

The Bisketene Radical Cation and Its Formation by Oxidative Ring-Opening of Cyclobutenedione

Krzysztof Piech and Thomas Bally*

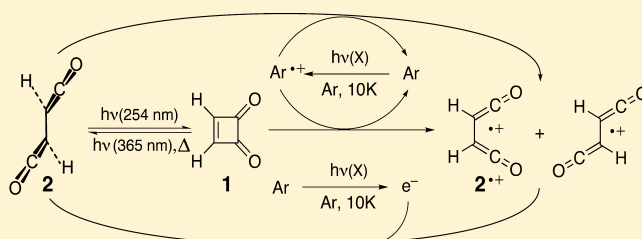
Department of Chemistry, University of Fribourg, CH-1700 Fribourg, Switzerland

Annette D. Allen and Thomas T. Tidwell

Department of Chemistry, University of Toronto, Ontario, Canada M5S 3H6

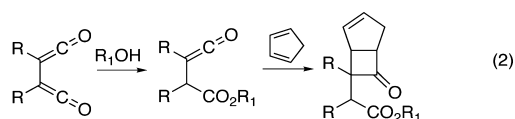
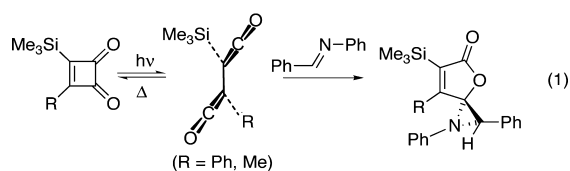
S Supporting Information

ABSTRACT: Parent cyclobutenedione **1** was photolyzed and ionized in an Ar matrix at 10K. The bisketene **2** that results in both cases (in the form of its radical cation after ionization) was characterized by its IR spectrum and by high-level quantum chemical calculations. Experiment and theory show that the neutral bisketene has only a single conformation where the two ketene moieties are nearly perpendicular, whereas the radical cation is present in two stable planar conformations. The mechanism of the ring-opening reaction, both in the neutral and in the radical cation, is discussed on the basis of calculations. In the latter case it is a nonsynchronous process that involves an avoided crossing of states.



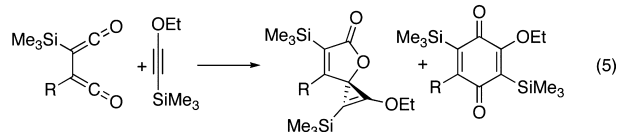
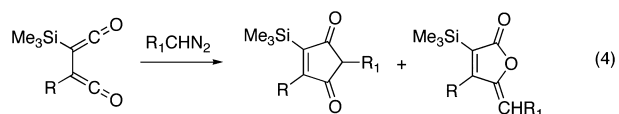
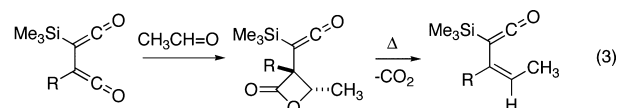
INTRODUCTION

Vicinal bisketenes are very reactive compounds^{1,2} and are also useful synthons that have been used to prepare mixed and symmetrical succinate esters,^{1f} butenolides,^{1f} symmetrical and mixed succinamides,^{2g} succinimides,^{2g} ester amides,^{2g} ortho esters,^{2e} and other species, including aziridines (eq 1).^{1d}



Bisketenes are more reactive than monoketenes resulting from the first reaction, and so selective reactions in which the two ketenyl groups are successively reacted first with one reagent and then with another are possible (eq 2).^{2g}

Thus, bisketenes react with aldehydes to give isolable β -lactones which on pyrolysis lose CO₂ to give vinylketenes (eq 3),^{1h} and reactions with diazoalkanes give cyclopentenones and lactones (eq 4).¹ⁱ Bisketenes also undergo [2 + 2] cycloaddition with cyclopentadiene forming spirobutenolides and ketenylcyclobutanones^{2i,j} and [4 + 2] cycloadditions with alkynes forming *p*-benzoquinones, together with spiro products of [2 + 1] cycloaddition with bicyclization (eq 5).^{2h} Reactions

