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Isomerization of Cubane Radical Cation

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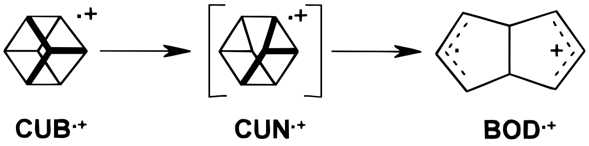
Upon ionization, cubane undergoes facile breaking of three C–C bonds leading to the bis-cyclobutenylium radical cation. This process is compared with the formation of the same product by cleavage of only one central bond in the *syn*-tricyclooctadiene radical cation. The kinetics of the isomerization process is also discussed, and it is concluded that a small barrier (2.5 kcal/mol) exists in contrast to the barrier-free transformation of the *syn*-tricyclooctadiene radical cation.

1. Introduction

Upon ionization, molecules containing small rings can reduce their strain by localizing spin and charge in one of the small ring bonds, which thereby undergoes significant elongation.[1] As a consequence, the activation energies for cleavage of such weakened bonds are substantially reduced compared with the parent neutral molecules. This situation is well illustrated by the radical cations of *syn*- and *anti*- tricyclo[4.2.0.0^{2,5}]octa-3,7-diene (TOD), which stood at the focus of our preceding studies on this subject.[2,3]

Cubane (CUB), the formal $2\pi+2\pi$ cycloaddition product of *syn*-TOD, is the most strained $(CH)_8$ hydrocarbon, containing 12 equivalent bonds in six four-membered rings.[4] At the full symmetry of CUB (O_h), its radical cation ($CUB^{\bullet+}$) has a triply degenerate ground state ($^2T_{2g}$)[5] that is subject to several modes of Jahn–Teller (JT) distortion. The electronic and molecular structure of $CUB^{\bullet+}$ is further complicated by the fact that another triply degenerate state ($^2T_{2u}$), itself JT active, lies within a few tenths of an electrovolt of the ground state.[5] Second-order vibronic coupling between the states on the resulting intertwined pair of JT surfaces may entail further distortion and a general flattening of the potential energy surface. Therefore, $CUB^{\bullet+}$ is expected to show a highly fluxional behavior.

Indeed, a time-resolved FDMR (fluorescence detected magnetic resonance) spectrum of CUB ionized by pulse radiolysis in liquid pentane was interpreted in terms of a radical cation with eight equivalent hydrogen atoms.[6] The same species was not detected after steady-state radiolysis of CUB in a Neon matrix at 4 K[7] or in Freon matrixes at 77 K.[8] Instead, it was found that ionized CUB rearranges to the bicyclo[3.3.0]-octa-2,6-diene-4,8-diyl radical cation ($BOD^{\bullet+}$), which had been generated earlier from semibullvalene or cyclooctatetraene.[9] It was proposed that $BOD^{\bullet+}$ arises from cuneane (CUN) to which CUB rearranges on ionization, but this hypothesis could not be verified experimentally.[8]



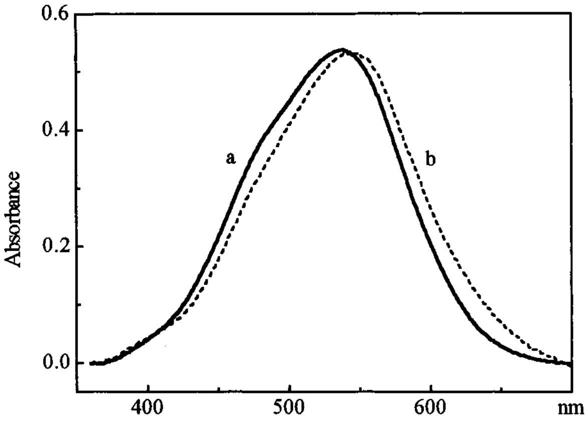


Figure 1. Absorption spectrum generated upon radiolysis (5 pulses, dose ≈ 5 kGy) of (a) CUB and (b) *syn*-TOD (0.01 M) in a glassy matrix of MCH (methylcyclohexane/1-chlorobutane (1 M)) at 77 K.

In our preceding study on *syn*-TOD, we had found that on ionization this valence isomer of CUB decays spontaneously to the bis(cyclobutenylium) radical cation ($BCB^{\bullet+}$).[2] Based on these findings, we will propose a reassignment of the rearrangement products of $CUB^{\bullet+}$ and discuss the kinetics of their formation.

