermal product from primarily formed cBD$^{\bullet+}$; and (4) tBD$^{\bullet+}$ is indeed formed as a primary photoproduct in what must then be a nonelectrocyclic pathway.

(1) This explanation can be discounted on the basis of the ESR results,[8] because the difference in proton coupling constants between tBD$^{\bullet+}$ and cBD$^{\bullet+}$ is expected to manifest itself at least in the highly resolved ENDOR spectra. With regard to the EA spectra, we note from our experience with longer polyene radical cations that the second, intense electronic transition is rather sensitive to conformational changes in the carbon framework, with shifts of up to 20 nm being observed for different "rotamers", while the weak first transition is much less affected.[26] It follows that we should expect a noticeable shift in the second band of BD$^{\bullet+}$ on going from the s-cis to the s-trans rotamer.[27]

(2) In order to minimize the contributions due to secondary photolyses, irradiations were effected at wavelengths where tBD$^{\bullet+}$ does not absorb. It is reasonable to assume that the same is true for eventually formed cBD$^{\bullet+}$ (see above). Immediate and complete conversion of cBD$^{\bullet+}$ to tBD$^{\bullet+}$ by secondary photolysis seems, therefore, unlikely, and hence, primarily formed cBD$^{\bullet+}$, if produced, should be detectable as a photochemical intermediate.

(3) Regarding a possible *thermal* cBD$^{\bullet+}$ $\rightarrow$ tBD$^{\bullet+}$ conversion, we note that this will not occur as readily as in the neutrals where it requires only 3–4 kcal/mol,[28] because removal of an electron from the π-HOMO of BD results in a *strengthening* of the central π-bond. We have attempted to calculate the potential surface for rotation around the central C–C bond in BD$^{\bullet+}$ and arrived at an estimate of 20–25 kcal/mol for the rotational barrier (see below). Thus, it seems unlikely that incipient cBD$^{\bullet+}$ formed from CB$^{\bullet+}$ would spontaneously rearrange to the observed s-trans rotamer by means of a thermally activated process at the temperatures prevailing in our experiments.[29]

(4) We are, therefore, left with the last of the above explanations, which is a nonelectrocyclic pathway connecting electronically excited CB$^{\bullet+}$ with ground-state tBD$^{\bullet+}$, involving perhaps an intermediate of the type proposed by Bauld et al.[4] (see Scheme I), which may have no perceptible persistency under our experimental conditions.

The question arises why excited CB$^{\bullet+}$ seems to avoid a concerted electrocyclic pathway for ring opening, even when this is not forbidden by symmetry. As Dunkin and Andrews have noted, "high stereospecificity [in a concerted electrocyclic rearrangement] is most likely to be found when the lowest excited state of the reactant can correlate directly with the ground state of the product".[2] They postulated that this condition is met by the $\pi \rightarrow \pi^*$ excited state of CB$^{\bullet+}$ "which is expected, therefore, to undergo ring-opening stereospecifically in a disrotatory manner".[2] However, the $^2A_2$ ($\pi \rightarrow \pi^*$) excited state of CB$^{\bullet+}$ is far from being lowest one (see above) and cannot be involved in our experiments.

According to the commonly accepted assignment of the PE spectrum of CB,[22,30] the lowest excited state of CB$^{\bullet+}$ (vertically above neutral CB) is $^2B_2$ with an electron removed from the antisymmetric cyclobutane Walsh MO. As can be seen from Figure 1, this state does not correlate with the BD$^{\bullet+}$ ground state along either of the two concerted electrocyclic pathways. On the other hand, the *second* excited $^2A_1$ state is predicted to rearrange adiabatically to ground-state BD$^{\bullet+}$ in a conrotatory manner. This prediction is confirmed by MNDO calculations according to which relaxation of the $^2A_1$ state of CB$^{\bullet+}$ within C_{2v} symmetry leads to a stationary point with a very long C_{sp^3}–C_{sp^3} bond of 2.57 Å which corresponds, however, to a *transition state*. Inspection of the normal mode associated with the negative force constant reveals the expected conrotatory twisting of the two CH_2 groups. Consequently, the system rearranges spontaneously to *s-cis*-BD$^{\bullet+}$ if only C_2 symmetry is maintained.

Conversely, the relaxed first excited $^2B_2$ state is stable toward concerted distortions of the CH_2 groups in either direction.

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[24] Shiotani, M.; Nagata, Y.; Sohma, J. *J. Phys. Chem.* **1984**, *88*, 4078.