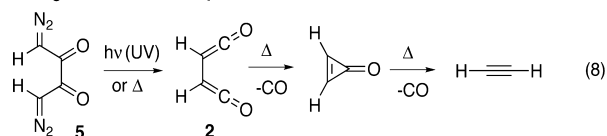
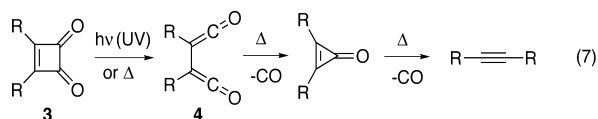
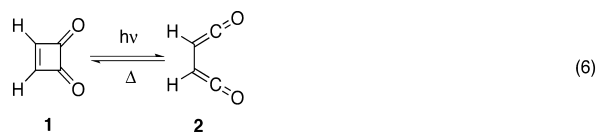


with fullerenes similarly give spiro products.^{2k} Pyrolysis of poly(bisketenes) leads to large-ring poly(acetylenes).^{2l}

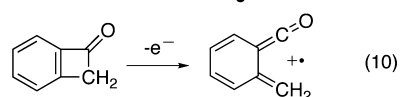
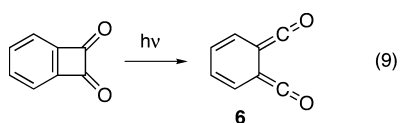
The photochemical ring-opening of cyclobutenediones is the most used way to prepare bisketenes, as these are generally less stable than the corresponding cyclobutenediones so thermal ring-opening is endothermic. The parent cyclobutenedione **1** upon photolysis in isooctane gave partial conversion to the bisketene **2**, as evidenced by the IR absorption at 2120 cm⁻¹ and the ¹H NMR signal at δ 3.20 (eq 6).^{2f} Pyrolysis of cyclobutenediones can lead to alkynes, presumably by spontaneous decarbonylation of the intermediate bisketenes and cyclopropanones (eq 7).^{1e}

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The parent bicyclic diketene **2** has also been generated and observed upon matrix photolysis in Ar at 10 K of the bis(diazo ketone) **5** and underwent decarbonylation to give cyclopropenone and then acetylene upon prolonged photolysis (eq 8).^{2a} Recently, dimethoxybicyclic diketene (**4**, R = OMe) was similarly generated in an Ar matrix from the dimethyl ester of squaric acid (**3**, R = OMe).^{2b} Photolysis of benzocyclobutenedione gave the bicyclic diketene **6** characterized in Ar at 11 K (eq 9),^{2c} and a variety of other unstable vicinal bicyclic diketenes have been generated in solution and characterized by time-resolved UV or IR spectroscopy.^{2d}



We had previously observed that upon ionization benzocyclobutenone undergoes spontaneous ring-opening to yield the radical cation of the quinoketene, 6-methylene-2,4-cyclohexadiene-1-ylidenemethanone (eq 10).³ We therefore wanted to see whether the ring-opening of cyclobutenedione could perhaps also be induced by ionization, thus opening a new avenue to the generation of bicyclic diketenes, e.g., by single-electron transfer.

Thus, we subjected parent cyclobutenedione **1** to photolysis in Ar matrices to characterize the resulting parent bicyclic diketene, **2**, and then to X-irradiation which partially converts neutral compounds that are contained in Ar matrices to their radical cations or to secondary products.⁴ This paper describes the results of these experiments and the accompanying quantum chemical calculations, which help to assign the spectra and understand the chemistry that we have observed.

RESULTS AND DISCUSSION

IR Spectra. Figure 1 sums up the results of the different experiments we did with cyclobutenedione. Obviously, on 254 nm photolysis, **1** is converted to **2**, as evidenced by the three strong IR bands that arise at 2114, 2127, and 2140 cm⁻¹. According to our (and previous)^{1a} calculations, the C₂ equilibrium conformation of **2** is twisted by nearly 90° and it shows a symmetric and an antisymmetric combination of the strongly IR-active ketene stretching vibrations. In addition, we found a shallow secondary minimum which corresponds to a planar C_{2h} (*trans*) structure, with only a single IR band in this

spectral region (the antisymmetric combination of ketene stretches is not IR active in this case), ca. 1 kcal/mol above the C₂ minimum (see Figure 2).

