Structure and Reactions of the Succinimidyl Radical: A Density Functional Study

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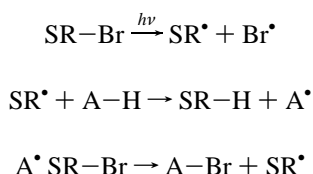
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Abstract: Recent density functionals and a variety of basis sets were employed in the study of three electronic states of the succinimidyl radical in C_{2v} symmetry: $^2A_1$ (σ_N), $^2B_1$ (π_N), and $^2B_2$ (σ_O). The lowest energy σ_O state is a genuine (local) minimum, as demonstrated by the harmonic vibrational analysis; the stationary points corresponding to the two remaining states are higher-order saddle points on the potential energy surface. Similar results were obtained with the Møller−Plesset method, while the complete active space calculations predict that the π_N state has the lowest total energy. The ring-opening reaction from the σ_O state is symmetry allowed and was calculated with the density functional theory to proceed via a true transition state. The β-scission process was found to exhibit a large secondary deuterium kinetic isotope effect, with $k_H/k_D = 1.2$. The infrared spectra of the open forms of the radical that result from β-scission reaction were calculated and compared to the calculated spectrum of β-bromopropanoyl isocyanate.
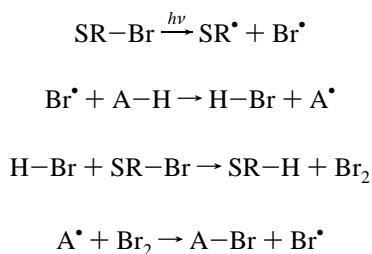
1. Introduction

The interest in the succinimidyl radical (SR) may be traced to the discovery made by Ziegler in 1942[1] that the compound *N*-bromosuccinimide (NBS) is an excellent brominating agent. The widespread use of NBS prompted the search for the mechanism of the bromination process. Two appeared within a decade of Ziegler's discovery. In the Bloomfield mechanism[2] the succinimidyl radical is the chain carrier:

$$SR{-}Br \xrightarrow{h\nu} SR^\bullet + Br^\bullet$$

$$SR^\bullet + A{-}H \rightarrow SR{-}H + A^\bullet$$

$$A^\bullet\ SR{-}Br \rightarrow A{-}Br + SR^\bullet$$

The succinimidyl radical chain appears to be functioning with unreactive substrates and is usually observed in the presence of olefins which act as a Br (or Br$_2$) sink. This mechanism could be accompanied by a competing ring-opening β-scission of the succinimide radical followed by the formation of β-bromopropanoyl isocyanate.

The Goldfinger mechanism[3] suggests that the active agent in the bromination by NBS is the bromine atom, generated in the photolytic first step of the Bloomfield mechanism, with NBS acting only as a low steady-state source of molecular bromine:

$$SR{-}Br \xrightarrow{h\nu} SR^\bullet + Br^\bullet$$

$$Br^\bullet + A{-}H \rightarrow H{-}Br + A^\bullet$$

$$H{-}Br + SR{-}Br \rightarrow SR{-}H + Br_2$$

$$A^\bullet + Br_2 \rightarrow A{-}Br + Br^\bullet$$

Bromination with reactive substrates appears to proceed via the bromine atom chain.

A. History of A Scientific Dispute. The succinimidyl radical was the object of a lively scientific controversy which related to the mechanism of bromination with NBS. In 1957, the research groups of Johnson[4] and Bartlett[5] independently reported detection of the β-bromopropanoyl isocyanate, a compound that may be produced in the opening of the succinimidyl radical ring and subsequent transfer with NBS. The observation of products formed from the succinimidyl radical seemed to support the Bloomfield mechanism. However, in 1963 Walling, Rieger, and Tanner,[6] as well as Pearson and Martin[7] and Russell *et al.*,[8] found no experimental evidence for the succinimidyl radical chain and concluded that bromination with NBS proceeds via the Goldfinger mechanism. In 1978, Skell *et al.*[9] unraveled the results of their search for the proof of the Bloomfield mechanism by suggesting that there is not one but two succinimide radical chains, due to two thermally accessible electronic states of the succinimidyl radical, $S_\sigma^\bullet$ and $S_\pi^\bullet$, which in effect behave as electronic isomers (analogous to the ones discovered in the chemistry of singlet and triplet states of carbenes). The ground state $S_\pi^\bullet$ would not lead to ring opening, while the excited state $S_\sigma^\bullet$ would. A rate constant for ring opening was estimated at $k > 10^8$ s^{-1}. The value of the rate constant for the reversible ring opening from $S_\sigma^\bullet$ was subsequently revised[10] to $k \approx 2 \times 10^7$ s^{-1}. In contrast with Skell's findings, studies on the bromination of substituted toluenes led Tanner *et al.*[11] to conclude that there was no

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evidence for the hypothesis of two states and proposed the mixed chain hypothesis: depending on the nature of the reactant either mechanism could be involved. Commenting on the two-state hypothesis of Skell they stated that if the two states of the radical existed they would be chemically indistinguishable. Walling *et al.*[12] performed accurate studies of the ring-opening reaction and found $k \approx 2 \times 10^4$ s^{-1} that would imply an inexplicably long lifetime of $S_\sigma^\bullet$, given that there was no clear mechanism to prevent this state from collapsing onto the ground state. They cautioned against uncritical interpretation of the succinimidyl radical reactions in terms of the $S_\sigma^\bullet$ and $S_\pi^\bullet$ states. Walling's paper met with a strong rebuke from Skell *et al.*,[13] who upheld the hypothesis of $S_\sigma^\bullet$ and $S_\pi^\bullet$ states being involved in the reactions of the succinimidyl radical, reiterated that $S_\sigma^\bullet$ is the ring opener, and strengthened their argument with the results of the ESR study of succinimidyl radical by Eberson and co-workers.[14] Subsequently Tanner, Walling, and their co-workers[15] reported results of new kinetic studies which led them to unequivocally state that the $S_\sigma^\bullet$ species was simply the ground state of the succinimidyl radical and the $S_\sigma^\bullet - S_\pi^\bullet$ hypothesis was at best unnecessary. Consequently, Skell *et al.*[16] withdrew the conclusions based on the $\sigma-\pi$ hypothesis in the imidyl systems, citing lack of definitive vidence. Skell summarized the main problems with the ground state of the imidyl system: (a) all calculations attested that the π_N state has the lowest energy; (b) the ESR study of Eberson and co-workers[14] attributed π symmetry to the ground state; (c) yet the facile ring-opening reaction indicated that either the symmetry selection rules ($S_\pi^\bullet \nrightarrow$ ICE$^\bullet$) are violated or else all known chemistry of the succinimidyl radical involving β-scission was that of the excited state.