[25] INDO calculations indicate that the 2,3-proton couplings should increase in going from tBD$^{\bullet+}$ to cBD$^{\bullet+}$. However, it seems unreasonable to explain the spectral differences in the two media in terms of wholly different conformations of BD$^{\bullet+}$: this would imply *complete* conversion of tBD to cBD$^{\bullet+}$ upon ionization in $CFCl_3$ (but not in CF_3CCl_3!) as well as *exclusive* formation of cBD$^{\bullet+}$ (tBD$^{\bullet+}$) upon photolysis of CB$^{\bullet+}$ in $CFCl_3$ (CF_3CCl_3), a set of results that would be very difficult to rationalize.

[26] (a) Hexatriene radical cation: Shida, T.; Kato, T.; Nosaka, Y. *J. Phys. Chem.* **1977**, *81*, 1095. Kelsall, B. J.; Andrews, L. *Ibid.* **1984**, *88*, 2723. Bally, T.; Nitsche, S.; Roth, K.; Haselbach, E. *Ibid.* **1985**, *89*, 2528. (b) Octatetraene radical cation: Bally, T.; Nitsche, S.; Roth, K. *J. Chem. Phys.* **1986**, *84*, 2577. Dunkin, I. R.; Andrews, L.; Lurito, J. T.; Kelsall, B. J. *J. Phys. Chem.* **1985**, *89*, 1701. Bally, T.; Haselbach, E.; Nitsche, S.; Roth, K. *Tetrahedron* **1986**, *42*, 6325. Andrews, L.; Lurito, J. T. *Ibid.* **1986**, *42*, 6343.

[27] LNDO/S-PERTCI calculations predict a shift of +3.5 nm for the first transition and +8.5 nm for the second transition in going from tBD$^{\bullet+}$ to cBD$^{\bullet+}$: Heidenreich, A.; Münzel, N.; Schweig, A. *Z. Naturforsch.* **1986**, *41A*, 1415.

[28] Experimental estimate: Squillacote, M. E.; Sheridan, R. S.; Chapman, O. L.; Anet, F. A. L. *J. Am. Chem. Soc.* **1979**, *101*, 3657. Best calculation: Bock, C. W.; George, P.; Trachtman, M. *Theor. Chim. Acta* **1984**, *64*, 293.

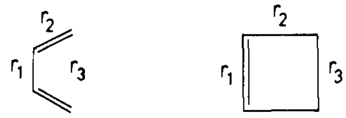
[29] A referee has pointed out that incipient CB$^{\bullet+*}$ may initially decay to *electronically excited* cBD$^{\bullet+*}$, which could subsequently undergo internal conversion to ground-state cBD$^{\bullet+}$, endowed with sufficient vibrational energy to cross over the barrier to tBD$^{\bullet+}$. However, there is no pronounced thermochemical bias in favor of tBD$^{\bullet+}$, and hence, it is expected that at least part of the hot cBD$^{\bullet+}$ should retain its conformation after thermalization. Otherwise, cBD$^{\bullet+}$ could not be regarded as a bona fide intermediate, and even if the CB$^{\bullet+}$ $\rightarrow$ tBD$^{\bullet+}$ decay happens to lead via a cBD$^{\bullet+}$ geometry, an electrocyclic process in the usual sense of the word is not involved.

[30] Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P. *Helv. Chim. Acta* **1977**, *60*, 2213.

Table II. Results of Theoretical Calculations for $CB^{\bullet+}$ and $BD^{\bullet+}$ [a]

molecule	state	$\Delta H_f°$, kcal/mol	geometrical parameters,[b] Å		
			r_1	r_2	r_3
CB	$^1A_1$	31.0	1.355	1.524	1.569
$CB^{\bullet+}$	$^2B_1$	242.3	1.450	1.513	1.568
	$^2B_2$	283.4	1.307	1.659	1.503
	$^2A_1$	270.5[c]	1.346	1.466	2.573
cBD	$^1A_1$	29.4	1.345	1.463	3.174
$cBD^{\bullet+}$	$^2A_2$	230.5	1.405	1.412	3.175
	$^2B_1$	289.5	1.376	1.510	3.091
tBD	^1A_g	29.0	1.344	1.466	
$tBD^{\bullet+}$	^2B_g	228.5	1.399	1.415	

[a] The MNDO Hamiltonian was employed and the RHF ("half-electron") procedure was used for open-shell systems. Geometries were optimized in C_{2v} symmetry, but all stationary points were characterized by diagonalizing the force constant matrix. [b] See scheme below. [c] System is a transition state (see text).



