has always been presented[14,17] as a concerted 1,3-migration of silicon. We are not of that view and believe that the path is similar to that found for the C_3H_4 surface[16] involving vinylcarbene, cyclopropene, and vinylidene intermediates as shown in Scheme II. Thus, the observed stereochemical outcome of inversion on silicon[14] is accommodated by a 1,2-Si migration with retention followed by a 1,3-Si migration with inversion. Further studies are currently in progress on the mechanistic details of silylallene isomerizations.

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Gas-Phase Generation of Singlet Oxygen by Reaction of Ozone with Organic Substances

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The reaction of ozone (O_3) with organic substances in the gas phase has been studied extensively because of the presence of ozone in the atmosphere.[1] One of us[2] has suggested that some ozone reactions occurring in polluted atmospheres may be sources of singlet oxygen. A number of liquid-phase reactions of ozone have been shown to give singlet oxygen.[3] Many of the methods used to gain evidence for singlet oxygen in the solution reactions of ozone are not readily adapted to the gas phase. We now report that we have used the 1.27-μm emission of $O_2(^1\Delta g)$ to gain evidence for the formation of singlet oxygen in the gas-phase reactions of ozone with a variety of organic substrates. These reactions are characterized by the transfer of one oxygen atom from ozone to the oxidized substrate concurrent with singlet oxygen production.

When oxygen gas containing triethylamine was mixed with oxygen gas containing ozone at atmospheric pressure,[4,5] singlet Δ oxygen was formed as evidenced by observing the 1.27-μm emission.[6,7] A record of the 1.27-μm emission and the quantity

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(4) The experimental apparatus was composed of $^1/_4$-in. stainless steel tubing with valves for flow control and dilution. Ozone was generated by passing oxygen (99.995%) through a Welsbach generator. Oxygen gas streams containing the organic substrates were generated by passing oxygen (99.995%) through a bubbler containing the liquid organic substrate.
(5) The concentration of the organic substrate in the gas phase was monitored by using gas chromatography with flame ionization detection. A Dasibi monitor was used to measure the ozone concentration.

Table I. Observed 1.27-μm Emission in the Reaction of Ozone with Organic Substances

reactant	reactant concn, ppm	O_3 concn, ppm	1.27-μm emission, mV	$^1O_2$ concn,[a] ppm
bkgd	0	0	0.3	0.000
control 1	297	0	0.3	0.000
control 2	0	2340	0.6	0.003
triethylamine	297	2340	15.0	0.109
diethyl sulfide	366	2290	7.0	0.050
methyl disulfide	337	2370	1.4	0.009
trimethyl phosphite	380	2330	1.6	0.011
triethyl phosphine	381	2330	0.8	0.005
N-methylpiperidine	351	2290	25.4	0.186

[a] The $O_2(^1\Delta g)$ concentration was established in chemical trapping experiments with 2,3-dimethyl-2-butene and therefore is a minimum concentration.

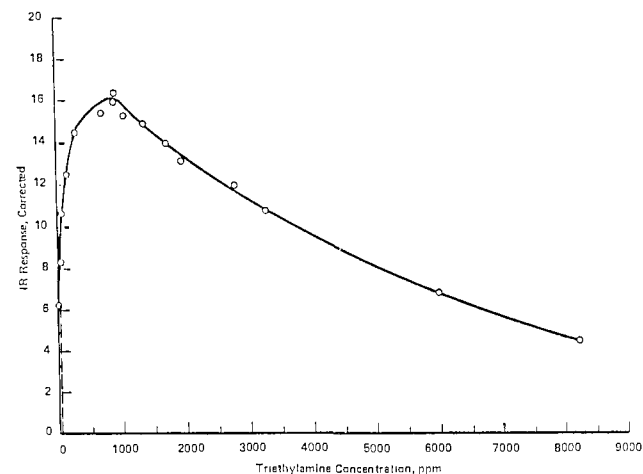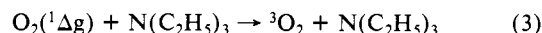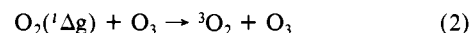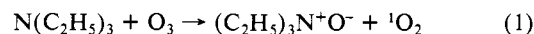**Figure 1.** Plot of $O_2(^1\Delta g)$ emission vs. triethylamine concentration at an ozone concentration of ~2350 ppm.

of $O_2(^1\Delta g)$ produced with several substrates is given in Table I. Control experiments in which oxygen containing ozone was passed through the optical detector gave signals near background level. Other control experiments with oxygen containing triethylamine also gave the same result.

