From the exact relations

$$\gamma_2 = X_X + Y_X - \gamma_t$$

$$\gamma_t = (X_X Y_X - k_{TX} k_{XT}[Q])/\gamma_2$$

we have

$$\gamma_t = \alpha \sim k_X K_x [Q] + \alpha^0,\ K_x = \frac{k_{XT}}{k_X + k_{TX}} \quad (A4)$$

which was obtained by putting $\gamma_2 \sim Y_x$, a necessary approximation to ensure that triplet quenching by ethyl iodide (heavy atoms) sustains a linear concentration, [Q], dependence as was observed experimentally (linear triplet quenching).

With the above restrictions, the initial triplet concentration $[^3M^*]_0$, and hence ϕ_T, is now defined, from eq A3

$$\frac{[^3M^*]_0}{[^1M^*]_0} = \phi_T = B_t \sim$$

$$\frac{k_{TM} + (k_{TX} k_{XE} K_e [Q]/[k_X + k_{TX}])}{k_M + k_E K_e [Q]} \quad (A5)$$

References and Notes

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(12) The fluorescence quenching observed in this investigation is more appropriately termed enhancement or negative quenching since $\partial r_F/\partial[Q] < 0$. We use the designation "quenching" to include both positive and negative quenching; its specific meaning will be revealed in context.
(13) The rate parameter nomenclature we use follows closely with that of Birks[9] (see also ref 1).
(14) A dissociative intersystem crossing process in $^1E^*$ could provide an additional route for populating $^3M^*$ which could be described by a lumped rate parameter, k_{TE}, to include such possibilities as

$$^1E^* \rightarrow {}^3M^*$$
$$^1E^* \rightarrow {}^3E^{**} \rightarrow {}^3M^*$$
$$^1E^* \rightarrow {}^3E^{**} \rightarrow {}^3M^{**} \rightarrow {}^3M^*$$
$$^1E^* \rightarrow {}^3M^{**} \rightarrow {}^3M^*$$

where two asterisks implies a higher excited state. It is not necessary to incorporate this process into Scheme I to explain external heavy-atom quenching of aromatic hydrocarbons and we ignore it for the sake of seeking a marginal mechanism.
(15) In the LRA of this function we treated $h - 1$ as the dependent variable since the propagated error in the product $r_F r_T$ makes this variable more uncertain than r_F.
(16) Exciplex internal conversion (k_{GE}) is unlikely to be efficient because of the large energy gap. Exciplex intersystem crossing (k_{XE}) to the triplet exciplex state, however, is an important quenching process in many cases[9] even when Q is not a heavy-atom quencher.[17]
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(18) We point out that the absolute magnitude of these rate ratios carries a significant uncertainty due to the 40% error in the determination of a_T for this system (Table III).
(19) We have examined the fluorescence response functions for the system DBA–3.0 mol $l.^{-1}$ ethyl iodide in cyclohexane at three emission wavelengths 410, 435, and 490 nm and were unable to fit these data to a single exponential impulse response. Analysis of the data for double exponential decay secured a well-behaved fit in each case implying the presence of a two-component fluorescent system. The amplitude of the shorter component $\tau \sim 0.3$–0.5 nsec was negative indicating the presence of an excited state reaction in the singlet manifold consistent with Scheme I. These results, although preliminary, offer direct support for $^1M^*$–Q photoassociation and demonstrate the presence of $^1E^*$ in this system. We plan a systematic temperature and concentration study of this and related systems employing nanosecond fluorescence techniques and will report on our findings in a future publication. In such a study careful attention must be given to controlling excitation lamp drifts and wavelength dependent transit time effects in the detector photomultiplier[20] since the decay times involved are short.
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An Investigation of Potassium Perchromate as a Source of Singlet Oxygen

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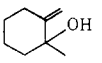
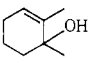
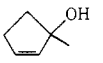
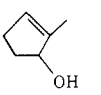
Received August 30, 1974

Abstract: Potassium perchromate undergoes aqueous decomposition with the concomitant generation of singlet oxygen. An upper limit for the yield of singlet oxygen, based on potassium perchromate, is estimated to be 6%. Use of the salt in a study of photodynamic reactions has demonstrated the occurrence of oxidative pathways other than those involving singlet oxygen and hence caution must be exercised in interpreting experiments employing the perchromate system as a source of singlet oxygen. In conjunction with this investigation the pH dependence of the rate of decomposition of CrO_8^{3-} in buffered solutions was investigated in the pH range from 10.0 to 12.5 using electron paramagnetic resonance (EPR) spectroscopy. The decomposition followed the approximate rate law $k = k'[H^+]$, with an order in hydrogen ion deviating slightly from unity, and $k' = 7 \times 10^7\ M^{-1}\ min^{-1}$. The thermal decomposition of solid K_3CrO_8 resulted in conversion to potassium chromate, potassium superoxide, and oxygen. No singlet oxygen was observed by EPR during thermal decomposition of the solid salt, establishing an upper limit for singlet oxygen of 0.1% of the ground state oxygen evolved.

In a recent communication from this laboratory[3] it was reported that potassium perchromate (K_3CrO_8) undergoes aqueous decomposition which, in the presence of singlet oxygen acceptors, results in the formation of typical singlet oxygen products and product distributions. These results were submitted as evidence that the oxygen evolved during the aqueous decomposition of potassium perchromate was, at least in part, in the excited singlet state $O_2(^1\Delta_g)$.

Table I. Product Distributions from Olefin Oxygenations

Olefin	Product alcohols A	Product alcohols B	K_3CrO_3 % A	K_3CrO_3 % B	Sensitized photooxygenation[a,b] % A	Sensitized photooxygenation[a,b] % B
			46	53	49	51
			82	18	89	11
	 		54, 5	41	53, 4	43

[a] See ref 22. [b] See ref 39.

Table II. Relative Reactivities of Olefins by Product Analysis

Olefin A	Olefin B	k_a/k_b K_3CrO_8	k_a/k_b Sensitized photooxygenation[a]
2-Methylpentene-2	1-Methylcyclopentene	2.7	2.0
2,3-Dimethylbutene-2	2-Methylbutene-2	41	41
2-Methylpentene-2	2-Methylbutene-2	0.90	1.3

[a] See ref 18.

