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Photoinduced electron transfer reactions of chloranil with small-ring hydrocarbons. Contrasting reactivities of radical cation intermediates

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Abstract

Products that result from the irradiation of chloranil with phenylcyclopropane and with 1,2-diphenylcyclobutene in various solvents have been identified. The cyclopropane gave products that derive from nucleophilic attack on the small-ring radical cation that is formed on electron transfer quenching of the quinone excited triplet state. Contrastingly, the cyclobutene ring remains intact following an analogous radical cation formation, but undergoes an addition in which (formally) the quinone is added across an allylic C–H bond. The results are consistent with the formation of radical ion pairs (triplet excited complexes, TECs) consisting of quinone radical anions and cations associated with the small-ring derivatives. Intra-ion-pair proton transfer and radical (ion) coupling reactions account for observation of the various products. Different pathways for photolysis of quinone and small-ring hydrocarbons in more polar media involving formation of free-radical ions were also established. The quenching of quinone excited triplet states and the appearance and decay of TEC-type and other intermediates were followed by laser flash photolysis. © 1997 Elsevier Science S.A.

Keywords: Chloranil; Small-ring hydrocarbons; Laser flash photolysis; Photochemical electron transfer; Radical cation intermediates

1. Introduction

The fate of radical cations generated from small-ring hydrocarbons via photochemical electron transfer has been the focus of investigation for some years. Issues that have been of special interest are the role of these simple structures as one-electron donors (the amplification of their reducing capabilities due to ring strain and other factors) [1], the evidence for the existence of the small-ring radical ion and its lifetime as a discrete intermediate [2], and the identification of secondary reaction products for both ring-closed and ring-opened species [3]. A variety of techniques including ESR, NMR/CIDNP, flash photolysis and photoproduct analysis have been used to identify radical cation structures and reaction pathways for a variety of small-ring systems that include quadricyclane [4], Dewar benzenes [5], cyclopropanes [6] and methylenecyclopropanes [7]. Much of the context of this work is related to the general observations of enhanced reactivity (reduced kinetic and thermodynamic stability) for organic molecules upon the gain or loss of electrons, and the adoption of relatively efficient pathways of fragmentation, addition or electrophile/nucleophilic capture (for reviews, see [8]).

In our laboratories, the high potential quinone chloranil (Q) has been employed as a sensitizer for conducting reactions via radical cations generated from many different electron donors. The strongly oxidizing triplet excited state of Q can react at near-diffusion-limited rates with modest electron donors such as simple arenes (e.g. methylnaphthalenes), cyclopolyenes and arylmethanols [9]. Radical ion intermediates, detected by laser flash photolysis, are generated upon Q triplet quenching under a variety of conditions. With the use of a non-polar solvent such as benzene, discrete triplet radical ion pair species have been detected by laser flash photolysis. Often the fate of the ion-pair species can be followed by direct observation in the convenient time domain of several hundred nanoseconds. In particular, the primary steps leading to triplet excited complexes (TECs) and the secondary steps such as proton transfers that lead to free-radical intermediates can be time-resolved and individual rate constants obtained [9]. Important distinctions that have been made in these studies are that (1) discrete radical ion pairs

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can indeed be generated in solvents of very low polarity, (2) the ion pair intermediates thus formed are of the contact type and constitute the low-lying triplet states associated with the charge-transfer (CT) complexes of the quinone and donor (assumed 1:1 complexation stoichiometry) and (3) reactions within the triplet ion pair complexes, taking place on the time scale of about 100 ns, can be directly inspected. Other pathways of reaction that result from electron transfer quenching of triplet Q, using small-ring hydrocarbons as electron donors in polar solvents, have been also documented, including valence isomerization of quadricyclane (to norbornadiene) and the ring opening of hexamethyl (Dewar benzene) [4,5].

In the present paper we wish to report on the radical ion chemistry that is invoked on photolysis of Q in the presence of two small-ring compounds that offer different opportunities for reaction of their radical ions. The divergent pathways that have been identified involve, for phenylcyclopropane, formation of a novel adduct with Q having a spiro structure, and for 1,2-diphenylcyclobutene, another type of adduct that is the result of proton transfer and radical coupling via an ion pair intermediate. The results offer further insight into the chemistry of these classes of radical cations, namely the possibility of nucleophilic cleavage of one-electron bonds [10] (for the cyclopropane) and the competition between ring–chain isomerization [11] vs. other pathways of decay (for the cyclobutene series).