Figure 1 is a plot of the 1.27-μm emission vs. triethylamine concentration at an ozone concentration of ~2350 ppm. The observed dependence on $N(C_2H_5)_3$ can be explained in terms of eq 1-3. Singlet oxygen was generated in the reaction of tri-

$$N(C_2H_5)_3 + O_3 \rightarrow (C_2H_5)_3N^+O^- + {}^1O_2 \qquad (1)$$

$$O_2(^1\Delta g) + O_3 \rightarrow {}^3O_2 + O_3 \qquad (2)$$

$$O_2(^1\Delta g) + N(C_2H_5)_3 \rightarrow {}^3O_2 + N(C_2H_5)_3 \qquad (3)$$

ethylamine with ozone (eq 1). Ozone (eq 2)[8] and triethylamine (eq 3)[9] are potent singlet oxygen quenchers and would be expected to remove $O_2(^1\Delta g)$ from the gas phase as seen in Figure 1. The singlet oxygen concentration passes through a maximum at a $N(C_2H_5)_3$ concentration that is ~35% of the required stoichiometric amount. This concentration is presumably dictated by the combined influence of eq 1-3. At higher triethylamine concen-

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(7) The 1.27-μm emission of singlet Δ oxygen was monitored by using a liquid nitrogen cooled germanium photodiode equipped with a 1.27 ± 0.02 μm band-pass filter. The IR region from 0.70 to 1.60 μm was scanned by replacing the band-pass filter with a Baush and Lomb Model 3 IR monochrometer. A narrow band was observed at 1.27 μm corresponding to the $^1\Delta g(\nu = 0) \rightarrow {}^3\Sigma(\nu = 0)$ transition of $^1O_2$ and a less intense band was also observed at 1.58 μm to the $^1\Delta g(\nu = 1) \rightarrow {}^3\Sigma_g^-(\nu = 0)$ transition of $^1O_2$.
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trations eq 3 begins to dominate and the $O_2(^1\Delta g)$ concentration decreases. The variation of IR emission with $N(C_2H_5)_3$ concentration provides powerful additional support for the presence of $O_2(^1\Delta g)$.

When the triethylamine concentration is held constant at ~324 ppm and the ozone concentration was increased from 65 ppm, the $O_2(^1\Delta g)$ concentration increases with increasing ozone concentration as indicated by the 1.27-μm emission and reaches a plateau maximum from an O_3 concentration of 270–480 ppm. The O_2-$(^1\Delta g)$ concentration decreased above an O_3 concentration of 480 ppm as the influence of eq 2 was felt.

Previous work in solution demonstrated that triethylamine oxide was the major organic product in the reaction of ozone with triethylamine.[10] Product studies are currently under way to characterize the product of the ozone–triethylamine reaction in the gas phase.

The results reported here indicate that the use of the 1.27-μm emission of $O_2(^1\Delta g)$ provides a powerful tool for investigating the question of the production of $O_2(^1\Delta g)$ in the gas-phase reactions of O_3 with organic substances. We plan to extend these studies to other examples where $O_2(^1\Delta g)$ is expected to be produced directly by reaction of O_3 with substrates such as certain olefins and sulfoxides, as well as to cases where O_3 reactions produce intermediates which have been shown to decompose to give an oxidized substrate and $O_2(^1\Delta g)$. The current results add support to the suggestion made by Pitts and co-workers,[10] ourselves,[2,6b,11] and others[12] that a variety of $O_2(^1\Delta g)$ generation processes can operate in polluted atmospheres to jointly contribute to the production of a significant concentration of $O_2(^1\Delta g)$.