Potassium perchromate, first prepared and isolated in 1905 by Riesenfeld et al.,[4] undergoes aqueous decomposition with the following stoichiometry.

$$4CrO_8^{3-} + 2H_2O \longrightarrow 4CrO_4^{2-} + 7O_2 + 4OH^-$$

The crystal structure of K_3CrO_8 determined by Stromberg and Brosset[5] in 1960 showed that the perchromate ion has $D_{2d}(\bar{4}2m)$ symmetry and consists of a chromium ion in oxidation state 5+ surrounded by four peroxide O_2^{2-} in which the geometrical arrangement of oxygen atoms around chromium is dodecahedral.[6]

Currently, there are many diverse methods available for generating $^1O_2$. However, each method (including, as this paper will show, K_3CrO_8) has at least one disadvantage associated with it. For example, O atoms, ozone, and mercury vapor present in microwave discharge techniques[7] are a constant source of concern. The dye-sensitized generation of singlet oxygen is, in some cases, complicated by sensitizer–substrate interactions which have plagued much of the work pertaining to the photodynamic effect.[8] The effect of hydrogen peroxide on the reaction is a drawback in the hypochlorite method of generating $^1O_2$.[9,10] The base hydrolysis of peroxyacetyl nitrate is, synthetically, without merit as a source of $^1O_2$, since PAN is a powerful oxidizing agent itself.[11] The decomposition of triphenyl phosphite ozonide is a potentially useful source of singlet oxygen, although direct oxidation of the substrate may occur under some circumstances with this source.[12,13] Diphenylanthracene endoperoxide undergoes smooth decomposition at 60° in benzene with liberation of $^1O_2$, but the reaction is limited to organic solvent systems.[14]

The results presented in our initial communication[3] suggested that the interesting salt, K_3CrO_8, might be employed as a relatively "clean" source of singlet oxygen in biological studies in contrast to interferences sometimes encountered in many of the techniques described above. We now, however, report the results of a more extensive investigation of the utility of K_3CrO_8 as a source of singlet oxygen, and these results show that great caution must be exercised when employing this salt as an $^1O_2$ source. In this paper we also report an electron paramagnetic resonance (EPR) investigation which determined the effect of pH on the aqueous decomposition of K_3CrO_8, and elucidated the nature of the products from the thermal decomposition of the paramagnetic perchromate anion. Previous EPR studies of K_3CrO_8 have been concerned primarily with characterization of the magnetic properties of the salt rather than with its chemical properties.[15-17]

Evidence for the Intermediacy of Singlet Oxygen from the Aqueous Decomposition of K_3CrO_8. Preliminary evidence for the involvement of singlet oxygen was obtained by isolating 2,3-dimethyl-3-hydroperoxybutene-1 in 35% yield (based on the starting olefin) after the simultaneous formation and decomposition of K_3CrO_8 in the presence of 2,3-dimethylbutene-2. The product hydroperoxide had infrared and NMR spectra identical with those of the product from sensitized photooxidations known to proceed by way of singlet oxygen.

In general, when a basic solution of potassium chromate is added to an aqueous methanol solution of H_2O_2 and substrate at 5°, a red-brown precipitate begins to form indicating formation of K_3CrO_8 with a simultaneous slow effervescence which increases upon warming to room temperature. The oxygenation product can then be isolated after reduction and aqueous work-up procedures. This procedure, which obviates the isolation of K_3CrO_8 as the dry salt, is useful with substrates which are unreactive toward basic hydrogen peroxide.

Three additional forms of evidence were obtained supporting the intermediacy of singlet oxygen from the aqueous decomposition of K_3CrO_8.[2]

(1) Product distributions from the reaction of K_3CrO_8 with three different singlet oxygen acceptors were compared with the characteristic singlet oxygen product ratios obtained from the dye-sensitized (Rose Bengal) photooxygenation of the same acceptors in methanol. The product hydroperoxides were then reduced to the corresponding alcohols with sodium borohydride before analysis by flame ionization chromatography. In this particular study, K_3CrO_8 was again simultaneously formed and decomposed in aqueous methanol (60:40, v/v) solution of the acceptor. As summarized in Table I, the product distributions obtained from the perchromate system are in good agreement with those obtained under dye-sensitized conditions, lending support to intermediacy of singlet oxygen.

(2) The relative reactivities of various pairs of olefins obtained from competition experiments under dye-sensitized conditions are also a parameter indicative of the involvement of singlet oxygen.[18] As shown in Table II, the relative reactivities of the indicated pairs of olefins obtained from the perchromate system are in reasonably good agreement with those obtained from sensitized photooxygenation. In these experiments the perchromate salt was simultaneously formed and decomposed in the presence of pairs of olefins,

and the amounts of the reduced hydroperoxides (alcohols) were determined by flame ionization chromatography.

(3) Spectral evidence supporting the presence of singlet oxygen in the aqueous decomposition of K_3CrO_8 was obtained by monitoring the weak emission at 1.27 μ which was detected with a liquid nitrogen cooled germanium photodiode which was described in our original communication.[3]

$$O_2(^1\Delta_g) \longrightarrow O_2(^3\Sigma_g) + h\nu\ (1.27\ \mu) \qquad (1)$$

The near-infrared detection system consisted of a chopper, 1.27 μ interference filter, liquid nitrogen cooled germanium photodiode, lock-in amplifier, and recorder.[19] Reactions were carried out in circular cuvettes 3 cm in diameter placed directly in front of the interference filter. The emission was easily observed simultaneously with the evolution of gas bubbles when a basic potassium chromate solution was mixed with a diluted hydrogen peroxide solution at room temperature. Moreover, upon the addition of water at ~45° to the pure, dry potassium perchromate salt, a sudden and strong emission was detected accompanied by an immediate and vigorous evolution of gas. The emission was monitored continuously for 20 min until it became too weak to detect.

The above results are characteristic of involvement of free singlet oxygen. As mentioned above, triphenyl phosphite ozonide is also a source of free singlet oxygen; however, under some circumstances, direct transfer of oxygen to substrate occurs with this $^1O_2$ source.[12,13] In the case of potassium perchromate, the good comparison of product distributions and relative reactivities with sensitized photooxidation support the involvement of free $^1O_2$ under the reported experimental conditions. Later evidence is presented suggesting oxidative pathways in addition to free $^1O_2$ with other types of substrates.