2. Experimental

Chloranil (Q) purchased from Aldrich was further purified by recrystallization from purified benzene followed by vacuum sublimation at 2.5 torr (at about 135 °C). The purified quinone gave rise to the characteristic shoulder in benzene (ε_{330} = 2200 M^{-1} cm^{-1}) [9](a). Tetrachlorohydroquinone (Aldrich) was purified by recrystallization from glacial acetic acid, followed by washing with distilled water, drying under vacuo and then vacuum sublimation. Baker HPLC grade benzene was purified by fractional distillation from P_2O_5, then stored over molecular sieves. Preparative irradiations were carried out using a Rayonet photochemical reactor with RUL-3500 lamps.

2.1. *Photoreaction of chloranil with phenylcyclopropane in chloroform*

A solution of phenylcyclopropane (603 mg, 5.10 mmol) and chloranil (1.20 g, 4.88 mmol) in 500 ml chloroform was irradiated at 350 nm for 3 h. Evaporation of solvent afforded a brown residue which was chromatographed on silica gel. Recrystallization of the primary fraction from chloroform and carbon tetrachloride provided colorless cubes, m.p. 160–161 °C. ^{1}H NMR (90 MHz, $CDCl_3$): δ 2.40 (1H, dddd), 3.07 (1H, dddd), 3.98 (1H, dd), 4.40 (1H, ddd) 4.63 (1H, ddd), 6.9–7.3 (5H, m). UV (acetonitrile): λ_{max} = 257.9 nm (ε = 11 060), 303 (sh, ε = 2530). MS (25 eV): 364 (1.0%, M^+), 329 (44), 327 (52), 118 (base), 117 (69). IR (KBr): 2990, 2900, 1681, 1610, 1576, 1451, 1259, 1150, 1114, 1101, 1010, 1003, 757, 723, 691. Anal. Calcd. for $C_{15}H_{10}O_2Cl_4$: C, 49.49%; H, 2.77%; Cl, 38.95%. Found: C, 49.69%; H, 2.65%; Cl, 38.82%.

2.2. *Photoreaction of chloranil with phenylcyclopropane in methanol*

A solution of phenylcyclopropane (601 mg, 5.08 mmol) and chloranil (1.2 g, 4.88 mmol) in 500 ml methanol was irradiated under nitrogen for 3 h at 350 nm. Evaporation gave a yellow residue which was chromatographed on silica gel, resulting in a single product fraction which after recrystallization from acetone was 1.155 g of colorless prisms, m.p. 132–133 °C. The pure material was identified as 3-methoxy-1-phenylpropyl 2,3,5,6-tetrachloro-4-hydroxyphenyl ether (**2**). ^{1}H NMR (90 MHz, $CDCl_3$): δ 2.22 (1H, ddt) 2.50 (1H, ddt) 3.20 (1H, ddd) 3.26 (3H, s), 3.46 (1H, td), 5.43 (1H, dd), 6.00 (1H, s), 7.4–7.4 (5H, m). UV (acetonitrile): λ_{max} = 210 (ε = 49 540), 303 (3390) 347 (970). IR (KBr): 3320, 2890, 1434, 1377, 1314, 1250, 1158, 1107, 958, 913, 900, 756, 696. MS (25 eV): 396 (M^+), 364, 248, 246, 149, 148, 131, 119, 117, 1056, 91, 45 (base). Anal. Calcd. for $C_{16}H_{14}O_3Cl_4$: C, 48.52%; H, 3.56%; Cl, 35.80%. Found: C, 48.43%; H, 3.64%; Cl, 35.61%.

2.3. *Preparation of 1,2-diphenylcyclobutene*

1,2-Diphenylcyclobutene was prepared by the method of Baumstark et al. [12]. White crystals were obtained in 80% yield, m.p. 52.2–52.90 °C, showing no impurities by TLC or HPLC analysis.

