The Mechanism for the Oxidation of Imines (Schiff Bases) with Peroxy Acids. An ab Initio Molecular Orbital Study

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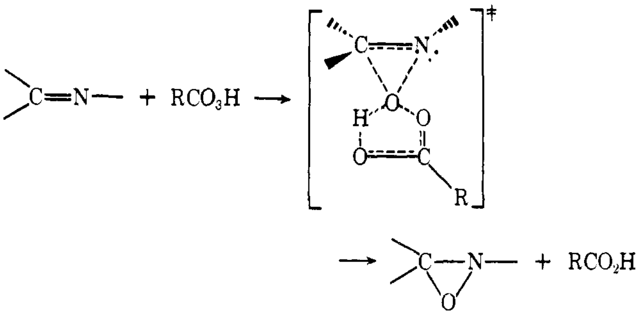
Abstract: The reaction of peroxyformic acid with methyleneimine has been studied by using STO-2G and STO-4G. Various plausible transition states presumably involved in a one-step mechanism and adducts involved in a two-step mechanism have been investigated. The formation of the corresponding oxaziridine is predicted to take place in a two-step process via an adduct intermediate resembling **B**. The transition state for the formation of the latter most probably resembles the one represented as **4**. The results are consistent with recently available experimental evidence.

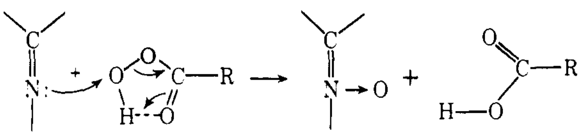
Introduction

Oxidation of imines (Schiff bases) with peroxy acids is a method of choice for the preparation of oxaziridines. Two mechanisms have been proposed for this reaction. The first one is analogous to olefin epoxidation and involves a one-step nucleophilic attack of π-bonding electrons on the electrophilic oxygen atom of the peroxy acid as shown in Scheme I.[1,2] The formation of relatively small amounts of nitrones in these reactions has been explained by the nucleophilic attack of N lone-pair electrons on the peroxy acid (Scheme II). The second mechanism resembles the Baeyer-Villiger oxidation of ketones, i.e., the first step of the reaction being the addition of peroxy acid to C═N to form an adduct which than collapses to oxaziridine in an internal nucleophilic (S_Ni) process (Scheme III).[3,4] In view of rather conflicting interpretations of complex kinetic and stereochemical data we felt it of interest to undertake an ab initio molecular orbital study of various plausible geometries of transition states (one-step mechanism) and adducts (two-step mechanism), and to analyze the implications of the obtained results on the mechanism of this reaction.

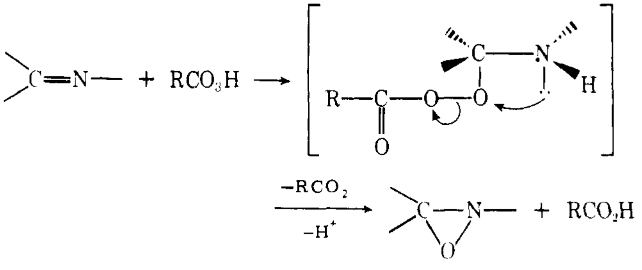
Scheme I



Scheme II



Scheme III



Method

In the present study, standard ab initio LCAO-SCF molecular orbital theory was used.[5] Molecular geometries were calculated by using the minimal STO-2G basis set. Unless otherwise stated, complete geometry minimization was performed. Molecular energies and charge distribution were than calculated by using the STO-4G basis set.

Results and Discussion

Peroxyformic and Formic Acid. The optimized geometries and all other data were taken from our previous study of these species.[6] The geometry of peroxyformic acid is shown in Figure 1. Calculated atomic orbital charges on the peroxidic oxygens are collected in Table I.

Methylenimine. $R(\mathrm{C{=}N}) = 1.283$ Å; $\angle \mathrm{C\text{-}N\text{-}H} = 108.1°$; $R(\mathrm{C\text{-}H}) = 1.080$ Å; $R(\mathrm{N\text{-}H}) = 1.080$ Å.[7]

Oxaziridine. $R(\mathrm{C\text{-}N}) = 1.465$ Å; $R(\mathrm{C\text{-}O}) = 1.423$ Å; $R(\mathrm{N\text{-}O}) = 1.428$ Å; $R(\mathrm{C\text{-}H}) = 1.083$ Å; $R(\mathrm{N\text{-}H}) = 0.999$ Å; $\angle \mathrm{H\text{-}C\text{-}H} = 116.5°$; $\angle(\mathrm{HCH})_{\mathrm{out}}\mathrm{C\text{-}N} = 150.6°$; $\angle(\mathrm{N\text{-}H})_{\mathrm{out}}\mathrm{C\text{-}N} = 150.5°$; $\angle \mathrm{C\text{-}N\text{-}H} = 110.5°$.