2. Results and Discussion

The transient optical spectrum obtained after radiolysis[10] of CUB in hydrocarbon glasses at 77 K is compared in Figure 1 with that obtained from *syn*-TOD under similar conditions and assigned to a mixture of $BCB^{\bullet+}$ (band at ~540 nm) and cyclooctatetraene radical cation ($COT^{\bullet+}$, shoulder at ~480 nm).[2] Obviously the two spectra are very similar, the main difference being a small blue shift in the spectrum generated from CUB, a shift which becomes more pronounced at lower temperatures. Although the maximum of the absorption lies at 530 nm following radiolysis of CUB at 30 K, it shifts toward 540 nm on annealing to 77 K and reaches 545 nm at temperatures >80 K.

We believe that this shift can be explained in terms of a matrix cage effect, which may prevent $BCB^{\bullet+}$ from attaining its equilibrium conformation. This effect would be expected to

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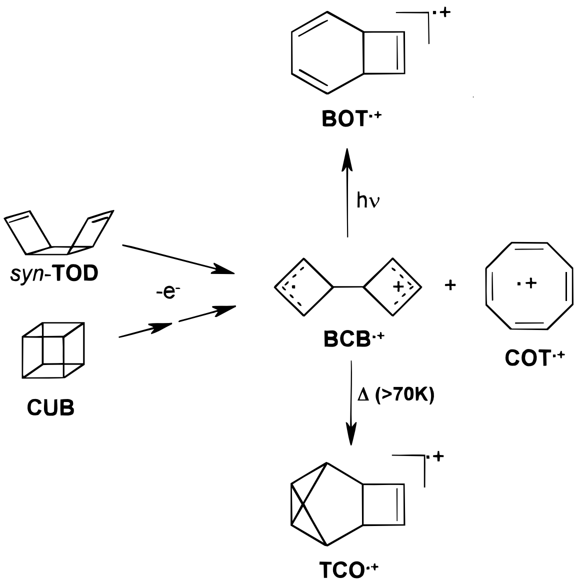
SCHEME 1: Products obtained by pulse radiolysis of *syn*-TOD and CUB and identified by electronic absorption (EA) spectroscopy.



primarily influence the angle between the four-membered rings, the critical quantity with regard to the overlap of the two allylic units and hence the position of the charge resonance (CR) transition responsible for the 545 nm band of BCB$^{•+}$.[2] Reducing this angle from the relaxed value leads to an increased splitting of the π-MOs and therefore in a blue shift of the CR transition.

At temperatures >70 K, the shift of the CR band of BCB$^{•+}$ coincides with its simultaneous isomerization to the radical cation of tetracyclo[4.2.0.0.^{2,4}0^{3,5}]octa-7-ene (TCO$^{•+}$)[2] (BCB$^{•+}$ → TCO$^{•+}$, Scheme 1). The decays are identical for the absorptions from ionized CUB and *syn*-TOD, and the same parameters of dispersive kinetics ($\tau_0 = 638$ s and $\alpha = 0.49$)[11,12] were found for both processes. In addition, photolysis of the two samples led to the same spectral changes, indicating the formation of bicyclo[4.2.0]octa-2,4,7-triene radical cation (BOT$^{•+}$)[2] (BCB$^{•+}$ → BOT$^{•+}$, Scheme 1), which confirms their assignment to the same products in both experiments.

This similarity finds further support in the electron spin resonance (ESR) spectra obtained after γ-irradiation of CUB and *syn*-TOD in $CF_2ClCFCl_2$ at 77 K, which are again nearly indistinguishable (cf. Figure 2a).[2] In the center, the spectra show the broad signals ascribed to the radical cation TCO$^{•+}$ which has been shown to arise by rearrangement of BCB$^{•+}$ at 77 K,[2] whereas in the wings, the characteristic quintet patterns of BOD$^{•+}$ [9] (i.e., the species observed in the previous Freon matrix study of ionized cubane[8]) stand out very clearly. The main difference between the CUB and *syn*-TOD results is that about a 2-fold larger relative yield of BOD$^{•+}$ is produced from cubane.

As in the case of *syn*-TOD, near infrared (NIR) photobleaching results in the generation of the multiplet spectrum of BOT$^{•+}$ (Figure 2b). Taking into account the somewhat poorer resolution of this spectrum recorded at 108 K compared with that obtained from *syn*-TOD at 113 K,[2] the yields of BOT$^{•+}$ and hence of its photoprecursor, TCO$^{•+}$, are comparable for the two solute systems. Thus, TCO$^{•+}$ and BOD$^{•+}$ are the major identified products after ionization of both *syn*-TOD and CUB at 77 K, with a slightly higher yield of the latter product in the case of CUB.