Estimate of Singlet Oxygen Yield. If k_d and k_a represent the primary pathways responsible for the loss of singlet oxygen

$$^1O_2 \xrightarrow{k_d} {}^3O_2 \qquad (2)$$

$$A + {}^1O_2 \xrightarrow{k_a} AO_2 \qquad (3)$$

then the instantaneous yield of product, Y_{AO_2}, from K_3CrO_8 oxygenations should be given by the following expression.[18]

$$Y_{AO_2} = Y_{t_{O_2}} \frac{k_a[A]}{k_d + k_a[A]} \qquad (4)$$

In this expression, Y_{1O_2} is the yield of singlet oxygen produced from a given amount of potassium perchromate. This relationship is valid only if [A] does not change during the reaction (conversions less than 10%).[18] An estimate of yield of singlet oxygen can be obtained by plotting $1/Y_{AO_2}$ against $1/[A]$ where A and AO_2 are the singlet oxygen acceptor and product, respectively.

$$1/Y_{AO_2} = 1/Y_{1_{O_2}}\left[\frac{\beta}{[A]} + 1\right] \qquad (5)$$

The intercept of such a plot is inversely proportional to the yield of singlet oxygen and the ratio of slope to intercept (k_d/k_a) is defined as β. Values of β have been determined for numerous acceptors by this technique.[18,20,21]

For this study the yield of singlet oxygen from K_3CrO_8 was determined using 2,3-dimethylbutene-2 as the acceptor and plotting $1/Y_{AO_2}$ against $1/[A]$. The validity of the mechanism for production of singlet oxygen from K_3CrO_8 can be measured in terms of the value of β obtained and comparing it to the value previously reported for dye-sensitized photooxygenations.[22] The value of β determined from the plot in Figure 1 is 0.007 which is in qualitative agreement with the previously reported value of 0.003.[22] From the intercept, an upper limit for the yield of singlet oxygen, based on potassium perchromate, is estimated to be approximately 6 ± 2%. The large uncertainty associated with both the intercept and the value of β is primarily due to the unavoidable and variable loss of product during the work-up of the aqueous reaction mixture before reduction of the product hydroperoxides and subsequent analysis by flame ionization gas chromatography. In addition, the above results are for the heterogeneous perchromate system and relations 4 and 5 are strictly true only for homogeneous systems which may also be a contributing source of the uncertainty in values of β and the intercept.

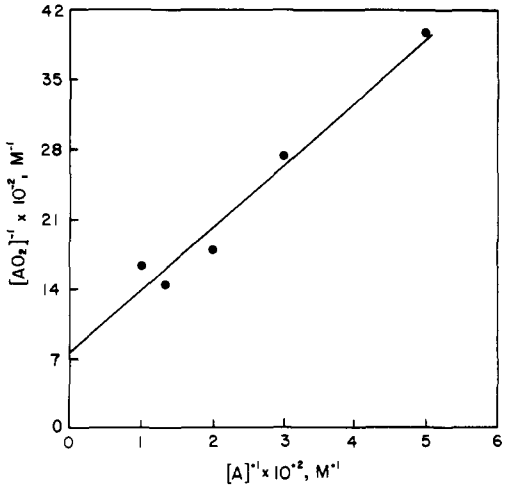


Figure 1. Determination of β value and yield of singlet oxygen for perchromate oxygenation of 2,3-dimethylbutene-2. Slope = 6.1 ± 0.8; intercept = 849 ± 250; β = 0.007 ± 0.002.

Inhibitory Effect of DABCO on Potassium Perchromate Oxygenations. DABCO (1,4-diazobicyclo[2.2.2]octane) is commonly employed[23] to test intermediacy of singlet oxygen, since it physically quenches $O_2(^1\Delta_g)$ with a known relative rate constant ("β" = 0.006)[24] but does not chemically react with it. Because DABCO is water soluble it appeared to be an ideal candidate to provide further evidence for the intermediacy of singlet oxygen in the aqueous perchromate system. Initial qualitative studies demonstrated that the addition of DABCO did indeed competitively inhibit product formation during perchromate oxygenation of 2,3-dimethylbutene-2 and other singlet oxygen olefinic acceptors such as 2-methylpentene-2.

However, a more definitive quantitative study revealed that DABCO inhibited the perchromate oxygenation of 2,3-dimethylbutene-2 with only 25% of its predicted inhibitory efficiency. This effect is graphically demonstrated in Figure 2. The ratio of product formation without quencher, to the amount formed in the presence of DABCO, $[AO_2]_0/[AO_2]_q$, is easily derived and is predicted to be governed by the following expression, where k_q is the rate constant for the physical quenching of singlet oxygen by DABCO.

$$\frac{[AO_2]_0}{[AO_2]_q} = 1 + \frac{k_q[Q]}{k_d + k_a[A]} \qquad (6)$$

When the concentration of acceptor, [A], is held constant, a plot of $[AO_2]_0/[AO_2]_q$ against [Q] should result in a straight line with a slope of $k_q/(k_d + k_a[A])$ and an intercept of 1.0. The predicted and experimentally determined behavior of 2,3-dimethylbutene-2 and DABCO are contrasted in Figure 2. It is evident from the slopes of the pre-

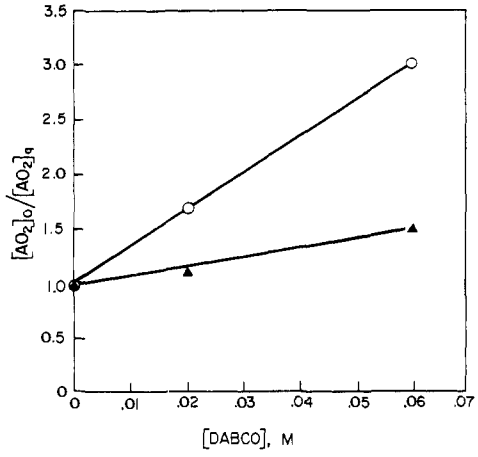


Figure 2. DABCO inhibition of perchromate oxygenation of 2,3-dimethylbutene-2. Predicted behavior (○), slope = 33.2 ± 0.6; observed behavior (▲), slope = 8.6 ± 1.2.