One-Step Mechanism. Six extreme, arbitrarily chosen geometries of plausible transition states were investigated.[8] As in our previous study,[6] all transition states were treated as isolated molecular entities. The reaction path, i.e., multidimensional surface for the transformation of the transition state to products, was not investigated. We assume that a higher barrier is not encountered on this path.

Complete geometry minimization was performed only for **1** (Figure 2). The exception is the imine part of the transition state, the geometry of which is taken from the free imine.[9] In all other transition states the same geometry parameters were employed except for the distance, r, and the orientation of the peroxy acid, which were systematically varied. Equilibrium energies of transition states **1–6**, together with distances, r, are summarized in Table II. The geometries are depicted in Figure 3.

Assuming the one-step mechanism to be the valid one, the first striking feature is the rather great similarity of the peroxy acid part of the transition state with that involved in epoxidation of ethylene.[6] Again, O—H, C═O, and O—O become slightly longer while the C—O and O···H bonds shorten. These findings seem to suggest intramolecular transfer of the proton during the reaction.

The inspection of charges (calculated as Mulliken populations) shows in all transition states under investigation a small but definite shift of electrons from imine to peroxy acid indicating a very weak electronic interaction between both par-

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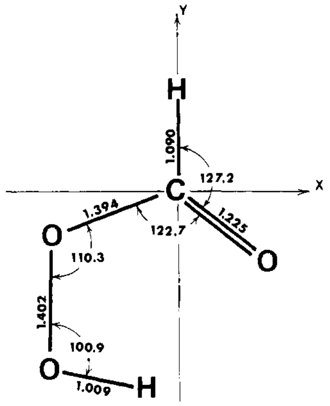

Figure 1. Optimized geometry of peroxyformic acid. Bond lengths and angles are in ångstroms and degrees, respectively.

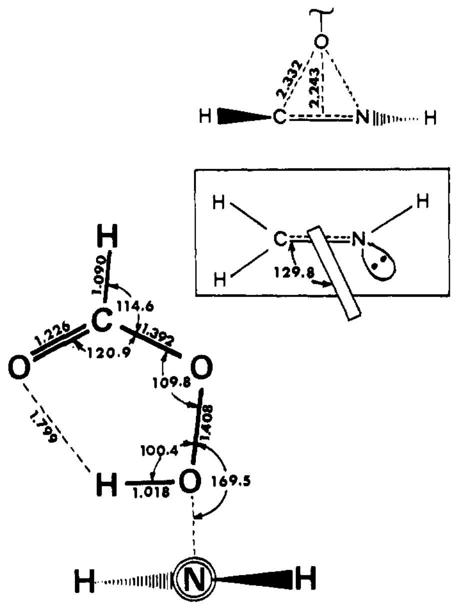

Figure 2. Optimized geometry of the transition state **1**. Bond lengths and angles are in ångstroms and degrees, respectively.

Table I. Calculated Atomic Orbital Charges of the Peroxidic Oxygens in Peroxyformic Acid

	STO-4G	
	O_6	O_7
2s	1.870	1.845
$2p_x$	1.358	1.365
$2p_y$	0.951	1.076
$2p_z$	1.996	1.866

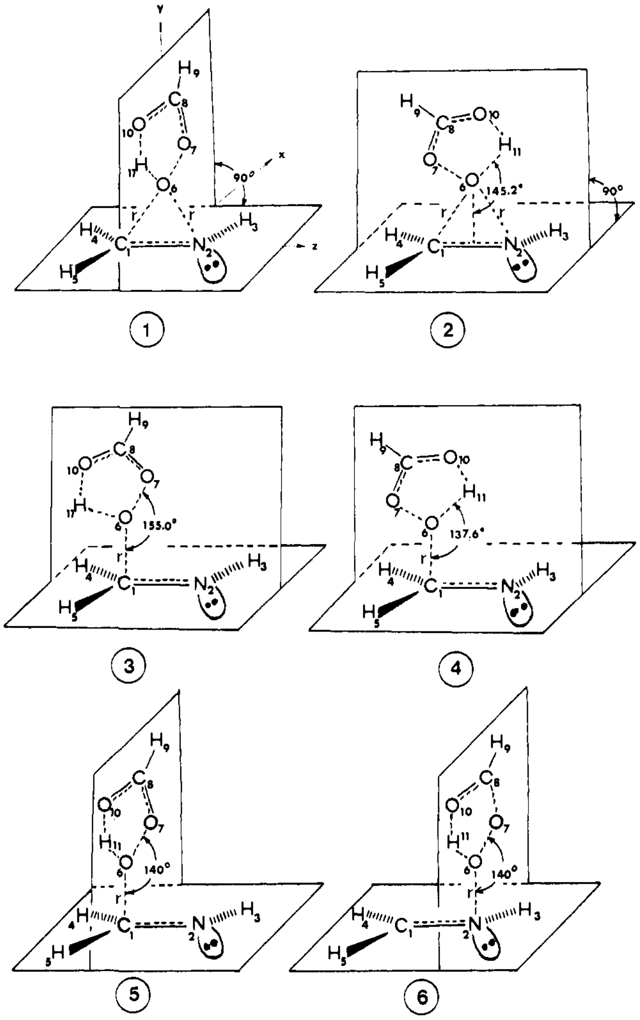

Figure 3. The geometries of transition state **1**–**6**.

