Cycloreversion of Formylcyclobutane Radical Anion: Two-Step Rotating Mechanism

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The [2+2] cycloreversion reaction of formylcyclobutane radical anion (c-C_4H_7-$CHO^{\bullet-}$) has been investigated at the UB3LYP level with the augmented Dunning's correlation-consistent polarized valence double-ζ basis set supplied with four even-tempered sp shells. Very diffuse p$-\pi$*-like singly occupied orbitals (SOMO) are found for the c-C_4H_7-$CHO^{\bullet-}$ and product $CH_2CHCHO^{\bullet-}$ radical anions, necessitating the use of a rather diffuse basis set for mechanistic study. The respective electron affinities of c-C_4H_7-CHO and CH_2CHCHO are calculated to be 5.4 and 16.1 kcal/mol, showing the ability to bind an extra electron. The intermediate structure $^{\bullet}(CH_2)_3CHCHO^-$ is found to be a valence-bound distonic anion apt to the elimination of C_2H_4. The present two-step "rotating" cycloreversion mechanism for c-C_4H_7-$CHO^{\bullet-}$ is formally similar to the biradical one for neutral cyclobutane structures, but with evidently lower potential barrier. For efficient electron-attachment catalysis, the extra electron should be trapped by suitable functional groups in some orbitals with substantial overlap with the σ*-orbitals of the cyclobutane structure.

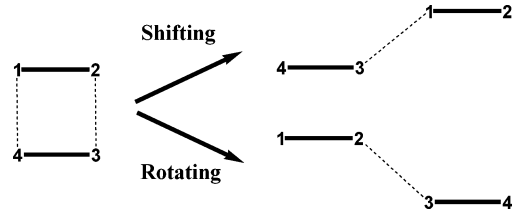
1. Introduction

The [2+2] cycloreversion reactions of cyclobutane derivatives are of both fundamental and practical importance in DNA photoenzymic repair,[1,2] photochemical energy storage,[3] and organic syntheses.[4] From the theoretical point of view, such reactions should be thermochemically forbidden (with large activation barrier) but photochemically allowed according to the Woodward−Hoffmann rules.[5] Indeed, the simplest cycloreversion of cyclobutane (c-C_4H_8) may occur via the stepwise biradical mechanism[6,7] over high activation barriers of 62.5 kcal/mol.[8] On the other hand, photochemical cycloreversion can only be practicable for some cyclobutane structures with efficient chromophore.

To overcome such problems for the cycloreversion of cyclobutane structures, the electron-transfer catalysis has been long postulated, especially for radical cation pericyclic reactions because of their abilities to form and cleave C−C bonds.[9−12] The radical cation reactions of quadricyclane,[13] pagodane,[14] and cyclobutane pyrimidine dimers[15,16] have also attracted considerable interest. Both the "shifting"[17,18] and "rotating"[19] cycloreversion mechanisms (Scheme 1) have been suggested for some simple cyclobutane radical cations such as c-$C_4H_8^{\bullet+}$. However, side reactions such as the intramolecular hydrogen migration of highly reactive radical cations can also occur in addition to the expected [2+2] ring cleavage.[19]

In contrast, very little is known about the corresponding radical anion pericyclic reactions of cyclobutane derivatives. We can find only two examples for such a radical anion process in the literatures. The first example is the electrolysis of dithymoquinone (TQ_2), a quinone cyclobutane dimer, resulting in its cleavage to the monomeric quinone with a rate constant