Table III. Comparison of Percent Destruction of Purine and Pyrimidine Bases Produced by Singlet Oxygen Generated by Microwave Discharge[a] and Potassium Perchromate[b]

Base	Percent destruction: Microwave discharge (exposure time, min)		Potassium perchromate
Uric acid	83	(45)	100
Guanine	69	(45)	53
Guanosine	69	(45)	30
Theophylline	57	(45)	48
Thymine	60	(90)	53
Theobromine	58	(90)	40
Thymidine	50	(90)	37
Caffeine	35	(180)	46
Uracil	28	(180)	60
Hypoxanthine	17	(180)	30
Cytosine	5	(180)	46
Inosine	3	(180)	25
Adenine	3	(180)	15

[a] I. Rosenthal and J. N. Pitts, Jr., *Biophys. J.*, 11, 963 (1971). [b] All exposures in carbonate buffer (pH 10.5).

dicted and experimentally determined lines that DABCO is inhibiting oxygenation only 25% as effectively as predicted. An explanation for this apparently anomalous behavior (predicted versus observed) may reside in the fact that the chosen relative rate constant ("β" = k_d/k_q = 0.006) for the physical quenching of $^1O_2$ by DABCO is for the solvent methanol, whereas the observed results are for an aqueous methanol (60:40, v/v) system. The rate constant for the decay of singlet oxygen, k_d, is a function of solvent and increases with the aqueous content of the solvent, in this case methanol.[25-28] Indeed, the value of k_q for quenching of singlet oxygen by DABCO may also be a function of solvent. For the aqueous methanol system employed, the value of k_d is probably greater than the value of k_d in pure methanol used in expression 6 for determining the predicted slope of the line in Figure 2. Consequently, the value of the predicted slope could be substantially smaller than the value used in Figure 2. Thus, if a somewhat larger value of k_d is chosen, then the predicted and observed values for DABCO inhibition of the perchromate oxygenation of TME are in good agreement.

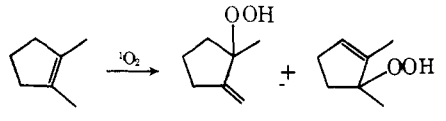
Reactivity of Purine and Pyrimidine Bases toward Perchromate Oxygenation. Photodynamic reactions,[8] which require a dye, visible light, and molecular oxygen, produce appreciable destruction of guanine moieties (although there is some disagreement with this view[29]) and, to a smaller extent, thymine moieties in nucleic acids by some oxidative pathway.[30] By analogy with dye-sensitized oxygenation of organic compounds, it has been suggested that singlet oxygen may be an active intermediate[31] in photodynamic reactions.[32]

The relative reactivity of various purine and pyrimidine bases in the photodynamic reaction compares favorably with relative percent destruction of the same purine and pyrimidine bases by singlet oxygen generated by both the hypochlorite method[33] and the microwave discharge method.[34]

In order to test the suitability of potassium perchromate as a source of singlet oxygen for the investigation of photodynamic reactions, a study, similar to those employing the hypochlorite and microwave discharge methods, was conducted. In this investigation, a constant amount of potassium perchromate was added to buffered solutions of the purine and pyrimidine bases and allowed to decompose. The percentage of base destruction was measured by uv spectrophotometry.

The results (see Table III) of the exposure of several purine and pyrimidine bases to perchromate oxygenation at pH 10.5 were compared, on a relative reactivity basis, to those obtained for exposures to singlet oxygen generated by the microwave discharge technique.[34] The random nature of the observed percent destruction of the selected purine and pyrimidine bases resulting from exposure to the aqueous decomposition of potassium perchromate, relative to that resulting from purine exposure to singlet oxygen generated by microwave discharge, suggests that the perchromate induced destruction involves at least one or more species in addition to singlet oxygen. The suggestion that singlet oxygen from potassium perchromate is responsible for at least some destruction is reinforced by the observation that DABCO inhibited the destruction of uracil. However, in a recent report by Hodgson and Fridovich,[35] it has been demonstrated that superoxide radical is also generated during the aqueous decomposition of K_3CrO_8. In view of this finding, the random nature of the perchromate results in Table III could be reasonably attributed to O_2^- which would enhance the destruction predicted by a purely singlet oxygen pathway.[36] A pathway involving oxidative destruction by way of a direct interaction with CrO_8^{3-} or possibly $HCrO_8^{2-}$, depending upon the pH of the reaction medium, cannot be ruled out either.

Limitations of Perchromate Oxygenations. Although it appears that the aqueous decomposition of K_3CrO_8 evolves singlet oxygen resulting in typical singlet oxygen reaction products with selected olefinic acceptors, it also is unmistakably clear that the oxidation of other substrates, such as some of the purine and pyrimidine derivatives, involves at least one additional oxidizing intermediate. Thus, the perchromate oxygenations of 1-2-dimethylcyclopentene resulted not only in the formation of the two expected singlet oxygen products (see reaction 7), but also in the production



(7)

of three unidentified products (30% of total product yield). One of the unidentified products, detected also in the dye-sensitized photooxygenation, was presumably due to free radical oxidation. However, the other two were apparently formed by some independent and undetermined pathway.

The same type of behavior was exhibited by 1-methylcyclohexene. Perchromate oxygenation resulted in formation

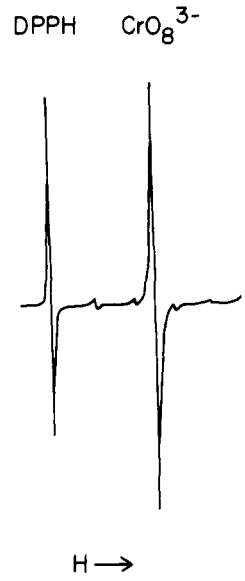
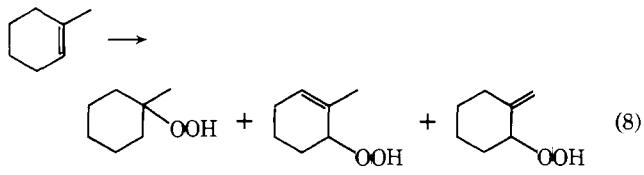


Figure 3. Perchromate resonance absorption in room-temperature aqueous solution buffered at pH 12.3 (with DPPH reference signal).

of the expected three singlet oxygen products (see reaction 8) which were generated by dye-sensitized oxygenation. In



(8)

addition, three unidentified products (~40% of total product yield), two of which were also found in the dye-sensitized oxygenation (~5% of total product yield), were detected in the perchromate oxygenation. Presumably at least one of these unidentified products arose by a process other than free-radical oxidation. The possibility of metal-catalyzed decomposition of the product hydroperoxides to yield unidentified products is not excluded.

