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Theoretical Exploration of the Photochemical Rearrangement of Oxaziridines

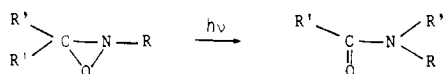
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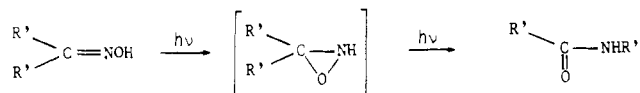
Abstract: The mechanism of the thermal and photochemical rearrangements of oxaziridines into amides has been explored through ab initio calculations using double- ζ plus diffuse basis sets and extensive CI. The lowest singlet excited state of the oxaziridine ring results from an $n \rightarrow \pi^*$ $\rightarrow \sigma^*_{\text{NO}}$ excitation and undergoes the breaking of the NO bond. The H(C) migration does not occur simultaneously; it should proceed on the ground state surface after deexcitation in the open geometry. The regioselectivity of the reaction would be due to an important barrier for the migration of the H atom in syn position with respect to the N lone pair.

Since their discovery by Emmons,² oxaziridines have drawn a great deal of attention in view of their practical and theoretical interest.³⁻⁵

Oxaziridines are photolabile^{3b,6} and in the singlet state, the major pathway for their decomposition is the rearrangement into amides with migration of one of the carbon substituents

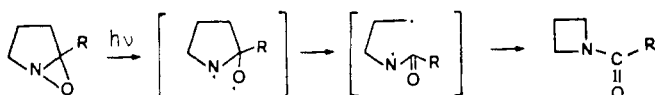


to nitrogen.⁷ This reaction is consistent with the suggestion that oxaziridines are intermediates in the photochemical conversion of oximes into the corresponding amides.⁷ According to Su-

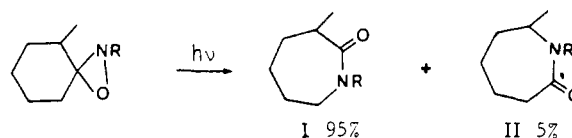


ginome et al.,^{8f} this photo-Beckmann rearrangement may be understood in terms of a rather simple scheme; singlet excited cycloalkane oximes "are rapidly transformed into intermediate oxaziridines. These oxaziridines undergo excitation to a singlet state and this is reorganized to give lactams without a further intermediate".

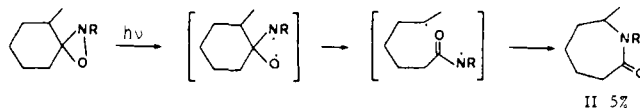
However, in the case of fused bicyclic oxaziridines, several authors^{6b,c} suggested that the rearrangement proceeds with a biradical intermediate via homolytic cleavage of the N-O bond.



But this free-radical mechanism is also brought into question by the results concerning the photochemical ring expansion of spiro oxaziridines.^{6d,9,10} The experimental data show that this reaction is highly stereoselective^{9,10} and regioselective.^{9,10}



In thermal reactions the degree of stereoselectivity is slightly lower but the lactam I is always the main product.^{10c} The regioselectivity observed rules against free-radical intermediates; should a radical mechanism be involved, the photolysis of spiro oxaziridines would be expected to give preferential cleavage of the C-C bond to the more highly substituted carbon atom

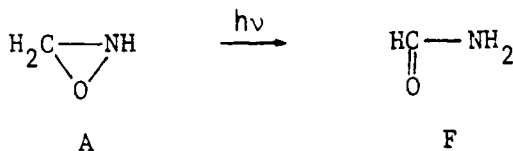


leading to the more stable free radical and to lactam II. Another remarkable feature¹⁰ appears in the rearrangement of the oxaziridines; the regioselectivity seems to be controlled by stereoelectronic requirements. The steric orientation of the nitrogen lone pair has not been considered so far. In fact, one may notice¹⁰ that the C-C bond which undergoes fragmentation lies quasi-antiperiplanar to the nitrogen lone pair and to one of the oxygen lone pairs.