Table II. Equilibrium Energies and Distances (r) in the Transition States and the Adducts

transition state or adduct	r, Å	E, au (STO-4G)
1	2.33	−355.349 69
2	2.57	−355.355 97
3	2.62	−355.357 71
4	2.62	−355.359 89
5	2.79	−355.360 61
6	2.83	−355.360 83
A		−355.355 55
B		−355.420 18
C		−355.297 03
D		−355.244 68

ticipating species. This, again, seems to support the experimentally determined electrophilic nature of peroxy acids. Negative charges on both peroxidic oxygen atoms (with O_6 being even slightly more negative than O_7) indicate, nevertheless, that the reaction is probably not just simply charge interaction controlled but must also involve some overlap control. This is particularly evident in the transition state **1** in which the electron-deficient p_y orbital of O_6 (the oxygen-oxygen bond axis) and the lowest unoccupied antibonding σ^* orbital (oriented in the same direction) of the peroxy acid are aligned nearly perpendicularly to the plane of the imine part.

"Unsymmetric" transition states are energetically more favorable than "symmetric" ones with the transition state for the peroxy acid attack on the nitrogen atom having the lowest energy. Thus, it seems safe to predict that at least the formation of nitrones (Scheme II) involves electrophilic attack of peroxy acid on the imine nitrogen atom, although we could not produce any convincing evidence that the N lone-pair electrons rather than π-bonding electrons are the nucleophilic center in this case.[4] The formation of the oxaziridine is according to this mechanism an exothermic reaction of 18.8 kcal/mol with the activation energy ranging from 1.5 to 4 kcal/mol (0.95 kcal/mol for nitrone). Unfortunately, there are no experimental data available to test this result.

Two-Step Mechanism. In view of the rather great complexity of the two-step mechanism we have investigated the geometry of the adduct only. Basically, three arbitrarily chosen geo-

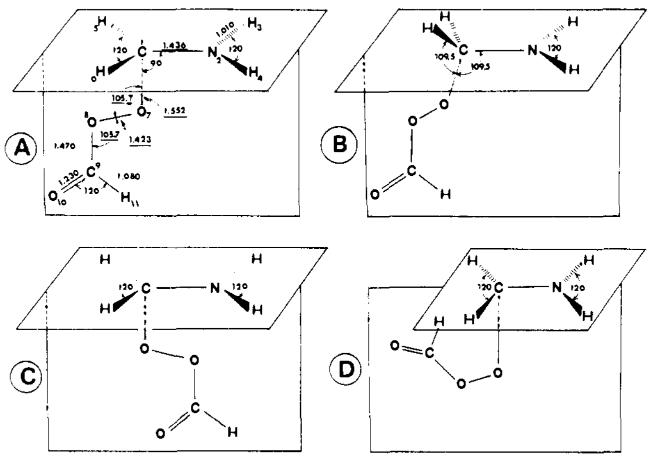

Figure 4. The geometries of adducts A–D. Underlined values are optimized.

metric arrangements (A, C, D) were investigated (Figure 4). Fairly extensive minimization was performed only in the case of conformation A, which has been found to possess the lowest energy. A considerably more stable conformation B resulted from the relaxation of the carbon atom to the tetrahedral one. B lies 36.3 kcal/mol below reactants and 17.5 kcal/mol below products. These results seem to support the experimental evidence which has been accumulated recently in favor of the two-step mechanism with the addition of peroxy acid to C=N of acyclic imines being the rate-determining step.[4,10-12] It seems quite probable that the transition state for the formation of the adduct resembles the one represented as **4** (reactant-like). The transition state for the second step (intramolecular nucleophilic reaction) is expected to be more product-like. The fact that an aliphatic imine reacts with hydrogen peroxide to form an adduct which is easily converted to an oxaziridine on gentle heating is also in accordance with the above-mentioned results.[13]