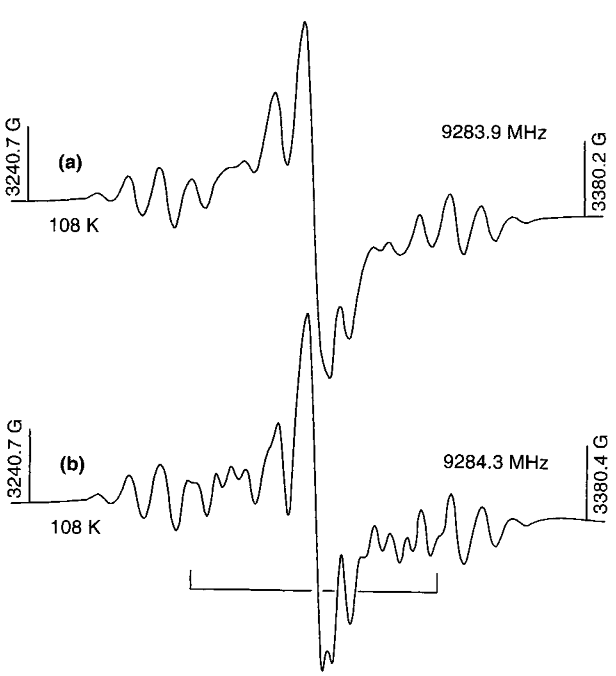
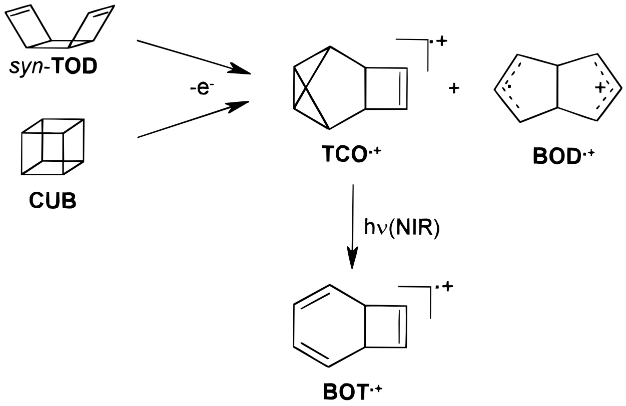


Figure 2. First-derivative ESR spectra showing (a) initial spectrum obtained on ionization of CUB in the $CF_2ClCFCl_2$ matrix, and (b) after illumination of the sample with NIR light (>840 nm). The NIR-induced signals displayed within the bracketed region of spectrum b are those of BOT$^{•+}$.[2,3]

SCHEME 2: Products obtained after γ-irradiation of *syn*-TOD and CUB at 77 K and identified by ESR spectroscopy.



Radiolytic oxidation of CUB in the CF_2BrCF_2Br matrix also gave ESR results that closely paralleled those for *syn*-TOD, although the spectra in this matrix were much more poorly resolved. Also, in either solute system, there was no detectable formation of the radical cation of 1,4-dihydropentalene (1,4-DHP$^{•+}$), the characteristic product obtained on ionization of *anti*-TOD in CF_2BrCF_2Br.[3] This result is clear evidence that ionized CUB does not follow the rearrangement pathway available to ionized *anti*-TOD.

Although the isomerization of *syn*-TOD$^{•+}$ as a precursor of BCB$^{•+}$ requires cleavage of only one C−C bond, analogous to the spontaneous ring opening of cyclopentadiene dimers to bisallylic cations on ionization,[13,14] the radical cation of CUB is a more remote precursor to BCB$^{•+}$ in that a cleavage of *three* bonds is required. In the case of 1,3-bishomocubane, CIDNP (chemically induced dynamic nuclear polarization) studies[15] and matrix photoionization[16] have ruled out any ring opening by rapid fragmentation of three C−C bonds. In contrast, such a process appears to occur very rapidly in the CUB radical cation, and it would therefore be interesting to probe the exact timing of the cleavages of the three bonds (note that once cyclorever-