The unusual and unpredicted behavior exhibited by the purines and pyrimidine bases in conjunction with the observation of not only typical singlet oxygen products but also unidentified oxidation products from certain singlet oxygen acceptors strongly suggests that at least one other oxidizing intermediate may be present during the aqueous decomposition of K_3CrO_8. In the olefinic oxygenation superoxide anion, O_2^- was ruled out on the basis of control experiments employing an excess of KO_2 in an aqueous methanol solution of the acceptor. (The reaction mixture was treated in the same manner as described for perchromate oxygenations, i.e., extracted with ether, reduced with $NaBH_4$, and analyzed by GC for the resulting alcohols.) However, it can be conjectured that the direct participation of CrO_8^{3-} or $HCrO_8^{2-}$, depending on pH, possibly provides an explanation of these unpredicted observations. Clearly, when using K_3CrO_8 as a singlet oxygen source, extreme caution should be exercised in attributing the results to $^1O_2$, particularly in the case of substrates of biological significance, as shown by the results from our study of the purine and pyrimidine bases.

Effect of pH on Aqueous Decomposition of Potassium Perchromate. A twofold increase in the yield of 2,3-dimethyl-3-hydroperoxybutene-1 from the perchromate oxygenation of 2,3-dimethylbutene-2 was observed upon lowering the pH of the unbuffered reaction mixture to 7 with a standard buffer. Since low conversions of acceptor were

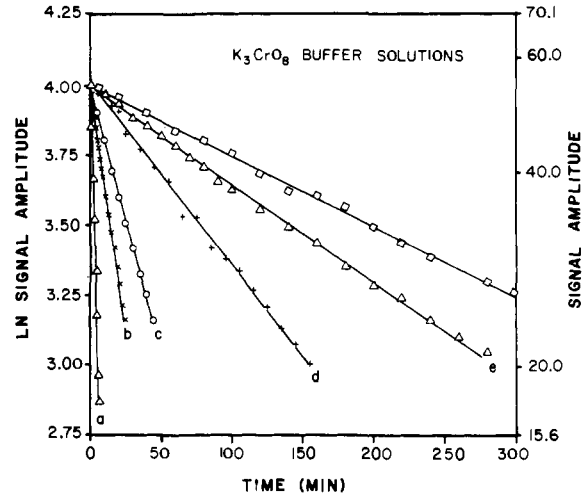


Figure 4. Decays of perchromate resonance absorptions in aqueous solutions buffered at pH's (a) 10.18, (b) 11.11, (c) 11.42, (d) 11.60, (e) 11.90, and (f) 12.39.

Table IV. Rate Constants for Decomposition of Perchromate in Room-Temperature Aqueous Buffered Solutions

pH of K_3CrO_8 buffer solutions	k, min^{-1}	pH of K_3CrO_8 buffer solutions	k, min^{-1}
10.18	0.151	11.60	0.00649
10.18	0.161	11.90	0.00334
11.11	0.0333	12.34	0.00299
11.42	0.0186	12.39	0.00242

maintained for these experiments, it appears that the yield of singlet oxygen from K_3CrO_8 increases twofold if the solution of K_3CrO_8 is buffered at pH 7. Qualitatively it also was noted that lower buffered pH's of the reaction medium resulted in increased rates of decomposition of the perchromate salt.

More quantitative determination of the effect of pH on the rate of aqueous decomposition was obtained by EPR measurements on buffered 6.5 mM solutions of K_3CrO_8 in the range of pH from 10 to 12.5. Well-behaved first-order decays were obtained after such systems had reached a constant pH (see Experimental Section) by repetitively monitoring the amplitude of the perchromate resonance absorption normalized to the absorption observed from a standard 2,2-diphenyl-1-picrylhydrazyl (DDPH) sample also in the resonant cavity of the X-band spectrometer. Figure 3 shows the perchromate resonance absorption observed for a room-temperature aqueous solution buffered at pH 12.34. This spectrum appears to be essentially identical to that reported previously for K_3CrO_8 in a room-temperature solution of H_2O_2.[37]

Figure 4 shows the decays observed for six different buffered systems, and the resulting half-lives and the corresponding pH's for these and two other determinations are listed in Table IV. The observation of pseudo-first-order decays is consistent with the following rate expression

$$d(CrO_8^{3-})/dt = -k(CrO_8^{3-}) \quad (9)$$

where for solutions of constant pH

$$k = k'(H^+)^n \quad (10)$$

Figure 5 shows a least-squares fit of the ln of the pseudo-first-order rate constants obtained above, against the corresponding pH. From (10) this fit yields an order in (H^+) of 0.85 ± 0.06 (one standard deviation). From the intercept, a value for k' of 7×10^7 M^{-1} min^{-1} was determined.

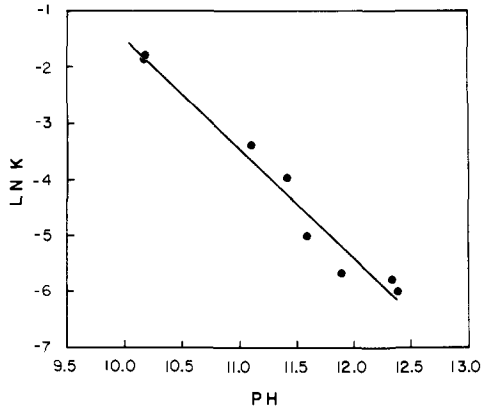


Figure 5. Effect of pH on rate of decomposition of perchromate in aqueous buffered solutions. Line is least-squares fit for $k = k'[H^+]$; $k' = 7 \times 10^7\ M^{-1}\ min^{-1}$.

