

end products¹⁶ rather than from direct observation of adduct radicals. McIntosh and Wan, however, observed the esr spectrum of $\text{Ph}_3\text{SiOCPh}_2\cdot$ formed by addition of the triphenylsilyl radical to the carbon-oxygen π bond of benzophenone.¹⁷

A full interpretation of the spectra we have observed in terms of details of radical structure awaits assignment of the nitrogen hyperfine coupling constants to the individual nonequivalent atoms and the resolution of the ^{29}Si coupling. That iminamino radicals resemble their iminoxy analogs⁵ in being σ radicals with a C-N-N bond angle considerably less than 180° is already clearly indicated by the coupling between the unpaired electron and *two* nonpara hydrogens of carbon-bound phenyl groups.

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References and Notes

- (1) Tetrahydrofuran or 1-methyltetrahydrofuran was added as solvent for solid triphenylsilane. Reaction mixtures were degassed and sealed.
- (2) An Eimac R-150-2 xenon lamp was focused on a Pyrex sample tube in the microwave cavity of a Varian E-3 esr spectrometer. Most irradiations were carried out at room temperature.
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- (10) These radicals have appreciable lifetimes. Pulsed photolysis experiments (*cf.* ref 15) indicated lifetimes to be ca. 0.1 sec at room temperature and >1 sec at -40° .
- (11) We have not yet succeeded in resolving ^{29}Si coupling due to insufficient signal-to-noise ratio.
- (12) An authentic sample was prepared by trimethylsilylation of benzophenone hydrazone. Satisfactory elemental analysis and spectroscopic properties were found.
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Catalysis of Peroxymonosulfate Reactions by Ketones

Sir:

The Baeyer-Villiger reaction of Caro's acid and ketones to produce esters is well known.¹ These reactions are usually conducted in acidic media. Hydrogen peroxide and acetone are also known to react in aqueous solution² and a variety of peroxides can be produced. In the course of a study of peroxymonosulfate ion (HSO_5^-) reactions in weakly al-

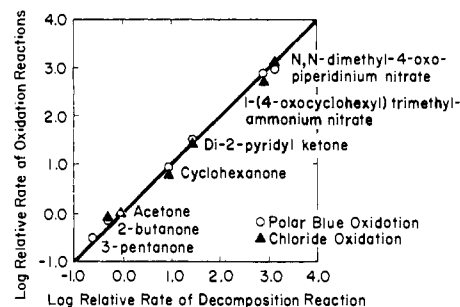


Figure 1. Linear free energy relationship for several ketones at pH 9.0.

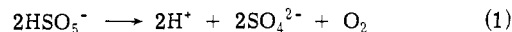
Table I. Catalysis of Peroxymonosulfate Reactions by Ketones

Ketone	Relative Rates of Reactions ^a		
	Decomposition ^b of peroxymonosulfate	Chloride ^c Oxidation	Polar Blue ^d Oxidation
None	<0.1	<0.1	<0.1
Acetone	1.0	1.0	1.0
Cyclohexanone	9.4	6.1	8.8
<i>N,N</i> -Dimethyl-4-oxopiperidinium nitrate	1400	1300	930

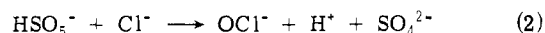
^a Each reaction was conducted at $2.7 \times 10^{-3} M \text{HSO}_5^-$ and pH 9.0. The rates in the presence of acetone have arbitrarily been taken as 1.0. Other rates are normalized to that of acetone at $5.0 \times 10^{-3} M$ (reactions are first-order in ketone). ^b Measured by iodometric titration. ^c The appearance of hypochlorite was followed spectrophotometrically at 292 μm . Chloride ion concentration was $2.4 \times 10^{-2} M$. ^d The disappearance of dye was followed spectrophotometrically at 620 μm . Dye concentration was $6.5 \times 10^{-5} M$.

kaline solutions, it was observed that ketones catalyze a number of reactions in an unexpected manner.

We present here results obtained on the catalysis of three reactions: (1) the decomposition of the peroxide



(2) the oxidation of chloride ion to hypochlorite ion



and (3) the oxidation of Polar Brilliant Blue GAW (an anionic dye) for which the complete stoichiometry is as yet unknown. Table I illustrates this catalysis for these three reactions in the presence of three ketones.

The rates of all three reactions are enhanced by the presence of the ketones, and the heterocyclic ketone, *N,N*-dimethyl-4-oxopiperidinium nitrate (hereafter referred to as ketone I), is particularly effective. (This compound is so active that a much lower concentration must be used to obtain accurate rate measurements.) Another very active catalyst is 1-(4-oxocyclohexyl)trimethylammonium nitrate.

It is evident from Table I that there is a marked parallelism among the three reactions suggesting that a common intermediate is involved. The effect is further demonstrated for seven ketones in Figure 1. As can be seen, an excellent linear free energy relationship is obtained. Also, Table I and Figure 1 show that a variety of ketone structures can be employed as catalysts for these reactions.