2.4. *Irradiation of 1,2-diphenylcyclobutene (DPC) with chloranil (Q)*

A solution of 1.2 g Q and 1.0 g DPC in 300 ml benzene was irradiated with 360 nm light from a Rayonet Photochemical reactor for 15 h. The course of the reaction was followed by TLC and HPLC. One main photoproduct was formed with several very small yield ones, one of which is the hydroquinone, QH_2. The main product was identified by evaporating the solvent and passing the residue through a short silica gel column followed by elution through a medium-pressure silica column, eluting with 17% ethyl acetate in hexane. The main fraction was recrystallized repeatedly from methanol to afford 0.20 g of purified material, m.p. 154.5–155 °C, identified as 1,2-diphenyl-3-(4-hydroxy-2,2,3,3-tetrachlorophenyl)cyclo-2-butene (**3**). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.006 (H4a, dd, 12.93, 3.93 Hz), 3.205 (H4b, d, 12.93 Hz), 5.679 (H3, d, 3.93 Hz), 5.864 (OH, broad multiplet), 7.24–7.36 (6H, m), 7.52–7.56 (4H, m), ^{13}C NMR (150 MHz, $CDCl_3$): 36.221 (C4), 75.948 (C3), 118.823 (3-Ph-4), 126.787 (1 or 2-Ph-2), 126.912 (1,2-Ph-2), 127.505 (3-Ph-

1), 127.866 (1,2-Ph-4), 128.212 (1,2-Ph-3), 128.424 (1,2-Ph-4), 128.934 (1,2-Ph-4), 133.504 (C2), 134.038 (C1), 145.643 (3-Ph-2 or 3), 145.778 (3-Ph-2 or 3). MS (70 eV): 454 (M + 2, 20.6%), 453 (M + 1, 11.0), 452 (M, 42.1), 451 (10.4), 450 (33.5), 417 (23.6), 415 (23.7), 207 (16.9), 206 (65.9), 205 (99.7), 204 (99.9), 203 (base), 202 (78.1). IR (KBr): 3390, 3010, 2940, 2905, 1436, 1383, 1318, 1276, 1200, 980, 892, 687. UV (MeOH): $\lambda_{max} = 296$ nm ($\varepsilon = 17\,700$). Anal: Calcd. for $C_{16}H_{12}O_2Cl_4$: C, 58.44%; H, 3.12%; Cl, 31.36%. Found: C, 58.27%; H, 3.22%; Cl, 31.14%.

2.5. *Laser flash photolysis*

The apparatus described elsewhere in detail [13] is comprised of a Quantel YG-581 Nd:YAG laser (with frequency doubling and tripling capability) interfaced with a LeCroy TR8818 100-megasample/sec digitizer along with an Apple Macintosh IIci computer. Other components include an Oriel 150-W xenon monitoring lamp, an Instruments SA H-20 monochromator with attached Kinetic Systems stepping-motor controller for computer controlled wavelength selection from 360 to 800 nm, and an RCA 4840 photomultiplier tube. Monitoring and laser beams were configured perpendicularly with a cell path length for the monitoring beam of 2 cm and that for the laser beam of 1 cm.

Each transient decay profile was averaged at least four times in order to improve the signal-to-noise ratio, and a set of transient decays at 10-nm wavelength intervals were collected to generate transient spectra. Each point in a spectrum of transient absorbance was generated by averaging 50–100 points around the specified time after the last pulse. All samples were photolyzed at room temperature using purified anhydrous benzene as solvent with argon sparging (usually 5 min ml^{-1}). Photoexcitation was carried out by irradiation of the chloranil absorption band (330 nm) using the third harmonic of the Nd:YAG laser (355 nm).

2.6. *Formation constants for charge-transfer complexes*

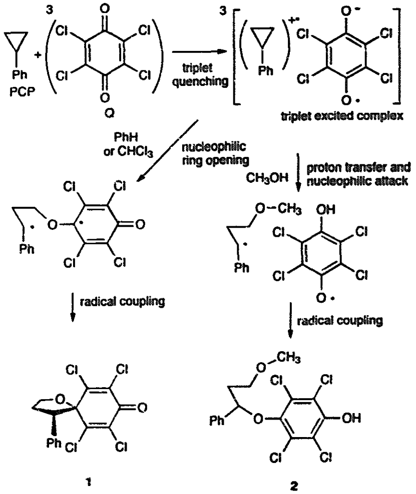
For hydrocarbon electron donors, ground state association with chloranil was detected in terms of long wavelength absorption bands which were not ascribable to the sum of spectra for Q and donor (see Fig. 4). Association constants, K_{ct}, and extinction coefficients for the complexes, ε_{ct}, could be obtained using the Benesi–Hildebrand spectrophotometric method [14]. The change in optical density CT absorption band maxima (ΔOD) was recorded for dilute Q solutions with added excess donor. Analysis of the slopes and intercepts of plots of [Q]/ΔOD vs. 1/[donor] ($r > 0.995$) gave values of K_{ct} and ε_{ct} (Table 1).

