Reaction of Peroxyacetyl Nitrate with Amines

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Summary Peroxyacetyl nitrate (PAN) has been found to react with primary amines and ammonia to yield amides, while the reaction of PAN with tertiary amines produces chemiluminescence from an unknown product.

PEROXYACETYL NITRATE (PAN) is the most common member of the family of peroxyacyl nitrates, which are formed in photochemically polluted atmospheres.[1] Because of the biological effects of PAN (**1**),[2] its biochemistry has been studied extensively,[3] but other than our initial studies of the reaction of PAN with olefins,[4] little of its chemistry has been reported.[5]

When ammonia, methylamine, or ethylamine was bubbled through a solution of PAN in $CDCl_3$ (*ca.* $0{\cdot}5$M), an exothermic reaction occurred immediately [equation (1)]. In each case, the major organic product was shown to be the corresponding acetamide (**2**) by comparison of its n.m.r. and i.r. spectra with those published.[6] Nitrous acid and nitrite ion were also formed. PAN was also reacted with ammonia and methylamine in the gas phase by mixing a stream of PAN with a stream of ammonia or methylamine. In each case, the product which condensed on the walls of the reaction vessel was shown to be the corresponding acetamide (**2**) by comparison of spectra.

$$\underset{(\mathbf{1})}{\mathrm{AcO{\cdot}O{\cdot}NO_2}} + \mathrm{RNH_2} \rightarrow \underset{(\mathbf{2})}{\mathrm{AcNHR}} + \mathrm{O_2} + \mathrm{HNO_2} \qquad \mathrm{R = H, Me, Et, Pr^n, Bu^n} \tag{1}$$

When liquid n-propylamine or n-butylamine was injected into a solution of PAN (*ca.* 0·5M in $CDCl_3$), a vigorous evolution of oxygen was noted. The only organic product observed from this reaction was the corresponding acetamide (**2**) whose spectra were compared with those of the independently synthesized acetamide.[7] The reaction was quite rapid, being complete less than one minute after mixing. The conversions of all amines studied, when reacted with PAN solutions, was in excess of 90% as determined by n.m.r. The apparent yield of acetamide from ammonia was less (50—60%), probably due to the poor solubility of the amide in $CDCl_3$.

The observation of singlet molecular oxygen chemiluminescence from the aqueous base catalysed decomposition of PAN[5b] [equation (2)] prompted us to look for

$$\mathrm{AcO{\cdot}O{\cdot}NO_2} + 2\mathrm{OH^-} \rightarrow \mathrm{AcO^-} + \mathrm{H_2O} + \mathrm{NO_2^-} + \mathrm{O_2}\ (\text{in part } {}^1\Delta_g) \tag{2}$$

emission from the reaction of PAN with primary amines. No chemiluminescence in the visible region was observed from the reactions of PAN with primary amines in the gas phase. No emission at 1·27 μm due to singlet oxygen (reaction 3)[8] was detectable from the reactions of PAN with methylamine (gas phase) or n-butylamine (in solution), although it is possible that any singlet oxygen generated in these reactions may be quenched by the amines [equation (3)].[9]

$$\mathrm{O_2}({}^1\Delta_g) \rightarrow \mathrm{O_2}({}^3\Sigma_g) + h\nu\ (1{\cdot}27\mu\mathrm{m}) \tag{3}$$

It is most interesting that the reaction of tertiary amines (triethylamine, *NN*-dimethylaniline) with PAN did yield chemiluminescence, both in solution (PAN bubbled through 0·1M solution of amine in acetone) and in the gas phase. Part of the observed emission appeared at the same wavelength as the fluorescence maximum (660 nm) of one of the reaction products. The remainder of the emission had a spectral distribution in the red region (> 715 nm) which was the same as that of electronically excited nitrogen dioxide (NO_2*). This was demonstrated by producing NO_2* in the same apparatus and monitoring its emission.† Studies are in progress to further characterize the reaction products and emitting species. These studies have been broadened to include secondary amines and other primary and tertiary amines. In addition, we are investigating the potential utility of the chemiluminescent emission for the monitoring of PAN in the atmosphere.

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† Generated from the reaction $O_3 + NO \rightarrow O_2 + NO_2$* (ref. 10).

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