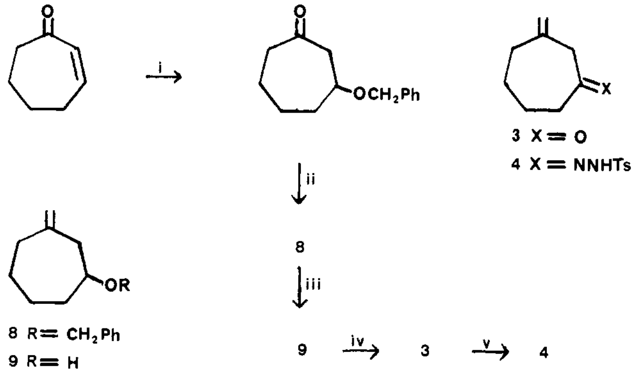
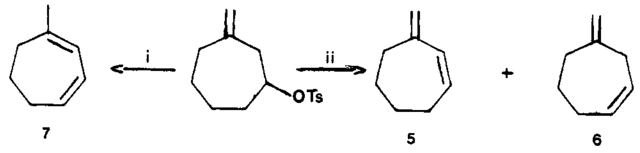
Scheme I[a]



[a] (i) Catalytic $PhCH_2ONa$, $PhCH_2OH$, room temperature, 12 h (62%). (ii) $Ph_3P{=}CH_2$, THF, room temperature, 15 h (76%). (iii) Na, NH_3 (l) (73%). (iv) PCC, NaOAc, CH_2Cl_2, room temperature, 4.5 h (85%). (v) NH_2NHTs, 1:1 MeOH-H_2O (90%)

Scheme II[a]



[a] (i) *t*-BuOK, Me_2SO, room temperature, 1 h. (ii) K_2CO_3, Me_2SO, 80 °C, 5 h.

geometry.[16] With such highly reactive species, there, of course, remains the possibility that the spectra reported[11b] for [3.1.1]-propellane are those of a decomposition product since toluene cannot be considered a particularly effective radical trap.

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A Search for Singlet Oxygen in the Disproportionation of Superoxide Anion

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A number of biological processes have been claimed to generate singlet oxygen $^1O_2$ ($^1\Delta_g$) which is harmful to biological molecules. Several explanations for the formation of $^1O_2$ in these enzymatic systems refer to superoxide anion $O_2^-\cdot$; they include reaction of $O_2^-\cdot$ with H_2O_2[1] (Haber-Weiss reaction), $OH\cdot$,[2] or itself[3] according to the elementary reaction 1 where $HO_2\cdot$ is the conjugate acid of $O_2^-\cdot$.

$$O_2^-\cdot + HO_2\cdot \xrightarrow{H^+} H_2O_2 + O_2(^1\Delta_g \text{ or } ^3\Sigma_g^-) \qquad (1)$$

In view of the biological implications of this reaction, many research workers have tried to determine whether disproportionation of $O_2^-\cdot$ yields O_2 in its $^1\Delta_g$ or $^3\Sigma_g^-$ state. On the basis of thermodynamic[4] or molecular orbital[5] considerations, it appears that $^1O_2$ could be generated by reaction 1. On the other hand, experimental determinations, using chemical[6] or radiolytic[7] sources of $O_2^-\cdot$, have led to contradictory results. The main difficulty in these studies arises probably from the very efficient quenching of $^1O_2$ by $O_2^-\cdot$ in water:[8]

$$O_2^-\cdot + {}^1O_2 \rightarrow {}^3O_2 + O_2^-\cdot \qquad (2)$$

To avoid this reaction, a low steady-state concentration of $O_2^-\cdot$ must be used; as a consequence, the catalyzed disproportionation of $O_2^-\cdot$ by impurities of water becomes the major pathway for the scavenging of $O_2^-\cdot$ unless highly purified water is used.[9] Another problem concerns the detection of $^1O_2$; the trap must react specifically with $^1O_2$ or at least it should lead to an oxidation product different from those obtained with other species present in the solution, namely, $^3O_2$, H_2O_2, $O_2^-\cdot$, $HO_2\cdot$. Finally, $O_2^-\cdot$ production must be homogeneous, and the $^1O_2$ trap must be water soluble to allow convincing kinetic treatment of experimental results. As far as we know, none of the preceding published works[6,7] fulfilled the above conditions. Consequently we designed a new technique for the detection of $^1O_2$, and we report that *reaction 1 does not produce* $^1O_2$.

The potassium salt of rubrene-2,3,8,9-tetracarboxylic acid (RTS) is water soluble in neutral and basic medium, giving a red solution which fades when reacting with $^1O_2$, yielding only the endoperoxide ($RTSO_2$):[10]

$$RTS + {}^1O_2 \rightarrow RTSO_2 \qquad (3)$$

To check the specificity of RTS toward $^1O_2$, it was shown that neither $^3O_2$ (1.2×10^{-3} M) nor H_2O_2 (0.1 M) reacted with an aqueous solution of RTS (2×10^{-4} M, pH 7.6), even after several days. In the same way, when a large excess of KO_2 (more than 100 times the stoichiometric amount) was added to an aqueous solution of RTS (2×10^{-4} M), no reaction occurred with the substrate.