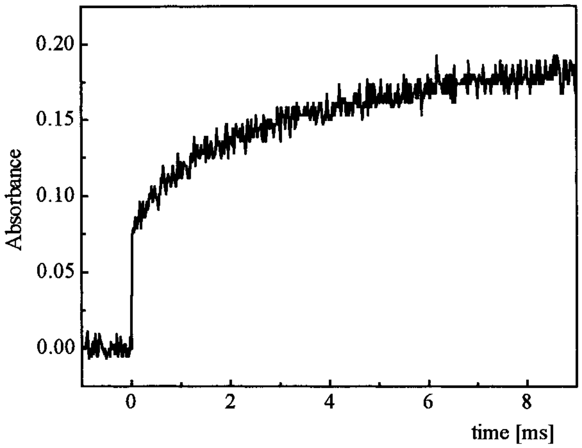


Figure 3. Absorption growth detected at 520 nm ($T = 82$ K) by pulse radiolysis of CUB solution (0.02 M, MCH). The sample was 10 mm thick and received a radiation dose of 0.5 kGy in a 2 μs electron pulse.

sion to *syn*-TOD$^{\bullet+}$ has occurred, the breaking of the third bond to yield BCB$^{\bullet+}$ requires no activation).[2]

As was mentioned in the previous paper,[2] the 540 nm transient absorption band arises within the resolution of the pulse radiolysis system when *syn*-TOD is used as a precursor. In contrast, the same band arises with a delay of a few milliseconds in the case of CUB (see Scheme 1 and Figure 3). There is no reason to assign this observation to a charge-transfer process because both neutral precursors, CUB and *syn*-TOD have very similar ionization potentials (IP = 9.0−9.1 eV).[5,17,18] Also, the growth rate of the 540 nm band does not depend on the concentration of CUB, which is what one would expect if charge-transfer processes between solvent (matrix) and solute molecules were involved.

The evidence just presented points toward the existence of a precursor that rearranges to BCB$^{\bullet+}$ within milliseconds at 80 K. This precursor seems to have a finite lifetime, and hence its rearrangement is associated with some activation barrier. In addition, this precursor does not seem to have any absorptions in the visible range. Thus, we conclude that this species represents the elusive CUB radical cation, which is consistent with the FDMR results of Qin et al.[6] If the absorption of the CUB radical cation lies <350 nm, its detection would be very difficult because this range is obscured by a strong absorption of the radiolysis by-products.

The temperature dependence of the 540 nm absorption growth rate is quite puzzling because a strong curvature of the Arrhenius plot is observed (Figure 4). Such a shape of the Arrhenius plot is often considered as an indication of the participation of quantum-mechanical tunneling in the observed processes. If we associate the tunneled mass with the four carbon atoms that presumably move most in the CUB$^{\bullet+}$ → *syn*-TOD$^{\bullet+}$ isomerization process, the barrier width (which can be considered as the average distance of movement for all atoms during this transformation) has to be assumed as very narrow (<0.05−0.1 Å). Such an interpretation is not without precedence and was used to explain the decay kinetics of the triplet biradicals.[19−21]

However, the fact that the strongest curvature of the Arrhenius plot is observed close to the glass transition temperature of the matrix may suggest that some matrix effects are responsible for this atypical behavior. However, dispersive kinetics cannot reproduce the observed curvature of the Arrhenius plot over such wide range of temperatures unless one assumes a nonphysically wide distribution of sites with correspondingly varying activation barriers.[11,21]

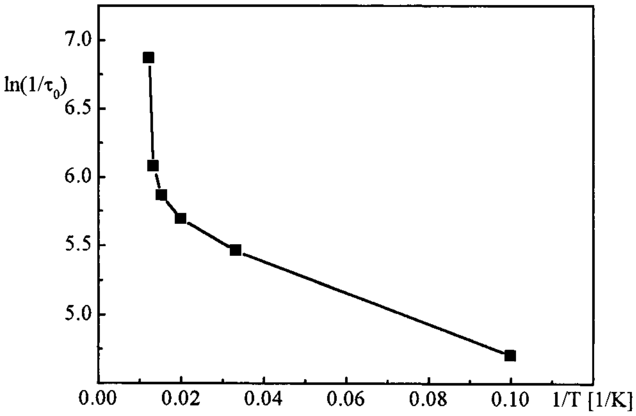


Figure 4. Rate constant of formation of the 540 nm absorption presented in the Arrhenius coordinates.

On the other hand, if the intrinsic barrier for rearrangement of the CUB radical cation to *syn*-TOD$^{\bullet+}$ (or directly to BCB$^{\bullet+}$) is low, but the process is slowed by a matrix cage effect, then we would expect the reaction rate to be constant over a wide temperature region where the matrix is rigid. When the matrix constraints are disappearing (i.e., close to and above the glassy transition temperature of the matrix), a pronounced acceleration of the process would set in. The whole process would then appear as a superposition of two dispersive processes involving similar activation energies; that is, guest rearrangement and host matrix relaxation.[22]

In any case, the delayed formation of the 540 nm absorption can be viewed as an indirect proof of stability of the primary radical cation (which, according to Qin et al.,[6] should be assigned to CUB$^{\bullet+}$). The activation barrier cannot be calculated unambiguously at present but, assuming that already at >80 K the rate is not perturbed by matrix effects and taking the preexponential factor $A = 10^{10}$ s^{-1}, one can estimate this barrier to be 2.5 kcal/mol.

