increasing photon energy and at 4000 Å (72 kcal/mol) shows no signs of leveling off. The curve shows no structure at 200-Å resolution.

Presumably the photon-induced reaction goes through the $(C_5H_9^+)^*$ complex. Any observation of product means that the $C_3H_5^+$ cation *must have* absorbed a photon, since C_2H_4 is transparent to below 3500 Å.[12] The $C_3H_7^+$ onset at 55 kcal/mol is higher than the endothermicity of reaction 1 by at least 33 kcal/mol. Hence, the threshold for the photon-induced reaction is not determined by the endothermicity of the reaction. The $C_3H_7^+$ onset may be determined either by the absorption of a photon by $C_3H_5^+$ or by the competitive unimolecular decomposition of $(C_5H_9^+)^*$. In either case, electronic excitation of the $C_3H_5^+$ by light must be possible at wavelengths at least as long as 5200 Å.

Reaction 2b is calculated[10] to be 6.5 kcal/mol endothermic for the formation of the cyclopropyl cation and 3.5 kcal/mol exothermic for the formation of the allyl cation.[9] Although internally excited $C_2H_4^+$ in reaction 2b may be energetically capable of producing the endothermic cyclopropyl cation product, it is quite possible that even if the cyclopropyl cation is formed, it rearranges to the more stable allyl structure[13] (especially on the time scale of our reactions (seconds)). More significantly, three different investigations[6,14] have presented experimental evidence which indicates that $C_3H_5^+$ produced in reaction 2b is formed in an exothermic reaction. It seems likely that allyl cation is the only possible exothermic product of this reaction, and hence we infer from these investigations[6,14] that the $C_3H_5^+$ ion whose electronic excitation we have studied is the allyl cation. (We cannot, however, completely rule out participation of the cyclopropyl or other isomeric cations.) Accordingly, we consider our results to provide evidence for the existence of an excited state of the allyl cation lying about 2.5 eV above the cation ground state.

Experimental data on the electronic spectrum of the allyl cation are very limited. Attempts have been made to observe the electronic spectrum of the allyl cation in highly acidic solutions.[15] The allyl cation system contains impurities and the ultraviolet spectrum is not known.[15] However, 1,1,3,3-tetramethylallyl cation is reported to show an absorption with maximum at 3050 Å (4.1 eV) in H_2SO_4.[15]

Semiempirical π-electron calculations for the allyl cation typically show the lowest excited singlet state lying near 5 eV.[16] Two recent theoretical calculations,[16,17] which explicitly consider σ excitations, indicate that excited states involving σ electrons lie as low or even lower in energy than the excited states that arise from excitation of a π electron. Our evidence for a low-lying excitation supports the need for explicit consideration of σ electrons in theoretical calculations for the allyl cation.

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(12) G. Herzberg, "Electronic Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1966, p 629.

(13) See M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, **93**, 4290 (1971), and references contained therein regarding cyclopropyl cation stability.

(14) G. C. Goode, A. J. Ferrer-Correia, and K. R. Jennings, *Int. J. Mass Spectrom. Ion Phys.*, **5**, 229 (1970).

(15) G. A. Olah, C. U. Pittman, Jr., and M. C. R. Symons, "Carbonium Ions," Vol. I, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N. Y., 1968, Chapter 5.

(16) S. D. Peyerimhoff and R. J. Buenker, *J. Chem. Phys.*, **51**, 2528 (1969).

(17) D. T. Clark and G. Smale, *Tetrahedron*, **25**, 13 (1969).

A New and Unique Chemical Source of Singlet Molecular Oxygen. Potassium Perchromate

Sir:

Potassium perchromate was first prepared and isolated in 1905 by Riesenfeld, *et al.*,[1] who found that this unusual salt liberates oxygen in aqueous solution according to the following equation.

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

The crystal structure of K_3CrO_8, determined by Stomberg and Brosset in 1960,[2] 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 groups (O_2^{2-}) in which the geometrical arrangement of the oxygen atoms around chromium is dodecahedral.[3]

Foote[4] has speculated that an enzyme bound or metal bound form of singlet oxygen might be the reactive species in certain biological oxygenations. We now wish to report unequivocal spectral evidence that potassium perchromate, upon aqueous decomposition, releases oxygen in the excited singlet state. In addition, chemical evidence is presented which demonstrates that at least some of the O evolved, either by simultaneous formation and decomposition of the salt or from the aqueous decomposition of the pure, dry salt, results in typical singlet oxygen reactions. We believe that the results, presented here for potassium perchromate, represent the first demonstration of a transition metal–oxygen complex which releases oxygen in the excited singlet state.

