3041

90° for 12 h under vacuum to give 30.3 g of (RR)-5, analysis for chlorine, 3.71%. Recovered from the filtrates was 1.8 g of crude and 1.3 g of chromatographed (RR)-4. The resin was refluxed 15 h with excess CH_3ONa in CH_3OH, washed, and dried to give 30.0 g of (RR)-6, 0.65% Cl, or 0.18 mequiv/g of Cl, 0.87 mequiv/g of CH_3O, and 0.073 mmol of host/g (based on the difference between (RR)-4 used and recovered, and consistent with the difference in percent Cl of chlorinated resin and (RR)-5). Almost one in every hundred benzene rings of the polymer carries a host, and the remaining polymer provides structural support, channels, and environment.

(8) A 60 by 0.75 cm (i.d.) stainless steel jacketed (insulated) column was packed by a balanced-density slurry method in 50% (v) CH_3CN–$CHCl_3$ at 3 ml/min (800–900 psi) and was washed with methanol and then chloroform. It contained 9.5 g of 250–325 mesh (RR)-6, and possessed a dead volume of 18.4 ml.

(9) Samples dissolved in a minimum of mobile phase solvent were injected on the column through an injection loop. Corrections (less than one-third of dead volume) were made for loop, detector, and tubing volumes. Chromatograms were run at constant flow rates of 0.36–2.0 ml/min with pressure drops of 350–700 psi. After runs, the columns were washed and stored under methanol.

(10) L. R. Snyder and J. J. Kirkland, "Introduction to Modern Liquid Chromatography", Wiley, New York, N.Y., 1974, pp 25–29, 35–37.

(11) The authors warmly thank Ms. Linda A. Domeier for preparing these compounds, which were characterized for the first time (ref 4a): p-$ClC_6H_4CHNH_3Cl(CO_2CH_3)$, mp 194–197°; p-$CH_3O_2CC_6H_4CH$-$NH_3Cl(CO_2CH_3)$, mp 200–201°. The corresponding acids are known, e.g., A. H. Neims, D. C. DeLuca, and L. Hellerman, Biochemistry, 5, 203 (1966).

(12) The methyl ester perchlorate salts of the phenylglycines gave: for the para chloro derivative, mp 82.5° for the less retained enantiomer, $[\alpha]^{25}_{578}$ +73.7° (c 0.83, MeOH), mp 82° for the more retained, $[\alpha]^{25}_{578}$ −69.5° (c 0.77, MeOH); for the para carbomethoxy derivative, less retained, mp 53.5°, $[\alpha]^{25}_{578}$ +75.9° (c 0.80, MeOH), more retained, mp 53°, $[\alpha]^{25}_{578}$ −76.0° (c 0.80, MeOH). The methyl ester perchlorate salts of p-fluorophenylalanine gave: mp 79° for the less retained, $[\alpha]^{25}_{578}$ +35.5° (c 0.80, MeOH); mp 79.5° for the more retained, $[\alpha]^{25}_{578}$ −33.8° (c 0.80, MeOH).

(13) The CD spectrum of all four phenylglycine and three phenylalanine methyl ester salts in MeOH (c 0.8 ± 0.1) gave Cotton effects at 215–220 nm ($\pi \rightarrow \pi^*$) whose sign was configuration dependent, and at 250–260 nm whose sign was configuration independent and negative. The ester salts of known configuration correlated as follows: (S)-phenylglycine, ~220 nm, $[\theta]$ = +1260°; (R)-p-hydroxyphenylglycine, ~215 nm, $[\theta]$ = −950°; (S)-phenylalanine, ~220 nm, $[\theta]$ = +800°; (S)-tyrosine, ~220 nm, $[\theta]$ = +1100°; (+)-p-chlorophenylglycine, less bound, ~215 nm, $[\theta]$ = +240° thus S configuration and (−)-p-chlorophenylglycine, more bound, ~215 nm, $[\theta]$ = −240°, thus R configuration; (+)-p-carbomethoxyphenylglycine, less bound, ~220 nm, $[\theta]$ = +300°, thus S configuration, and (−)-p-carbomethoxyphenylglycine, more bound, ~220 nm, $[\theta]$ = −310°, thus R configuration;(+)-p-fluorophenylalanine, less bound, ~220 nm, $[\theta]$ = −275°, thus R configuration, and (−)-p-fluorophenylalanine, more bound, ~220 nm, $[\theta]$ = +280°, thus S configuration.

(14) G. D. Y. Sogah and D. J. Cram, unpublished results.

(15) S. C. Peacock and D. J. Cram, J. Chem. Soc., Chem. Commun., in press.