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Biosynthesis of 7,8-Didemethyl-8-hydroxy-5-deazariboflavin, the Chromophoric Moiety of Coenzyme F420

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Methanogenic bacteria contain a variety of unusual cofactors such as coenzyme F_{420},[1] coenzyme F_{430},[2] methanopterin,[3] methanofuran,[4] and coenzyme M,[5] which are involved in the process of methanogenesis. We have shown earlier that cultures of *Methanobacterium thermoautotrophicum* excrete substantial

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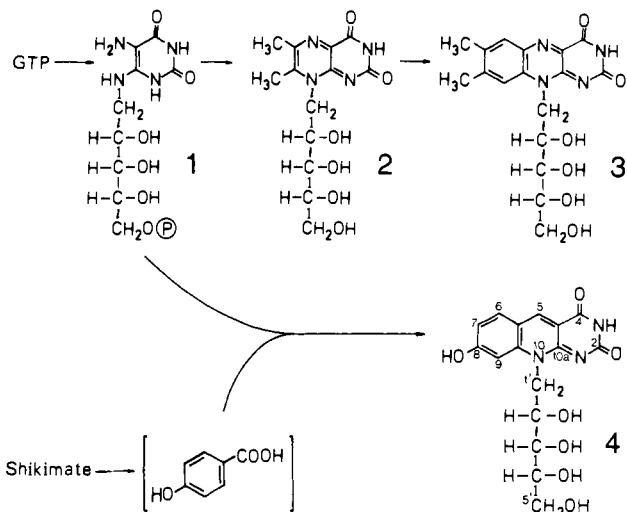(5) Taylor, C. D.; Wolfe, R. S. *J. Biol. Chem.* 1974, *249*, 4879.

Figure 1. Proposed pathway for the biosynthesis of 7,8-didemethyl-8-hydroxy-5-deazariboflavin (**4**).

amounts of 7,8-didemethyl-8-hydroxy-5-deazariboflavin (**4**, Figure 1), the chromophoric moiety of coenzyme F_{420}, into the culture medium.[6]

The structural similarity of riboflavin (**3**) and its deaza analogue **4** raises the question whether the two types of chromophores are produced by similar metabolic pathways. The biosynthesis of riboflavin has been studied extensively in eubacteria and in fungi.[7] The pathway starts from GTP and leads through several steps to 5-amino-6-(ribitylamino)-2,4(1*H*,3*H*)-pyrimidinedione 5′-phosphate (**1**) (Figure 1).[8] The addition of a pentose-derived four-carbon moiety,[9] which could be isolated only recently,[10] yields the pteridine derivative, 6,7-dimethyl-8-ribityllumazine (**2**). The xylene ring of riboflavin then arises by an unusual dismutation of the lumazine.[7]

Little is known about the biosynthesis of deazaflavins. Tracer studies have shown the incorporation of ^{14}C into coenzyme F_{420} from position 2 but not from position 8 of guanine.[11] Isotope from [1-^{13}C]glycine was incorporated into position 10a of the deazaflavin chromophore.[12] These data suggest that the pyrimidine ring of deazaflavins is biosynthesized from a purine in analogy with riboflavin. However, the origin of the carbocyclic ring of deazaflavins is unknown. It was only shown that tyrosine and the methyl group of methionine are not incorporated.[11]

^{13}C incorporation studies have been useful in the elucidation of the biogenesis of the xylene ring of riboflavin using a variety of labeled precursors.[9] Similar studies in *Methanobacteria* are limited by the poor uptake of complex nutrients. However, detailed information can be obtained even with simple precursors, such as acetate, by pattern recognition methods.[9] With this strategy in mind we have studied the incorporation of [1-^{13}C]acetate in *M. thermoautotrophicum* Marburg. The organism was grown at 65 °C in 14 L of a minimal medium supplemented with 5 mM [1-^{13}C]acetate in an atmosphere containing 20% CO_2 and 80% H_2. The pH of the culture medium was maintained at 6.0 by the addition of sodium bicarbonate. **4** was isolated from the culture

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