A similar stereoelectronic control has also been suggested for other fragmentation reactions^{11,12} in the ground state.

The present work tries to explore the mechanism of this photorearrangement using the instruments of quantum chemical descriptions. Since the excited state involved may be rather unusual, we preferred to use an accurate ab initio extended basis set description rather than an unreliable semi-empirical model. A correct configuration interaction (CI) treatment was required in order to deal with excited states and bond-cleavage situations. These methodological choices compelled us to restrict our analysis to the smallest model molecule and to a few points of the potential surface for the reaction



What is hoped from these calculations is an answer to the following points:

- (1) What is the nature of the singlet excited state of the oxaziridine ring?
- (2) Does the N-O bond tend to break in this excited state?
- (3) Does the C-H bond (representing in our model the C-C bond of the experimentally studied molecules) break simultaneously or after a preliminary NO breaking; does this event proceed in the excited state or in the ground state surface after deexcitation?
- (4) May one explain a difference between the two C-H (C-C) bonds according to their syn or anti position with respect to the nitrogen lone pair?

I. Method

The basis set is of (double- ζ + diffuse) quality. The double ζ basis set was taken from Clementi's optimized Slater AOs¹⁴ converted into three Cartesian Gaussian functions according to Huzinaga's formulas.¹⁵ It has been augmented by a set of 3s and 3p AOs on each heavy atom, the exponents of which are 0.020, 0.025, and 0.030 for C, N, and O, respectively, as suggested by earlier works on excited-states problems at the same level of accuracy.¹⁶

The calculation of atomic integrals and the SCF step were performed according to the IBMOLH program, in a closed-shell formalism. The closed-shell picture would not be reliable for the intermediates where chemical bonds are broken, but a large CI procedure always follows the SCF step. The same set of ground-state SCF MOs are used for all states in the CI process. The CI result was approached through the iterative CIPSI algorithm¹⁷ which combines variation (for the strongest interactions) and perturbation (for the remainder) techniques. A zeroth-order wave function of the state m , ψ_m^0 , is obtained by diagonalization of the Hamiltonian restricted to the subspace S of n_s most determinants, selected from preliminary iterations of the process

$$P_s = \sum_{K \in S} |K\rangle \langle K|$$

$$P_s H P_s |\psi_m^0\rangle = E_m |\psi_m^0\rangle$$

$$|\psi_m^0\rangle = \sum_{K \in S} C_{mk} |K\rangle$$

Then ψ_m^0 is perturbed to the second order in energy by its interaction with the determinants which do not belong to the subspace S .

$$\epsilon_m^2 = \sum_{I \notin S} \frac{\langle \psi_m^0 | H | I \rangle \langle I | H | \psi_m^0 \rangle}{E_m^0 - E_I^0} \quad (1)$$

If a determinant $|I\rangle$ is involved in the first-order wave function ψ_m^1 with a coefficient $C_{mI}^1 = \langle \psi_m^0 | H | I \rangle / (E_m^0 - E_I^0)$ larger than a given threshold, $|I\rangle$ is added to the set S and the process is repeated. In practice the subspace involves up to 50 determinants, going to triply excited states, and the determinants I represent single and double substitutions from any determinant of S . Their number goes to eight hundreds of thousands in our calculations. The set of virtual MOs was reduced to 18 MOs representing the Rydberg MOs resulting from the diffuse AOs, and the valence antibonding MOs.

Besides the ground state, the lowest triplet and singlet excited states have been calculated for all geometries.