SCHEME 1



of 3.0 s^{-1}.[20] The experimental results have been interpreted by the mechanism of one-electron reduction of TQ_2 followed by ring cleavage of the $TQ_2^{\bullet-}$ radical anion, but it seems that further study is still required to verify this mechanism and to make clear if the distonic radical anion intermediate is involved. The second example is the photoenzymic catalytic repair of DNA cyclobutane pyrimidine dimers, which has been extensively examined.[21] Such a reaction may be initiated by electron transfer from the enzyme to the dimer substrate[22] with rate constants in excess of 10^6 s^{-1}.[23] The stepwise, as well as concerted, cycloreversion mechanism with the first C−C bond cleavage as part of the rate-determining step has been suggested by previous experimental data.[22,24,25] Recent calculations[26,27] based on AM1 and HF/6-31G(d) optimization have found both the initial ring opening and the subsequent dissociation transition structures for the splitting of radical anions of pyrimidine cyclobutane dimers; however, the ring-opening transition structure disappears at higher MP2/6-31G(d)//HF/6-31G(d) and B3LYP/6-31+G(d) levels,[27,28] suggesting the one-step splitting mechanism. As will be demonstrated below, rather diffuse basis sets are required for a reliable description of such radical anions systems, and thus the contradictions between these studies[26−28] and experiments[22,24,25] should be due to the insufficiency of the used basis sets.

Very recently, we have performed a B3LYP/6-31++G(d,p) investigation on the cycloreversion of the idealized c-$C_4H_8^{\bullet-}$ model system.[29] Interestingly, the two-step "rotating" cyclo-

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reversion mechanism involving the distonic $^{\bullet}CH_2CH_2CH_2CH_2^-$ tetramethylene radical anion intermediate has been found, with the cycloreversion barrier slightly lower by about 8 kcal/mol than the corresponding biradical one for neutral *c*-C_4H_8. However, the *c*-$C_4H_8^{\bullet -}$ radical anion is unstable with respect to electron detachment.[29] Therefore, it is still of interest to determine the detailed mechanism for radical anion cycloreversion of cyclobutane derivatives and its efficiency for electron-attachment catalysis. In the present study, we have chosen the radical anion of polar formylcyclobutane (*c*-C_4H_7-$CHO^{\bullet -}$) as a model system for three practical reasons. First, the polar *c*-C_4H_7-CHO molecule with high dipole moment (~3.3 D) larger than 2.5 D should be able to trap an extra electron in the dipole- or valence-bound state.[30] Second, this molecule closely resembles the crucial cyclobutane structures of the cyclobutane pyrimidine dimer and thus can be used to study the role of functional substituent groups on the radical anion mechanism. Third, for the present relatively small system, detailed theoretical calculations with sufficiently diffuse basis sets required for radical anions (especially for the possible dipole-bound state)[31] should be applicable.

2. Computational Methods

The GAUSSIAN 98 program package[32] was used for all calculations. To obtain reliable electron affinities of the closed-shell *c*-C_4H_7-CHO and CH_2CHCHO molecules and to describe possible dipole-bound intermediates, normal valence basis sets (such as 6-31G) should be augmented with extra diffuse sets designed to reliably describe the distribution of the extra electron.[31] Considering the range and direction of dipole moments of these molecules, we have chosen the recommended basis set[31] consisting of the aug-cc-pVDZ[33] supplied with four even-tempered sp shells centered on the α-carbon atoms with exponents 0.005, 0.001, 0.0002, and 0.00004 (labeled as aug-cc-pVDZ+4(sp) latter on). To describe the electron-attachment and cycloreversion processes consistently and accurately, size-extensive correlated methods should be used. The highly correlated CCSD(T)[35,36] method with this rather diffuse basis set is computationally too demanding for the present $[C_5H_8O]^{\bullet -}$ systems. Fortunately, the hybrid density functional theory (DFT)[37−39] B3LYP methods are computationally not very demanding in giving accurate structures and energies comparable with the MP2[34] and CCSD(T) methods but with relatively smaller spin contaminations on open-shell systems.[40,41]

