trien backbone, and a medium intensity band or doublet in the 1550 cm^{-1} region, which has been assigned to the C=N and/or C=C stretching modes. In addition, the highest *m/e* peak in the mass spectra of Ni(AT)Br and Ni(TAT)Br is that due to the (parent ion − HBr).

Typical proton nmr spectra are shown in Table I.

Table I. Nmr Spectra of Ni(AT)NO_3 and Ni(TAT)NO_3 in $CDCl_3$

Ni(AT)NO_3, δ^a	Ni(TAT)NO_3, δ^a	Band	Assignment
5.88 (2.3)^b	6.23 (2)^b	Broad singlet	-NH-
4.70 (1.2)	5.20 (1)	Sharp singlet	=CH-
3.13^c (13)	3.12^c (13)	Overlapping multiplets	-CH_2-
1.87 (6)	1.93 (3)	Sharp singlet	-CH_3

^{a} Measured in ppm downfield from internal TMS at 60 MHz. ^{b} Relative areas are shown in parentheses. ^{c} Center of gravity of complex pattern.

In each case, absence of any resonances which might be assigned to -NH_2 protons and the presence of a singlet attributed to the vinyl proton are consistent only with formation of a fully condensed macrocyclic ligand containing one partially delocalized six-membered chelate ring.

The template reactions described here should provide the first general synthetic route to metal complexes containing corrin-type ligands, *i.e.*, macrocyclic, Schiff base ligands with a single, partially delocalized negative charge. General application of these techniques is expected to result in the synthesis of many new complexes of this type, including those containing the backbone of the corrin ring.

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The Lifetime and Quenching Rate Constant for the Lowest Triplet State of Sulfur Dioxide

Sir:

Previous attempts to determine the lifetime of optically excited sulfur dioxide triplet molecules in the gas phase have not been successful.[1] A measurement of this quantity is necessary for the solution of the following important problem related to sulfur dioxide photochemistry. The only available triplet lifetime estimate ($\tau_0 = (7 \pm 1) \times 10^{-3}$ sec), made by Caton and Duncan, was based on an excitation of sulfur dioxide by electric discharge. The lifetime showed no detectable dependence on pressure of sulfur dioxide up to 300 μ. However the rate constant data of Strickler and Howell[2] and Rao, Collier, and Calvert[3] suggest that a significant decrease (from 35 to 75%) should have been observed over the pressure range used by Caton and Duncan.

We wish to report the findings of a study in which we have determined the lifetime of sulfur dioxide triplet species which have been generated in two distinct photochemical ways: (1) direct laser light excitation of sulfur dioxide to the first excited triplet state ($^3SO_2$) by absorption at 3828.8 Å within the "forbidden" triplet ← singlet band; and (2) flash photolytic excitation of sulfur dioxide to the first excited singlet state ($^1SO_2$) with subsequent triplet population by intersystem crossing.

