Consequently, this rule can now be used for the determination of the absolute configuration of chiral six-membered-ring ketones from the ^{13}C NMR spectra of their (2*R*,3*R*)-2,3-butanediol acetals. This is an important extension of a method which was primarily elaborated for the determination of the enantiomeric excess of chiral ketones.[12]

Acknowledgment. We are very indebted to Prof. G. Snatzke, who confirmed very recently the 3*R* configuration of the 3-(1-nitroalkyl)cyclohexanones **47**, **49**, and **50** (Table IV) from the CD spectra.

Registry No. (4*R*)-**36** acetal, 105969-74-2; (4*S*)-**36** acetal, 105969-76-4; (2*R*)-**38** acetal, 105969-75-3; (2*S*)-**38** acetal, 106034-29-1; (3*R*)-**39** acetal, 106034-27-9; (3*S*)-**39** acetal, 106034-28-0; (3*R*)-**47**, 105969-77-5; (3*S*)-**47**, 106034-30-4; **48**, 105969-78-6; **49**, 105969-79-7; (3*R*)-**50**, 105969-80-0; (3*S*)-**50**, 106034-31-5; **51**, 106034-32-6; **52**, 106034-33-7; **53**, 105969-81-1; **55**, 106034-34-8; **56**, 105969-82-2; **57**, 105969-83-3.

Theoretical Study of the Photodecomposition of *s*-Triazine

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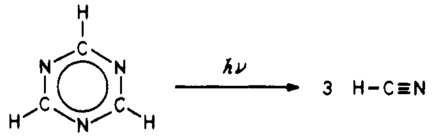
Abstract: The reaction mechanism of the photodissociation of *s*-triazine $C_3H_3N_3$ is examined with the ab initio molecular orbital method. The decomposition which leads to three equivalent HCN molecules is a symmetry-allowed reaction in the ground state under the C_{3h} symmetry, and the symmetric transition state is found to be a true transition state. The activation energy is estimated to be ca. 100 kcal/mol. In the excited states, all low-lying states increase the energies along the reaction coordinate. This means that the electronically excited *s*-triazine must experience the radiationless transition to the ground state and decompose synchronously. We can conclude that the triple dissociation of *s*-triazine occurs on the potential surface of the ground state and is a one-step concerted reaction.

I. Introduction

s-Triazine $C_3H_3N_3$ is a high-symmetry species with aromaticity like benzene. It is, however, known that *s*-triazine easily decomposes by photolysis. *s*-Triazine behaves very differently in photochemical processes compared with the complexity in the case of benzene. While various isomerization processes take place in the excited states of benzene, *s*-triazine simply decomposes to three HCN molecules.



(1)

Ondrey and Bersohn measured the kinetic energies of HCN fragments by laser pulse photolysis at two different wavelength.[1] There is a kind of paradoxical result, where HCN molecules have an average kinetic energy of 10 kcal/mol when they use 248-nm light, while in the case of higher energy excitation, i.e., 198 nm, they observed the translational energy of only 2 kcal/mol. At the same time, Goates, Chu, and Flynn observed the vibrationally excited products HCN by infrared fluorescence spectroscopy.[2]

Since the decomposition reaction 1 seems to be very simple compared with many photodissociation reactions,[3] there are still remaining questions on the mechanism, e.g., whether *s*-triazine decomposes to three HCN molecules simultaneously or step wisely. It is obvious that the energy used in this photodecomposition (115–148 kcal/mol) is not enough to break three CN bonds at one time.

It is very interesting to explore the reaction mechanism and energetics for this photodissociation theoretically. We have applied the ab initio molecular orbital method to investigate the potential energy surfaces of *s*-triazine in the ground and excited states. The equilibrium geometries and the structure of the transition state in the ground state are determined by using the analytical energy gradient method.[4] The excitation energies are evaluated with configuration interaction method.

II. Synchronous Decomposition Pathway in the Ground State

In order to explore the possibility of the triple dissociation of *s*-triazine to produce three equivalent HCN molecules, one can apply the conservation rule of the orbital symmetries to find out the continuity of the electronic structure during the reaction.[5] Assuming the least motion pathway which keeps C_{3h} symmetry, one can find that all occupied orbitals of *s*-triazine smoothly correlate to the linear combination of three HCN molecular orbitals. This means that the triple dissociation is a symmetry-allowed reaction in the ground state. As a result of searching the geometry of the transition state under the C_{3h} symmetry, we obtain the structure shown in Table I.