3. Results

When a benzene solution of phenylcyclopropane (PCP) and chloranil (Q) was irradiated at 350 nm on a preparative scale, an addition reaction took place, yielding the spiro structure **1** indicated in Scheme 1. The product was isolated as a crystalline solid, purified by recrystallization, and characterized by NMR and other spectral data. Although the chemical yield of **1** was high (86%), the quantum efficiency for this process was rather low (0.069). The quantum yield was enhanced (0.30) by using chloroform as solvent, while the chemical yield remained high (80%). Laser flash photolysis experiments were carried out for Q and the potential electron donor PCP, using the frequency-tripled output of a Nd/YAG laser (355 nm, typically 80 mJ per 7 ns pulse) and the detection system described previously [15]. Flash excitation of Q, alone in chloroform solvent, led to formation of the triplet transient with $\lambda_{max} = 510$ nm that has been previously identified [9]. On similar irradiation of 0.49 mM Q in the presence of 3.3 mM PCP in chloroform, the transient spectrum was altered, displaying peaks at 520 and 450 nm. The phototransient features were identified as the radical cation of phenylcyclopropane [16] and the radical anion of chloranil [9](b) respectively. The two transients decayed with similar time constants, obeying first-order kinetics. The transients

Table 1
Data for charge-transfer complexation of chloranil and hydrocarbon donors in acetonitrile

Substrate	ε/M^{-1} cm^{-1}	K/M^{-1}	λ_{max}/nm
DPC	91	4.2	500 sh
trans-Stilbene	1250	0.92	500



Scheme 1.

were assumed to comprise a contact triplet radical ion pair (a TEC intermediate, note Scheme 1) [9]; a lifetime for this triplet excited complex was obtained (τ = 220 ns for the decay monitored at 520 nm).

In contrast, the formation of the spiro adduct **1** was not detected on irradiation of phenylcyclopropane in methanol. Instead, there was a clean conversion yielding structure **2** that incorporates the starting materials and a molecule of methanol (isolated in 57% yield). With acetonitrile solvent neither of these products was detected, but intractable material was obtained. Laser flash experiments in which PCP was irradiated in methanol or acetonitrile revealed weak absorption at 520 and 450 nm, again associated with the cyclopropane and Q radical ions, respectively. The observations are consistent with the quenching of Q triplets by electron transfer and formation of radical ion pair intermediates, observable only during the laser flash, whose lifetime is consequently shorter than the detection limits of the instrumentation. The initial weak transient evolved into a secondary transient absorbing at 430 nm identified as the chloranil semiquinone radical [9](b,c) that decayed very slowly (microsecond time domain) by second-order kinetics. The results for photolysis of PCP in polar media were consistent with electron transfer quenching of Q triplets giving rise to radical ion pairs that decay predominantly by charge recombination. Free-radical ions that escape solvent cages are subject to several secondary decay steps, including capture by solvent and radical coupling, a pattern of behavior shown previously for several types of donors on photolysis in the presence of Q [9].

Irradiation of a benzene solution of 1,2-diphenylcyclobutene (DPC) and chloranil proceeds inefficiently (Φ = 0.025), but rather cleanly, to give a single photoproduct that is a one-to-one adduct having the structure **3**, 1,2-diphenyl-3-(2,3,5,6-tetrachloro-4-hydoxyphenyl)cyclobutene, with a few other unidentified products in very low yield. The source of the quantum inefficiency was shown not to involve a lack of reactivity of the excited state of chloranil with ground state DPC. Laser flash photolysis experiments revealed that the quinone triplet (λ_{max} = 510 nm) is quenched near the diffusion-controlled limit.