In recent work on the succinimidyl radical Lind *et al.*[17] revised the value of the rate constant for the ring-opening reaction in aqueous solutions to be $k = 8 \times 10^4$ s^{-1}. In studies of intramolecular hydrogen transfer in imidyl radicals, Chow *et al.*[18] unequivocally concluded that the ground state of imidyl radicals must have a σ electronic configuration.

B. ESR Studies. The results of ESR studies regarding the nature of the ground state of the radical appear to be inconclusive. In an early paper Hedaya *et al.*[19] mentioned an unpublished ESR study of the succinimidyl radical by Hedaya and Kasai, who assigned the observed ESR spectrum to the β-(isocyanatocarbonyl)ethyl radical. The first ESR of a single crystal at 26 K was published by Eberson and co-workers,[14] who concluded that the succinimidyl radical is in a π ground state. However, the most recent argon matrix isolation ESR studies done at 4 K by Kasai[20] showed that the ESR spectrum is of the open chain β-(isocyanatocarbonyl)ethyl radical (ICE)

rather than that of the succinimidyl radical. Kasai remarked that in Eberson's work[14] either the succinimidyl radical was stabilized by the crystal or crystallization from aqueous solution resulted in hydrogen bonding which stabilized the σ_O state and prevented the ring-opening reaction. In their more recent work Eberson *et al.*, using the spin-trapping method, could not detect the open form of the succinimidyl radical in solution.[21]

C. Previous Computational Studies. Several theoretical investigations of the succinimidyl radical, both semiempirical and *ab initio*, have been undertaken. The first calculations of the radical were performed at the INDO level by Koenig *et al.*,[22] who investigated C_{2v} and C_s structures of the radical. The relative ordering of the three calculated states were π_N (0) < σ_N (36) < σ'_O (61 kcal/mol). The states π_N and σ_N were calculated by assuming that the radical possessed the C_{2v} symmetry, while the results for the σ'_O state were obtained with assumed C_s symmetry, with one short and one long carbonyl bonds. Furthermore, it was found that only a σ state of the radical opens to the ground state of the β-(isocyanatocarbonyl)-ethyl radical, while the π state leads to an excited state. The MNDO results of Clark[23] predicted that the σ_N state of the succinimidyl radical is 14 kcal/mol above the π_N state. The first *ab initio* study was reported by Apeloig and Schreiber.[24] Their UHF results obtained with the STO-3G basis set indicated that the ground state is the π_N state, while the excited state σ_N is 20 kcal/mol higher. We found, however, that the UHF wave function for the doublet state of the radical, expanded in the minimal STO-3G basis set, is strongly contaminated with higher multiplicities, leading to $\langle S^2 \rangle$ greater than 2, significantly larger than the value of $^3/_4$ expected in the radical.[25] MNDO calculations were reported by Dewar *et al.*,[26] who found that only σ_N yields the β-(isocyanatocarbonyl)ethyl radical in the ground state. The estimated activation energy for the ring-opening process was $E_a = 12.9$ kcal/mol and the predicted rate constant was $k \approx 2 \times 10^4$ s^{-1}. Two more advanced *ab initio* calculations followed: Petrongolo and Peyerimhoff[27] used the MR CISD method with a DZV basis set and, after non-gradient geometry optimization, found the ordering of states π_N (0) < σ_O (12) < σ_N (16 kcal/mol), using a full-CI estimate of the potential energy surface. Hillier *et al.*[28] performed a series of calculations from UHF to CI//CAS and found in their best set of results (CISD calculations with the 6-31G(d) basis set performed at the geometry optimized with the CAS method and employing the 3-21G basis set) that π_N (0) < σ_N (5 kcal/mol).

2. Details of Present Calculations

The motivation for the present study originated from the recognition that there is no definitive computational resolution of the conflict between the facile opening of the radical's ring and the presumed π symmetry of the succinimidyl radical's ground electronic state. The few *ab initio* calculations performed for the succinimidyl radical utilized small basis sets and did not evaluate the energy hessian. As a consequence of the lack of the hessian, the question whether the stationary points represent genuine minima on the potential energy

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Table 1. Calculated Structural Parameters[a] and the Spin Expectation Values for the $\pi_N(^2B_1)$ State of the Succinimidyl Radical

param[b]	4-31G		4-31G(d,p)		6-311G(d,p)		6-311G++(2df,2pd)	
	UHF	B3LYP	UHF	B3LYP	B3LYP	B3PW91	B3LYP	B3PW91
CO	1.255	1.244	1.215	1.221	1.216	1.215	1.215	1.213
CN	1.371	1.409	1.380	1.404	1.405	1.402	1.404	1.401
C_4C_6	1.516	1.528	1.520	1.530	1.530	1.524	1.526	1.520
C_6C_7	1.539	1.537	1.532	1.530	1.531	1.524	1.528	1.522
OCN	121.8	121.8	121.5	121.7	121.7	121.6	121.6	121.6
CNC	108.5	107.4	107.7	107.3	107.4	107.2	107.5	107.3
NCC	112.7	112.4	112.9	112.5	112.4	112.5	112.3	112.4
CCC	103.1	103.9	103.2	103.8	103.9	103.9	103.9	104.0
$\langle S^2 \rangle$	1.300	0.792	1.119	0.782	0.780	0.782	0.780	0.781
N_{imag}[c]	0	1	0	1	2	1		

[a] Bond lengths in Å, bond angles in deg. [b] See Figure 1 for the definition of atoms. Here the atomic indices were dropped whenever possible without creating ambiguity. [c] Number of imaginary frequencies found in the harmonic vibrational analysis.

surface was never asked, and the genuine ground state of the radical was never definitely identified.

The principal tool used in the present work was the density functional theory (DFT), which was shown to perform well in the studies of radicals.[29,30] Two features of the DFT approach make it particularly attractive in the studies of large radicals: the basis set convergence is rapid and the spin contamination is less severe.[31]

Two recent density functionals were used in the present work: the combination of Becke's 3-parameter exchange[32] and Lee–Yang–Parr correlation[33] functionals (denoted in this work as B3LYP), and the same exchange functional with the Perdew–Wang correlation functional[34] (denoted as B3PW91). In spite of the widespread use of the Becke3-LYP combination (facilitated perhaps by its availability in the Gaussian92/DFT program[35]), Becke's parametrization was accomplished with the Perdew–Wang functional.