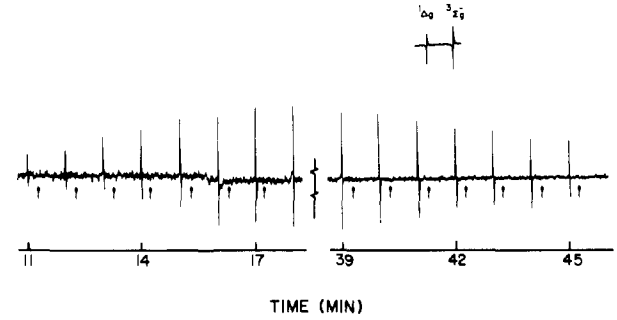


Figure 6. Resonance absorption by ground state oxygen evolved during smooth thermal decomposition of K_3CrO_8 for 30 sec repetitive scans. Arrows show position at which singlet oxygen absorption should appear. Inset shows resonance absorption due to singlet oxygen generated by microwave discharge relative to absorption by ground state oxygen.

In a previous study of the kinetics of the aqueous decomposition of the tetraperoxy chromate ion, Quane and Earley used either a pH-stat to monitor H^+ or followed the appearance of CrO_4^{2-} spectrophotometrically.[38] (They did not monitor CrO_8^{3-} directly as was possible in the present EPR study.) These workers obtained data in the pH range from 8.0 to 10.0. Although they suggested that a more complex rate law than (3) might be required, our data for pH to 12.5 do not require such and can be explained on the basis of a rate-determining protonation of CrO_8^{3-} followed by decomposition of $HCrO_8^{2-}$ as suggested by the previous authors. In fact, the value of 7×10^7 determined here for k' is in very good agreement with values of 1.25×10^8 and $5 \times 10^7\ M^{-1}\ min^{-1}$ obtained in the lower pH region by Quane and Earley for aqueous unbuffered (with pH-stat) and ammonia buffered solutions, respectively.

EPR Investigation of the Thermal Decomposition of K_3CrO_8. The observation of singlet oxygen as a product in the aqueous decomposition of K_3CrO_8 led us to investigate the products of thermal decomposition as well.

In initial experiments, the neat salt was rapidly heated under vacuum in the magnetic resonance spectrometer to a temperature of 150–170° in order to promote explosive decomposition. The magnetic field was chosen so as to be at one of the first derivative maxima of the transition of singlet oxygen (as confirmed for singlet oxygen produced in a microwave discharge). Under these conditions, no resonance absorption due to $O_2(^1\Delta_g)$ was observed. In similar experiments for which the field chosen corresponded to a first derivative maximum for the transition in ground state oxygen, a very strong resonance absorption was observed simultaneously with the visual observation of explosive decomposition.

In an effort to minimize any possible pressure quenching by ground state oxygen and to obtain data under more controlled conditions, the perchromate salt was mixed in approximately a 50–50 mixture with potassium chromate. This procedure resulted in a smooth decomposition of K_3CrO_8 at approximately 145° which lasted typically 30 to 45 min, depending upon temperature. During the smooth decomposition of the salt, the pressure in the cavity was estimated to be always less than 1 Torr, based on the observed resonance absorption line widths. Figure 6 shows a typical series of spectra for a smooth decomposition of K_3CrO_8 taken for a 30-sec repetitive scan rate. The scans were over a range of field encompassing both an $O_2(^1\Delta_g)$ resonance line and a ground state absorption. The only absorption observed was that due to ground state oxygen which was generated in the course of the decomposition. This absorption had a maximum signal-to-noise ratio during the decomposition of 30. In an analogous repetitive scan experiment for microwave discharge production of up to 5% $O_2(^1\Delta_g)$, the ratio of the ground state to singlet oxygen resonance absorptions was 1.4–2.3 (see inset Figure 6). From these data, an upper limit for the production of $O_2(^1\Delta_g)$ from the controlled thermal decomposition of K_3CrO_8 was determined to be 0.1% of all the oxygen molecules generated. Because the geometry of the flow system was expected to lead to significantly greater quenching of $O_2(^1\Delta_g)$ generated in the microwave discharge, as opposed to singlet oxygen produced in the decomposition, this upper limit is considered conservative. We note here that the tentative observation, reported previously as a footnote in ref 3, that $O_2(^1\Delta_g)$ is produced from the thermal decomposition of K_3CrO_8 is now known to have been an artifact resulting from thermal emission being detected by the germanium photodiode used in the previous study.

The observation that $O_2(^1\Delta_g)$ is not produced in any significant quantity during the thermal decomposition of neat K_3CrO_8 is consistent with the results of Wasserman et al.[39] They observed evolution of $O_2(^1\Delta_g)$ for the decomposition of diphenylanthracene endoperoxide in benzene at 60°, but not for the thermal decomposition of the neat samples of the endoperoxide.

Following the gas phase investigation, EPR spectra were obtained at 77K for the solid residue from the thermal decomposition. A single, fairly symmetric line was observed with a line width of approximately 400 G. As shown in Figure 7, this spectrum corresponds closely to that obtained from examination of a sample of neat potassium superoxide (KO_2) obtained under similar experimental conditions (and our KO_2 spectrum appears identical to that reported by Bennett et al.[40]). On this basis, we assign the absorption observed following thermal decomposition of K_3CrO_8 to O_2^-. Measurements of the amplitudes of the resonance absorptions for the decomposition product and for neat KO_2 indicate that approximately 30% of the decomposition product is KO_2.

The only other product identified in the thermally decomposed sample was K_2CrO_4. This salt was identified by its uv absorption spectrum (λ_{max} = 372 nm). Uv measurements established that K_3CrO_8 was quantitatively converted (based on chromium) to K_2CrO_4.

$$K_3CrO_8 \longrightarrow K_2CrO_4 + KO_2 + O_2$$

Experimental Section

Preparation of Potassium Perchromate. The following procedure is a slight modification of the method of Riesenfeld et al.[4] A solu-

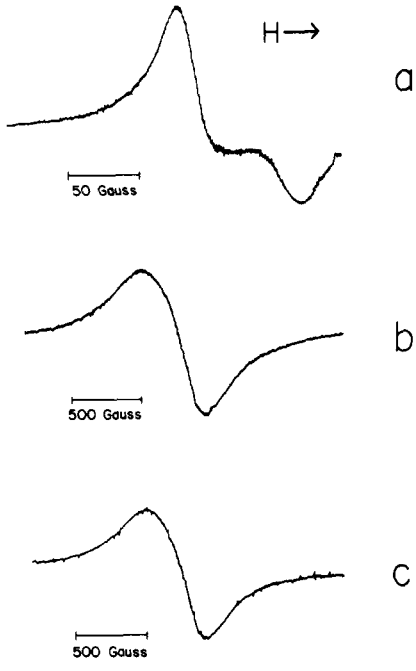


Figure 7. (a) Resonance absorption due to neat K_3CrO_8 sample; (b) absorption observed after thermal decomposition of K_3CrO_8; (c) absorption observed for neat sample of KO_2. All spectra were obtained for samples at 77°K.