However, the activation enthalpy for the decay of the metastable *trans*-C_{2h} to the twisted C₂ equilibrium structure is vanishingly small, if it exists at all (high-level calculations, as they are used in the G4 procedure, place the transition state found by DFT calculations ca. 1 kcal/mol *below* the C_{2h} minimum; see Table S1 in the Supporting Information). Thus, the C_{2h} structure of **2** is unlikely to persist, and although the presence of both conformers of **2** in the matrix would nicely explain the observation of three bands, we favor an interpretation of the three bands as being due to a site splitting, as it is invariably observed in matrix IR spectra of compounds with cumulated double bonds. As the last of these bands is broader than the other two, and it peaks at 2140 cm⁻¹, i.e., almost exactly where CO absorbs in Ar matrices, we also cannot exclude that some CO is expelled in the course of the photolysis, although we will show below that this is rather unlikely.

Why are bicyclic diketenes **2** twisted almost 90°? Probably for two reasons: first, the HOMO of **2** is as π-antibonding along the central C–C bond as the adjacent π-MO is bonding, so the π bond order along this bond is almost zero, in contrast to butadiene where the lowest π-MO is much more bonding than the HOMO is antibonding, which results in a positive π-bond order.⁵ Second, the perpendicular geometry minimizes the unfavorable dipole interactions between the two C=O groups which prevail in the planar structures, in particular in the C_{2v} one.

If, instead of exposing an Ar matrix containing **1** to UV light, it is subjected to 90 min of X-irradiation, the green difference spectrum (b) in Figure 1 is obtained (for an explanation of the events that occur on X-irradiation of Ar matrices, see Methods).

At first sight this spectrum looks very similar to spectrum (a); i.e., the two peaks of **1** decrease and the three of **2** increase, albeit with different relative intensities than after photolysis of **1**. However, closer inspection reveals some new bands between 2150 and 2300 cm⁻¹ that had not arisen upon photolysis (see the enlargement in Figure 1), some of which we will assign to the radical cation of **2**.

It is known that, after ca. 90 min of X-irradiation, the amount of charged species that are formed in an Ar matrix levels off because they are then reneutralized by the electrons that roam through the matrix at the same rate as they are formed by scavenging the holes. If the formed radical cations do not undergo any chemistry, additional X-irradiation results in no spectral changes. However, if the incipient radical cations rearrange, as it is the case here, then the *rearranged* cations get reneutralized and the formation of rearranged neutral (in our case **2**) can continue, in principle indefinitely.

The results of further X-irradiation (orange difference spectrum (c)) are shown to demonstrate that, under these conditions, no additional **2**^{•+} is formed (the three bands labeled “c” do not increase) because it is continually reneutralized to give more **2**, as evidenced by the increase of its characteristic triplet of bands (see Methods). In addition, this experiment shows that the two small peaks labeled “n” also continue to increase, which indicates that they cannot belong to charged species but must be due to a neutral byproduct that may perhaps form upon loss of CO (unfortunately, CO escapes our detection because its comparatively weak IR absorption lies within the strong triplet of peaks of **2**, and spectrum (c) does