In order to establish convergence of the DFT results with basis set size, several standard library basis sets were employed in this work: they varied from the small, unpolarized DZV 4-31G basis set and its polarized counterpart 4-31G(d,p) to the larger 6-311(d,p) and 6-311++G-(3df,2pd) basis sets. (Note that despite the notation, the 6-311G basis set is TZV only in the p-space while it has only DZV quality in the s-space.[36])

For comparison, Møller–Plesset perturbation theory (MP2) and Complete Active Space (CAS) calculations were done using the smaller basis sets 4-31G and 4-31G(d,p).

Preliminary geometry optimizations were performed using the unrestricted Hartree–Fock method (UHF). The stationary points were determined using gradient techniques, and their character was identified by the analytical evaluation of the energy hessian. In all UHF, MP2, and DFT calculations the Gaussian 94 program[37] was used. The CAS geometry optimizations were executed using GAMESS-US[38] and HONDO[39] programs.

3. Results and Calculations

A. Search for the Ground State. Geometry optimization was done assuming the C_{2v} symmetry of the radical for three electronic states, each with a different distribution of the unpaired electron. In the $\pi_N(^2B_1)$ state, the unpaired electron is delocalized over the imidyl fragment O–C–N–C–O of the

radical in orbitals that are perpendicular to the plane of the ring. In the $\sigma_N(^2A_1)$ state, the electron is mainly localized on the nitrogen atom in an orbital lying in plane of the ring. Finally, in the $\sigma_O(^2B_2)$ state, the unpaired electron is again delocalized over the imidyl fragment, this time, however, in the plane of the ring. The calculated structural parameters for the three states are collected in Tables 1–3. As expected, the values of $\langle S^2 \rangle$ decrease substantially on going from UHF to DFT. The nature and relative ordering of the investigated states change, depending on the choice of basis set and theoretical procedure. The energy gap between the π_N state on one hand and σ_N and σ_O on the other changes significantly when going from the UHF to DFT energies: the largest change is observed for the σ_O state calculated with the smaller basis sets. As the basis sets increase, the UHF–DFT gap slightly decreases. More interesting, however, is the relative ordering of the three states as predicted using the DFT. The B3LYP π_N–σ_N energy gap decreases to less than 1 kcal/mol, making the σ_N state thermally accessible at room temperature; the B3PW91 functional with the two largest basis sets brings about the ordering $E(\sigma_N) < E(\pi_N)$. However, when polarization functions are added, it is the σ_O state (Table 3) that becomes the lowest energy state, with B3PW91 placing the σ_O state about 1 kcal/mol lower than the B3LYP. (The state σ_O is predicted to be the lowest energy state already with a 4-31G(d) basis set.) Thus the relative ordering of the three states is predicted to be $E(\sigma_O) < E(\pi_N) < E(\sigma_N)$ at the B3LYP level and $E(\sigma_O) < E(\sigma_N) < E(\pi_N)$ at the B3PW91 level.

It must be stressed that all three states were calculated by imposing the C_{2v} symmetry on the nuclear framework of the radical. Two lower symmetries were investigated: (a) the radical was constrained to the C_s symmetry and the electronic state was $^2A'$, with the initial geometry of the radical taken from the work of Hillier *et al.*[28] and (b) all symmetry restrictions were removed (i.e. the radical possessed the C_1 symmetry) and the electronic state was ^2A. In both of these cases the geometry optimization process leads to the nuclear configuration of the

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Table 2. Calculated Structural Parameters,[a] Relative Energies,[b] and the Spin Expectation Values for the $\sigma_N(^2A_1)$ State of the Succinimidyl Radical

param[c]	4-31G		4-31G(d,p)		6-311G(d,p)		6-311G++(2df,2pd)	
	UHF	B3LYP	UHF	B3LYP	B3LYP	B3PW91	B3LYP	B3PW91
CO	1.202	1.223	1.178	1.202	1.198	1.196	1.197	1.196
CN	1.373	1.387	1.371	1.380	1.381	1.377	1.378	1.374
C_4C_6	1.526	1.551	1.528	1.549	1.549	1.541	1.545	1.539
C_6C_7	1.546	1.548	1.541	1.541	1.542	1.535	1.539	1.534
OCN	128.2	130.2	128.3	130.5	130.5	130.4	130.3	130.3
CNC	120.8	119.6	121.2	120.0	120.3	120.5	120.2	120.3
NCC	103.6	104.3	103.3	104.1	103.9	103.7	104.0	103.8
CCC	106.0	105.9	106.1	105.9	106.0	106.1	106.0	106.0
$\langle S^2 \rangle$	0.767	0.754	0.763	0.754	0.754	0.754	0.754	0.755
ΔE^b	17.6	1.8	11.0	1.8	0.8	−0.1	0.3	−0.6
N_{imag}^d	1	1	1	2	2	3		

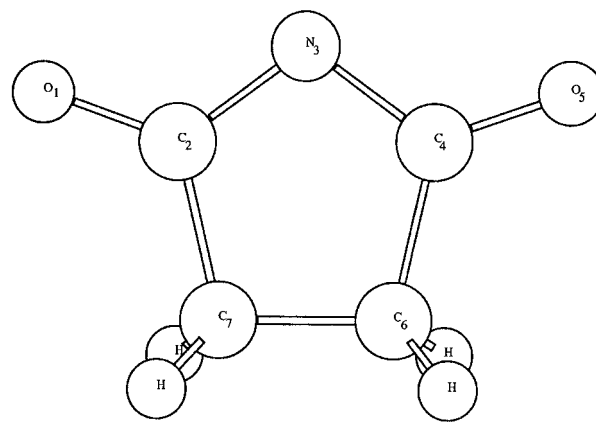[a] Bond lengths in Å, bond angles in deg. [b] Relative energies, $\Delta E = E_{tot}(^2A_1) - E_{tot}(^2B_1)$, in kcal/mol. [c] See Figure 1 for the definition of atoms. [d] Number of imaginary frequencies found in the harmonic vibrational analysis.