In the present study, all relevant structures are fully optimized at the UB3LYP/aug-cc-pVDZ+4(sp) level. Both the tight SCF convergence threshold and the quadratic convergence method[42] are shown to be useful in dealing with the convergence difficulty encountered for calculations with very diffuse functions. Harmonic frequencies are further calculated to verify whether they are true minima or transition structure (without and with only one imaginary frequency, respectively) and to give zero-point vibrational energy (ZPVE) corrections. Intrinsic reaction coordinate (IRC)[43] calculations are carried out to determine the relationship between transition structures and minima. The atomic charges and spin densities are calculated according to the Mulliken population analysis scheme. Indeed, rather small spin contaminations are observed for radical anions as reflected by the spin-squared expectation values ($\langle S^2 \rangle$ within 0.75−0.77 compared to the ideal value of 0.75). Unless specified otherwise, the fully optimized geometries and ZPVE-corrected energies (RE_0) are used in the following discussions.

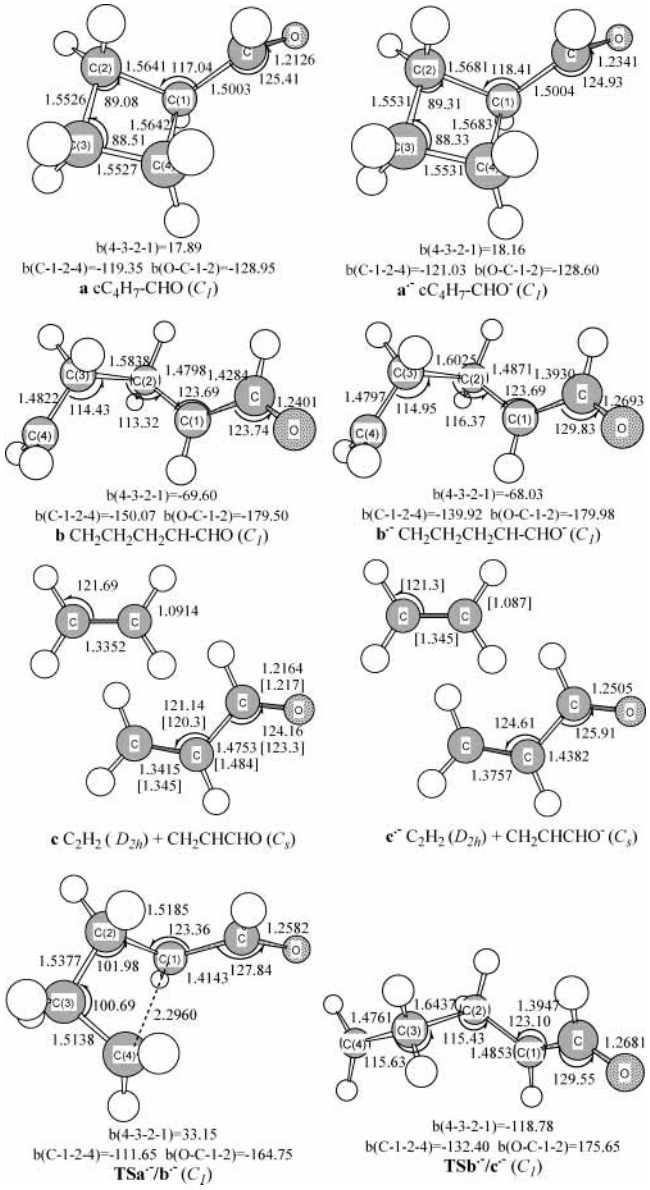

Figure 1. The UB3LYP/aug-cc-pVDZ+4(sp) optimized geometries. The bond lengths are in angstroms and bond angles in degrees, with some available experimental data in brackets for comparison.

3. Results and Discussions

The optimized geometries of all involved structures are shown in Figure 1. The calculated $\langle S^2 \rangle$, ZPVE, total energies, and relative energies are collected in Table 1. The detailed Cartesian coordinates and the harmonic frequencies (as well as infrared intensities) of all fully optimize structures are given in the Supporting Information for clarity. The frontier molecular orbitals of some important intermediates are given in Figure 2. Finally, the schematic reaction profiles for the cycloreversion of *c*-C_4H_7-$CHO^{\bullet -}$ are depicted in Figure 3.