Although, due to convergence problems, we have not been able to examine the stability of this state toward other distortions, it may well be that the primary deactivation pathway for this ion is internal conversion to high vibrational levels of the $^2B_1$ ground state which may subsequently engage in a (nonelectrocyclic) thermal rearrangement analogous to that observed in the gas phase.[31] However, this mechanism can only occur if the $^2A_1$ hypersurface is bypassed on the way from (vertically populated) $^2A_2$ to the lowest excited state $^2B_2$. In view of the substantial geometry differences between the two excited states, with $^2A_1$ having actually a dissociative C_{sp^3}–C_{sp^3} bond, this is at least conceivable.

It is interesting to note in this context that photochemical cyclization of $BD^{\bullet+}$ to $CB^{\bullet+}$ is not observed, although in this case the *lowest* excited state of $BD^{\bullet+}$ correlates with the $CB^{\bullet+}$ ground state (directly in the conrotatory and perhaps with a slight activation barrier in the disrotatory mode). Obviously, this reaction could only proceed in a concerted synchronous fashion when starting from the s-cis rotamer of $BD^{\bullet+}$. The absence of photochemical recyclization may be taken as another indication that the photoproduct of $CB^{\bullet+}$ is $tBD^{\bullet+}$ and *not* $cBD^{\bullet+}$.

(c) Calculations. The results of our calculations of $CB^{\bullet+}$ and $BD^{\bullet+}$ are summed up in Table II. Note in particular the pronounced geometry differences between the various states of the two cations, in accord with expectations based on the shape of the MO's from which an electron is removed. The surfaces involved in the $cBD^{\bullet+} \rightarrow tBD^{\bullet+}$ rearrangement are pictorially represented in Figure 4, which illustrates the difficulties encountered in locating the transition state for this reaction: Depending on whether the forward or the backward reaction was calculated, different states with different geometries were obtained at 90° (see inset drawings depicting the geometries and the singly occupied MO's at points A and B), and no saddle point connecting these two structures was found.

The reason for this is that the $cBD^{\bullet+} \rightarrow tBD^{\bullet+}$ interconversion is a state symmetry forbidden process in C_2, i.e., the point group shared by both species. True transition states (saddle points) for such reactions do not exist within single-determinant models, because the surfaces for different states truly "cross", leading to singularities on the hypersurface. This is no longer true in principle if all symmetry is destroyed, but in practice, it is very difficult to find the true transition state, since the system tends to retain the leading configuration in a reaction coordinate calculation and, thus, climbs toward the target product excited state.

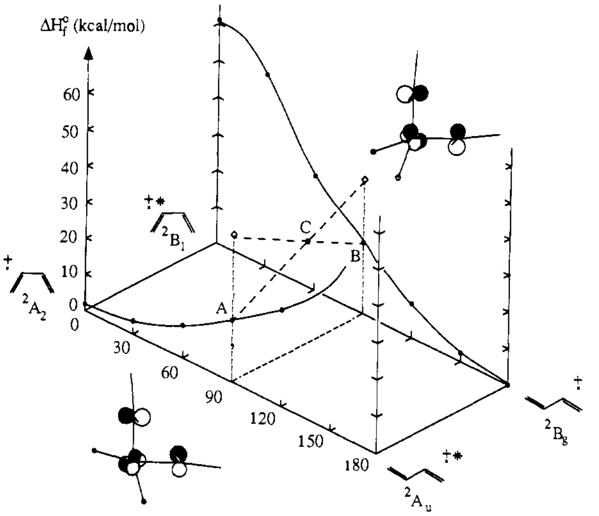


Figure 4. Results of MNDO calculations of the $cBD^{\bullet+} \rightarrow tBD^{\bullet+}$ interconversion. Energies are plotted relative to ground-state $tBD^{\bullet+}$. The MOPLOT drawings on the lower left and upper right indicate the different geometries and singly occupied MO's obtained for the forward and backward reactions, respectively (points A and B). The squares correspond to the energies of state B at the geometry of A and vice versa (discussion see text).

We have made various attempts to find a ≈90° twisted $BD^{\bullet+}$ geometry at which a 2 × 2 CI calculation would give similar weight to the leading configurations of the two states, hoping that this could serve as a starting point for locating the transition state on a CI surface. However, all our "trial and error" searches were unsuccessful. The crossing point C between the lines connecting state A at the geometry of state B and vice versa (≈29 kcal/mol above $cBD^{\bullet+}$) may thus be regarded as an upper limit for the calculated rotation barrier in $BD^{\bullet+}$.