When a basic solution of potassium chromate is added to an aqueous methanol solution of H_2O_2 and 2,3-dimethylbutene-2 at 5°,[5] a red-brown solid begins to form, indicating formation of K_3CrO_8, with a simultaneous slow effervescence which increases upon warming the solution to room temperature. From the solution, 2,3-dimethyl-3-hydroperoxybutene-1 can be isolated in 35% yield whose infrared and nmr spectra are identical with those of the product from sensitized photooxidation.

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(1) E. H. Riesenfeld, H. E. Wohlers, and W. A. Kutsch, *Ber.*, **38**, 1885 (1905).

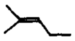
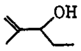
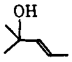
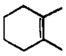
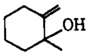
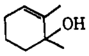
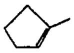
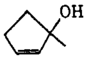
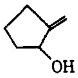
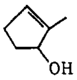
(2) R. Stomberg and C. Brosset, *Acta Chem. Scand.*, **14**, 441 (1960).

(3) For a discussion of the chemical bonding in K_3CrO_8, see J. D. Swalen and J. A. Ibers, *J. Chem. Phys.*, 37, 17 (1962).

(4) C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968).

(5) 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.

Table I. Product Distributions from Olefin Oxygenations

Olefin	Product alcohols A	Product alcohols B	K_3CrO_8 % A	K_3CrO_8 % 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 4. [b] C. S. Foote, *Pure Appl. Chem.*, **27**, 635 (1971).

Product distributions from olefins that give more than one product in the perchromate system were compared with the characteristic singlet oxygen product ratios obtained from corresponding dye-sensitized photooxygenations in methanol using Rose Bengal as the sensitizer. This method was used effectively by Foote and coworkers.[6] The experimental technique involved was the same as that described above for TME except that the product hydroperoxides were reduced to the corresponding alcohols with sodium borohydride before analysis by flame ionization chromatography. The results are summarized in Table I. As can be seen, the two reactions give product ratios which are nearly identical.

Product distributions were repeated with 1,2-dimethylcyclohexene and 1-methylcyclopentene using the pure, dry perchromate salt. In this procedure, the isolated salt was added to a cooled 60% aqueous methanol solution of the olefin which was allowed to warm to room temperature and react with continuous effervescence overnight. The singlet oxygen product ratios obtained by this method were nearly identical with those reported in Table I for the two substrates. In the case of 1-methylcyclopentene, an additional product was observed which may be due to radical oxidation but which was not identified.

The relative reactivities of various pairs of olefins from competition experiments have also been determined with the perchromate salt and compared with those obtained from dye-sensitized photooxygenations. The method has been described previously.[7] In these experiments the perchromate salt was simultaneously formed and decomposed in the presence of pairs of olefins and the amounts of product alcohols were determined by flame ionization chromatography. From Table II, it can be seen that reasonably good agreement is obtained by the two different methods of generating singlet oxygen in determining the relative rates of pairs of olefins.

From these data alone, it is highly probable that singlet oxygen, released from potassium perchromate, is the oxidizing species and the perchromate salt itself is not directly involved. In addition, we have obtained unequivocal spectral evidence for the presence of $O_2(^1\Delta_g)$ by monitoring the emission at 1.27 μ due to the following process.

$$O_2(^1\Delta_g) \longrightarrow O_2(^3\Sigma_g^-) + h\nu$$

Table II. Relative Reactivities of Olefins by Product Analysis

Olefin A	Olefin B	K_3CrO_8 k_a/k_b	Sensitized photooxygenation[a] k_a/k_b
2,3-Dimethylbutene-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 7.