Oxygen and hypochlorite production measurements clearly indicate the stoichiometry shown in eq 1 and 2. However, with certain ketones side reactions such as the Baeyer-Villiger oxidation of the ketone and chlorination of the ketone by hypochlorite ion³ can complicate the overall reaction. For instance, with cyclohexanone a significant loss (15–30%) of ketone can be observed and only about 70% of

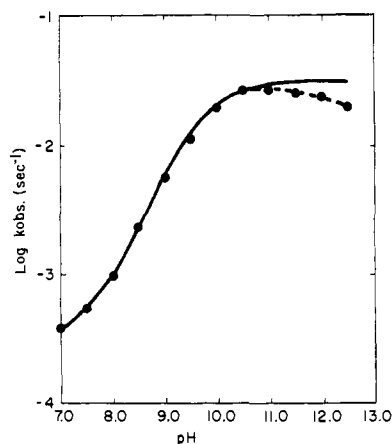


Figure 2. Variation of decomposition rate with pH for the peroxymonosulfate-cyclohexanone system. Reactions were conducted at $2.7 \times 10^{-3} M$ HSO_5^- , $10^{-2} M$ cyclohexanone, 28° , and $\mu = 0.15$. Solid line is calculated assuming $K_a = 2.3 \times 10^{-10} \text{ mol/l.}$, $k_1 = 6.9 \times 10^4 \text{ l.}^2 \text{ mol}^{-2} \text{ sec}^{-1}$ and $k_2 = 3.0 \times 10^{-2} \text{ l. mol}^{-1} \text{ sec}^{-1}$.

Table II. Effect of Cyclohexanone Concentration on the Observed Rate of Decomposition of Peroxymonosulfate^a

Ketone concentration, M	$10^3 k$ (Obsd), ^b sec^{-1}
1.0×10^{-3}	0.99
3.0×10^{-3}	2.7
5.0×10^{-3}	4.5
7.5×10^{-3}	6.1
10.0×10^{-3}	8.4

^a At $2.7 \times 10^{-3} M$ HSO_5^- , pH 9.0, $\mu = 0.15$. ^b A linear regression analysis of $\log k_{\text{obsd}}$ vs. \log concentration gave $n = 0.92$.

the theoretical yield of oxygen is evolved.⁴ However, with the quaternary ketone I very little oxidation would be expected and greater than 90% yield of oxygen is obtained.⁴

Small amounts of ketone can decompose large quantities of peroxymonosulfate indicating that the ketone is indeed a catalyst. For example, the turnover number (defined as the number of peroxide molecules decomposed for each ketone molecule oxidized) for ketone I is about 40. No loss of acetone is observed during the course of a decomposition run with this ketone and thus the turnover number for acetone must be very large. Also turnover numbers of greater than 1 are indicated for the other ketones shown in Figure 1.

The kinetics of the decomposition reaction have been studied and the rate law was found to be

$$-d[\text{HSO}_5^-]/dt = k_1 [\text{HSO}_5^-][\text{ketone}][\text{OH}^-]$$

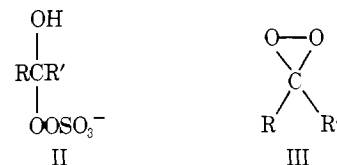
The loss of HSO_5^- is pseudo-first-order when ketone concentration and pH are held constant (the uncatalyzed reaction is second order in peroxide⁵); plots of $\log [\text{HSO}_5^-]$ against time are linear through two half-lives which indicate this kinetic order in peroxide concentration. Variation in ketone concentration showed that at low ketone concentration the rate was essentially proportional to the amount of ketone present (Table II).

A plot of \log rate against pH is shown in Figure 2. This profile also differs from the symmetrical profile found for the uncatalyzed decomposition reaction.⁵ At no point is the slope exactly one; however, HSO_5^- is half ionized near pH 9.5 and this results predictably in a leveling-off beginning at this pH. Below pH 8 another leveling begins; as yet the nature of this less important process is unestablished. The shape of this profile can be explained by the use of the K_a value for HSO_5^- of $2.3 \times 10^{-10} \text{ mol/l.}$, a k_1 value of $6.9 \times 10^4 \text{ l.}^2 \text{ mol}^{-2} \text{ sec}^{-1}$, and a k_2 value of $3.0 \times 10^{-2} \text{ l. mol}^{-1} \text{ sec}^{-1}$, where k_2 is a constant for the possible rate term ($-d[\text{HSO}_5^-]/dt = k_2 [\text{HSO}_5^-][\text{ketone}]$). Below pH 11

the agreement is good; however, these rate terms do not explain the small decline in rate observed above pH 11. Above pH 11 the enolization of the ketone may become important.

The rate law for the oxidation reactions appear to be more complicated than that for the decomposition reaction although the rate is dependent on peroxide, ketone, and pH in a manner similar to that found for decomposition. The rate of oxidation of reductant S also depends on reductant concentration. For $\text{S}^- = \text{Cl}^-$, the yield of oxygen production (decomposition of peroxide) decreases⁴ with increases in $[\text{Cl}^-]$ suggesting Cl^- and HSO_5^- compete for a reactive intermediate. In no case, however, was it possible to obtain 100% yield of hypochlorite. At a Cl^- to HSO_5^- molar ratio of about 40 only a 75% yield of hypochlorite is obtained. The failure to achieve 100% yield may be due to a side reaction (*i.e.*, chlorination of ketone).

The Polar Blue oxidations when followed by dye color disappearance showed apparent first-order behavior in dye concentration; however, this is open to several interpretations. Nonetheless, these results also suggest the involvement of an unusually reactive intermediate. The initial step in all three reactions is believed to be the nucleophilic addition of peroxymonosulfate to the carbonyl carbon to form an adduct (II). This adduct is analogous to the stable adduct 2-hydroxy-2-hydroperoxypropane formed in aqueous alkaline solutions of hydrogen peroxide and acetone.⁶ It is unlikely though that adduct II is the reactive intermediate. Smitherman's ¹⁸O isotopic work⁷ which will be published later clearly indicates that the dioxirane compound III is an intermediate in the decomposition reaction. Whether this is involved in the oxidation reactions is not known at this time.



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Molecular Twisting as a Mode of Excited State Decay. Mechanistic Organic Photochemistry^{1,2}

Sir:

Many years ago we noted that most photochemical reactions proceed directly to ground state of product.³ In the case of $n-\pi^*$ reactions this was revealed by following the