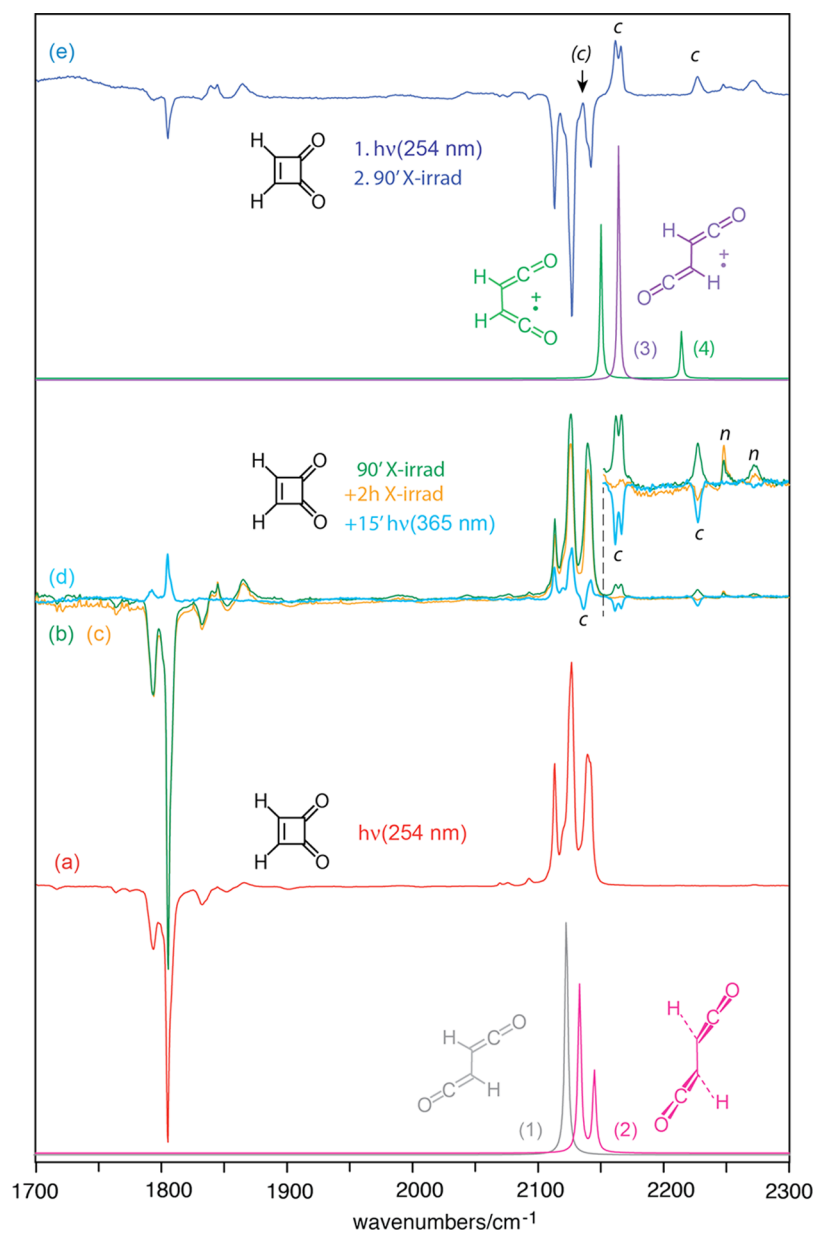


Figure 1. Difference spectra for (a) photolysis of **1** at 254 nm, (b) 90 min. X-irradiation of **1**, (c) additional 2 h of X-irradiation of **1**, (d) subsequent photolysis at >515 nm, and (e) X-irradiation of a sample of **1** that had previously been photolysed to give **2**. Bands in spectra c–e labeled “c” are due to cations, and those labeled “n” are neutral species (see the discussion in text). The spectra of the different species (traces 1–4) are from B3LYP/6-31G* calculations, scaled by 0.968 for the neutrals, 0.960 for the cations.

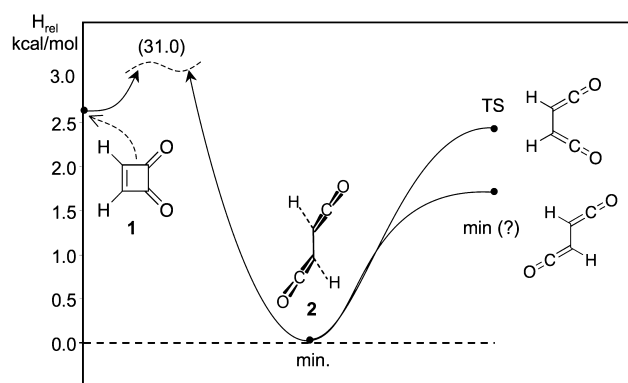


Figure 2. G4 potential surface for the conversion of **1** to **2** and the interconversion of different conformers of **2**.

not reveal any evidence for the characteristic pair of intense bands at 1780 and 1880 cm^{-1} of cyclopropanone.^{6,7}

As X-irradiation of an Ar matrix containing **1** resulted also in the increase of some weak bands in the near-UV part of the spectrum (which otherwise looks too nondescript to serve as a valid source of chemical information), we decided to expose the ionized sample to 365 nm irradiation. This did indeed result in a decrease of the bands labeled “c” in Figure 1d, and the rise of the triplet of peaks of **2**, which suggests that this photolysis led to some reneutralization of 2^{*+} . At the same time, the peaks of **1** also grow, albeit only to a small extent, indicating that a small amount of recyclization takes place. The most interesting aspect of that experiment is, however, that a band at ca. 2130 cm^{-1} decreases, in concert with the other bands labeled “c”, which suggests that this band belongs to the same species.