Table 3. Calculated Structural Parameters,[a] Relative Energies,[b] and the Spin Expectation Values for the $\sigma_O(^2B_2)$ State of the Succinimidyl Radical

param[c]	4-31G		4-31G(d,p)		6-311G(d,p)		6-311G++(2df,2pd)	
	UHF	B3LYP	UHF	B3LYP	B3LYP	B3PW91	B3LYP	B3PW91
CO	1.217	1.245	1.195	1.223	1.218	1.216	1.217	1.215
CN	1.356	1.366	1.346	1.355	1.354	1.351	1.352	1.350
C_4H_6	1.557	1.564	1.559	1.569	1.570	1.562	1.566	1.558
C_6C_7	1.502	1.513	1.496	1.502	1.502	1.497	1.500	1.494
OCN	123.7	123.6	123.5	123.9	124.1	124.0	124.1	123.9
CNC	108.7	107.9	107.6	107.3	107.6	107.4	107.8	107.5
NCC	112.6	113.2	113.6	113.8	113.6	113.7	113.5	113.6
CCC	103.0	102.8	102.5	102.5	102.6	102.6	102.6	102.7
$\langle S^2 \rangle$	0.804	0.757	0.796	0.756	0.756	0.756	0.757	0.757
ΔE^b	54.6	1.7	45.3	−0.9	−1.0	−1.9	−1.5	−2.5

[a] Bond lengths in Å, bond angles in deg. [b] Relative energies, $\Delta E = E_{tot}(^2B_2) - E_{tot}(^2B_1)$, in kcal/mol. [c] See Figure 1 for the definition of atoms.

C_{2v} symmetry, with the electronic state of the $^2B_2$ symmetry as the lowest energy level.

Analysis of the energy hessian brings about a surprising result that only the σ_O state is a genuine minimum on the potential energy surface. Of the two other states π_N is a minimum at the UHF level for the two smallest basis sets (no UHF calculations were done with the larger basis sets) and a saddle point at the DFT level starting with the 4-31G basis set; the σ_N state is a saddle point for both UHF and DFT methods. The order of the saddle point depends on the basis set (see the values of N_{imag} in the last row of Tables 1 and 2). As mentioned above, when the nuclear configurations of the π_N and σ_N states are distorted along a mode corresponding to the negative curvature of the potential energy surface and the geometry is optimized in the resulting C_1 symmetry, the optimization process leads to the σ_O state with C_{2v} symmetry.

While the energy gaps depend on the basis set, the geometries of the three states are converged already at the 4-31G(d,p) level. The differences in the geometries calculated with B3LYP and B3PW91 functionals differ slightly, with the B3PW91 bond lengths being 0.002−0.008 Å shorter than the B3LYP bonds. Similarly, bond angles differ insignificantly.
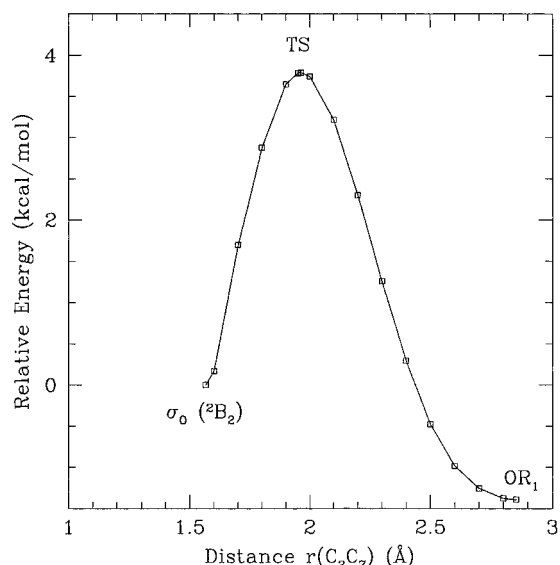
B. Ring-Opening Reaction. The σ symmetry of the ground state of the radical is consistent with the experimentally observed facility with which the radical opens[12,17] and the readiness with which the open forms of the radical cyclize.[40] With the σ symmetry of the ground state allowing for the β-scission, we studied the energy change in the course of the ring-opening reaction by performing complete geometry optimization of all structural parameters for a range of values of the reaction

(40) Kaushal, P.; Roberts, B. P.; Ryan, E. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1587. Kaushal, P.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1559.

Figure 1. Structure of the succinimidyl radical.

coordinate, the C_2-C_7 distance. The energy changes during the β-scission process are shown on Figure 2. The highest-energy point was shown to be a genuine transition state point by the harmonic vibrational analysis. The relative energies of the transition state are shown in Table 4 and the fully optimized parameters are collected in Table 5. The length of the cleaved C_2-C_7 bond is almost 2 Å in the transition state.

Following the reaction path from the transition state leads first to the structure OR_1 of the β-(isocyanatocarbonyl)ethyl radical, with an energy 1−4 kcal/mol below that of the parent succinimidyl radical (Table 4), and a characteristic geometrical structure (Table 6 and Figure 4). The second structure of the open radical, OR_2, which is effected from OR_1 by the rotation around N_3-C_4 bond, was found to be slightly more stable (Tables 6 and 4 and Figure 5). Harmonic vibrational frequency analyses have shown that both OR_1 and OR_2 are genuine minima.

Figure 2. Energy profile for the β-scission reaction using basis 4-31G(d) with the B3LYP density functional.

Table 4. Total and Relative Energies Calculated in Large Basis Sets

property	6-311(d,p)		6-311++G(2df,2pd)	
	B3LYP	B3PW91	B3LYP	B3PW91
	C_{2v}: $^2B_2(\sigma_O)$			
$E_{tot}{}^a$	−360.0635	−359.9224	−360.0955	−359.9528
ΔE^b	0.0	0.0	0.0	0.00
	C_{2v}: $^2A_1(\sigma_N)$			
$E_{tot}{}^a$	−360.0607	−359.9195	−360.0926	−359.9499
ΔE^b	1.8	1.8	1.8	1.82
	C_{2v}: $^2B_1(\pi_N)$			
$E_{tot}{}^a$	−360.0619	−359.9193	−360.0931	−359.9489
ΔE^b	1.0	1.9	1.5	2.45
	C_s: $^2A'(TS^c)$			
$E_{tot}{}^a$	−360.0599	−359.9168	−360.0920	−359.9474
ΔE^b	2.3	3.5	2.2	3.39
	C_1: $^2A(OR_1{}^d)$			
$E_{tot}{}^a$	−360.0713	−359.9256	−360.1022	−359.9547
ΔE^b	−4.9	−2.0	−4.2	−1.2
	C_1: $^2A(OR_2{}^e)$			
$E_{tot}{}^a$	−360.0745	−359.9286	−360.1047	−359.9569
ΔE^b	−6.9	−3.9	−5.8	−2.57

^{a} Total energy, in atomic units. ^{b} Relative energy $\Delta E = E_{tot} - E_{tot}(^2B_2)$, in kcal/mol. ^{c} Transition state; see Figure 3. ^{d} Open radical structure; see Figure 4. ^{e} Open radical structure; see Figure 5.