As shown in Figure 1, the B3LYP-calculated geometries for the closed-shell molecules of acrolein CH_2CHCHO (C_s) and ethylene C_2H_4 (D_{2h}) are very close to the experimental values[44] within 0.01 Å and 1°. Though no experimental geometries are available for the closed-shell structure **a** (*c*-C_4H_7-CHO (C_1)), our B3LYP calculations shows that it has near-planar symmetry along the equatorial formyl group nearly perpendicular to the cyclobutyl ring, with its cyclic C−C single bond lengths being very close to the experimental values (1.555 Å) for cyclobutane[44]

TABLE 1: The UB3LYP/aug-cc-pVDZ+4(sp) Calculated Spin-Squared Expectation Value ($\langle S^2 \rangle$), Total Energies (TE_e, in hartrees), Zero-Point Vibrational Energies (ZPVE, in hartrees), Total Energies with ZPVE (TE_0, in hartrees), and Relative Energies with ZPVE Corrections (RE_0, in kcal/mol)[a]

species	$\langle S^2 \rangle$	TE_e	ZPVE	TE_0	RE_0
a$^{\bullet-}$ (*c*-C_4H_7-$CHO^{\bullet-}$)	0.75	−270.571863	0.117648	−270.454215	−5.4
b$^{\bullet-}$ ($^{\bullet}(CH_2)_3CHCHO^-$)	0.76	−270.549657	0.111520	−270.438136	+4.7
c$^{\bullet-}$ ($C_2H_4 + CH_2CHCHO^{\bullet-}$)	0.75	−270.562714	0.109657	−270.453058	−4.7
TSa$^{\bullet-}$/**b**$^{\bullet-}$	0.77	−270.539187	0.112602	−270.426585	+11.9
TSb$^{\bullet-}$/**c**$^{\bullet-}$	0.76	−270.546331	0.111339	−270.434992	+6.6
a (*c*-C_4H_7-CHO)	0.00	−270.564860	0.119295	−270.445565	0.0
b ($^{\bullet}(CH_2)_3CHCHO^{\bullet}$)	0.97	−270.487269	0.112750	−270.374519	+44.6
		[−270.485188]			[+45.9]
c ($C_2H_4 + CH_2CHCHO$)	0.00	−270.539283	0.111939	−270.427343	+11.4

[a] The energies for triplet structure $^{\bullet}(CH_2)_3CHCHO^{\bullet}$ are indicated in brackets.