tion of 16.8 g (0.087 mol) of potassium hydroxide in 200 ml of water was cooled to −5° in an ice-salt bath until crystals began to form. Hydrogen peroxide (30 cm^3, 30%; 0.50 mol) was then added dropwise with stirring while maintaining the temperature below −3°. An immediate red-brown color developed along with reddish-brown crystals. After addition was complete the solution was stirred for an additional 1.5 hr at −3°, then placed in a freezer at −10° overnight. The solid mass was allowed to warm slightly (not above 0°) and broken up with a spatula. The crystals were filtered with suction and washed with cold (10°) 95% ethanol until the filtrate became clear. The crystals were finally washed and dried with anhydrous ether and stored in a desiccator (20.1 g; 80% yield).

Determination of Production Distributions by Simultaneous Formation and Decomposition of Potassium Perchromate. Typically, 500–800 mg of the olefins listed in Table I were dissolved in 200 ml of methanol to which was added 100 ml of water, and the solution was cooled to 0–5°. Hydrogen peroxide (30%; 20 ml) was then added. A solution of 3.5 g of potassium hydroxide and 16.8 g of potassium chromate in 200 ml of water was then added dropwise to the above solution, maintaining the temperature below 10° during the addition. After addition was complete, the cooling bath was removed and the reaction mixture was allowed to warm to room temperature with continuous stirring for approximately 16 hr. The reaction solution was then decanted from the unreacted potassium perchromate and extracted with three 200-ml portions of ether. The extracted hydroperoxides were dried over anhydrous sodium sulfate and filtered, and the ether solution was evaporated to a final volume of 50–80 ml. The hydroperoxides were reduced to the corresponding alcohols with a fourfold excess of sodium borohydride with cooling and the product alcohols were analyzed on a Varian (Model 1200) flame ionization vapor phase chromatograph using a 10 ft × ⅛ in. column of 10% UCON WS on 100–120 Chromosorb P. Product distributions were identical and independent of whether they were obtained by simultaneous formation and decomposition of the perchromate salt or whether obtained by addition of the pure dry salt to an aqueous methanol (60:40, v/v) solution of the substrate.

Comparison and Verification of Product Distributions by Dye-Sensitized Photooxygenation. In all perchromate oxygenations, products and product distributions were compared with those obtained from the dye-sensitized photooxygenation of the same acceptor. The reaction vessel consisted of a small immersion irradiation apparatus[41] fitted with a Sylvania DWY, 650-W lamp. Typically, 10 mg of Rose Bengal (triplet sensitizer) was used in 120 ml of methanol to which was added ~800 mg of olefinic acceptor. Irradiation at 60 V for 5–10 min corresponded to approximately 10–20% conversion of the olefin to the product hydroperoxides. The product hydroperoxides were reduced and analyzed by flame ionization gas chromatography as described above. For all olefins listed in Table I, the product distributions have been independently determined and reported previously.[22,42]

Relative Reactivities of Pairs of Olefins. The relative reactivities of various pairs of olefins (see Table II) to perchromate oxygenation were determined in competition experiments and compared with those obtained from dye-sensitized oxygenation. The method has been described in detail elsewhere.[18] Typically, predetermined, weighed amounts (estimated from known relative rates) of the two olefins were oxygenated by potassium perchromate in aqueous methanol (60:40, v/v) and the products were analyzed in exactly the same manner described above for the product distributions. The same two olefins were then oxygenated by dye sensitization in the same manner as described for product distribution determination. In both methods, the conversion of acceptor was less than 10% in order to assure accurate determination of the relative reactivities as required by this method. The absolute yields of product alcohols were not determined. Instead, the ratio of product alcohols from the olefin pair in the perchromate oxygenation was simply determined by comparison to that produced in dye-sensitized oxygenation of the same pair in which the relative rates were known from previous work.[18,22]

Identification of Product from the Perchromate Oxygenation of 2,3-Dimethylbutene-2. Potassium chromate (16.9 g, 0.087 mol) and potassium hydroxide (3.5 g, 0.065 mol) in 200 ml of water were slowly added at 5° to 300 ml of 33% aqueous methanol containing 30 ml of 30% hydrogen peroxide and 2.1 g (0.025 mol) of 2,3-dimethylbutene-2. After aqueous work up of the solution, as described above for the product distributions, 2,3-dimethyl-3-hydroperoxybutene-1 was isolated in 35% yield based on starting olefin and whose infrared NMR spectra, and GC retention times of reduced hydroperoxide, were identical with those of the product from dye-sensitized photooxygenation.

Determination of the Yield of Singlet Oxygen from Potassium Perchromate. Various amounts of 2,3-dimethylbutene-2 (420, 315, 210, 139.4, and 84 mg; 5.0, 3.75, 2.5, 1.66, and 1.00 mmol) were each dissolved in 500 ml of aqueous methanol (60:40; v/v). To each solution was added 3.000 g (0.001 mol) of potassium perchromate. Complete decomposition of potassium perchromate occurred in each solution as indicated by the characteristic clear, light yellow appearance of potassium chromate in solution. Each reaction solution was extracted with ether, the volume was reduced, and the product hydroperoxides were reduced with a fourfold excess of sodium borohydride. To each solution of the product alcohols was added a 2-ml aliquot of a 5.00×10^{-3} M internal standard solution of isoamyl alcohol (0.4471 g in 100 ml of methanol). The absolute yields of product alcohol for each solution were determined by flame ionization gas chromatography after calibration of the detector with a standard solution of pure 2,3-dimethyl-3-hydroxybutene-1 and isoamyl alcohol. The plot shown in Figure 1 was derived from these data.