Another estimate of this barrier can be obtained from the photoelectron spectrum of BD:[30] This shows two bands separated by 2.43 eV, which arise (in LCBO parlance) through ionization from the negative (π^-) and the positive combinations (π^+) of the two ethylenic π-orbitals in BD, respectively. Assuming that the π^-/π^+ energy splitting is symmetric and goes to zero for an orthogonal arrangement of the double bonds leads to a resonance energy in planar $BD^{\bullet+}$ of 0.5 × 2.43 eV, i.e., 28 kcal/mol. Hyperconjugative effects will entail a slight lowering of the rotational barrier which is, therefore, expected to lie in the 20–25 kcal/mol range.

Conclusions

The primary product of the photochemical ring opening of $CB^{\bullet+}$ is found be the s-trans rotamer of $BD^{\bullet+}$. Since (a) a secondary isomerization of thermalized *s-cis-* to *s-trans-*$BD^{\bullet+}$ can be excluded and (b) the corresponding photochemical process is unlikely to occur under the present experimental conditions, we conclude that the photochemical ring opening of $CB^{\bullet+}$ does not proceed in a concerted electrocyclic fashion. Instead, we propose that electronically excited $CB^{\bullet+}$ decays to vibrationally excited ground-state $CB^{\bullet+}$ which may subsequently rearrange to $tBD^{\bullet+}$ via a nonelectrocyclic pathway such as that postulated previously on the basis of semiempirical and ab initio calculations.[4]

Orbital correlation diagrams are of little use in discussions of *thermal* $M^{\bullet+}$ electrocyclic reactions, because such processes are invariably state symmetry forbidden. Consequently, the reactants must lose all symmetry in order to cross over to the product ground-state surface, and therefore, the premises on which orbital correlation diagrams are based (maintenance of symmetry in the course of the reaction) are invalidated. This is not necessarily

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(31) It is interesting to note that $BD^{\bullet+}$ obtained from $CB^{\bullet+}$ in the gas phase shows *identical* ion–molecule chemistry to $tBD^{\bullet+}$ formed from genuine tBD,[5a] although one would expect differences in the behavior of the two rotamers, especially when cycloaddition reactions are used to probe the configuration of the ions. It therefore seems that the thermal $CB^{\bullet+} \rightarrow BD^{\bullet+}$ rearrangement also leads to $tBD^{\bullet+}$ as a primary product, in accord with theoretical predictions.[4]

(32) Kurreck, H.; Kirste, B.; Lubitz, W. *Electron Nuclear Double Resonance Spectroscopy*; VCH Publishers: New York and Weinheim, 1988; (a) Chapter 2; (b) p 314.

(33) Gerson, F.; Huber, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 495.

(34) Gerson, F.; Qin, X.-Z. *Chem. Phys. Lett.* **1988**, *153*, 546.

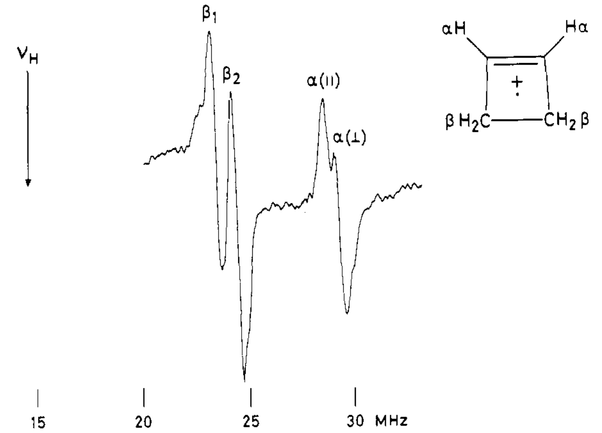

Figure 5. ^1H ENDOR spectrum of $CB^{\bullet+}$ in a CF_3CCl_3 matrix at 135 K.

true for the corresponding *photochemical* processes where some reactant excited state always correlates adiabatically with the product ground state along a concerted synchronous pathway. However, these reaction modes will only occur if the lowest reactant excited state is the one that shows this feature, as is the case for photochemical cyclizations of linear conjugated polyene cations. However, these reactions could only be observed if the prerequisite s-cis conformation of the reactant polyene can be prepared in stable form prior to the envisaged photochemical reaction.