The structures of the $O_1C_2N_3$ fragment in both OR_1 and OR_2 closely resemble the experimental geometry[41] of the isocyanic acid HNCO: the $O_1C_2N_3$ angle is about 1° larger than the experimental value of 172.6°, the O_1C_2 bond is about 0.01 Å shorter than that in HNCO (1.166 Å), while the C_2N_3 bond length is essentially identical with that of the CN bond (1.214 Å).

In order to better convey the evolution of geometry from that of the succinimidyl radical to that of OR_2, the structural changes are summarized in Table 7 for B3PW91 with the largest basis set. The most conspicuous is the opening of the $O_1C_2N_3$ bond angle to almost linear 172°. Further rotation along the N_3-C_4 and C_4-C_6 bonds leads to the second structure of the open radical with a slightly lower energy (Tables 4 and 6 and Figure 5).

The expectation value of the spin before projection, $\langle S^2 \rangle$, changes from 0.76 for the σ_O and the transition state to 0.75

(41) Yamada, K. *J. Mol. Spectrosc.* **1980**, *79*, 323.

Table 5. Structural Data^a for the Transition State

param^b	6-311G(d,p)		6-311G++(2df,2pd)	
	B3LYP	B3PW91	B3LYP	B3PW91
O_1C_2	1.188	1.183	1.186	1.181
C_2N_3	1.278	1.270	1.275	1.267
N_3C_4	1.394	1.391	1.391	1.388
C_4O_5	1.199	1.198	1.199	1.197
C_4C_6	1.554	1.548	1.548	1.543
C_6C_7	1.490	1.483	1.487	1.480
C_2C_7	1.929	1.962	1.924	1.970
$O_1C_2N_3$	147.2	149.2	147.3	149.5
$C_2N_3C_4$	117.9	118.7	118.1	119.0
$N_3C_4O_5$	123.5	123.5	123.4	123.3
$N_3C_4C_6$	112.6	113.0	112.7	113.1
$C_4C_6C_7$	107.3	107.9	107.4	108.1

^{a} Bond lengths in Å, bond angles in deg. ^{b} See Figures 1, 3, 4, and 5 for the definition of atoms.
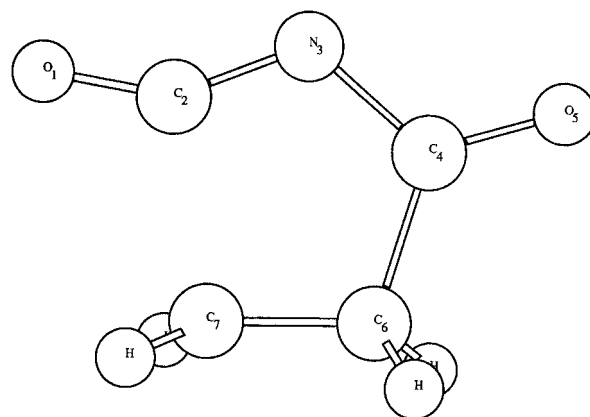
Figure 3. Structure of the succinimidyl radical in the transition state.
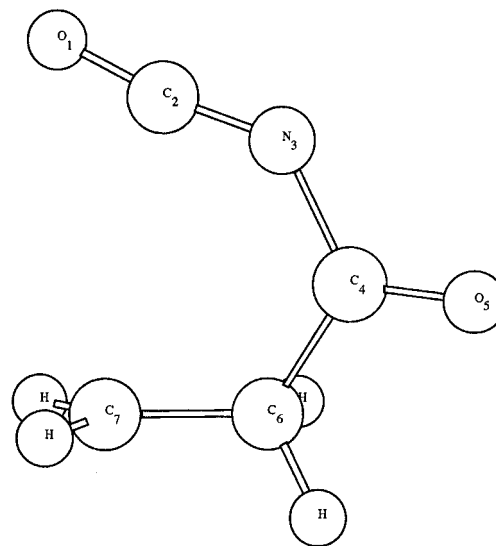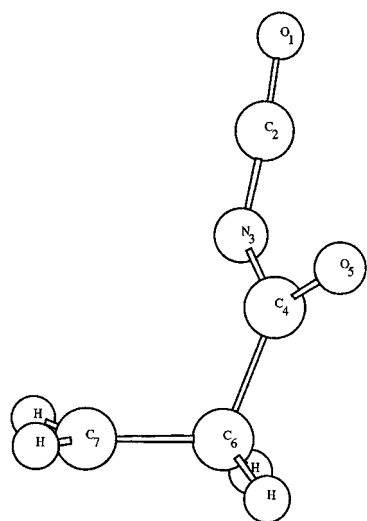

Figure 4. Open radical structure OR_1.

for the open-ring structures OR_1 and OR_2. The change of atomic spin densities during the ring-opening reaction is shown in Table 9. Already in the transition state most of the unpaired electron is located at the carbon atom C_7, which in the open radical structure OR_1 becomes the sole carrier of the unpaired spin. In the two open structures, the C_7 atom is in the planar environment, consistent with the sp^2 hybridization.