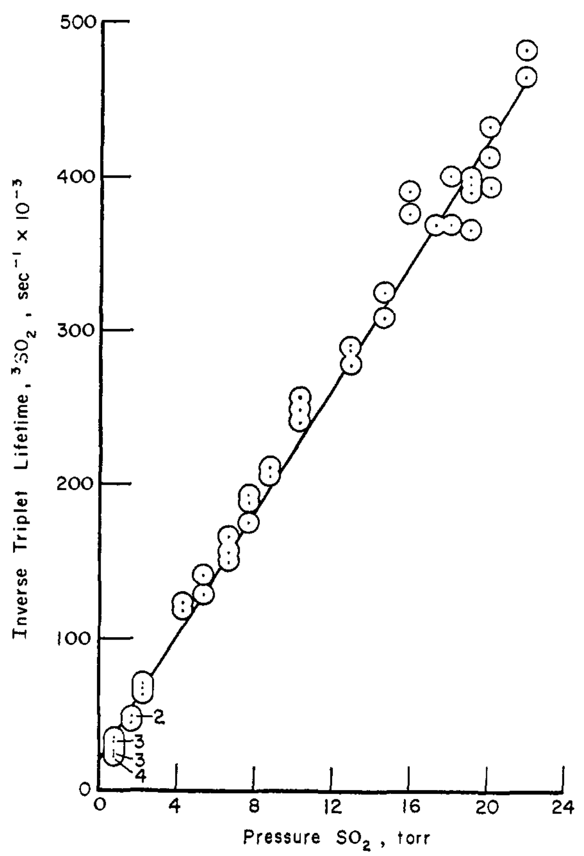

Figure 1. Plot of the inverse sulfur dioxide triplet lifetime *vs.* pressure of sulfur dioxide; data from the laser-excited sulfur dioxide experiments at 3828.8 Å.

The experimental details and the complete results of this study will be published elsewhere. A brief description is given here. The laser pulse of 3828.8-Å wavelength was generated from the output of a 75-MW ruby laser (6943 Å) by Raman shifting (1344 cm^{-1}) using nitrobenzene, followed by frequency doubling. About 50 kW of power at 3828.8 Å resulted in a half-intensity peak duration of 20 nsec. The intensity of phosphorescence emission was monitored at right angles to the excitation beam by a spectrally filtered phototube whose output was traced on an oscilloscope and photographed. For the apparatus employed in this work, pressures of SO_2 in the range 1–25 Torr gave signals which were sufficient to allow lifetime estimates with reasonable accuracy. The analog data from both the laser and the flash systems were digitized semiautomatically and reduced using least-squares computer programs. In the laser study, excitation occurred only in reaction I. Triplet decay in this system was by the reactions 1, 2, and 3. The lifetime data from the laser system are summarized in Figure 1.

The flash system employed in the second method was a flash photolysis apparatus with a 6-μsec half-intensity peak width. It was constructed to follow the phosphorescence intensity of the filtered, highly collimated beam

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(1) R. B. Caton and A. B. F. Duncan, *J. Amer. Chem. Soc.*, **90**, 1945 (1968).

(2) S. J. Strickler and D. B. Howell, *J. Chem. Phys.*, **49**, 1947 (1968).

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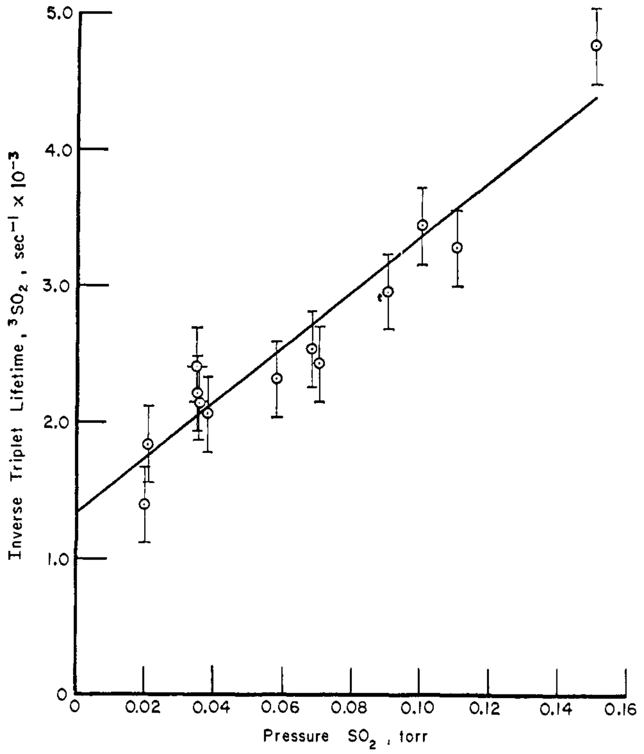

Figure 2. Plot of the inverse sulfur dioxide triplet lifetime *vs.* pressure of sulfur dioxide; data from the flash photolytic excitation of sulfur dioxide (2500–3300 Å).