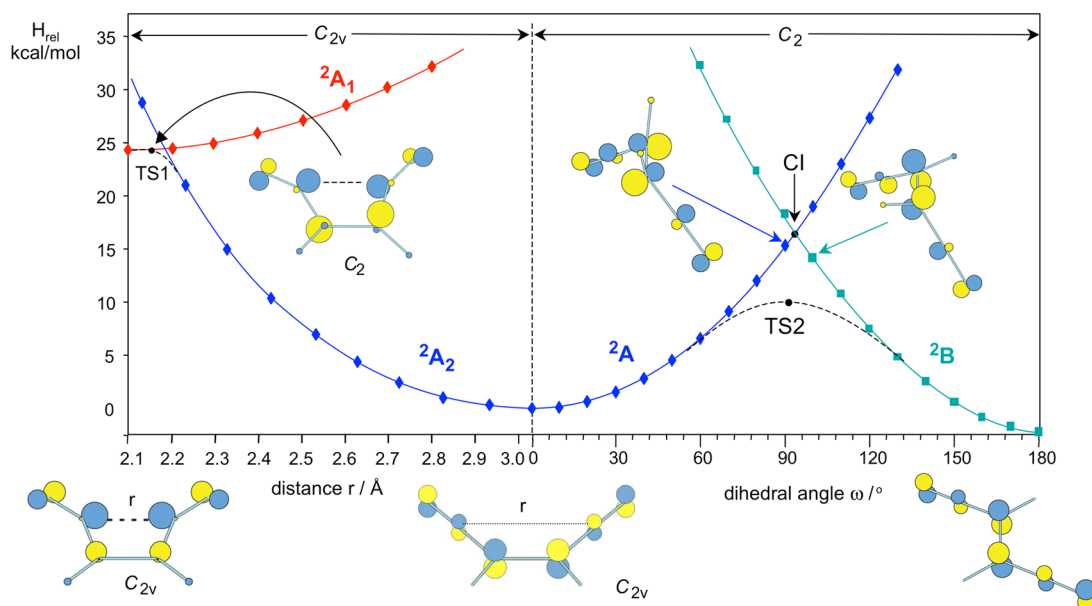


Figure 3. B3LYP/6-31G* potential surfaces for the interconversion of $1^{\bullet+}$ to *cis*- $2^{\bullet+}$ and for the interconversion of the latter to *trans*- $2^{\bullet+}$. The orbital plots represent the singly occupied MO (SOMO) in each state.

Finally, we preformed **2** by photolysis of **1** before X-irradiation, which gave rise to the difference spectrum (e) at the top of Figure 1. This time the bands of **2** decrease (because **2** is ionized), and the same bands above 2150 cm^{-1} increase as in the experiment where **1** had been ionized (green spectrum (b)). The “c” band at 2130 cm^{-1} does not point up as much as it should because its increase is overcompensated by the decrease of the 2140 cm^{-1} band of **2**, but the mere fact that this latter band is much smaller in the difference spectrum (d) than in the others indicates that some other absorption must be increasing in this region.

The above-described observations lead us to conclude that we see three IR-absorptions of $2^{\bullet+}$, at 2140 , $2162/2166$ (double peak) and 2227 cm^{-1} . Quantum chemical calculations of $2^{\bullet+}$ reveal that it exists in two stable conformations, *cis* (C_{2v}) and *trans* (C_{2h}), the first of which shows a pair of widely spaced ketene stretching vibrations while the second shows only one IR-active band in this region, due to its symmetry (see simulated spectra 3 and 4, respectively, in Figure 1). These results allow us to propose that the double peak at ca. 2164 cm^{-1} belongs to the *trans* conformer (calculated spectrum 3), while the peaks at 2140 and 2227 cm^{-1} (calculated spectrum 2) belong to the *cis* conformer of $2^{\bullet+}$.