The arrangement of the hydrogen atoms in the open-ring structure OR_1 is similar to one of the limiting structures that Kasai postulated[20] in order to explain the complexity of the ESR spectrum of the β-(isocyanatocarbonyl)ethyl radical: the dihedral angle $H_\alpha-C_7-C_6-H_\beta$ is 18° from the ESR analysis, and

Table 6. Calculated Structural Data[a] for the Two Open Structures, OR$_1$ and OR$_2$

	OR$_1$				OR$_2$			
	6-311G(d,p)		6-311G++(2df,2pd)		6-311G(d,p)		6-311G+(2df,2pd)+	
param[b]	B3LYP	B3PW91	B3LYP	B3PW91	B3LYP	B3PW91	B3LYP	B3PW91
O$_1$C$_2$	1.164	1.162	1.162	1.161	1.160	1.158	1.158	1.157
C$_2$N$_3$	1.213	1.214	1.210	1.212	1.217	1.216	1.215	1.215
N$_3$C$_4$	1.417	1.410	1.412	1.405	1.426	1.420	1.421	1.416
C$_4$O$_5$	1.196	1.196	1.196	1.196	1.200	1.199	1.200	1.198
C$_4$C$_6$	1.542	1.535	1.537	1.531	1.526	1.520	1.523	1.518
C$_6$C$_7$	1.488	1.484	1.485	1.480	1.493	1.489	1.489	1.486
C$_2$C$_7$	3.008	2.922	3.057	2.880	2.999	2.971	4.140	4.112
O$_1$C$_2$N$_3$	172.9	172.2	173.1	171.9	173.9	173.8	174.0	173.9
C$_2$N$_3$C$_4$	135.2	134.8	135.5	134.7	130.6	130.8	130.8	130.8
N$_3$C$_4$O$_5$	120.8	120.8	120.6	120.7	123.0	123.0	122.9	123.0
N$_3$C$_4$C$_6$	115.7	115.8	115.8	116.2	111.9	111.9	112.3	112.2
C$_4$C$_6$C$_7$	114.7	115.3	114.2	115.7	110.9	110.8	110.9	110.7
N$_3$C$_4$C$_6$C$_7$	52.2	45.8	55.8	41.6	67.4	66.0	68.9	67.5

[a] Bond lengths in Å, bond angles in deg. [b] See Figures 1, 3, 4, and 5 for the definition of atoms.

Figure 5. Open radical structure OR$_2$.

Table 7. Changes of Structural Parameters[a] for the $\sigma_O(^2B_2)$, TS, OR$_1$, and OR$_2$ Systems

param[b]	$\sigma_O \to$ TS	TS $\to$ OR$_1$	OR$_1 \to$ OR$_2$
O$_1$C$_2$	−0.034	−0.020	−0.004
C$_2$N$_3$	−0.083	−0.055	0.003
N$_3$C$_4$	0.038	0.017	0.011
C$_4$O$_5$	−0.018	−0.001	0.002
C$_4$C$_6$	−0.015	−0.012	−0.013
C$_6$C$_7$	−0.014	0.000	0.006
C$_2$C$_7$	0.412	0.910	1.232
O$_1$C$_2$N$_3$	25.6	22.4	2.0
C$_2$N$_3$C$_4$	11.5	15.7	−3.9
N$_3$C$_4$O$_5$	−0.6	−2.6	2.3
N$_3$C$_4$C$_6$	−0.5	3.1	−4.0
C$_4$C$_6$C$_7$	5.4	7.6	−5.0
N$_3$C$_4$C$_6$C$_7$	0.0	41.6	25.9

[a] Changes in bond lengths in Å and bond angles in deg, calculated using B3PW91 functional and 6-311++G(2df,2pd) basis set. Negative values signify reduction of the corresponding parameter in the transition. [b] See Figures 1, 3, 4, and 5 for the defintion of atoms.

its value calculated using B3LYP with 6-311G(d,p) basis set is 11°. The other limiting structure, for which Kasai estimates H$_\alpha$−C$_7$−C$_6$−H$_\beta$ = −29°, was not identified in the present study. Given that the calculated harmonic frequency of the α-CH$_2$ plane oscillations is only 129 cm^{-1}, the rotation of the α-CH$_2$ group around the C$_6$−C$_7$ bond should cost little energy. This rotation was studied using the 6-311G(d,p) basis set with the B3LYP functional; for the range of torsional angle equal to the

Table 8. Calculated Structural Parameters[a] of β-Bromopropanoyl Isocyanate

distance[b]		angle[b]	
O$_1$C$_2$	1.158	O$_1$C$_2$N$_3$	173.9
C$_2$N$_3$	1.219	C$_2$N$_3$C$_4$	130.3
N$_3$C$_4$	1.426	N$_3$C$_4$O$_5$	122.9
C$_4$O$_5$	1.200	N$_3$C$_4$C$_6$	112.4
C$_4$C$_6$	1.516	C$_4$C$_6$C$_7$	112.4
C$_6$C$_7$	1.524	N$_3$C$_4$C$_6$C$_7$	54.1
C$_7$Br$_8$	1.978	C$_6$C$_7$Br$_8$	111.0
		C$_4$C$_6$C$_7$Br$_8$	178.1

[a] Bond lengths in Å and bond angles in deg, calculated using B3LYP functional and 6-311G(d,p) basis set. [b] See Figures 1, 3, 4, and 5 for the definition of atoms.

Table 9. Total Atomic Spin Densities[a] of the σ_O State of the Succinimidyl Radical, the Transition State, and the OR$_1$ Structure of the Open Radical

atom[b]	σ_O	TS	OR$_1$
O$_1$	0.42	0.25	0.00
C$_2$	−0.03	−0.05	0.00
N$_3$	0.09	0.15	0.00
C$_4$	−0.03	0.01	0.04
O$_5$	0.42	0.03	0.02
C$_6$	0.06	−0.04	−0.09
C$_7$	0.06	0.65	1.10

[a] Basis 6-311(d,p), density functional B3LYP, Mulliken population analysis. [b] For the notation, see Figures 1, 3, and 4.

optimized value of H$_\alpha$−C$_7$−C$_6$−H$_\beta$ = ±25°, the total energy changed only by about 0.3 kcal/mol.

The bromine atom, released in the photolytic dissociation of NBS, may attack the C$_7$ carbon atom to form β-bromopropanoyl isocyanate. The geometry of one possible conformer of the product compound was optimized using the basis set 6-311G(d,p) with the density functional B3LYP. The calculated structure of the molecule, shown in Figure 6 with structural parameters collected in Table 8, was found to be a minimum under harmonic vibrational analysis.