taken from a position within the cell which was blind to the direct lamp flash. The monitored light was that which prevailed after the decay of the bulk of both the scattered incident light from the cell walls and the singlet sulfur dioxide emission. The pressure range employed (0.02–0.15 Torr) and the time at which the phosphorescence signal was monitored were selected by a computer analysis of the kinetic system, which maximized the triplet to singlet concentration ratio. Less than 0.01% of the signal could have been due to singlet emission in these experiments. The tail of the intensity of the scattered light from the flash lamp gave a small but very reproducible decay curve, which was subtracted from the total signal at a given time to derive the phosphorescence intensity–time data for each experiment. In these flash experiments excitation of sulfur dioxide occurred in reaction II; triplet formation, and excited singlet and triplet molecule decay, resulted from the series of reactions 1–8. The pressure dependence of the triplet lifetime data obtained from the flash system is summarized in Figure 2.

$$SO_2 + h\nu\ (3828.8\ \text{Å}) \longrightarrow {}^3SO_2 \tag{I}$$

$${}^3SO_2 \longrightarrow SO_2 + h\nu_p \tag{1}$$

$${}^3SO_2 \longrightarrow SO_2 \tag{2}$$

$$\left.\begin{array}{l} {}^3SO_2 + SO_2 \longrightarrow SO_3 + SO \\ {}^3SO_2 + SO_2 \longrightarrow 2SO_2 \end{array}\right\} \tag{3}$$

$$SO_2 + h\nu\ (2500\text{–}3300\ \text{Å}) \longrightarrow {}^1SO_2 \tag{II}$$

$${}^1SO_2 + SO_2 \longrightarrow 2SO_2 \tag{4}$$

$${}^1SO_2 + SO_2 \longrightarrow {}^3SO_2 + SO_2 \tag{5}$$

$${}^1SO_2 \longrightarrow SO_2 + h\nu_f \tag{6}$$

$${}^1SO_2 \longrightarrow SO_2 \tag{7}$$

$${}^1SO_2 \longrightarrow {}^3SO_2 \tag{8}$$

Obviously the triplet lifetime is a marked function of the sulfur dioxide pressure, as seen in Figures 1 and 2. From the slope of these inverse lifetime *vs.* pressure plots, the value of k_3 is estimated to be $(3.8 \pm 0.1) \times 10^8$ and $(3.9 \pm 0.7) \times 10^8$ l./mole sec from the laser and the flash experiments, respectively. The near identity of the values of k_3 derived from the very different experiments suggests that the reactivity of the triplet toward SO_2 is not a strong function of the vibrational level in which the triplet is first formed. It appears probable that vibrational equilibration of the triplet is practically complete for all of the conditions employed here.

The intercepts of the Figures 1 and 2 give in theory estimates of $k_1 + k_2$. The scatter in the data from the laser experiments and the range of pressures of SO_2 at which a useful intensity of signal could be obtained are such that extrapolation of the data to zero pressure is very inaccurate. However the data from the flash experiments, obtained at much lower pressures, provide a meaningful estimate of the intercept. These data give $k_1 + k_2 = (1.3 \pm 0.3) \times 10^3$ sec^{-1}. The lifetime of the triplet of sulfur dioxide at zero pressure $[1/(k_1 + k_2)]$ is estimated to be $(7.9 \pm 1.7) \times 10^{-4}$ sec. This result is a factor of 10 lower than that reported by Caton and Duncan.

It seems probable that the emission which was excited by electric discharge in sulfur dioxide by Caton and Duncan did not originate from a triplet sulfur dioxide molecule which was vibronically equivalent to that formed photochemically.

There is fair agreement between the triplet lifetime estimated in this work ($\tau = (7.9 \pm 1.7) \times 10^{-4}$ sec) and the values measured by Greenough and Duncan[4] by optical excitation of triplets in solid SO_2 at 77°K ($\tau = (5.0 \pm 1.0) \times 10^{-4}$ sec), and that estimated by McKenzie and Thrush[5] from chemiluminescence studies of excited SO_2 formed on O-atom association with SO at the wall ($\tau = (7.6 \pm 1.6) \times 10^{-4}$ sec). Since the systems are so very different from that used here, the agreement may be fortuitous.

The laser system is being redesigned to allow measurements at much lower sulfur dioxide pressures which will allow also a meaningful estimate of the $k_1 + k_2$ value from the laser system. A complete report of these results will be published later.

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