II. Geometries

The dimension of the basis set and the cost of the CI procedure prevented both an optimization of the initial (A) and final (F) products geometries and an extensive study of the potential surfaces between them. The geometries of the oxaziridine (A) and formamide (F) have been taken from experiment. Since the unsubstituted oxaziridine has not been synthesized, a reasonable guess of its geometry had to be done, as in previous calculations of this molecule.^{5b,c} Lehn et al.^{5b} had built their geometry from a comparison with oxiranes, aziridines, and hydroxylamines, while Csizmadia et al.^{5c} had estimated their geometry from X-ray data concerning a substituted oxaziridine. The same procedure has been used here, using the various X-ray results now available,^{18a-c} and led to the geometry reported in Table I. As concerns the final product (formamide), the geometry was taken from Kitano and Kutchitsu's¹⁹ recent results.

The choice of the intermediate points (B-E) on the surface will be discussed later on.

III. Results

1. Oxaziridine. The Fock energies of the valence occupied and lowest unoccupied canonical SCF MOs have been given in Table II. The occupied levels compare fairly well with previous Csizmadia values.^{5c} The highest occupied MO, which would correspond to a 12.05-eV ionization potential according to the Koopmans theorem, is a linear combination of the " π " lone pairs of N and O. The lowest virtual MOs are completely different since they become Rydberg MOs of very low energies. In the virtual orbital approximation, which represents the excited state with a single determinant using the canonical MOs, the vertical transition energies are given by

$${}^1,3\Delta E_{(i \rightarrow j^*)} = \epsilon_{j^*} - \epsilon_i - J_{ij^*} + (2,0)K_{ij^*} \quad (2)$$

In Csizmadia's^{5c} calculation, the lowest transitions were at 6.86 eV for the triplet and 8.40 eV for the singlet. In the basis set used in this work, a strong competition occurs between various single excitations. For instance,

$$12 \rightarrow 13 (n \rightarrow \pi^* \rightarrow \sigma^*_{\text{Rydberg}}) \quad {}^3\Delta E = 9.31 \text{ eV}$$

$${}^1\Delta E = 9.33 \text{ eV}$$

and

$$12 \rightarrow 25 (n \rightarrow \pi^* \rightarrow \sigma^*_{\text{valence}}) \quad {}^3\Delta E = 9.07 \text{ eV}$$

$${}^1\Delta E = 10.70 \text{ eV}$$

The interaction between them will lead to lower energy excited states, of a mixed valence-Rydberg character. The CI process actually leads to the following values after the second-order correction:

$$S_0 \rightarrow T_1 \quad \Delta E = 4.61 \text{ eV}$$

$$S_0 \rightarrow T_2 \quad \Delta E = 4.96 \text{ eV}$$

$$S_0 \rightarrow S_1 \quad \Delta E = 5.59 \text{ eV}$$

The result for the singlet compares fairly well with the ab-

Table I. Coordinates of the Various Nuclei in Studied Geometries (A–F) (bohr)

geometry	coordinates	N	O	C	H _A ^a	H _S ^a	H(N)
A	x	0	2.835	1.467	1.316	1.316	-0.695
	y	0	0	2.276	3.199	3.199	-0.624
	z	0	0	0	1.598	-1.598	1.751
B	x	0	3.449	1.767	1.643	1.643	-0.695
	y	0	0	2.055	3.077	3.077	-0.591
	z	0	0	0	1.540	-1.540	1.762
C	x	0	4.367	2.216	2.118	2.118	-0.695
	y	0	0	1.557	2.904	2.904	-0.578
	z	0	0	0	1.267	-1.268	1.766
D _A	x	0	3.581	1.916	-0.507	2.232	-0.400
	y	0	0	1.828	2.449	3.468	-1.570
	z	0	0	0	1.447	-1.080	1.107
D _S	x	0	3.581	1.916	2.232	-0.507	-0.400
	y	0	0	1.828	3.468	2.449	-1.570
	z	0	0	0	1.080	-1.447	1.107
E _A	x	0	4.346	2.276	-0.062	2.289	-0.400
	y	0	0	1.352	2.697	3.199	-1.556
	z	0	0	0	1.036	-0.738	1.128
E _S	x	0	4.346	2.276	2.289	-0.062	-0.400
	y	0	0	1.352	3.199	2.697	-1.556
	z	0	0	0	0.738	-1.036	1.128
F	x	0	4.327	2.329	-1.597	2.218	-0.102
	y	0	0	1.121	1.102	3.244	-1.938
	z	0	0	0	0	0	0

^a H_A, H_S: hydrogens respectively anti and syn toward the nitrogen lone pair.