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References and Notes

(1) W. D. Emmons, *J. Am. Chem. Soc.*, **79,** 5739 (1957).
(2) V. Madan and L. B. Clapp, *J. Am. Chem. Soc.*, **91**, 6078 (1969); **92,** 4902 (1970).
(3) E. Schmitz, R. Ohme, and D. Murawski, *Chem. Ber.*, **98,** 2516 (1965).
(4) Y. Ogata and Y. Sawaki, *J. Am. Chem. Soc.*, **95,** 4687, 4692 (1973).
(5) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51,** 2657 (1969).
(6) B. Plesničar, M. Tasevski, and A. Ažman, *J. Am. Chem. Soc.*, **100,** 743 (1978).
(7) The last two values were not optimized; nevertheless, the positive charge on the hydrogens decreases in the order $H_3 > H_5 > H_4$, which is the same as in the completely optimized structure (J. M. Howell, *J. Am. Chem. Soc.*, **98,** 886 (1976); N. D. Epiotis, R. L. Yates, J. R. Larson, C. R. Kirmaier, and F. Bernardi, *ibid.*, **99,** 8379 (1977)).
(8) The term "transition state" is used throughout the paper rather loosely. Arbitrarily chosen molecular arrangements **1–6,** believed to be near the transition state, were selected on the grounds of chemical intuition and probably do not have zero gradient and only one negative force constant for molecular motion (J. W. McIver, Jr., and A. Komornicki, *J. Am. Chem. Soc.*, **94,** 2625 (1972); J. W. McIver, Jr., *Acc. Chem. Res.*, **7,** 72 (1974)).
(9) After completing this study we have optimized also the C–N distance of the transition state 1 and found, in accordance with the results of our previous study of the epoxidation reaction, that it becomes slightly longer as compared to free imine (1.288 Å).
(10) C. Bełzecki and D. Mostowicz, *J. Org. Chem.*, **40,** 3878 (1975).
(11) D. R. Boyd, D. C. Neil, C. G. Watson, and W. B. Jennings, *J. Chem. Soc., Perkin Trans. 2,* 1813 (1975).
(12) M. Bucciarelli, A. Forni, I. Moretti, and G. Torre, *J. Chem. Soc., Perkin Trans. 2,* 1339 (1977).
(13) E. Höft and A. Rieche, *Angew. Chem.*, **77,** 548 (1965).

The 147-nm Photolysis of Monosilane[1]

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Abstract: The 147-nm photolysis of SiH_4 results in the formation of H_2, Si_2H_6, Si_3H_8, and a solid hydridic silicon film. Two primary processes are involved, namely, (a) $SiH_4 + h\nu \rightarrow SiH_2 + 2H$ and (b) $SiH_4 + h\nu \rightarrow SiH_3 + H$, with $\phi_a = 0.83$ and $\phi_b = 0.17$. The quantum yields depend on the pressure of SiH_4 but at 2 Torr are $\Phi(-SiH_4) = 4.4 \pm 0.6$, $\Phi(Si_2H_6) = 1.29 \pm 0.08$, $\Phi(Si_3H_8) = 0.46 \pm 0.01$, and $\Phi(Si_{wall}) = 0.5$; the quantum yields for H_2 formation were not measured. A mechanism is proposed, which incorporates the known reactions of SiH_2 and SiH_3 radicals, and is shown to be in accord with the experimental facts.

Direct photochemical decomposition of silicon hydrides can occur only for light of wavelength less than 200 nm. While the vacuum ultraviolet photochemistry of methylsilane[2,3] and dimethylsilane[4] has been studied in some detail, only a brief report of the direct photolysis of monosilane,[5] the simplest member of the series, has appeared in the literature.

The $Hg(^3P_1)$-photosensitized decompositions of monosilane[6-10] and the methylsilanes[9] occur predominantly through the formation and subsequent reaction of monovalent silyl radicals, reactions that apparently are more complex in monosilane[9,11,12] than in the methylsilanes.[9] Since the vacuum ultraviolet photolysis of the methylsilanes results mainly in the formation of divalent silylene radicals,[2-4] one may expect the direct photolysis of monosilane to be quite different from the photosensitized decomposition.

As part of a general program concerned with the radiation and photochemical decomposition of gaseous silicon and germanium hydrides, we have studied the 147-nm photolysis of monosilane at 305 K. This paper is a report of our results.

Experimental Section

The photolyses were carried out in a cylindrical cell that had a diameter of 1.9 cm and a length of 13.4 cm. One end of the photolysis cell contained a pinhole leak, with a diameter of 2×10^{-3} cm, that led directly into the ionization region of a time of flight mass spectrometer. The opposite end of the cell was a lithium fluoride window that was common to both the photolysis cell and the light source. The cell was connected via ¼-in. stainless steel and 6-mm Pyrex tubing to large reservoirs containing the reactant gases.

The light source was a xenon resonance lamp in which resonance radiation at 147 (98%) and 130 nm (2%) was produced in an elec-

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