The simulated infrared spectra of all stable structures were compared in Figure 7. The IR spectrum of the succinimidyl radical differs considerably from that of the open radical forms OR$_1$ and OR$_2$. The most prominent peak in the spectrum of the succinimidyl radical, calculated at 768 cm^{-1}, corresponds to the in-plane deformation of the ring, effected by asymmetric streches of the CN and CO bonds. The two adjacent peaks, at 489 and 811 cm^{-1}, arise from similar deformations. The spectrum of the open forms of the radical and of the brominated product is dominated by the intense band in the 2335−2338-
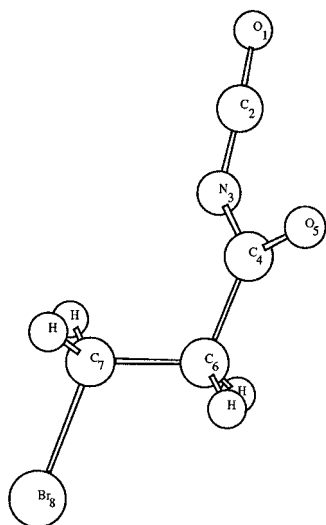
Figure 6. Structure of β-bromopropanoyl isocyanate.

cm^{-1} range, due to the asymmetric stretch of the NCO moiety. The band around 1800 cm^{-1} corresponds to the carbonyl stretch. Finally, the third most intense peak in the spectrum of OR_2 and β-bromopropanoyl isocyanate, found around 1450 cm^{-1}, represents the symmetric NCO stretch. The two strong bands observed experimentally[4,5] at 1733−1735 and 2247−2250 cm^{-1} correlate well with the calculated carbonyl and isocyanato group stretches, respectively.

Assuming that molecules behave like rigid rotors and harmonic oscillators, the rate constant of the ring-opening reaction may be evaluated from the transition state theory.[42] However, while the calculated absolute rate constant may be significantly different from the experimental values, better agreement may be expected from the ratio of the rate constants for isotopically substituted species. The secondary deuterium kinetic isotope effects in the β-scission process were estimated using the formula:[43]

$$\frac{k_H}{k_D} = \frac{Q_{TS}^H}{Q_{TS}^D}\frac{Q_{SR}^D}{Q_{SR}^H}\exp\left[\frac{-(\delta E_o^{TS} - \delta E_o^{SR})}{RT}\right]$$

where δE_o^{TS} is the difference between the total molar vibrational zero-point energies for the light and heavy transition state (TS), δE_o^{SR} is the analogous quantity for the reactant succinimidyl radical, and Q represents the partition function. For the perdeuterated succinimidyl radical, the value of k_H/k_D is 1.2 using the B3LYP functional with the 6-311(d,p) basis set. The same value is obtained for the isotopic substitution at the β-carbon C_6, while, surprisingly, there is no secondary kinetic isotope effect (*i.e.* $k_H/k_D = 1.0$) for the substitution at the α-carbon C_7.

C. MP2 and CAS Studies. The MP2 and CAS studies were performed for the π_N, σ_N, and σ_O states in C_{2v} symmetry using the two smallest basis sets. In the MP2 calculations the seven core orbitals, corresponding to the 1s orbitals of the heavy atoms, were frozen. The CISD calculations were performed for the three states at the B3PW91/6-311G++(2df,2pd) geometry. The CISD expansion contained over 200 000 terms in the 4-31G basis, and over 1 000 000 when the 4-31G(d,p) basis was used. The active orbitals for the CAS studies (see Tables 10−12) were those involved in configurations with large weights and resulted

(42) Glasstone, S.; Laidler, K. J.; Eyring, H. *The Theory of Rate Processes*; McGraw-Hill: New York, 1941.
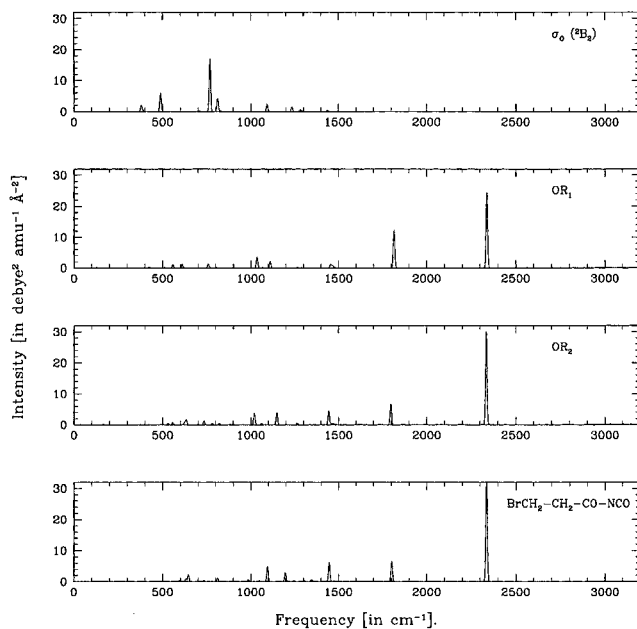(43) Maskill, H. *The Physical Basis of Organic Chemistry*; Oxford University Press: Oxford, 1993.

Figure 7. Calculated IR spectra using basis 6-311(d,p) with the density functional B3LYP.

Table 10. Structural Parameters[a] for the $\pi_N(^2B_1)$ State of the Succinimidyl Radical

param[b]	4-31G			4-31G(d,p)		
	B3LYP	MP2	CAS[c]	B3LYP	MP2	CAS[c]
CO	1.244	1.202	1.238	1.221	1.181	1.208
CN	1.409	1.473	1.391	1.404	1.462	1.396
C_4C_6	1.528	1.539	1.518	1.530	1.526	1.521
C_6C_7	1.537	1.540	1.536	1.530	1.518	1.531
OCN	121.8	122.2	121.9	121.7	122.1	121.6
CNC	107.4	106.7	108.1	107.3	106.5	107.5
NCC	112.4	111.1	112.3	112.5	111.1	112.5
CCC	103.9	105.5	103.6	103.8	105.7	103.7

[a] Bond lengths in Å, bond angles in deg. [b] See Figure 1 for the definition of atoms. [c] The active space selected was $1a_2^2 2a_2^2 2b_1^2 3b_1^1 3a_2 4b_1 5b_1$. Size of the CAS expansion was 392 configurational space functions (CSF).