Table II. Fock Energies of Oxaziridine SCF MOs (eV)

SCF MOs	this work ^a	Csizmadia ^{5c}		
virtual	25	7.183		
	17	2.095		
	16	1.224		
	15	1.088	6.312	
	14	0.980	6.095	
	13	0.544	5.034	
	occupied	12	-12.054	-11.945
		11	-13.877	-13.632
		10	-14.394	-13.931
		9	-16.136	-15.428
		8	-18.748	-18.285
		7	-21.033	-20.190
		6	-25.876	-25.060
		5	-29.360	-29.414
		4	-40.488	-40.053
3		-307.228	-308.697	
2		-424.041	-425.428	
1		-559.002	-560.635	

^a Geometry A (see Table I).

sorption near 210 nm (5.85 eV) observed for substituted compounds.^{7a,10}

The lowest triplet wave function corresponds to a $n \rightarrow \pi^*$ Rydberg excitation where the (12 → 25) excitation is the only valence component:

$$\psi_{T_1}^0 = 0.57(12 \rightarrow 13) + 0.39(12 \rightarrow 14) + 0.30(12 \rightarrow 25) + 0.27(12 \rightarrow 18) + 0.27(12 \rightarrow 24) + 0.27(12 \rightarrow 20) + \dots \quad (3)$$

The "hole" actually is located on the 12 level, i.e., on the N and O " π " lone pairs; to understand the nature of the "particle" one must remember that the 12 lowest (13–24) virtual MOs are Rydberg, while the MO numbered 25, which is the lowest valence excited MO, is mainly the σ^*_{NO} antibonding MO of the NO bond.

The corresponding excited-state singlet wave function illustrates the valence-Rydberg mixing:

$$\psi_{S_1}^0 = 0.62(12 \rightarrow 25) + 0.31(12 \rightarrow 26) - 0.30(12 \rightarrow 21) - 0.27(12 \rightarrow 20) + 0.22(12 \rightarrow 27) - 0.21(12 \rightarrow 22) + \dots \quad (4)$$

where the valence excitation $n \rightarrow \pi^*$ ($12 \rightarrow 25$) is the main component.

The antibonding character of the excitation should favor a breaking of the NO bond.

2. Breaking of the NO Bond. Two geometries (B and C) with increasing values of the NCO angle (NCO = 80 and 109°, respectively) have been studied. The latter corresponds to the sp^3 hybridization of the carbon atom and should describe a complete breaking of the NO bond. The HCN and HCO angles values and the orientation of the NH bond have been kept. The 109° results (geometry C) will be discussed in some detail.

The ground state can no longer be represented in a satisfactory mode with a single determinant. The SCF closed-shell result is 3.42 eV (78.7 kcal/mol) above the initial state (A), but the MOs 12 (HOMO) and 13 (LUMO) have been deeply changed. The highest occupied MO ($\epsilon = -11.4$ eV) is a bonding σ MO between two hybrids located on N and O, while the lowest empty MO with a very low energy ($\epsilon = 1.605$ eV) is the corresponding antibonding MO (contaminated by Rydberg AOs). The SCF ground-state determinant is an unsatisfactory mixture of ionic and covalent forms.