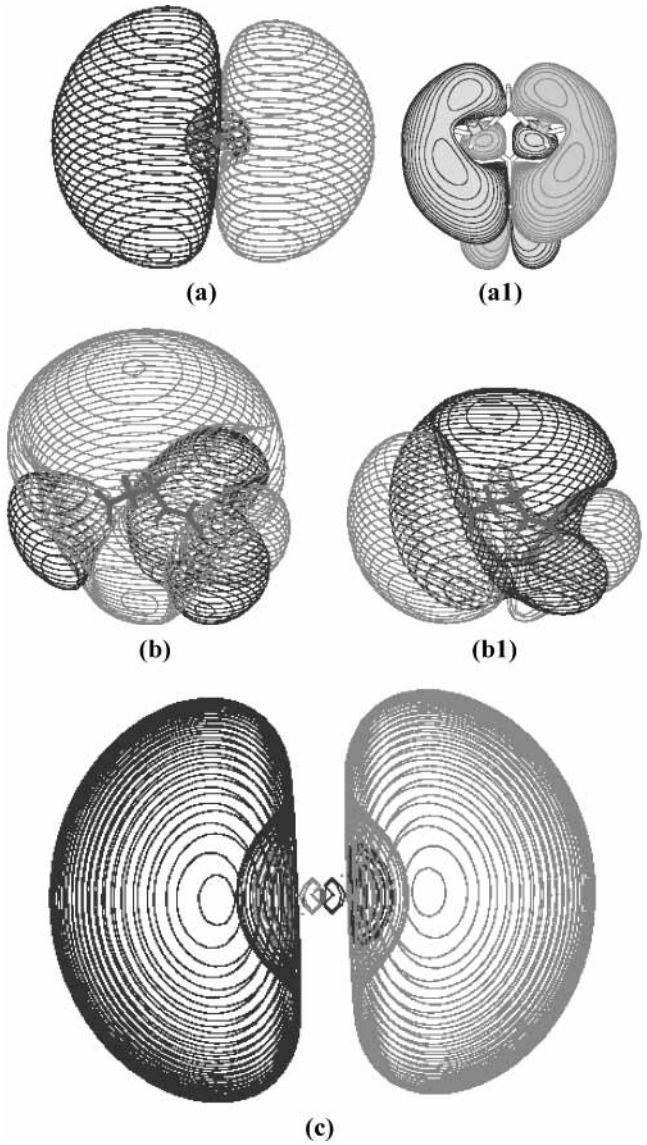

Figure 2. (a) The SOMO of *c*-C_4H_7-$CHO^{\bullet-}$ under and above the butyl ring at the 0.00008 contour surface; (a1) The SOMO of *c*-C_4H_7-$CHO^{\bullet-}$ at the 0.006 contour surface enlarged 15 times; (b) the highest doubly occupied orbital of $^{\bullet}(CH_2)_3CHCHO^-$ at the 0.00008 contour surface enlarged 15 times; (b1) the third SOMO of $^{\bullet}(CH_2)_3CHCHO^-$ at the 0.00008 contour surface enlarged 15 times; and (c) the SOMO of $CH_2CHCHO^{\bullet-}$ under and above the molecular plane at the 0.00008 contour surface. For parts a1, b, and b1 the molecular skeletons are also shown.

within 0.01 Å. The calculated dipole moments for *c*-C_4H_7-CHO and CH_2CHCHO are 3.3 and 3.4 D, respectively, with the latter being close to the experimental value of 3.12 D.[44] These dipole

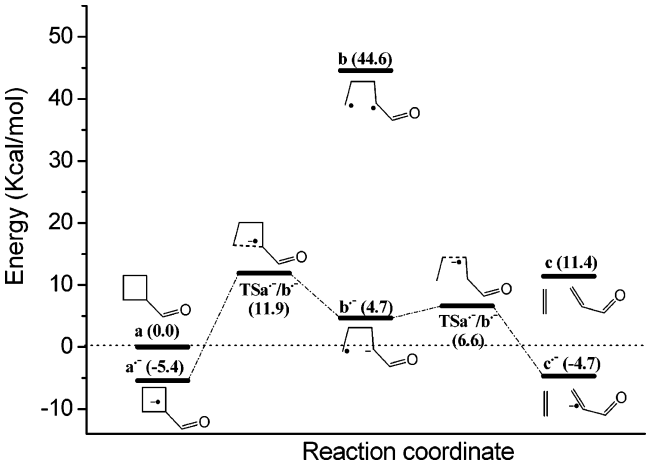

Figure 3. The schematic reaction profiles for the cycloreversion reactions of the *c*-C_4H_7-$CHO^{\bullet-}$ radical anion at the UB3LYP/aug-cc-pVDZ+4(sp) level with the ZPVE corrections.

moment values are evidently larger than the threshold of 2.5 D for the formation of dipole-bound anion.[30]