(16) D. H. McDaniel and H. C. Brown, J. Org. Chem., 23, 420 (1958).

(17) F. Suzuki and M. Oki, Bull. Chem. Soc., 48, 596 (1975), observed that intramolecular attractive forces of the π–π variety between differently substituted benzene rings accounted for the dominant conformation of 9-benzyltriptycenes.

(18) African–American Institute, AFGRAD Fellow.

G. Dotsevi Y. Sogah,[18] D. J. Cram*

Contribution No. 3550, Department of Chemistry
University of California at Los Angeles
Los Angeles, California 90024
Received November 17, 1975

Enhanced Dimol Emission of Singlet Oxygen by Cyclic Tertiary Diamines

Sir:

One criterion for the presence of singlet oxygen ($^1O_2$) in chemical and biological systems is the inhibition of the process under investigation by specific quenchers of $^1O_2$.[1,2] Tertiary amines have been studied extensively in this regard, and have been shown to inhibit product formation in several systems,[3,4] as well as inhibiting $^1O_2$ dimol emission at 634 nm in the gas phase[3,4] produced in the following reaction:

$$O_2(^1\Delta_g) + O_2(^1\Delta_g) \rightarrow 2O_2(^3\Sigma_g^-) + h\nu$$
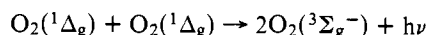
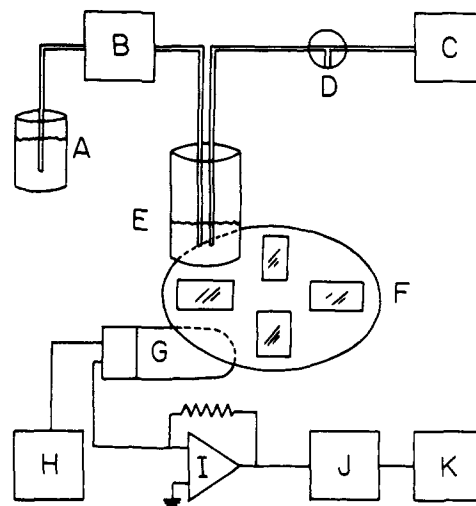The proposed mechanism for amine quenching is through the formation of a charge-transfer complex.[3–9] We wish to report

Figure 1. Experimental apparatus for detecting $^1O_2$ dimol emission and effects of added tertiary diamines. The production of $^1O_2$ in the peroxide/hypochlorite reaction is initiated by pumping 0.4 M NaOCl from reservoir (A) using a peristaltic pump (B) to the reaction flask (E) containing 5.0 ml of 1.2 M H_2O_2. The emitted light passes through a filter wheel (F) containing interchangeable interference filters and falls on a red-sensitive photomultiplier (G) powered by a high voltage supply (H). The resulting current is converted to voltage by operational amplifier (I), put through a low-pass filter (J) and displayed on a strip chart recorder (K). Air was bubbled through the reaction mixture by a pump (C). To test the effect of added tertiary amines, 1.0-ml solutions of these compounds were injected through a three-way stopcock (D) directly into the air line and carried to the reaction mixture.

here a *stimulation* of $^1O_2$ dimol emission by certain cyclic tertiary diamines in aqueous solution.

$^1O_2$ was produced from the reaction of NaOCl and H_2O_2[1,2,10] in a scintillation vial above a red-sensitive photomultiplier tube RCA 4832 (formerly C31025C). Interchangeable interference filters, which transmitted light at 634, 670, and 703 nm, were placed between the reaction vial and the photomultiplier tube. $^1O_2$ specific dimol emission occurs at 634 and 703 nm with little light emitted at 670 nm. Thus a comparison of light transmitted by these three interference filters can be used to differentiate $^1O_2$ specific emission from other types of chemiluminescence. The current from the photomultiplier tube was converted to voltage by an operational amplifier (Model 310J, Analog Devices, Norwood, Mass.) and displayed on a strip chart recorder after passive attenuation and low-pass filtering. A schematic of the experimental set-up is shown in Figure 1. A preliminary report of this apparatus has appeared.[11]