Calculations. In order to understand and explain the apparently spontaneous ring-opening of the radical cation of cyclobutenedione, we explored the potential surfaces for this process and for the interconversion of the two conformers of the bisketene radical cation. The results of these efforts are depicted in Figure 3, which shows that, indeed, there is almost no barrier for the decay of $1^{\bullet+}$, for two reasons: first the reaction, which had been only slightly exothermic in neutral **1**, is now exothermic by 21.7 kcal/mol (on a G4 enthalpy scale), and second, the electron that is removed on ionization comes from the HOMO which is σ -bonding along the C–C bond that links the two carbonyl groups in **1**, which leads to a substantial weakening of that bond. This expresses itself for example in the fact that, at the equilibrium structure of $1^{\bullet+}$, that C–C bond has a length of 2.1 \AA .

However, to decay to *cis*- $2^{\bullet+}$ the system must pass from the $2A_1$ surface of ground-state $1^{\bullet+}$ to the $2A_2$ surface of *cis*- $2^{\bullet+}$, and to do that, the symmetry must be lowered to C_2 (where both states become $2A$). This is indeed what is found at the transition state (TS in Figure 3) which lies, however, only 0.57 kcal/mol above $1^{\bullet+}$, on a G4 enthalpy scale, which explains why the decay to $2^{\bullet+}$ is spontaneous.

From the IR spectra in Figure 1 we concluded that we see *both* stable conformations of $2^{\bullet+}$, so the question poses itself how *trans*- $2^{\bullet+}$ can be reached. From the right side of Figure 3 we see that the interconversion of the two conformers of $2^{\bullet+}$ involves a state crossing, even in C_2 symmetry; i.e., at 90° there is a conical intersection (CI) between the $2A$ and the $2B$ surfaces.

Ground-state reactions always circumvent conical intersections; their transition states lie in the “moat” that surrounds them. The only way for $2^{\bullet+}$ to pass from the $2A$ to the $2B$ surface is by localizing the SOMO, and hence the spin, in one-half of the molecule (which leads to a total loss of symmetry), so the coefficients in the other half can re-emerge with the opposite sign (see MOs near the CI in Figure 3).

Unfortunately, as we have explained before,⁸ such transformations cannot be followed by any quantum chemical method that accounts for dynamic electron correlation (which cannot be ignored when one compares localized and delocalized species!). Therefore, we are unable to provide a reliable prediction for the activation energy for the *cis*–*trans* interconversion of $2^{\bullet+}$, and we must content ourselves with an estimate of around 10 kcal/mol .

The question remains how *trans*- $2^{\bullet+}$ is formed from $1^{\bullet+}$. In experiments where Ar-matrices are exposed to X-irradiation, the ionization of added substrates occurs by charge transfer from $\text{Ar}^{\bullet+}$ (or, more precisely, $\text{Ar}_n^{\bullet+}$, because charge or spin are not localized on single Ar atoms in an Ar crystal), a process which is invariably quite exothermic. As Ar is a very poor heat conductor, the excess energy that is thus imparted on the incipient substrate cations is only hesitatingly dissipated, and is therefore available to surmount small activation barriers. The spontaneous ring-opening of $1^{\bullet+}$ endows nascent $2^{\bullet+}$ with an

additional eV of excess energy, and perhaps the two combined effects suffice to make it possible for a part of *cis*- $2^{\bullet+}$ to cross over to *trans*- $2^{\bullet+}$. However, we cannot exclude that *trans*- $2^{\bullet+}$ arises by a different mechanism, directly from $1^{\bullet+}$, as in the case of the radical cation of cyclobutene which undergoes a concerted ring-opening to yield the radical cation of *trans*-butadiene.⁹

CONCLUSION

We have generated the radical cation of cyclobutenedione, $1^{\bullet+}$, by X-irradiation of an Ar matrix containing **1**, and observed its spontaneous decay to the radical cation of bisketene $2^{\bullet+}$ (buta-1,3-diene-1,4-dione) which is in large part reneutralized to **2** by the electrons liberated by the X-irradiation of Ar. This allowed us to characterize for the first time parent **2** and its radical cation by matrix IR spectroscopy. The spectra, and the accompanying quantum chemical calculations, lead us to the conclusion that neutral **2** exists only in the form of a single conformer where the two ketene moieties are nearly perpendicular, whereas $2^{\bullet+}$ has two stable planar conformers, both of which are formed on ionization of **2**. According to high-level calculations the decay of $1^{\bullet+}$ to $2^{\bullet+}$ is virtually activationless, whereas the interconversion of the two conformers of $2^{\bullet+}$ involves a barrier that cannot be precisely calculated but is probably in the vicinity of 10 kcal/mol, because it involves a state crossing.