It is well-known that some polar molecules can bind an extra electron to form both dipole-bound and valence anions,[46] with the former providing an efficient "doorway" for the formation of the latter.[47−49] Generally, the dipole-bound electron occupies an extremely diffuse orbital on the positive end of electrostatic dipole potential with rather smaller binding energies. As a prototypical example, the experimental electron affinities (EA) are about 0.3 and 6.0 kcal/mol, respectively, for the respective dipole-bound and valence anion states of nitromethane CH_3-NO_2 (∼3.5 D).[49] Though some aromatic aldehyde radical anions such as *c*-C_6H_5-$CHO^{\bullet-}$, *c*-C_4H_4O-$CHO^{\bullet-}$, and *c*-C_4H_4S-$CHO^{\bullet-}$ have been observed by the ESR technique,[50] it is still of interest to make clear the nature of some aliphatic aldehyde radical anions as those of *c*-C_4H_7-CHO and CH_2CHCHO molecules with dipole moments larger than 2.5 D.

As shown in Figure 1, the optimized geometries of radical anion **a**$^{\bullet-}$ (*c*-C_4H_7-$CHO^{\bullet-}$ (C_1)) are very close to those of neutral **a** (*c*-C_4H_7-CHO (C_1)) within 0.004 Å and 1° except for the longer C═O bond (by ∼0.02 Å) of the former. Such structural change can also be reflected by the evidently reduced (by ∼171 cm^{-1}) C═O stretching frequency (1612 cm^{-1}) of **a**$^{\bullet-}$, while the remaining vibration frequencies are only 10−40 cm^{-1} lower than those of structure **a**. The highest SOMO of radical anion **a**$^{\bullet-}$ is rather diffuse (see Figure 2a) with the respective populations on the four even-tempered sp shells being 0.009, 0.088, 0.792, and 0.006, suggesting enough diffuse shells for this structure. This orbital resides mainly under and above the plane of the cyclobutyl group (see Figure 2a) but still shows extensive overlapping with the σ^*-orbitals of the cyclic C−C

bonds (see Figure 2a1). Such π-shaped SOMO is obviously different from the spherically shaped ones of normal dipole-bound anions such as $H_2O{\cdot}NH_3^{\bullet-}$ and $CH_3CN^{\bullet-}$.[31] The calculated EA value (5.4 kcal/mol) of $\mathbf{a}^{\bullet-}$ is too large to be accounted for only by the weak dipole−electron interaction that should be less than 0.3 kcal/mol considering the dipole moment 3.3 D of *c*-C_4H_7-CHO. These results suggest that the *c*-C_4H_7-$CHO^{\bullet-}$ radical anion possesses both dipole-bound and valence nature, and it require very diffuse basis sets for a reliable description.

Very similar results can also be found for the $CH_2CHCHO^{\bullet-}$ (C_s) product radical anion. It shows large geometry differences from its neutral partner CH_2=CHCHO (C_s) especially for its C=O bond length elongated by 0.034 Å due to the interconversion between possible resonance structures CH_2=CH−$CHO^{\bullet-}$ ↔ $^{\bullet}CH_2$−CH=CHO^{-}. Such structural features of $CH_2CHCHO^{\bullet-}$ can also be reflected by its evidently reduced (by 165 cm^{-1}) C=O stretching frequency (1595 cm^{-1}). The highest SOMO of $CH_2CHCHO^{\bullet-}$ (see Figure 2c) resides under and above the molecular plane, and is even more diffuse than that of structure $\mathbf{a}^{\bullet-}$ (*c*-C_4H_7−$CHO^{\bullet-}$), with the respective populations on the four even-tempered sp shells being 0.003, 0.006, 0.083, and 0.553. The large population (0.553) on the most diffuse sp shell suggests that an even larger basis set is needed for $CH_2CHCHO^{\bullet-}$, though it is enough for neutral CH_2-CHCHO. Thus, the calculated EA (16.1 kcal/mol) value will be slightly increased by extending the basis set due to a better description of the negative system.[31] The EA of $CH_2CHCHO^{\bullet-}$ is 10.7 kcal/mol higher than that of *c*-C_4H_7-$CHO^{\bullet-}$, which may be due to the lack of resonance structures for the latter. These results confirm again the role of using a very diffuse basis set in the present mechanistic study involving radical anions.