NaOCl as Clorox (0.4 M) was added by an LKB peristaltic pump at a rate of 1.4 ml/min into 5 ml of 1.2 M H_2O_2 in a scintillation vial. An air bubbler was used to promote uniform mixing and by 45 s after the onset of $^1O_2$ generation a steady state light emission had been reached. At that time, 1.0-ml solutions of various nitrogen-containing compounds were injected through the air line and carried to the reaction vial. By 45 s after the addition of the tertiary amine or an equivalent amount of distilled water, a new steady state light emission was observed and data were expressed as percent change in light emission caused by the addition of amine. Among the tertiary amines tested were 1,4-diazabicyclo[2.2.2]octane (DABCO, I) its monocyclic analogue N,N'-dimethylpiperazine (II) and
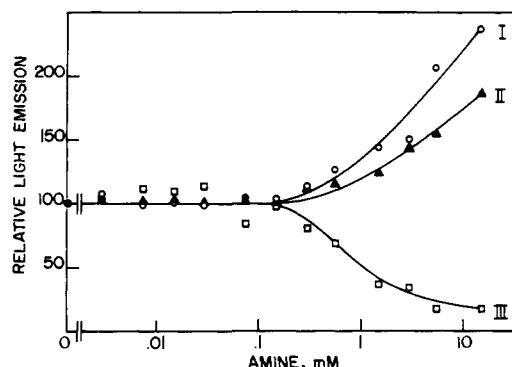
I II III

Communications to the Editor
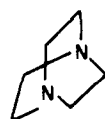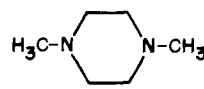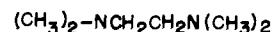
Figure 2. The effect of adding varying concentrations of the tertiary diamines, DABCO (I), II, or III, on the $^1O_2$ dimol emission produced by the $^1O_2$ generating system, peroxide/hypochlorite.

its acyclic analogue N,N,N',N'-tetramethylethylenediamine (III).

As can be seen in Figure 2, at final concentrations above 1.5 × 10^{-4} M, both DABCO and II stimulated total light emission whereas the acyclic analogue III inhibited dimol emission. This light emission had the same relative amount of light passing the 634 and 703 nm interference filters, either in the presence or absence of the tertiary diamines. In all cases, the light emission at 670 nm was <1% of that observed at 634 nm. Therefore, even in the presence of tertiary diamines the light emission remains characteristic of $^1O_2$.[12] NaN_3 has also been reported to quench the chemical reactivity of $^1O_2$.[13,14] When added at a final concentration of 0.013 M, NaN_3 decreased $^1O_2$-specific light emission to <5% of a control sample. NaN_3 was also effective in inhibiting the light emission stimulated by DABCO. The final pH at the conclusion of each experiment ranged from 8.4 to 9.0 in the presence or absence of tertiary diamines. The amines, when added to either the H_2O_2 or the NaOCl alone, did not produce detectable light. Furthermore, when the reaction was allowed to go to completion by continuing the addition of NaOCl until all the peroxide was consumed, no difference was observed in the duration of light emission in the presence or absence of DABCO. This would indicate that the enhanced light emission in the presence of the tertiary amine was not due to an acceleration in the overall rate of the peroxide/hypochlorite reaction.

Thus, while DABCO reduces the extent of 634-nm gas-phase emission observed from radiofrequency discharge generated $^1O_2$[3,4] and quenches the chemical reactivity of $^1O_2$ in aqueous systems,[5-9] we have observed an enhancement of 634 and 703 nm emission from aqueous solutions in which $^1O_2$ has been formed chemically. This phenomenon is also seen with the monocyclic analogue II of DABCO but not with the acyclic analogue III of DABCO and may indicate that steric factors play a role in this reaction. The increased $^1O_2$ dimol emission observed in this system could be attributed to a change in either the localized concentration of $^1O_2$ in solution or in the rate or extent of nucleation of oxygen bubbles. The reaction of tertiary amines with $^1O_2$ has been proposed to be through a charge-transfer complex,[3] which might increase $^1O_2$ lifetime and actually facilitate dimol emission. Any possible effect on nucleation is unknown.

In either case, the $^1O_2$ would still be made unavailable for chemical reactions and thus the DABCO and II could simultaneously enhance dimol emission while still quenching the chemical reactivity of $^1O_2$.[15]

References and Notes

(1) T. Wilson and J. W. Hastings, *Photophysiology*, **5**, 49–95 (1970).
(2) D. R. Kearns, *Chem. Rev.*, **71**, 395–427 (1971).
(3) C. Ouannes and T. Wilson, *J. Am. Chem. Soc.*, **90**, 6527–6528 (1968).
(4) E. A. Ogryzlo and C. W. Tang, *J. Am. Chem. Soc.*, **92**, 5034–5036 (1970).