For moderately high concentrations of DPC (benzene solvent), the flash experiment revealed that the Q triplet transient at 510 nm was replaced by a broad absorption that appeared to have a component at 510 nm in early time domains but dominated by absorption peaking at about 450 and 480 nm (Fig. 1). These latter features were assigned again to the chloranil radical anion (λ_{max} = 450 nm) and the anticipated absorption due to the cyclobutene radical cation (by analogy to the spectrum of the *cis*-stilbene cation, with λ_{max} = 508 nm in acetonitrile [17]). The composite 450/480 nm transient observed on flash photolysis of the Q/DPC pair in a solvent of low polarity was assumed to be another intermediate of the TEC-type [9](b). In the time domain of several hundred nanoseconds, the absorption region of 440–500 nm decayed in a relatively uniform fashion. A lifetime for this species was obtained by monitoring the first-order decay of the transient at 480 nm (τ = 150 ns) (Fig. 2).

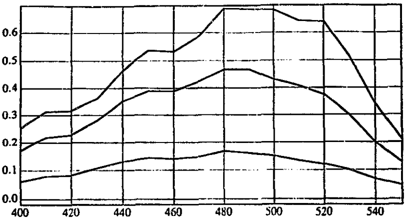


Fig. 1. Phototransient spectra for solution of 0.81 mM DPC and 0.52 mM Q in benzene irradiated at 355 nm. From the top the curves represent the change in absorbance vs. wavelength in nm at 74 ns after the flash followed by 148 and 297 ns.

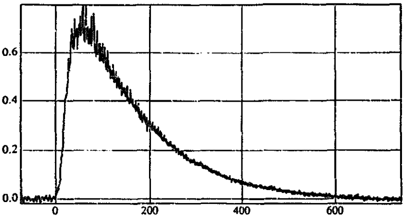


Fig. 2. The decay curve for the transient monitored at 500 nm for the flash experiment shown in Fig. 1.

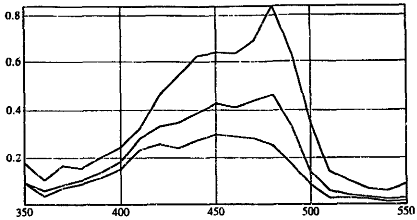


Fig. 3. Phototransient spectra for solution of 3.88 mM DPC and 0.36 mM Q in acetonitrile irradiated at 355 nm. From the top the curves represent the change in absorbance vs. wavelength in nm at 200 ns after the flash followed by 3 and 6 μs.

The radical ion intermediates could also be obtained on flash photolysis of Q in the presence of DPC in acetonitrile. As shown in Fig. 3, a somewhat more distinct series of bands could be discerned assignable as before to DPC$^{+\bullet}$ (λ_{max} = 480 nm), Q$^{-\bullet}$ (λ_{max} = 450 nm) (and probably including, at longer time frames, the quinone species, QH$^{\bullet}$, with λ_{max} = 430 nm as previously reported [9](a)). Notably, the phototransients observed on photolysis of Q and DPC in the polar solvent correspond to free-radical ions, since they appear at delay times well past 1 μs ($\tau_{1/2} \approx 3.5$ μs at 480 nm), much longer than the decay times of contact ion pairs

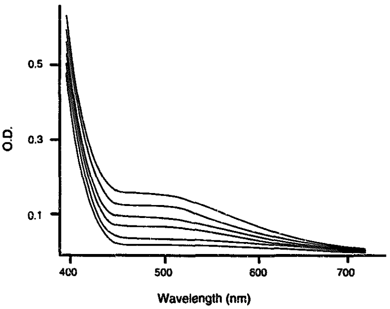


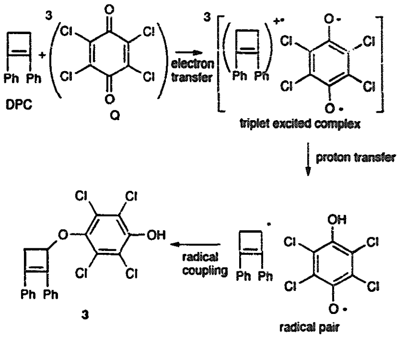
Fig. 4. Absorption spectra obtained for chloranil (Q) (5.1 mM) in the presence of DPC (0–0.156 M) in acetonitrile.

(TEC intermediates) that are generated in a non-polar medium [9].