METHODS

Cyclobutenedione **1** was synthesized according to the procedure described in ref 2f.

For the matrix isolation experiments, **1** was mixed in a 1:1000 ratio with a 9:1 mixture of Ar and N₂ (where the latter is added to improve the optical quality of the matrices) in a 2000 mL storage vessel to a total pressure of 100 mbar, about half of which was deposited over ca. 1 h on a CsI window held at 20 K inside the cold head of a closed-cycle cryostat. After the deposition was complete, the heater of the cryostat was switched off, so the temperature of the matrix descended to 10 K. Photolysis was done with a low-pressure Hg lamp (254 nm) or a medium-pressure Hg/Xe lamp fitted with an interference filter (365 nm) or a cutoff filter (>515 nm). X-irradiation was effected by means of a source tube containing a tungsten anode that was operated at 40 kV/40 mA, which gives off Bremsstrahlung that under these conditions peaks at ca. 0.5 Å/2.5 keV. Under the impact of this radiation, electron-hole pairs form in the Ar matrix, a few of which separate and diffuse (in the form of polarons) through the solid until they are trapped by added substrates or impurities with a lower oxidation or reduction potential, respectively, than Ar.

Initially, we added an equivalent of methylene chloride to serve as electron scavenger,⁴ but it turned out that this did not make any difference so we assume that the electrons are scavenged either by **1** or by some impurities such as CO₂ (however, we found no evidence for the formation of $1^{\bullet-}$ or $2^{\bullet-}$). As the radical cations that are formed by hole trapping accumulate, they begin to contribute increasingly to the scavenging of electrons, until a steady state is attained (after ca. 90 min under our experimental conditions) where holes and electrons are scavenged at the same rate.

If the primary radical cations are chemically stable, longer X-irradiation leads to no further spectral changes, except for the slow formation of side products. If, however, the primary radical cations undergo fragmentation or rearrangement, the electrons will be scavenged by the secondary cations to yield rearranged or fragmented neutral species, as it is the case in the example shown in this paper. On continuing X-irradiation those species continue to accumulate past the point where the cation production has leveled off, and they may thus become much more prominent than the primary cations, as in the present case.

In the quantum chemical calculations, all structures (minima and transition states) were first optimized by the standard B3LYP/6-31G* method which also served to compute vibrational frequencies (which were scaled by 0.968 for neutrals and 0.960 for radical cations for comparison with experiment) and IR intensities. Subsequently, the structures were reoptimized and their energies were computed according to the G4 composite protocol¹⁰ which is expected to yield heats of formation to an accuracy of 0.65 kcal/mol, and probably even more accurate relative energies. All calculations were done with the Gaussian program suite,¹¹ the B3LYP and G4 energies are given in the Supporting Information.

An interesting problem occurred in the case of the C_{2h} structure of **2** that resides in a shallow minimum at the B3LYP level (which is also used to optimize structure within the G4 protocol, albeit with a much larger basis set), but where the transition state for its decay to the orthogonal equilibrium structure lies ca. 1 kcal/mol below the C_{2h} structure at the (empirically corrected) CCSD(T) level that is used in G4. This shows that such composite protocols should not be used blindly but with a measure of circumspection.

ASSOCIATED CONTENT

Supporting Information

Complete ref 11; results of B3LYP and G4 calculations for **1**, **2**, and their radical cations, including Cartesian coordinates for all stationary points. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: thomas.bally@unifr.ch.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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(7) A reviewer has suggested that these bands may be due to reaction of the ketenecarbene $\text{O}=\text{C}=\text{CH}-\ddot{\text{C}}-\text{H}$ that arises upon loss of CO from **2** (or its radical cation) with the 10% N_2 that we add to our matrices to improve their optical quality to form diazopropenone ($\text{O}=\text{C}=\text{CH}-\text{CH}=\text{N}=\text{N}$), which may have bands in the 2100–200 cm^{-1} region. Unfortunately, we have no way to confirm or reject this interesting hypothesis which we consider, however, improbable for various reasons.

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