to sulfones.[1] In addition, some olefins which have special structural features give epoxides upon ozonolysis, and these products have been explained by postulating an intermediate π or σ complex[2-4] which subsequently loses molecular oxygen and gives the epoxide. The observation that olefin stereochemistry is preserved in the epoxide so produced perhaps lends support to these explanations.[3]

We have been convinced for some time that the oxygen evolved in some or all of these reactions probably has singlet multiplicity. Corey and Taylor have made a similar suggestion.[5]

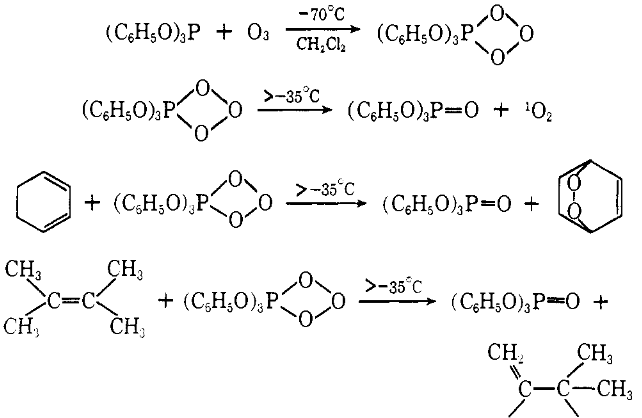
We wish to report that one such oxidation evolves oxygen which undergoes typical singlet oxygen reactions. This observation strongly suggests that the oxygen involved in a wide range of such oxidations probably has singlet multiplicity. The case examined in detail is based on the report by Thompson[6] that triaryl and trialkyl phosphites are oxidized rapidly and quantitatively to phosphates by ozone. In particular, Thompson found that some triaryl phosphites formed 1:1 adducts with ozone at low temperature; these adducts could be used to oxidize other added materials. We have observed that the oxygen formed during the decomposition of this adduct will undergo singlet oxygen reactions.

A number of recent reports have provided strong evidence for the involvement of singlet oxygen in photochemical oxidation and provided useful techniques for diagnosing the presence of singlet oxygen.[5,7-12] We have taken advantage of these techniques to test for the presence of singlet oxygen in the ozone oxidations of triaryl phosphites to phosphates.

We have shown that the adduct between triphenyl phosphite and ozone prepared at −70° can be used to convert 1,3-cyclohexadiene (1.5:1; adduct:diene ratio) into 5,6-dioxabicyclo[2.2.2]octene-2 (norascaridol) in 67% yield, mp (on samples recrystallized from pentane) 90–91°, some gas evolution (lit.[13] mp 88.5°). The material obtained is identical (nmr and infrared spectra) with that formed by photochemical oxidation.

The triphenyl phosphite–ozone adduct also converts an equimolar amount of 2,3-dimethylbutene-2 to 2,3-dimethyl-3-hydroperoxy-butene-1 (53% yield, bp 52–54° (9 mm); lit.[7] bp 55° (12 mm)); the product had infrared and nmr spectra identical with those of the product of photosensitized oxidation. In both reactions a quantitative yield of triphenyl phosphate was obtained. These reactions are typical of those which have been ascribed[5,7-12] to the presence of singlet oxygen generated by chemical or photochemical techniques.

Chart I. Reaction Scheme for Oxidation of Singlet Oxygen Acceptors by Phosphite–Ozone Adduct



A summary of the reaction scheme is given in Chart I. The exact nature of the phosphite–ozone adduct is still in doubt, but Thompson[6] has suggested the structure shown on the basis of ^{31}P nmr data. In the reactions described, the phosphite–ozone adduct was formed at −70° in methylene chloride by passing in an oxygen–ozone stream until the blue color of ozone persisted. Excess ozone was then removed by nitrogen purge. A cold solution of the cyclohexadiene or tetramethylethylene in methylene chloride was then added, and the reaction mixture was allowed to warm slowly to $\sim -30°$. This temperature was maintained for several hours and then continued warming to room temperature was permitted. Control experiments in the absence of singlet oxygen acceptors showed rapid oxygen evolution at −10°.

An orange solution of rubrene was bleached when treated with a nitrogen-purged solution containing the triphenyl phosphite–ozone adduct beginning at $\sim -35°$. No bleaching occurred at −70° in this same solution. If a nonpurged solution was used, bleaching did occur at −70°, indicating that the nitrogen purge successfully removes ozone and that the bleaching which occurs beginning at $\sim -35°$ in the purged solution is due not to ozone but most likely to the evolved oxygen.

The phosphite–ozone adduct is a convenient source of singlet oxygen in which the oxygen can be liberated in a controlled rate to accomplish the desired oxidation in high yield. We are continuing similar investigations to determine whether singlet oxygen can be detected in the other ozone oxidations referred to above.

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The Mercury(II)-Catalyzed Isomerization of the Sulfur-Bonded Monothiocyanate Complex of Chromium(III)[1]

Sir:

It was reported earlier that the reaction of mercury(II) with the sulfur-bonded monothiocyanate complex

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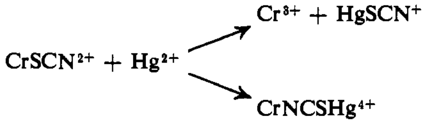
(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

of chromium(III) produces Cr^{3+} and $HgSCN^{+}$.[2,3] We now find, however, that this reaction proceeds *via* two parallel paths. One path produces Cr^{3+} and $HgSCN^{+}$, while the other yields the binuclear complex $CrNCSHg^{4+}$ (eq 1). The latter complex is also formed by the reaction of mercury(II) with the nitrogen-bonded monothiocyanate complex of chromium(III) and can be reconverted to $CrNCS^{2+}$ by the addition of chloride ions. This communication is concerned with the above reaction scheme, which we believe affords the first example of a metal-catalyzed linkage isomerization of a metal complex which does not proceed by an electron-transfer mechanism.