The acyclic structure $\mathbf{b}^{\bullet-}$ ($^{\bullet}(CH_2)_3CHCHO^{\bullet-}$ (C_1)) shows an interesting distonic radical anion structure. This structure is obviously a valence-bound anion with the highest orbital being the doubly occupied π*-orbital on the CHCHO$^{\bullet}$ moiety (see Figure 2b) with the third highest orbital being the singly occupied p orbital on the end carbon atom SOMO (Figure 2b1). These orbitals with their total populations on four even-tempered sp shells less than 0.00003 are evidently more compact than the SOMO's of *c*-C_4H_7-$CHO^{\bullet-}$ and $CH_2CHCHO^{\bullet-}$. The C=O bond of $\mathbf{b}^{\bullet-}$ is evidently longer than those of *c*-C_4H_7-$CHO^{\bullet-}$, as reflected by a smaller C=O stretching frequency (1607 cm^{-1}). Note that the structure $\mathbf{b}^{\bullet-}$ might dissociate easily into CH_2-CH_2 and $CH_2CHCHO^{\bullet-}$ due to the rather weak $^{\bullet}CH_2CH_2\cdots CH_2$-$CHCHO^{-}$ bonding (1.6025 Å) as the result of the electronic effects of the adjacent electron-withdrawing radical and the electron-donating anion centers.

To approximately estimate the EA of structure $\mathbf{b}^{\bullet-}$ and the cycloreversion barrier of neutral formylcyclobutane *c*-C_4H_7-CHO, we have also optimized the neutral acyclic structure **b** ($^{\bullet}(CH_2)_3CHCHO^{-}$ (C_1)) (see Figure 1) at the B3LYP level. The optimized geometries are very similar to those of $\mathbf{b}^{\bullet-}$ but with shorter C=O and CH_2CH_2−CH_2CHCHO bonds. Of course, the accurate treatment on singlet (but not triplet) biradicals should require correlated multiconfiguration methods such as MRCI. However, such a method with very diffuse basis set is computationally too demanding for the present system. Fortunately, structure **b** is a distonic structure with only weak coupling between two distant radical centers. The $\langle S^2\rangle$ value for intermediate **b** is 0.97 (Table 1), suggesting a spin contamination of about 50% from the first triplet state if it is assumed that only this state has a contribution. Within the same assumption, the energy of structure **b** should have been overestimated[45] by 1.3 kcal/mol and its singlet−triplet splitting is only 2.6 kcal/mol. By considering the spin contamination, the EA value of singlet **b** is estimated to be 38.6 kcal/mol while the cycloreversion barrier for *c*-C_4H_7-CHO is about 43.3 kcal/mol.

We now discuss the cycloreversion mechanism of radical anion $\mathbf{a}^{\bullet-}$ (*c*-C_4H_7-$CHO^{\bullet-}$). Though both the "shifting" and the "rotating" cycloreversion mechanisms[17−19] for radical cation *c*-$C_4H_8^{\bullet+}$ may also be suggested for radical anion $\mathbf{a}^{\bullet-}$, the former should involve a rather high barrier as shown in our previous calculations on *c*-$C_4H_8^{\bullet-}$.[29] Since the ring structure of *c*-C_4H_7-CHO is almost unperturbed upon electron attachment, the cycloreversion of $\mathbf{a}^{\bullet-}$ should involve a stepwise mechanism similar to the biradical one for neutral cyclobutane.[6,7] Indeed, the ring-opening transition structure $\mathbf{TSa}^{\bullet-}/\mathbf{b}^{\bullet-}$ for *c*-C_4H_7-$CHO^{\bullet-}$ is located at one long C−C bond length of 2.296 Å adjacent to the formyl group, with the ($\mathbf{a}^{\bullet-} \rightarrow \mathbf{b}^{\bullet-}$) barrier being only 17.3 kcal/mol. Further dissociation of intermediate $\mathbf{b}^{\bullet-}$ ($^{\bullet}(CH_2)_3CHCHO^{-}$) may occur via the weak $^{\bullet}CH_2CH_2\cdots CH_2$-$CHCHO^{-}$ bonding into $\mathbf{c}^{\bullet-}$ ($CH_2CHCHO^{\bullet-} + C_2H_4$), which is rather easy with a barrier of only 2.0 kcal/mol. Obviously, the two-step "rotating" cycloreversion mechanism is involved for *c*-C_4H_7-$CHO^{\bullet-}$, with the rate-determining step being the initial ring-opening process over a barrier of 17.3 kcal/mol.