Table 11. Structural Parameters[a] and Relative Energies[b] for the $\sigma_N(^2A_1)$ State of the Succinimidyl Radical

param[c]	4-31G			4-31G(d,p)		
	B3LYP	MP2	CAS[d]	B3LYP	MP2	CAS[d]
CO	1.223	1.237	1.213	1.202	1.209	1.188
CN	1.387	1.405	1.379	1.380	1.385	1.376
C_4C_6	1.551	1.555	1.524	1.549	1.537	1.526
C_6C_7	1.543	1.560	1.549	1.541	1.536	1.544
OCN	130.2	129.2	127.7	130.5	129.5	127.9
CNC	119.6	120.6	120.0	120.0	121.6	120.5
NCC	104.3	103.2	104.0	104.1	103.6	102.5
CCC	105.9	106.4	106.0	105.9	106.7	106.1
ΔE^b	1.8	−17.7	8.1	1.8	−8.8	6.3

[a] Bond lengths in Å, bond angles in deg. [b] Relative energies, $\Delta E = E_{tot}(^2A_1) - E_{tot}(^2B_1)$, in kcal/mol. [c] See Figure 1 for the definition of atoms. [d] The active space selected was $1a_2^2 2a_2^2 2b_1^2 3b_1^1 11a_1^1 3a_2 4b_1 5b_1$. Size of the CAS expansion was 542 CSFs.

in relatively compact CAS expansions. The optimized MP2 and CAS results are compared with the density functional B3LYP values in Tables 10−12. There is a fair agreement in the calculated geometries, with the $\sigma_O(^2B_2)$ state showing the largest discrepancies. However, the energy ordering of the three states is quite different. The DFT method predicts that the states have fairly similar energies: the 4-31G ordering of the states, π_N (0) < $\sigma_N \approx \sigma_O$ (2 kcal/mol), changes upon addition of the

Table 12. Structural Parameters[a] and Relative Energies[b] for the $\sigma_O(^2B_2)$ State of the Succinimidyl Radical

param[c]	4-31G			4-31G(d,p)		
	B3LYP	MP2	CAS[d]	B3LYP	MP2	CAS[d]
CO	1.245	1.254	1.251	1.223	1.225	1.227
CN	1.366	1.308	1.333	1.355	1.358	1.327
C_4C_6	1.564	1.577	1.529	1.569	1.564	1.531
C_6C_7	1.513	1.523	1.527	1.502	1.496	1.518
OCN	123.6	123.4	122.8	123.9	123.6	122.5
CNC	107.9	107.2	108.7	107.3	106.6	107.4
NCC	113.2	113.6	113.6	113.8	114.1	114.6
CCC	102.8	102.8	102.1	102.5	102.6	101.7
ΔE^b	1.7	−18.6	37.2	−0.9	−14.2	32.8

[a] Bond lengths in Å, bond angles in deg. [b] Relative energies, $\Delta E = E_{to}3t(^2B_2) - E_{tot}(^2B_1)$, in kcal/mol. [c] See Figure 1 for the definition of atoms. [d] The active space selected was $2a_2^2 3b_1^2 11a_1^2 12a_1^2 9b_2^2 3a_2 4b_1 5b_1$. Size of the CAS expansion was 582 CSFs.

polarization functions to σ_O (0) < π_N (1) < σ_N (3 kcal/mol). As stated earlier, it is only the σ_O state that is a true minimum on the basis of the harmonic vibrational analysis. The MP2 method predicts that the σ_O state has the lowest energy regardless of the basis set, with the ordering of σ_O (0) < π_N (19) < σ_N (37 kcal/mol) for the 4-31G basis and σ_O < σ_N (5) < π_N (14 kcal/mol) for the polarized basis 4-31G(d,p). The lowest-energy σ_O state is predicted to be a minimum, while the higher states are the 1st- and 2nd-order saddle points for the 4-31G and 4-31G(d,p) basis sets, respectively. Finally, the CAS calculations consistently predict that π_N is the ground state, with the ordering π_N (0) < σ_N (19) < σ_O (37 kcal/mol) and π_N (0) < σ_N (6) < σ_O (33 kcal/mol) for the unpolarized and polarized basis sets, respectively. The magnitude of π_N−σ_N splitting in the 4-31G(d,p) basis set is very close to the best value of about 5 kcal/mol obtained by Hillier *et al.* in their CISD calculations.[28] The harmonic vibrational analysis could not be done for the CAS wave function: the presently available code lacks the analytical hessians for the CAS wave function; the numerical evaluation of the hessian requires that the symmetry be lowered from C_{2v} to C_1 and as a result the wave functions mix. Consequently, we were not able to determine the nature of the stationary points obtained with the CAS method. In our CISD single-point calculations using the 4-31G(d,p) basis at the DFT-optimized geometry the ordering was π_N (0) < σ_N (2) < σ_O (22 kcal/mol) without the Davidson correction[44] and π_N (0) < σ_N (4) < σ_O (16 kcal/mol) with the Davidson correction included to estimate the effect of higher excitations.

4. Conclusions

Using the DFT methodology, we found that the ground electronic state of the succinimidyl radical is of σ symmetry,

which allows for facile β-scission leading to the ground electronic state of the open β-(isocyanatocarbonyl)ethyl radical. The overall isomerization is found to be exothermic by 3−6 kcal/mol, in agreement with experimental findings. The reaction is expected to exhibit an unusually large secondary deuterium kinetic isotope effect for β-substituted hydrogens.

We found that the MP2 method also predicts the σ_O state to have the lowest total energy. In agreement with the DFT results, this state is a minimum on the potential energy surface. On the other hand, the CAS method conforms to all earlier computational results by predicting that the ground state is the π_N character. The energy gap between the lowest and highest states is more pronounced for MP2 and CAS methods (14−33 kcal/mol); the DFT splitting is much smaller (about 3 kcal/mol). This difference may result from the lack of convergence of the MP2 and CAS results with respect to basis set size: while the 4-31G(d,p) basis set appears to be sufficient for converging the DFT results, it is most certainly inadequate to secure the convergence of results for the MP2 and CAS methods. It appears that a thorough CAS study with large basis sets, including geometry optimization and analytical harmonic vibrational analysis, may be required for additional information about the nature of the ground state of the succinimidyl radical.

The most intriguing result of the present work is that the two states which were traditionally used to analyze the chemistry of the succinimidyl radical, namely the π_N and σ_N states, do not correspond to minima on the potential energy surface, and may not be invoked in the analysis of the ESR results. In this context it is puzzling that the ESR studies of Eberson and co-workers[14] detected a π ground state of the radical. A possible solution to this dilemma may stem from the fact that the calculations were done for an isolated molecule in the gas phase, while the experiments were performed for a crystal. The crystalline environment of the radical may not only affect the geometry of the radical (see the asymmetric X-ray structure of the succinimide in the work of Mason[45]), but it may also change the nature of the potential energy surface and alter the ordering of the energy levels. The experimental conditions that are perhaps closest to the gas-phase environment of computational work are those created by Kasai in the argon matrix ESR studies of the radical.[20]

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