In accord with prior reports [9] regarding combination of Q with electron donors, addition of DPC to solutions of the quinone led to formation of a ground state charge-transfer complex. For observation of CT absorption as a resolved band (or a shoulder) absorbing in the visible, high concentrations of DPC (up to 0.156 M, acetonitrile solvent) were required (Fig. 4). The CT absorption data were subjected to a Benesi–Hildebrand analysis [12] (absorbance monitored at 500 nm as a function of DPC concentration, and assuming a 1:1 stoichiometry for Q/DPC complexation) that provided an equilibrium constant (K) and extinction coefficient (ε) for CT absorption (Table 1). Data were also obtained for comparison, regarding complexation of Q with other model "diaryl alkenes". The complexation constant for Q/DPC was similar to that obtained for *trans*-stilbene; values in the range of $K = 0.6–3.2\ M^{-1}$ have been previously reported for complexation of Q and condensed ring aromatic hydrocarbons in chloroform solvent [18]. Steady irradiation of the CT complex (combinations of Q and DPC at high concentration in CH_3CN or C_6H_6) resulted in no net photochemical change, under circumstances in which the principal absorber is not the uncomplexed quinone. These results are consistent with a documented mechanism for photoexcitation of ground state complexes that involves formation of a singlet radical ion pair (the CT excited species) and subsequent decay via return electron transfer in the singlet manifold [9,19].

4. Discussion

The mechanisms proposed for photoreactions of chloranil and the small-ring electron donors are outlined in Schemes 1 and 2. The key features include formation of the chloranil triplet after photoexcitation, followed by electron transfer yielding a triplet excited complex. Cyclopropane radical cations derived from chloranil by irradiation have been characterized by CIDNP techniques [20]. The reaction anticipated



Scheme 2.

for PCP$^{+\bullet}$ is attack on the intact ring system by nucleophiles [6]. For situations in which the nonpolar solvents benzene and chloroform are employed, this nucleophile is the radical anion and the result is cycloaddition to form **1**. Methanol provides the presumed nucleophile when it is the solvent and results in its incorporation in the alternative product **2** as observed by others [3](a)[21].

Cyclobutene radical cations are known to isomerize to butadiene radical cations [3,22]. The DPC radical cation of this study is given enough time to rearrange (at least several hundreds of nanoseconds). Nonetheless, products associated with ring opening have not been isolated and phototransients have been assigned without resort to invocation of ring-opened intermediates (the λ_{max} for the relevant butadiene cation would be expected around 410 nm [11]). These results are similar to those of Kawamura et al. [11] for 1,2-diphenyl-3,3,4,4,-tetramethylcyclobutene. Apparently, the substitution pattern of the cyclobutene becomes the crucial factor as to whether rearrangement occurs or not. In the case of DPC the diene product would have the phenyl groups at the internal diene positions where they will only minimally stabilize the diene cation radical. Thus the rearrangement may not occur because it is endoergonic.

Another feature that is especially noteworthy in this system is the very slow proton transfer step that is observed under circumstances in which a proton adjacent to a charge site in the radical cation of a TEC intermediate is available to delivery to the quinone counter radical anion. For the reported chloranil reactions with arenes [9](a,b), the rate of proton transfer is relatively high (about $10^6\ s^{-1}$) resulting in the appearance of free radicals associated with the electron donor (formally, the loss of hydrogen atom at benzyl positions). Such radicals are not observable in the present case, even though they are indicated as precursors to the final products. Since proton transfer does not compete effectively with back electron transfer, the concentrations of these radicals remains low. This slow proton transfer may be associated with the greater p character for CH bonds associated with strained small rings [1]. The alternative decay of the Q/DPC TEC intermediate via return electron transfer (triplet recombination, in lieu of proton transfer) occurs with a rate constant (6.6×10^6 s^{-1}) similar to that reported for other triplet excited complexes [9](a).

The sharply contrasting behavior of the cyclopropane system and the cyclobutene system observed in this series of experiments may be a reflection of intrinsic differences in the nature of the radical cations as previously characterized [16,23]: cyclopropane is a σ type, while the cyclobutene is primarily a π type. In the π type the electron deficiency in the π bonds gives rise to characteristic chemical behavior such as cis–trans isomerization. The σ type, also referred to as a one-electron bond, exhibits nucleophilic addition and single bond cleavage [16].

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