3. Conclusion

The results presented here clearly indicate that CUB and its [$2\pi+2\pi$] cycloreversion product, *syn*-TOD, give rise to the same product on ionization; that is, the bis(cyclobutenylium) radical cation, BCB$^{\bullet+}$. However, a clear difference is observed with regard to the kinetics of the formation of BCB$^{\bullet+}$ which occurs within the duration of the ionizing electron pulse in the case of *syn*-TOD, but with a delay of some milliseconds in the case of CUB. From this result we conclude that the ring opening of CUB$^{\bullet+}$ is an activated process, in contrast to that of *syn*-TOD that occurs spontaneously.

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References and Notes

(1) see, e.g.; Roth, H. D.; Schilling, M. L. M. *Can. J. Chem.* **1983**, *61*, 1027.

(2) Bally, T.; Bernhard, S.; Matzinger, S.; Roulin, J.-L.; Sastry, G. N.; Truttmann, L.; Zhu, Z.; Marcinek, A.; Adamus, J.; Kamiński, R.; Gębicki, J.; Williams, F.; Chen, G.-F.; Fülscher, M. *Chem. Eur. J.* **2000**, *6*, 858.

(3) Bally, T.; Bernhard, S.; Matzinger, S.; Truttmann, L.; Zhu, Z.; Roulin, J.-L.; Marcinek, A.; Gębicki, J.; Williams, F.; Chen, G.-F.; Roth, H.-D.; Herbertz, T. *Chem. Eur. J.* **2000**, *6*, 849.

(4) Eaton, P. E.; Cole, T. W. *J. Am. Chem. Soc.* **1964**, *86*, 3158.

(5) Bischof, P.; Eaton, P. E.; Gleiter, R.; Heilbronner, E.; Jones, T. B.; Musso, H.; Schmelzer, A.; Stober, R. *Helv. Chim. Acta* **1978**, *61*, 547.

(6) Qin, X.-Z.; Trifunac, A. D.; Eaton, P. E.; Xiong, Y. *J. Am. Chem. Soc.* **1991**, *113*, 669.

(7) Knight, L. B, Jr.; Arrington, C. A.; Gregory, B. W.; Cobranchi, S. T., Liang, S.; Paquette, L. *J. Am. Chem. Soc.* **1987**, *109*, 5521.

(8) Qin, X.-Z.; Trifunac, A. D.; Eaton, P. E.; Xiong, Y. *J. Am. Chem. Soc.* **1990**, *112*, 4565.

(9) Dai, S.; Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1990**, *112*, 2835, 2837.

(10) Details of the pulse radiolysis system based on electron linear accelerator are given elsewhere: Karolczak, S.; Hodyr, K.; £ubis, R.; Kroh, J. *J. Radioanal. Nucl. Chem.* **1986**, *101*, 177.

(11) Płonka, A. *Annu. Rep. Prog. Chem.* **1989**, *85*, 47.

(12) Marcinek, A.; Gębicki, J.; Płonka, A. *J. Phys. Org. Chem.* **1990**, *3*, 757.

(13) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1985**, *107*, 716.

(14) Momose, T.; Shida, T.; Kobayashi, T. *Tetrahedron* **1986**, *42*, 6337.

(15) Roth, H. D.; Schilling, M. L. M.; Abelt, C. J. *Tetrahedron* **1986**, *42*, 6157.

(16) Andrews, L.; Dunkin, I. R., Kelsall, B. J.; Lurito, J. T. *J. Phys. Chem.* **1985**, *89*, 821.

(17) Gleiter, R.; Heilbronner, E.; Hekman, M.; Martin, H.-D. *Chem. Ber.* **1973**, *106*, 28.

(18) Martin, H.-D.; Mayer, B. *Angew. Chem.* **1983**, *95*, 281.

(19) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 3857.

(20) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 4688.

(21) Sponsler, M. B.; Jain, R.; Coms, F. D.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2240.

(22) Płonka, A.; Paszkiewicz, A. *J. Chem. Phys.* **1992**, *96*, 1128.