A correct description of the ground state involves the (12 → 13)² doubly excited determinant and to a lesser extent the (12 → 13) single excitation. To build the ψ_m^0 wave functions, a set of 34 determinants has been selected, among which 18 are singly excited and 15 doubly excited. The ground-state wave function

$$\psi_0^0 = 0.83\phi_0 + 0.26(12 \rightarrow 13) - 0.45(12 \rightarrow 13)^2 + \dots \quad (5)$$

confirms the dominant covalent character of the ground state. If the MOs 12 and 13 were expanded on two hybrids a_N and b_O without polarization,

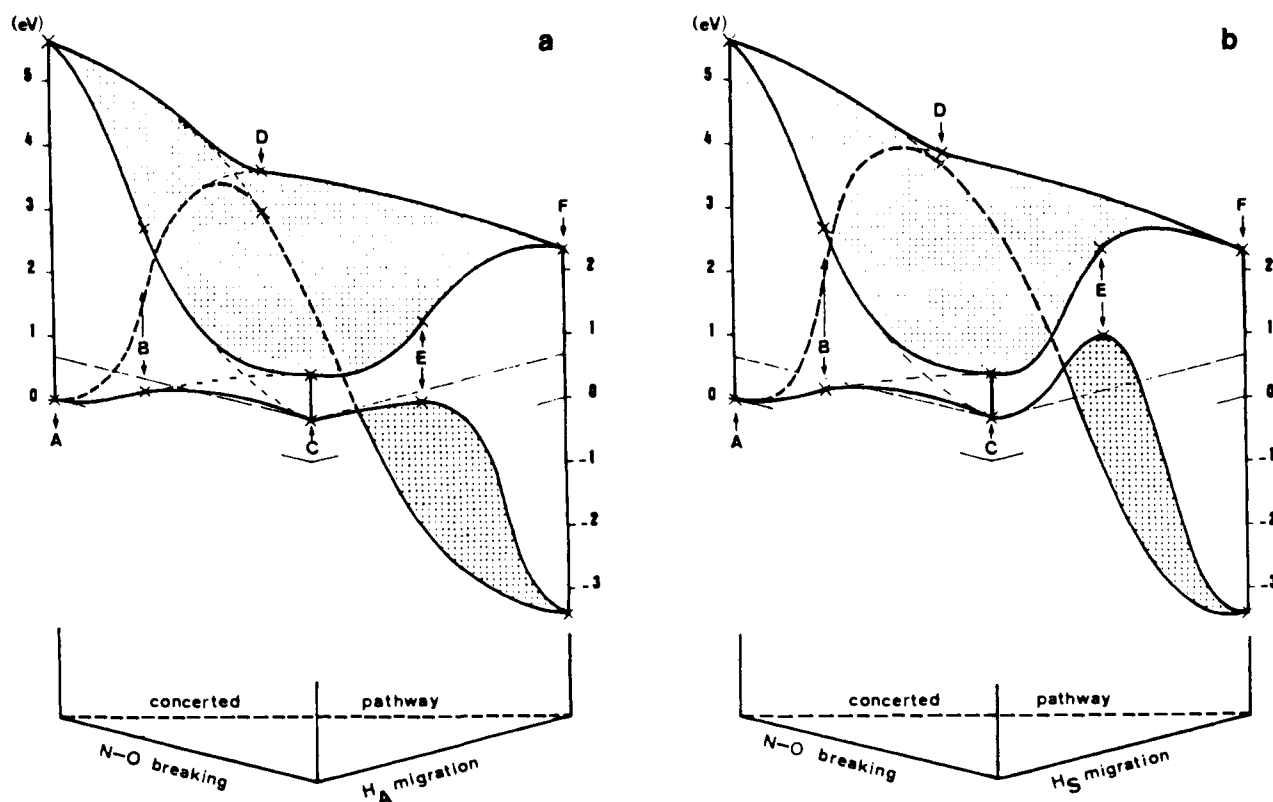


Figure 1. (a) Ground and singlet excited states surfaces for the oxaziridine (A)→formamide (F) reaction for the migration of the H(C) atom in anti position with respect to the N lone pair. The geometries (A-F) are explained in the text and given in Table I. (b) Same comments as in Figure 1a for the migration of the H(C) atom in syn position.