It is interesting that the cycloreversion mechanism for radical anion $\mathbf{a}^{\bullet-}$ (*c*-C_4H_7-$CHO^{\bullet-}$) formally resembles the biradical ones[6,7] for neutral cyclobutane but with a much lower potential barrier (44.6 vs 17.3 kcal/mol) as shown in Figure 3. Similar observations have also been obtained for the smaller *c*-$C_4H_8^{\bullet-}$ model system (62.5 vs 37.3 kcal/mol),[29] though *c*-C_4H_8 is unable to bind an extra electron. Different from the *c*-$C_4H_8^{\bullet-}$ system, the *c*-C_4H_7-$CHO^{\bullet-}$ radical anion is stable with respect to electron detachment and the cycloreversion barrier for *c*-C_4H_7-$CHO^{\bullet-}$ is evidently lower by about 20 kcal/mol, suggesting the crucial role of functional substituent groups. Thus, the *c*-C_4H_7-CHO molecule may bind an extra electron to facilitate the initial cycloreversion as well as the subsequent dissociation processes, with the overall barrier being reduced to only 12 kcal/mol.

According to our calculations, the evident reduction of the cycloreversion barrier for *c*-C_4H_7-$CHO^{\bullet-}$ can be mainly due to the intramolecular electron transfer from the diffuse SOMO into the σ*-orbitals of the breaking cyclic C−C bond. The extensive overlap between such diffuse SOMO and σ*-orbitals (see Figure 2a1) may assist such an electron-transfer process. After the initial ring-opening step, the extra electron is stabilized by the CHCHO moiety leading to the distonic radical anion intermediate $^{\bullet}(CH_2)_3CHCHO^{-}$ that is rather unstable toward C_2H_4 elimination. Obviously, the rotating of the formyl group within the *c*-C_4H_7-$CHO^{\bullet-}$ radical anion may change the direction of the dipole moment away from the cyclobutane structure, and thus may disturb such an SOMO → σ*-orbitals electron-transfer process. It seems that at least two factors are important for efficient radical anion catalysis. First, some functional groups are required to trap the extra electron because of the incapability of the cyclobutane structure itself. Second, the appropriate conformation with respect to the cyclobutane structure of such a functional group is needed for substantial overlap between SOMO and the σ*-orbitals of the cyclobutane structure.

Noticing the structural similarity between *c*-C_4H_7-CHO and the pyrimidine cyclobutane dimers, the high facility of radical anion cycloreversion of the latter can be easily understood. On one hand, the large dipole moments of pyrimidine dimers (∼7.0 D) can trap an extra electron that will be further stabilized by charge delocalization over the pyrimidine rings with electron-withdrawing carbonyl groups. On the other hand, the suitable conformation with two pyrimidine rings being proximately

perpendicular to the cyclobutane structure may facilitate the electron transfer from SOMO into the cyclobutane structure. New calculations taking both electron-correlation and a larger basis set into account are still required for a deeper understanding of the photoenzymic repair mechanism of DNA.

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Supporting Information Available: Listing of Cartesian coordinates and harmonic frequencies of all fully optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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