$$CrSCN^{2+} + Hg^{2+} \begin{cases} \nearrow Cr^{3+} + HgSCN^{+} \\ \searrow CrNCSHg^{4+} \end{cases} \quad (1)$$

The $CrSCN^{2+}$ was prepared as described earlier[2] except that its concentration was determined by the addition of V^{2+}, which produces an equivalent amount of thiocyanate ion.[4,5] The kinetics of reaction 1 were studied at 25° and 1 M ionic strength ($HClO_4$–$NaClO_4$) on the flow apparatus which has been described elsewhere.[6] The concentration ranges used were: $(CrSCN^{2+}) = 3 \times 10^{-5}$ to 5.4×10^{-4} M, $(Hg^{2+}) = 2 \times 10^{-3}$ to 1×10^{-1} M, and $(HClO_4) = 0.05$ to 1.0 M. Mercury(II) was always in sufficient excess to ensure pseudo-first-order conditions. The reaction was followed at 262 mμ where a decrease of absorbance due to the disappearance of $CrSCN^{2+}$ was observed, and also at 235 mμ where an increase in absorbance due to the formation of $HgSCN^{+}$ and $CrNCSHg^{4+}$ occurred. The rate constants calculated from the absorbance changes at the two wavelengths were identical within the experimental error of the measurements.

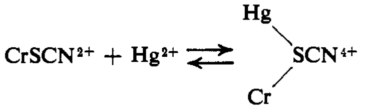
The rate of the reaction is first order with respect to each of the two reactants and the rate law has the form

$$-\frac{d(CrSCN^{2+})}{dt} = \left\{k_1 + \frac{k_2}{(H^+)}\right\}(CrSCN^{2+})(Hg^{2+})$$

with $k_1 = 5.4 \times 10^2$ M^{-1} sec^{-1} and $k_2 = 5.4 \times 10^2$ sec^{-1} at 25°. In the original solution of chromium(III) monothiocyanate there was always some $CrNCS^{2+}$ present with a concentration of approximately one-half of that of $CrSCN^{2+}$. The reaction of $CrNCS^{2+}$ with mercury(II) proceeds too rapidly to be detected on the stopped-flow apparatus.

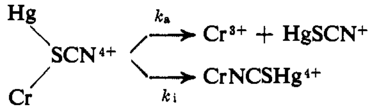
The yields of the products of reaction 1 were determined in the following manner. Hydrochloric acid was added to an aliquot of the reaction mixture in order to decompose the $CrNCSHg^{4+}$ complex into $CrNCS^{2+}$. The concentration of $CrNCS^{2+}$ was then determined spectrophotometrically.[7] Hexaaquochromium(III) was determined spectrophotometrically as chromate ion,[8] after the products were separated on a Dowex 50W-X8 ion-exchange column. The ratio of Cr^{3+} to $CrNCS^{2+}$ formed in reaction 1 was found to be 1.32 ± 0.12[9] and to be independent of the hydrogen ion concentration. This ratio may be compared with the ratio of Cr^{3+} to $CrNCS^{2+}$ formed in the spontaneous aquation and isomerization of $CrSCN^{2+}$ which is equal to 0.39.[10] The addition of mercury(II) to the complex thus makes the aquation path predominate, although a significant amount of isomerization still occurs.

The relatively slow rate of reaction 1 indicates that the rate-determining step is not substitution on mercury(II). We propose, therefore, that reaction 1 proceeds by a rapid preequilibrium step, which may involve the formation of the sulfur-bonded binuclear complex



$$CrSCN^{2+} + Hg^{2+} \rightleftharpoons \overset{Hg}{\underset{Cr}{SCN^{4+}}} \quad K$$

followed by the decomposition of this complex *via* two parallel paths



$$\overset{Hg}{\underset{Cr}{SCN^{4+}}} \begin{cases} \xrightarrow{k_a} Cr^{3+} + HgSCN^{+} \\ \xrightarrow[k_i]{} CrNCSHg^{4+} \end{cases} \quad (2)$$

The value of K is not large enough to cause departure from the pseudo-first-order kinetics under the experimental conditions used ($K < 1$ M^{-1} at 25° and $\mu = 1$ M).

The mechanism of the mercury(II)-catalyzed isomerization may be similar to the one previously proposed for the spontaneous isomerization of $CrSCN^{2+}$. The mechanism proposed for the spontaneous isomerization involves the formation of an intimate ion pair, with the internal return of the ion pair being rapid compared to its dissociation. Interaction of the metal orbitals with the π system of thiocyanate may also be important during the isomerization process.[11]

The above reaction scheme assumes that the mercury(II) attacks the sulfur atom of $CrSCN^{2+}$ (adjacent attack). This seems reasonable because mercury is a soft metal, and because steric factors should not be too unfavorable for adjacent attack since the Cr–SCN angle is less than 180°. Alternatively, the mercury(II) could attack the nitrogen atom of $CrSCN^{2+}$ (remote attack) to form $CrSCNHg^{4+}$ and the isomerization could then proceed by the rotation of the thiocyanate group (or the concerted sliding motion of $(H_2O)_5Cr^{3+}$ and Hg^{2+}) *via* a π-bonded transition state. Further studies of these reactions are in progress.

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(11) The spontaneous and mercury(II)-catalyzed isomerization may proceed by the $(H_2O)_5Cr^{3+}$ sliding along the π system of the SCN^- or of $HgSCN^+$. This type of mechanism may have some features in common with the mechanism of the more familiar type of ligand migration or insertion reaction.

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