(5) D. Bellus, H. Lind, and J. F. Wyatt, *J. Chem. Soc., Chem. Commun.*, 1199–1200 (1972).
(6) I. B. C. Matheson and J. Lee, *J. Am. Chem. Soc.*, **94**, 3310–3313 (1972).
(7) R. H. Young and R. L. Martin, *J. Am. Chem. Soc.*, **94**, 5183–5185 (1972).
(8) W. F. Smith, Jr., *J. Am. Chem. Soc.*, **94**, 186–190 (1972).
(9) R. H. Young, R. L. Martin, D. Feriozi, D. Brewer, and R. Kayser, *Photochem. Photobiol.*, **17**, 233–244 (1973).
(10) A. U. Khan and M. Kasha, *J. Am. Chem. Soc.*, **92**, 3293–3300 (1970).
(11) C. F. Deneke and N. I. Krinsky, Abstracts, 3rd Annual Meeting, American Society for Photobiology, Louisville, Ky., June 22–26, p 45 (1975).
(12) R. J. Browne and E. A. Ogryzlo, *Proc. Chem. Soc., London*, 117 (1964).
(13) N. Hasty, P. B. Merkel, P. Radlick, and D. R. Kearns, *Tetrahedron Lett.*, 49–52 (1972).
(14) C. S. Foote, T. T. Fujimoto, and Y. C. Chang, *Tetrahedron Lett.*, 45–48 (1972).
(15) Supported in part by NIH Grant AM 17745, NSF Grant BMS 74-18145, and by the Charlton Fund, Tufts University School of Medicine.

Carl F. Deneke, Norman I. Krinsky*

Department of Biochemistry and Pharmacology
Tufts University School of Medicine
Boston, Massachusetts 02111

Reduction of Molecular Nitrogen to Hydrazine. Structure of a Dinitrogen Complex of Bis(pentamethylcyclopentadienyl)zirconium(II) and an ^{15}N Labeling Study of Its Reaction with Hydrogen Chloride

Sir:

We recently reported the synthesis and isolation of a dinitrogen complex of bis(pentamethylcyclopentadienyl)zirconium(II), $[(C_5Me_5)_2ZrN_2]_2N_2$ (**1**), and noted further that on treatment with HCl one of the three N_2 ligands was reduced to hydrazine in 86% yield according to eq 1.[1]

$$[(C_5Me_5)_2ZrN_2]_2N_2 + 4HCl \rightarrow 2(C_5Me_5)_2ZrCl_2 + 2N_2 + N_2H_4 \quad (1)$$
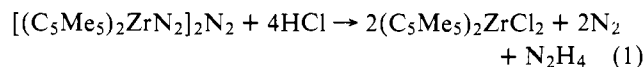
The ready protonation and reduction of N_2 in **1** is of considerable interest in view of a general lack of such reactivity for other isolated dinitrogen complexes.[2] Accordingly we have investigated the structure of **1** and have carried out an ^{15}N labeling study to determine which dinitrogen ligand is reduced to hydrazine in the reaction with HCl.

The structure of **1** as recently determined by single-crystal x-ray diffraction methods is illustrated in Figure 1. The binuclear structure consists of two $(\eta^5-C_5Me_5)_2ZrN\equiv N$ moieties bridged by a third dinitrogen ligand. Terminal and bridging dinitrogen ligands are bound end-on with essentially linear $Zr—N\equiv N$ and $Zr—N\equiv N—Zr$ arrangements; NN distances are 1.116 (8), 1.114 (7), and 1.182 (5) Å, respectively.

The ^1H NMR spectrum of **1** at 5° (toluene-d_8) shows the expected two singlets attributable to the pairwise equivalent $(\eta^5-C_5Me_5)$ rings.[1] ^{15}N NMR data for $[(C_5Me_5)_2Zr(^{15}N_2)]_2(^{15}N_2)$ also support a solution structure for **1** identical with that in the crystalline state. Thus at −28° (toluene-d_8), the 18.25-MHz ^{15}N NMR spectrum for **1**-$(^{15}N_2)_3$ consists of two doublets attributable to the two ^{15}N nuclei of the two equivalent terminal dinitrogen ligands ($^1J_{^{15}N-^{15}N}$ = 6.2 Hz) centered 89.8 and 160.4 ppm upfield of a third singlet resonance due to the two ^{15}N nuclei of the μ-N_2. The ^{15}N NMR spectrum for **1**-$(^{15}N\equiv^{14}N)_3$ exhibits the same spectrum with the exception that the two upfield doublets now appear as the expected singlets. The results of a variable temperature ^1H and ^{15}N NMR study of **1** will be reported in a forthcoming full paper.[3]

We have also investigated the possibility that the terminal dinitrogen ligands are substitutionally more labile than the μ-N_2. Table I summarizes the results of our studies of the ex-