

a valence band near 340 nm. None of the $O_2(^1\Delta)$ states has previously been reported. Their assignment is currently in progress.

The equilibrium between excited iodine atoms and oxygen has been examined by monitoring the time-dependent I^* ($\equiv I(^2P_{1/2})$) concentration following creation of this species by pulsed laser photolysis of iodine-containing precursors. A double-exponential decay is observed which reflects a fast approach to equilibrium followed by a slower relaxation of the equilibrated mixture. Data obtained with the I^* precursors HI and CH_3I show that the rate constant for the reaction $I^* + O_2 \rightarrow I + O_2$ is insignificant compared with that for the reaction $I^* + O_2 \rightarrow I + O_2(^1\Delta)$. Data obtained from the precursors $i-C_3F_7I$, $n-C_3F_7I$, C_2H_5I and CF_3I suggest that $O_2(^1\Delta)$ is rapidly relaxed by the precursor itself, by the precursor radical or by some product formed in a reaction between the precursor radical and oxygen. The rate constant for the process $I^* + O_2 \rightarrow I + O_2(^1\Delta)$ has been found to be $(8.8 \pm 0.9) \times 10^5 \text{ s}^{-1} \text{ Torr}^{-1}$, while that for the process $I^* + O_2 \rightarrow I + O_2$ is $(0.3 \pm 1.3) \times 10^5 \text{ s}^{-1} \text{ Torr}^{-1}$.

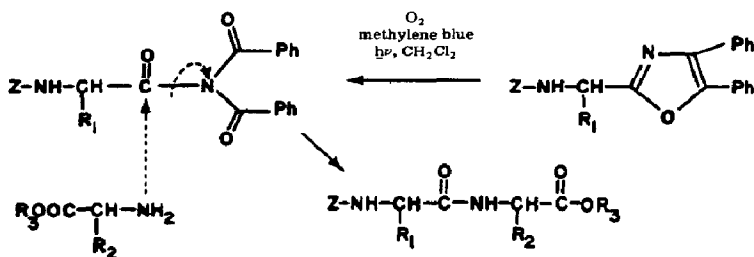
Electronic-to-vibrational energy transfer from $I^*(5^2P_{1/2})$ to $I_2(25 < v < 43)$ has been observed. I^* was created by pulsed laser photolysis of either I_2 -Ar mixtures at 475 nm or CF_3I - I_2 -Ar mixtures at 266 nm, while the resulting vibrational distribution of I_2 was monitored by laser-induced fluorescence on the $I_2(B \leftarrow X)$ transition. The experimental results are consistent with a nascent I_2 product distribution which is inverted, with a substantial fraction of the I_2 molecules formed in $v > 30$. Roughly 2% of the I^* deactivations result in $I_2(v = 40)$. The rate constants for vibrational relaxation of $I_2(v = 40)$ by argon, helium and I_2 at room temperature are $(7.3 \pm 0.3) \times 10^5 \text{ s}^{-1} \text{ Torr}^{-1}$, $(1.0 \pm 0.2) \times 10^6 \text{ s}^{-1} \text{ Torr}^{-1}$ and $(1.8 \pm 0.4) \times 10^6 \text{ s}^{-1} \text{ Torr}^{-1}$ respectively. These results have important implications for the mechanism of I_2 dissociation in the chemical oxygen-iodine laser. A chain-branching mechanism consisting of the steps $I^* + I_2 \rightarrow I + I_2(20 < v < 40)$, $I_2(20 < v < 40) + O_2(^1\Delta) \rightarrow 2I + O_2$ and $O_2(^1\Delta) + I \rightarrow O_2 + I^*$ may be responsible for the dissociation.

Recent applications of singlet oxygen reactions in synthesis[†]

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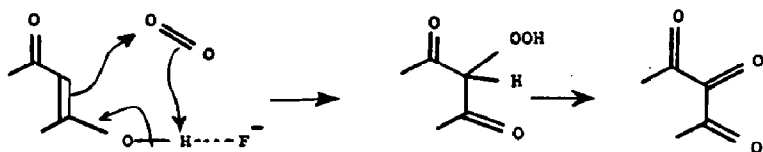
The reactions of singlet oxygen with oxazoles have provided a novel method for protecting carboxyl groups which may then be regenerated in an activated form:



Recent use of this procedure in the synthesis of dipeptides is discussed.

[†]Abstract of a paper presented at the COSMO 84 Conference on Singlet Molecular Oxygen, Clearwater Beach, FL, U.S.A., January 4 - 7, 1984.

A singlet oxygen reaction which has potential use in synthesis is the oxidation of β -dicarbonyl derivatives leading to vicinal tricarbonyl systems. Thus, while enols of β -diketones show only sluggish reactivity or no reaction with singlet oxygen, the presence of fluoride ion in the reaction medium promotes rapid uptake of singlet oxygen leading to 1,2,3-tricarbonyl products or their hydrates. This reaction most probably results from electron enrichment in the double bond through hydrogen bonding. Another method for forming vicinal tricarbonyls from β -diketones involves the formation of α -enamines followed by singlet oxygen oxidative cleavage:



Synthetic applications are discussed.