The near-infrared detection system consisted of a chopper, 1.27-μ interference filter, liquid nitrogen-cooled germanium photodiode, lock-in amplifier, and recorder.[8] 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 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 observation of $O_2(^1\Delta_g)$ in this system does not exclude the possibility that $O_2(^1\Sigma_g^+)$ may be formed initially since it would rapidly deactivate to the $^1\Delta_g$ state.[9]

Potassium perchromate provides a convenient source of singlet oxygen which can be liberated at a controlled rate depending on aqueous content of the solvent and temperature. The salt appears to have ideal characteristics for work in aqueous systems where a singlet oxygen source is desired which is free of hydrogen peroxide (present in the hydrochlorite method), free of O atoms and mercury vapor (present in microwave discharge techniques), and free of sensitizer–substrate interactions which have complicated much of the work pertaining to the photodynamic effect.[10]

Singlet oxygen has been postulated as being the active intermediate in the destruction of nucleic acids and their component bases in aerobic photodynamic reactions.[11] We are presently investigating the possibility of using this salt as an aqueous source of singlet oxygen in reactions related to the photodynamic effect. In addition, the chemistry of K_3CrO_8 with substrates unreactive toward singlet oxygen is being investigated.[12,13]

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(6) C. S. Foote, S. Wexler, and W. Ando, *Tetrahedron Lett.*, 4111 (1965).

(7) R. Higgins, C. S. Foote, and H. Cheng, *Advan. Chem. Ser.*, **No. 77**, 102 (1968).

(8) R. P. Wayne and J. N. Pitts, Jr., *J. Chem. Phys.*, **50**, 3644 (1969).

(9) R. P. Wayne, *Advan. Photochem.*, **7**, 400 (1969).

(10) J. D. Spikes and R. Livingston, *Advan. Radiat. Biol.*, **3**, 29 (1969).

(11) C. S. Foote, *Science*, **162**, 963 (1968).

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(12) It has been suggested by a referee that O_2^-, generated during the aqueous decomposition of potassium perchromate, may be the actual source of singlet oxygen. Although O_2^- is quite probably generated in the K_3CrO_8 decomposition, Khan has shown, in the case of potassium superoxide, that if any excited molecular oxygen is formed from O_2^-, it is in the $^1\Sigma$ state and is rapidly quenched by water and hence would not be detected in our system.

(13) NOTE ADDED IN PROOF. We have recently detected O_2 ($^1\Delta$ spectral emission) from the thermal decomposition of the pure dry potassium perchromate salt which will be described in a forthcoming communication.

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Metalloporphyrin Photochemistry. A Ruthenium(II) Porphyrin Photodimer with a Metal-Metal Bond

Sir:

We wish to report a novel and facile photoreaction of ruthenium(II) porphyrins which apparently involves photochemical ejection of a CO ligand with subsequent formation of a dimer. Whereas complexes containing two metalloporphyrins linked *via* an oxo bridge,[1] two porphyrins bound to one metal,[2] and one porphyrin bound to two metals[3] have been previously prepared, the present reaction is apparently the first case involving formation of a metalloporphyrin dimer linked through a metal-metal bond.

Irradiation of degassed benzene or pyridine solutions of ruthenium(II) carbonyletioporphyrin I pyridinate[4] (**1**) with visible or ultraviolet light leads quantitatively to photoproduct **2a**. The reaction can be followed by changes in the uv-visible spectra (Figure 1) (isosbestic points at 532, 436, 422, 408, and 391 nm) resulting in loss of the characteristic metalloporphyrin spectrum or by loss of the carbonyl stretching frequency at 1931 cm^{-1} in the ir.[5] In a typical "preparative" experiment a suspension of 0.04 g of **1** in 4 ml of pyridine was irradiated with a medium-pressure mercury lamp (Pyrex filter) for 36 hr; formation of crystals of the highly insoluble **2a** was observed as the irradiation progressed. The crystals were recovered by filtration and recrystallized (with difficulty) from pyridine. Irradiation of the octaethylporphyrin analog of **1** under the same conditions led to the octaethylporphyrin derivative **2b** which proved to be easier to purify and generally much more soluble in organic solvents. Elemental analysis shows that **2a** has lost CO and contains pyridine and ruthenium etioporphyrin in a 1:1 ratio. *Anal.* Calcd for $(C_{32}H_{36}N_4Ru)_x \cdot (C_5H_5N)_x$: C, 67.66; H, 6.29; Ru, 15.39; O, 0.0. Found: C, 68.02; H, 6.08; Ru, 14.90; O, 0.13.