$$12 \sim (a_N + b_O)/\sqrt{2}$$

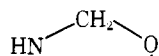
$$13 \sim (a_N - b_O)/\sqrt{2}$$

the wave function might be described as

$$\psi^0 \approx |\phi_0 + (12 \rightarrow 13)|/\sqrt{2} \approx (|a_N \bar{b}_O| + |b_O \bar{a}_N|)/\sqrt{2} \quad (6)$$

The actual polarities of the NO region lead to a deviation from this ideal formula to the coefficients of eq 5. The zeroth-order barrier height from the initial state (A) is lowered to 1.24 eV (28.6 kcal/mol).

The lowest triplet state is given by the (12→13) excitation, and represents the triplet component of the diradical open form



$(\bar{a}b - b\bar{a})/\sqrt{2}$. T_1 and S_0 are nearly degenerate, as may be expected ($T_1 \lesssim S_0$).

The lowest singlet excited state is essentially due to the (11→13) excitation. The 11 MO is localized on the oxygen " π " lone pair. At this level of description, the excited singlet remains therefore a $n \cdot \pi^* \rightarrow \sigma^*_{\text{NO}}$ excitation.

The second-order result shows an inversion of the S_0 and S_1 levels. This defect could not in practice be overcome by improving the variational CI since the first-order wave function already involves 7.5×10^5 determinants! This result suggests, however, that an avoided crossing occurs between 80 and 109° in the singlet manifold as pictured in Figure 1. The second-order corrections lower the ground-state barrier height for the ring opening to 0.67 eV (15.4 kcal/mol), which agrees with the easy thermal decomposition of NH oxaziridines.^{2,10}

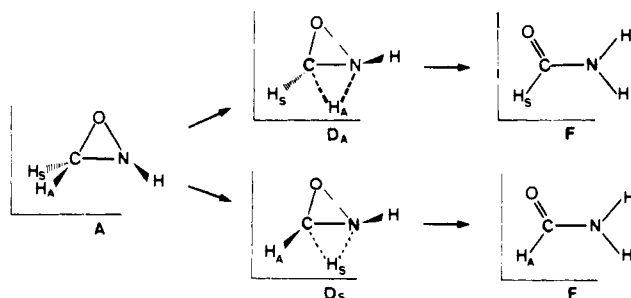
The analysis of the intermediate geometry (B) ($\text{NCO} = 80^\circ$) shows that the excited-state energy decreases regularly when opening the NO bond.

3. Migration of an H(C) Hydrogen to Give the Final Product.

The final product, i.e., formamide (geometry F), ground- and excited-states energies, calculated with the same method, have been extensively studied elsewhere¹³ and are in good agreement with experiment and with most recent calculations.²⁰ Formamide appears to lie 3.39 eV (78.1 kcal/mol) below the initial oxaziridine (instead of 3.75 eV in Csizmadia's calculation^{5c}). To reach the final product, two main directions may be assumed.

The first one is a direct rearrangement, corresponding to synchronous NO opening and H migration. As a typical point on this pathway, the geometry D has been built by giving to all geometrical parameters half of their variation between the initial (A) and final (F) values. The two H atoms are no longer equivalent, according to their initial syn (H_S) or anti (H_A) position with respect to the nitrogen lone pair in oxaziridine.

The migration pathway of the hydrogen atom (H_A or H_S) has been taken according to the least motion principle so that in the final product H_A and H_S are in a cis position relative to each other.