Table I summarizes the geometries of equilibrium structure and the transition state determined by using the various types of basis sets.[6] In order to confirm whether the calculated structure is a true transition state or not, we have performed the vibrational analysis. As shown in Table II, we find that the force constant of the symmetric structure has only one imaginary frequency. This reveals the existence of the concerted reaction pathway although the energy barrier is high. It is noticeable that the decomposition of *s*-triazine in the ground state is the one-step reaction via symmetric transition state, and this reaction obeys the Woodward–Hoffmann rule. The activation energy corrected by the zero-point vibration energy is calculated to be 110 kcal/mol within the theory of SCF level by using the 6-31G** basis set. Since the effect of electron correlation would reduce the energy at the transition state, we estimate the barrier height to be ca. 100 kcal/mol.

Figure 1b shows the normal coordinate for the imaginary frequency at the transition state. This nuclear motion clearly shows that the H–C–N bending mode will be excited in HCN

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[1] Ondrey, G. S.; Bersohn, R. *J. Chem. Phys.* **1984**, *81*, 4517.

[2] Goates, S. R.; Chu, J. O.; Flynn, G. W. *J. Chem. Phys.* **1984**, *81*, 4521.

[3] Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978.

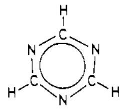
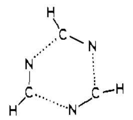
[4] Dupuis, M.; Spangler, D.; Wendoloski, J. J. *NRCC Software Catalog*; Program No. QG01 "GAMESS", 1980; Vol. 1.

[5] Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press: New York, 1970.

[6] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

0002-7863/87/1509-1370$01.50/0

Table I. Molecular Structures and Their Energies of s-Triazine and Its Transition State of Triple Dissociation[d]

	basis set	STO-3G	3-21G	6-31G	6-31G**	experiment
s-triazine	total energy	−275.13795	−277.10111	−278.53526	−278.70076	
	(rel energy)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)
	R_{CN}	1.3535	1.3302	1.3313	1.3180	1.3381[a]
	R_{CH}	1.0909	1.0666	1.0665	1.0756	1.084
	∠NCN	126.42	123.57	123.68	125.57	126.8
	∠HCN	116.79	118.22	118.16	117.21	116.6
3 H—C≡N	total energy	−275.02563	−277.06225	−278.48495	−278.63141	
	(rel energy)	(70.5)	(24.4)	(31.6)	(43.5)	(43.2[b])
	R_{CN}	1.1529	1.1371	1.1441	1.1328	1.1532[c]
	R_{CH}	1.0700	1.0502	1.0527	1.0590	1.0655
transition state	total energy	−274.92833	−276.96062	−278.37401	−278.51544	
	(rel energy)	(131.5)	(88.2)	(101.2)	(116.3)	
	$R_{C\text{-}N}$	1.1846	1.1770	1.1835	1.1691	
	$R_{C\cdots N}$	1.9300	1.8792	1.8881	1.8929	
	$R_{C\text{-}H}$	1.0786	1.0560	1.0570	1.0623	
	∠N–C•••N	118.18	118.92	118.80	120.21	
	∠C–N•••C	121.82	121.08	121.20	119.79	
	∠H–C–N	148.82	146.87	146.08	145.60	

[a] Lancaster, J. E.; Stoicheff, B. P. *Can. J. Phys.* **1956**, *34*, 1016. [b] Bystron, K. *J. Chem. Thermodyn.* **1982**, *14*, 865. [c] *Landolt-Börnstein New Series Group II*; Hellwege, K.-H., Hellwege, A. M., Eds.; Springer: Berlin, 1976; Vol. 7, p 126. [d] The total energies are in hartree, and the values in parentheses (kcal/mol) are the relative energies to the equilibrium of s-triazine. The units of bond distances and bond angles are in Å and deg.

Table II. Vibrational Frequencies (cm^{-1}) for s-Triazine and Its Transition State of Triple Dissociation Calculated by Using Two Different Basis Sets

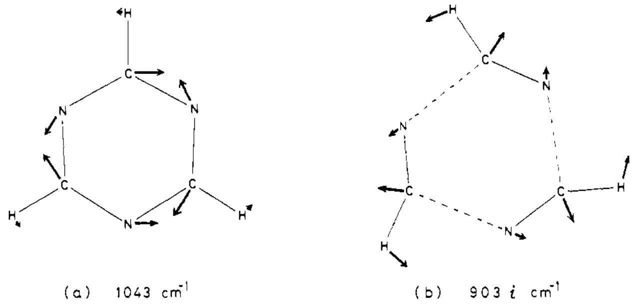
	s-triazine			transition state	
	STO-3G	3-21G		STO-3G	3-21G
A₁′	1097	1074	A′	991i	903i
	1260	1273		643	687
	3700	3432		1153	1146
				2058	1913
A₂′	904	1043		3806	3565
	1532	1516			
			E′	353	329
E′	741	760		587	583
	1322	1251		1254	1225
	1589	1546		2310	2132
	1835	1688		3807	3562
	3700	3421			
			A″	325	423
A₂″	862	842		915	940
	1004	1098			
			E″	149	220
E″	439	460		938	965
	1150	1185			

molecules after dissociation. This result is consistent with the observed fact by Goates et al., where three HCN molecules are produced equivalently in energy distribution and their ν_2 bending mode is highly excited.[2]