Mass spectral analysis reveals that **2a** is a dimer of the starting material. High-resolution spectrometry indicates that the parent ion has a composition[6] of $Ru_2C_{64}H_{72}N_8$; the peaks occur in the clusters expected for the ruthenium isotopes. Little fragmentation is evident except for the usual peaks corresponding to loss of methyl groups; a notable feature of the mass spectrum is the condensed clusters at one-half (spacing every 0.5 mass unit) and one-third the parent ion mass which correspond to doubly and triply charged ions of **2a**. The nmr spectrum of **2b** (Table I) shows only the resonances expected for the three types of porphyrin protons in octaethylporphyrin in the expected ratios, indicating that the porphyrin ring has not been altered.[7] From the nmr spectrum, together with the fact that loss of CO accompanies formation of **2**, it is apparent that the dimer must result *via* metal-metal bonding; since each ruthenium is bound to four porphyrin nitrogens and one pyridine and the complex is diamagnetic,[10] the ruthenium-ruthenium bond is formally a double bond.[11,12]

Table I. Proton Chemical Shifts of Ruthenium(II) Octaethylporphyrin Complexes[a]

Compd	Bridge protons	$-CH_2CH_3$	$-CH_2CH_3$	Pyridine α	Pyridine β	Pyridine γ
Ruthenium(II) carbonyl-octaethylporphyrin pyridinate	9.75 s (4 H)	3.88 q (16 H)	1.82 t (24 H)	1.07 m (2 H)	4.76 m (2 H)	5.65 m (1 H)
2b	7.61 s (4 H)	5.92 m (16 H)	1.45 t (24 H)	2.6 m (2 H)	5.3 m (2 H)	nd

[a] $CDCl_3$ solutions, chemical shifts in ppm downfield from tetramethylsilane; s = singlet, t = triplet, m = multiplet, q = quartet, nd = not detectable.

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(1) I. A. Cohen, *J. Amer. Chem. Soc.*, **91**, 1980 (1969); E. B. Fleischer and T. S. Srivastava, *ibid.*, **91**, 2403 (1969).

(2) M. Whalley, *J. Chem. Soc.*, 866 (1961); J. A. Elvidge, *ibid.*, 169 (1961).

(3) D. Ostfeld, M. Tsutsui, C. P. Hrung, and D. C. Conway, *J. Amer. Chem. Soc.*, **93**, 2548 (1971).

(4) (a) M. Tsutsui, D. Ostfeld, and L. M. Hoffman, *ibid.*, **93**, 1820 (1971); M. Tsutsui, D. Ostfeld, J. N. Francis, and L. M. Hoffman, *J. Coord. Chem.*, **1**, 115 (1971); (b) B. C. Chow and I. A. Cohen, *Bioinorg. Chem.*, 1, 57 (1971).

(5) No other significant differences are apparent between the ir of **1** and **2a**.

(6) Loosely bound pyridine is lost from **2a** in the mass spectrometer. This is also observed for **1**.

(7) Lack of resolution of the methylene protons is probably caused by nonequivalence of the geminal protons due to axial dissymmetry. This has been observed for tin(II) octaethylporphyrin[8] as well as other similar compounds.[9]

(8) D. G. Whitten, J. C. Yau, and F. A. Carroll, *J. Amer. Chem. Soc.*, **93**, 2291 (1971).

(9) B. W. Roberts, A. Wissner, and R. R. Rimerman, *ibid.*, **91**, 6208 (1969); W. L. Meyer and R. B. Meyer, *ibid.*, **85**, 2170 (1963).

(10) This is indicated by the relatively sharp nmr spectrum of the dimer. The nmr also appears to rule out structures wherein the dimer results from nitrogen lone pair coordination to the ruthenium of a second molecule since such a structure would have multiple proton resonances unless rapid equilibration occurs.

(11) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Wiley-Interscience, New York, N. Y., 1966, p 720.

(12) Interestingly Chow and Cohen[4b] report that irradiation of the carbonyl-tetraphenylporphyrin-ruthenium(II) complex in pyridine leads to carbon monoxide ejection and formation of the monomeric ruthenium(II) porphyrin dipyridinate. We have obtained a product having an identical spectrum with their product in preliminary experiments.