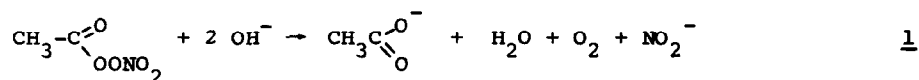


THE BASE-INDUCED DECOMPOSITION OF PEROXYACETYLNITRATE

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Peroxyacetyl nitrate (PAN), a highly reactive, biologically important photochemical air pollutant (1), decomposes in the presence of base (2,3) according to reaction 1. Whereas this stoichiometrically correct reaction in no way sug-



gests a mechanism for the decomposition, on the basis of spin conservation it is possible that molecular oxygen in either the $^1\Sigma_g^+$ or $^1\Delta_g$ excited state might be formed. We wish to report that, in fact, singlet oxygen is a product of reaction 1, and to suggest that singlet oxygen may, therefore, be important in oxidations involving PAN and its homologues, the peroxyacetyl nitrates.

Spectroscopic investigations of the emissions from $\text{O}_2(^1\Sigma_g^+)$ and $\text{O}_2(^1\Delta_g)$ have been undertaken by Bowen and Lloyd (4), Khan and Kasha (5) and Ogryzlo et al. (6). In our study, the presence of $\text{O}_2(^1\Delta_g)$ was determined by monitoring the emission at 1.27μ due to process 2. The near infrared detection system consisting of a



chopper, monochromator and liquid-nitrogen-cooled germanium photodiode, has been previously described (7). Reactions were carried out in one cm square cuvettes placed in front of the entrance slit of the monochromator. Dilute solutions of PAN (0.2 - 0.3M in benzene) were treated with aliquots of 0.4M potassium hydroxide in benzene-methanol (9:1). An immediate, vigorous and short-lived evolution of

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oxygen occurred and simultaneously emission at 1.27 μ was observed. Although the decomposition of PAN and the subsequent quenching of the singlet oxygen were too rapid to permit the entire emission spectrum to be obtained, point-by-point scanning between 1.1 and 1.4 μ showed that emission was observed only at 1.27 μ . The observation of $O_2(^1\Delta_g)$ in this system does not exclude the possibility that $O_2(^1\Sigma_g^+)$ may be formed initially in reaction 1 since deactivation from the $^1\Sigma_g^+$ state to the $^1\Delta_g$ state is possible (8).

The use of methanolic potassium hydroxide to effect the decomposition caused a significant attenuation of the emission intensity. This result is not unexpected if the correlation (9) between the efficiency of quenching of $O_2(^1\Sigma_g^+)$ and the magnitude of the intermolecular potential between $O_2(^1\Sigma_g^+)$ and the quenching species may be extended to $O_2(^1\Delta_g)$ systems. Attempts to quench the emission with tetramethylethylene (TME), an efficient scavenger (10) of $O_2(^1\Delta_g)$, gave inconclusive results because of a competing reaction involving only PAN and TME. Similar results were found for ethanethiol; further work on all of these processes is in progress.

The extreme reactivity of PAN in chemical and in biological in vitro and in vivo systems is well documented, but little understood. PAN is known to be an important cause of eye irritation and plant damage in polluted urban atmospheres (1b,11) and studies with simpler systems have shown that it can act as both an acetylating and oxidizing agent (12). The results presented here suggest that singlet molecular oxygen may have to be considered not only as a possible environmental oxidant (13) but also in the elucidation of the mechanism(s) of oxidation by PAN.

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