III. Comparison with Other Termolecular Reactions

Figure 1a shows the fourth lowest vibrational mode in equilibrium structure of ground-state s-triazine, which corresponds to the reaction coordinate of the triple dissociation. This mode is originating the formation of the Kekulé structure; it is the so called ν_{14} vibration in benzene.[7] The fact that the curvature of the reaction coordinate reflects to the height of the energy barrier may be seen as the difference of the vibrational frequencies of the bond alternating mode for benzene (1154 cm^{-1})[8] and s-triazine (904 cm^{-1}).

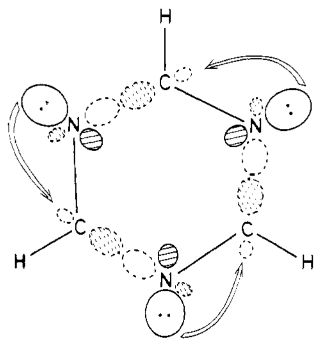
Although the orbital symmetry rule also shows that the termolecular decomposition of benzene is an allowed reaction, the dissociation of benzene to three acetylenes does not take place because of the considerable high-energy barrier. Bach, Wolber, and Schlegel calculated the barrier height from benzene to three acetylenes to be ca. 180 kcal/mol.[9]



(a) 1043 cm^{-1} (b) 903 i cm^{-1}

Figure 1. (a) One of the A_2' vibrational modes of s-triazine in the ground state calculated with the 3-21G basis set. (b) Reaction coordinate at the transition state of triple dissociation of s-triazine.

Scheiner and Schaefer calculated the transition state of the triple dissociation of s-tetrazine $C_2H_2N_4$ very recently.[10] The barrier height of the decomposition of tetrazine to two HCN and N_2 molecules is estimated to be less than 51.8 kcal/mol which is about half of the barrier in the case of s-triazine. The stability of azabenzene seems to decrease as the number of nitrogen atoms in the aromatic ring increases. This may be understood by taking into account that the CN σ bond rupture is promoted by the orbital interaction between the lone-pair orbital on nitrogen and the anti-bonding orbital of C–N σ bond. In the case of s-triazine, following orbital interaction would be important for the triple dissociation. Although the orbital interaction from the lowest lone pair orbital to the highest C–N σ^* orbital is energetically disfavored, this electron delocalization would be necessary because of the symmetry constraint.



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(7) Ziegler, L. D.; Hudson, B. S. *Excites States*; Academic Press: New York, 1982; Vol. 5, p 41.

(8) Osamura, Y. *Nippon Kagaku Kaishi* **1986**, 1384.

(9) Bach, R. D.; Wolber, G. J.; Schlegel, H. B. *J. Am. Chem. Soc.* **1985**, *107*, 2837.

(10) Scheiner, A. C.; Scuseria, G. E.; Schaefer, H. F. *J. Am. Chem. Soc.* **1986**, *108*, 8160.

Table III. Vertical Excitation Energies (in eV) of *s*-Triazine Calculated by Singly Excited Configuration Interaction (SECI) and n + π Full Configuration Interaction[a]

	tot energy of the ground state $^1A_1$	SECI −227.10111 hartree	3n + 6π full CI[b] −277.17729 hartree
$n \rightarrow \pi^*$ triplet	$^3A_2''$	4.88	4.71
	$^3E''$	5.36	5.20
	$^3A_1''$	6.54	5.92
$\pi \rightarrow \pi^*$ triplet	$^3A_1'$	4.32	4.59
	$^3E'$	6.17	5.91
	$^3A_2'$	7.25	8.32
$n \rightarrow \pi^*$ singlet	$^1A_1''$	5.90	5.23
	$^1E''$	6.18	5.58
	$^1A_2''$	6.68	5.93
	$^1E''$	9.82	8.53
$\pi \rightarrow \pi^*$ singlet	$^1A_2'$	7.52	5.80
	$^1A_1'$	8.38	9.27
	$^1E'$	9.91	9.39

[a] The geometry of *s*-triazine used is the equilibrium structure determined by the RHF method with the 3-21G basis set. [b] Concerning all possible configurations for 12 electrons among three lone pair orbitals and six π orbitals.

Generally speaking, such termolecular decomposition pathway via a single transition state seems to be very unusual. This reaction,

$$ABC \rightarrow A + B + C \qquad (2)$$

however, becomes exoteric by coupling the concept of the Woodward–Hoffmann rule and the quantum chemical calculation. The example of the termolecular reaction is first established for the photodissociation of glyoxal[11] and is followed by experiments.[12]

IV. Excited States of *s*-Triazine

Even if the triple dissociation of *s*-triazine is a concerted reaction in the ground state, its energy barrier is still too high for the dissociation to proceed thermally. When this energy is supplied by a photon, the termolecular decomposition may become possible.