DABCO Inhibition of Perchromate Oxygenation of 2,3-Dimethylbutene-2. A set of three solutions of 0.0100 M (420.0 mg) 2,3-dimethylbutene-2 in 500 ml of aqueous methanol (60:40, v/v) was prepared. To each solution was added 1.120 g (2.000×10^{-2} M) of DABCO and 3.360 g (6.000×10^{-2} M) of DABCO (1,4-diazobicyclo[2.2.2]octane), respectively. Potassium perchromate (3.000 g, 0.010 mol) was added to each solution and allowed to completely decompose to the clear yellow color of potassium chromate. Each solution was extracted with ether, and the hydroperoxide was reduced and analyzed by flame ionization gas chromatography as described above for yield of singlet oxygen determinations. The possibility of perchromate oxidation of DABCO seems unlikely in view of the linear quenching plot obtained in Figure 2 and which is predicted by expression 6.

Relative Reactivities of Purine and Pyrimidine Base with Potassium Perchromate. Solutions of 100 ml of 1.000×10^{-3} M purine or pyrimidine were prepared using a sodium bicarbonate-sodium hydroxide buffer of pH 10.5. To measure the initial uv absorbance, a part of the solution was diluted to 8×10^{-5} M using the buffer

solution and the uv spectra was recorded on a Cary 15 spectrometer using buffer as a blank. As a typical example, theophylline gave an absorbance maximum of 0.95 at 275 nm. While stirring vigorously, 50 mg of the perchromate salt was decomposed in 50.0 ml of 10^{-3} M theophylline solution. The solution was then diluted 12.5-fold with buffer and the uv spectrum was recorded, using as a blank the solution resulting from decomposing 50 mg of perchromate salt in 50.0 ml of pure buffer, and diluted 12.5-fold with buffer. In this way, the absorbance due to the potassium chromate was canceled. After treatment with perchromate, theophylline showed an absorbance maximum of 0.44 at 275 nm indicating 53% destruction.

To test the effect of the potassium chromate solution on theophylline, a solution of 3.36×10^{-4} M K_3CrO_4 and KOH in buffer was prepared with theophylline and the uv spectrum was recorded using as a blank a similar solution without theophylline. The net absorbance was 0.93 at 275 nm showing the purine was unaffected by chromate.

To test for quenching by DABCO, a solution of 10^{-3} M uracil at pH 10.5 was prepared containing 10^{-2} M DABCO. After 12.5-fold dilution, the initial uv absorbance at 282 nm was 0.41 using 8.0×10^{-4} M DABCO/buffer solution as a blank. After treating 50.0 ml of DABCO-containing uracil solution with 5.0 mg of perchromate and diluting 12.5-fold with buffer, the absorbance was 0.35 using a blank prepared by decomposing 50 mg of perchromate in 1.00×10^{-2} M DABCO/buffer solution and diluting 12.5-fold. The net destruction with and without DABCO was 15 and 45%, respectively, possibly indicating the reaction was quenched by DABCO.

Determination of Rate of Aqueous Decomposition by EPR. A Varian V4502 X-band, electron paramagnetic resonance spectrometer with a 6 in. magnet was employed.

Solutions (6.5 mM) of K_3CrO_8 were prepared in aqueous media buffered at six pH's between 10 and 12.5. Some change in buffer pH occurred (typically 0.2–0.3 pH units) when 200 mg of salt was dissolved in 100 ml of the buffer solution, but the pH then remained constant indefinitely. The pH was determined several times during a run for the parent solution from which the EPR sample was aliquoted. A Leeds and Northrup Model 7403 pH meter was employed and it was recalibrated for each measurement series against standard buffers obtained from Beckman. Rate data were used only for times for which the pH was shown to be constant. Samples were studied in a Varian V-4548 Aqueous Solution Sample Cell Accessory in a Model E-4531-type resonant cavity modified with high-impedance modulation coils. Power levels were chosen to avoid saturation of signals. Modulation amplitude was kept nominally less than half the line width in all cases and in no case exceeded 0.5 G.

At the klystron frequency used, the K_3CrO_8 central resonance line for the solution studied appeared at a nominal field dial setting of 3375 g. Decay data were obtained by repetitive sweeps through the K_3CrO_8 central resonance line at intervals of 1, 2.5, 5, or 10 min. To normalize the observed signal amplitude for long-term spectrometer instability, the field region was sufficiently large to include the resonance absorption by a solid sample of DPPH taped to the outside of the solution cell.

EPR Investigation of Thermal Decomposition. Solid K_3CrO_8 was ground in a mortar and pestle to a fine powder which was then introduced either into a 4 mm o.d. tube of GE type 204 quartz or into an Erlenmeyer flask for solid or gas phase studies, respectively. The Erlenmeyer flask was constructed for attachment to a gas phase flow system. Gaseous products from the decomposition flowed into a Varian V-4531 large sample access cylindrical cavity through a 25 mm o.d. GE type 204 quartz tube. The distance between the base of the flask and the center of the resonance cavity was 23 cm. An untrapped Welch 1402B vacuum pump was used to evacuate the flow tube. Pressure was measured by means of a silicone oil manometer. A side tube just above the sample flask was used to introduce singlet oxygen for calibration purposes. Singlet oxygen was produced by flowing a mixture of 90% O_2 and 10% Ar through a Raytheon microwave power generator discharge operated at approximately 50% power. EPR signals from $O_2(^1\Delta_g)$ were scanned before and after each K_3CrO_8 decomposition in order to verify spectrometer stability during each run. For low-temperature studies solid samples were placed in a quartz dewar filled with liquid N_2 which was placed in turn in the same rectangular cavity used in the pH studies.

Samples and Instruments. Olefin samples were purchased from Chemical Samples Co. and all other chemicals were procured through standard sources. When necessary, olefins were purified by passage through silica gel to remove traces of peroxides. Infrared spectra were obtained on a Perkin-Elmer Model 221 spectrophotometer, and nuclear magnetic resonance spectra were recorded on a Varian A-60A using tetramethylsilane as an internal standard. Ultraviolet spectra were taken on a Cary Model 15 recording spectrophotometer. All solvents were used as received.

Acknowledgment. This work was supported by Grant 5RO1-AP:00771-4 from the Environmental Protection Agency, and by Grant GP 34524 from the National Science Foundation. The contents of this paper do not necessarily reflect the views and policies of the Environmental Protection Agency or National Science Foundation, nor does mention of trade names or commercial products constitute endorsement or recommendation for use. The authors thank Mr. Dennis Fitz, for his able assistance in the purine and pyrimidine reactivity study, and Drs. K. R. Darnall and J. L. Sprung, for review of the manuscript at several stages of its preparation.

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