The assumed geometries D_A and D_S for the migration of H_A and H_S , respectively, are given in Table I. The calculated energies for D_A and D_S lead to rejection of such a direct path for the ground and excited states. The ground-state surface is

very high in energy: 2.94 eV (80 kcal/mol) above the initial oxaziridine^{1A} for anti migration and 3.68 eV (100 kcal/mol) for the syn migration. The excited-state energy remains also very high; moreover, a careful study of the wave functions suggests that an avoided crossing occurs between geometries A and D. In the singlet excited state there is no reason to begin the H migration simultaneously with the NO cleavage and the simple NO breaking seems much more likely.

The second direction would start from the broken NO bond (geometry C) to allow a migration of H_A or H_S atoms from the carbon to the nitrogen. Geometries E_A and E_S were determined as middle points between geometries C and F according to the same procedure as geometries D_A and D_S (Table I). The main results are the following.

As concerns the ground state, the point E_A (anti migration) is lower than the point C by 0.189 eV (5.14 kcal/mol) suggesting that after the NO cleavage no barrier (or a weak barrier only) prevents the subsequent migration of the proton. On the contrary the point E_S (syn migration) is 0.86 eV (19.8 kcal/mol) above the point C; a barrier should occur in the ground-state surface after the NO bond breaking for the syn hydrogen migration.

As concerns the singlet excited state, one may notice already that the lowest $n\pi^*$ singlet excited state of the final product (geometry F) is higher in energy than our relaxed singlet excited state (geometry C). The formamide geometry certainly should not be reached in the singlet excited surface; for both migrations of the hydrogen atom, the energy increases when starting from geometry C to reach geometry E. For the syn migration, an important barrier is likely between C to F. For the anti migration, the singlet excited state at geometry E_A has a lower energy than the $^1n\pi^*$ excited state of formamide (F), but a barrier should occur between geometries E_A and F on the singlet surface since the $^1n\pi^*$ excitation of formamide is not known to lead to a possible reverse H migration!

From the preceding numerical results and qualitative discussions, a rough representation of potential surfaces of the ground and excited singlet states has been drawn in Figure 1 (a and b) for the anti and syn hydrogen migration.

IV. Discussion

The few calculated points of the hypersurfaces do not allow quantitative considerations, but they suggest a possible mechanism for the ground- and excited-states reactions.

The thermal reaction does not proceed through a direct concerted procedure (geometries D_A and D_S). This conclusion seems logical according to Dewar;²¹ reactions involving the concerted breaking of two bonds should need high activation energies and are therefore rare. The reaction starts with the breaking of the N–O bond; the subsequent H migration should be easier (perhaps without barrier) for the anti hydrogen than for the syn hydrogen, which certainly meets a significant barrier.

The photochemical reaction also avoids a direct concerted mechanism. The excited singlet relaxes to a low-energy hole of the potential surface corresponding to a breaking of the NO bond; this relaxation is induced by the proper nature of the lowest absorption which is a $n \rightarrow \sigma^*_{NO}$ excitation. Then the molecule cannot reach the formamide geometry in the excited state since the $^1n\pi^*$ excited state of this compound is significantly higher in energy than the relaxed geometry lowest excited singlet. The most likely process is therefore a deexcitation on the ground-state surface near the open geometry C, and the subsequent migration of the hydrogen atom as in the ground-state reaction, favoring the anti migration. The slight differ-

ence in regioselectivity between thermal and photochemical reactions may be explained by differences in vibrational energies.

The photoreaction would proceed through a three-events mechanism: (1) photochemical breaking of the NO bond; (2) deexcitation on the ground-state surface; (3) hydrogen migration on the S₀ surface.

The sequence of these three steps is continuous and, since the dissociation of the CH bond occurs without activation (or a small activation energy), one may understand the lack of experimental evidence for a stable intermediate species.^{10a,b}

The easy breaking of the CH bond in the anti position with respect to the nitrogen lone pair may be explained in terms of $n \rightarrow \sigma^*$ conjugation as suggested by Epitotis²² for the stereo-electronically controlled reactions observed by Deslongchamps.¹²

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References and Notes

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