There are many low lying excited states involving the electron excitations among three lone pair orbitals and six π orbitals. Table III shows the vertical excitation energies obtained by the singly excited configuration interaction (SECI) for all valence electrons and the full CI calculation in the n and π space (2520 configurations) with the 3-21G basis set. The result shows the lowest excited singlet state is the $n \rightarrow \pi^*$ state (5.23 eV above the ground state), and the lowest singlet $\pi \rightarrow \pi^*$ state is located only 13 kcal/mol above the lowest $n \rightarrow \pi^*$ state. In general, theoretical calculation overestimates the excitation energy, especially for $\pi \rightarrow \pi^*$ excitation. We, thus, could not specify the electronic states generated in Ondrey and Bersohn's experiment. The laser pulses of two wavelengths, 193 and 248 nm, seem to generate the different excited states, $\pi \rightarrow \pi^*$ with larger internal energy and $n \rightarrow \pi^*$ with less internal energy, of *s*-triazine.

In order to investigate the possibility of the photodissociation via electronically excited states, we calculate the potential energy surfaces of *s*-triazine qualitatively by using SECI method. We have found that the energies of all low lying $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excited states increase along the dissociation path and that these states correlate to the excited states of HCN which are energetically high. We have also examined the energy variation in the excited states by breaking the symmetry, such as out-of-plane displacement, distorsions of ring, single bond scission, etc. None of these shows stabilization or dissociation.

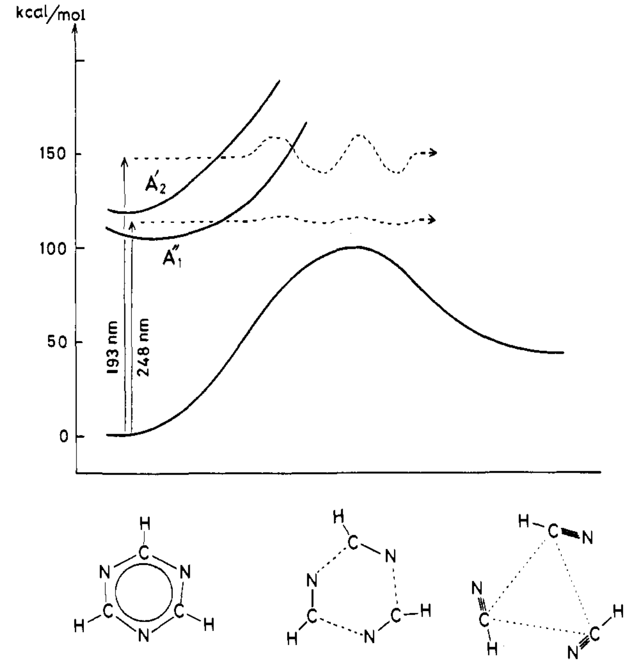

Figure 2. Speculative potential energy surfaces of the photodissociation of *s*-triazine.

Consequently, *s*-triazine has the stable equilibrium structures in $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ states (probably D_{3h} or C_{3h} symmetry).[13] Since all low lying excited states need very high energy to dissociate to excited HCN molecules, one can conclude that the radiationless transition has to occur to lead to the triple dissociation. Figure 2 illustrates a speculative summary of the potential energy surfaces.

V. Concluding Remarks

The unimolecular triple dissociation is possible to occur in an aromatic ring containing nitrogen atoms in the concerted manner. The synchronous decomposition pathway of *s*-triazine to three equivalent HCN molecules has the energy barrier of ca. 100 kcal/mol in the electronically ground state, and this reaction is found to be a one-step concerted reaction obeying the Woodward–Hoffmann rule. It may be concluded on the mechanism of photolysis that *s*-triazine dissociates through the internal conversion to the ground state from the excited singlet states since the potential energy surfaces show the energy increase in the low lying $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ states along the reaction path.

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Registry No. *s*-Triazine, 290-87-9.

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(11) Osamura, Y.; Schaefer, H. F.; Dupuis, M.; Lester, W. A. *J. Chem. Phys.* **1981**, *75*, 5828.

(12) (a) Saito, K.; Kakumoto, T.; Murakami, I. *J. Phys. Chem.* **1984**, *88*, 1182. (b) Hepburn, J. W.; Buss, R. J.; Butler, L. J.; Lee, Y. T. *J. Phys. Chem.* **1983**, *87*, 3638.

(13) Jug, K.; Hahn, G. *J. Comput. Chem.* **1983**, *4*, 410.