We found single-determinant theory an inadequate tool for calculating reaction paths for $M^{\bullet+}$ isomerizations which are formally symmetry forbidden, because the distortions that are necessary for achieving a transition from reactant to product ground-state surfaces cannot be identified on uphill regions of potential surfaces. Presumably, MC-SCF procedures are required to obtain wave functions that are sufficiently sensitive to such distortions to allow the correct reaction paths to be identified. Much theoretical research remains to be done before we can begin to devise rules for $M^{\bullet+}$ isomerizations which are as widely applicable as those used so successfully in discussions of the corresponding neutral reactions.

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Appendix

The ^1H ENDOR spectrum of $CB^{\bullet+}$ (Figure 5) exhibits two pairs of signals above $\nu_H = 14.56$ MHz, the frequency of the free proton. The two signals at 23.64 (β_1) and 24.68 MHz (β_2) are essentially isotropic, their positions being given by $|a/2| - \nu_H$ where $a = 76.40$ and 78.48 MHz, respectively[32a] (the high-frequency counterparts at $|a/2| + \nu_H = 52.76$ and 53.80 MHz are not accessible to our radio-frequency source). Each of the two coupling constants a, which can be converted into 2.73 and 2.80 mT, must be due to two methylene β-protons. The second pair of ENDOR signals at 28.70 and 29.51 MHz have a shape that is characteristic of a parallel and a perpendicular feature, respectively.[32b,33] Their positions are given by $\nu_H + |A_\parallel/2|$ and $\nu_H + |A_\perp/2|$ and they are associated with anisotropic coupling constants of the olefinic α-protons, $A_\parallel = 28.28$ MHz or 1.009 mT and $A_\perp = 29.90$ MHz or 1.067 mT (the corresponding signals at $\nu_H - |A_\parallel/2| = 0.42$ MHz and $|A_\perp/2| - \nu_H = 0.39$ MHz could not be detected because of the poor sensitivity of our ENDOR instrument in this low-frequency region). The isotropic value calculated from the above data is 1.048 mT, and since $|A_\parallel| < |A_\perp|$, its sign should be negative.[34]

Photochemical Activation of Distal Functional Groups in Polyfunctional Molecules. Activation of a β Carbon-Chlorine Bond by the Trimethylsilyl Enol Ether Chromophore via (π^* + σ^*) LUMO Mixing[1]

Brad D. Maxwell,[†] John J. Nash,[†] Harry A. Morrison,*[,†] Michael L. Falcetta,[‡] and Kenneth D. Jordan[‡]

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, and Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260. *Received March 10, 1989*

Abstract: *exo*-6-Chloro-2-(trimethylsiloxy)norbornene (ExoCl) and *endo*-6-chloro-2-(trimethylsiloxy)norbornene (EndoCl) have been synthesized in order to compare their spectroscopic and photochemical properties with those predicted by ab initio computations. The latter indicate a large contribution of C–Cl σ^* character in the LUMO of ExoCl but not EndoCl. This interaction leads to significant observable differences between the ultraviolet absorption and electron transmission spectra of the exo and endo isomers. Photolysis (254 nm) of this isomer in hexane containing (±)-*sec*-butylamine as an acid scavenger leads to homolysis of the C–Cl bond and reduction to 2-(trimethylsiloxy)norbornene (TMSNB). The reaction is quite clean with the quantum efficiency of disappearance for ExoCl (0.066 ± 0.001) comparable to that for appearance of TMSNB (0.069 ± 0.001). Photolysis of the endo isomer is appreciably less efficient ($\Phi_{dis} = 0.0079 \pm 0.0005$), as anticipated from the lack of σ^*/π^* mixing predicted and observed for the LUMO of this isomer.

The mixing of π^* and σ^* molecular orbitals in the lowest unoccupied molecular orbital (LUMO) of polyfunctional molecules represents a common mechanism for spectroscopic and photochemical interaction between distal functionalities.[2] In particular, one may expect that a C–Cl bond remote from, but propitiously placed with respect to, a π chromophore could generate such a mixed LUMO, the potential consequence of which would be the labilization of the C–Cl bond upon population of a primarily π

[†] Purdue University.

[‡] University of Pittsburgh.

(1) Abstracted, in part, from: Maxwell, B. D. Doctoral Dissertation, Purdue University, Dec 1988. Organic Photochemistry. 79. Part 78: Wu, Z.; Morrison, H. *Photochem. Photobiol.*, in press. Presented in part at the Third Chemical Congress of North America, Toronto, Canada, June 5–10, 1988.

(2) Morrison, H. A. *Rev. Chem. Intermed.* **1987**, *8*, 125–145.

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