In order to study the dismutation of $O_2^-\cdot$ at low steady-state concentrations, a buffered solution (phosphate 3×10^{-3} M, pH 7.6) saturated with oxygen or air containing sodium formate (0.16 M) and RTS (2×10^{-4} M) was irradiated by using a ^{60}Co γ source. The disappearance of RTS was monitored by its absorbance at 539 nm and HPLC.[10] Under such conditions, $H\cdot$ and

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0002-7863/81/1503-4965$01.25/0

OH· radicals produced from water radiolysis react with formate giving $COO^{-}\cdot$ radicals. Then $COO^{-}\cdot$ and e_{aq}^{-} react with O_2 to generate $O_2^{-}\cdot$ as the sole radical species:[11]

$$H_2O \rightarrow OH\cdot,\ H\cdot,\ e_{aq}^{-},\ H_2,\ H_2O_2 \tag{4}$$

$$OH\cdot + HCOO^{-} \rightarrow H_2O + COO^{-}\cdot \tag{5}$$

$$H\cdot + HCOO^{-} \rightarrow H_2 + COO^{-}\cdot \tag{6}$$

$$COO^{-}\cdot + O_2 \rightarrow O_2^{-}\cdot + CO_2 \tag{7}$$

$$e_{aq}^{-} + O_2 \rightarrow O_2^{-}\cdot \tag{8}$$

At pH 7.6, $O_2^{-}\cdot$ disappears essentially by reaction 1,[9] and if $^1O_2$ is produced, it will react with RTS[12] or will be quenched either by $O_2^{-}\cdot$ or by water (reactions 3, 2, and 9, respectively).

$$^1O_2 \xrightarrow{H_2O} {}^3O_2 \tag{9}$$

Assuming that $^1O_2$ yield is 100% for reaction 1, the radiolytic yield of RTS disappearance is expressed as

$$G(\text{-RTS}) = G(O_2^{-}\cdot)k_3[\text{RTS}]/[2(k_3[\text{RTS}] + k_9)]$$

where $G(O_2^{-}\cdot) = 6$ molecules per 100 eV and $k_9/k_3 = 1.5 \times 10^{-3}$ M;[12] thus $G(\text{-RTS}) = 0.35$. The experimental value obtained with oxygen saturated solutions is $G(\text{-RTS}) = 0.05 \pm 0.01$ molecule per 100 eV (3×10^{18} eV cm^{-3} < dose < 30×10^{18} eV cm^{-3}).

This low yield cannot be attributed to the generation of $^1O_2$ because no endoperoxide $RTSO_2$, which had been shown to be stable under these conditions, could be detected by HPLC. Furthermore, we have observed higher G values in presence of air; so it must be assumed that *another reaction occurred between RTS and one of the radicals* $COO^{-}\cdot$ *or* e_{aq}^{-}.

In order to check this hypothesis, the effects of these species upon RTS were investigated by using a pulse radiolysis method. Electron pulses were produced by an accelerator (Febetron 708), and the kinetics were followed by rapid spectrophotometry.[14] The doses were homogeneously delivered in solutions saturated with nitrogen or nitrous oxide in order to produce e_{aq}^{-} and $COO^{-}\cdot$ (reactions 4, 5, 6) or $COO^{-}\cdot$[13] alone (reactions 4–6, 10).

$$e_{aq}^{-} + N_2O + H_2O \rightarrow OH\cdot + N_2 + OH^{-} \tag{10}$$

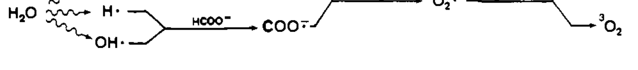
Under such conditions, no reaction could be detected between $COO^{-}\cdot$ and RTS. On the contrary, e_{aq}^{-} reacted efficiently with RTS, leading to a rapid one-electron reduction followed by a dismutation of the intermediate:

$$\text{RTS} + e_{aq}^{-} \rightarrow \text{RTS}^{-}\cdot \tag{11}$$

$$2\text{RTS}^{-}\cdot + 2H_2O \rightarrow \text{RTSH}_2 + \text{RTS} + 2OH^{-} \tag{12}$$

Kinetic study of the competing reactions involved in the decay of e_{aq}^{-} with or without RTS led to the value $k_{11} = (3 \pm 1)10^9$ M^{-1} s^{-1}.

All experimental results observed by γ radiolysis may be explained by the following scheme:



According to this scheme

$$G(\text{-RTS}) = G_{e_{aq}^{-}}k_{11}[\text{RTS}]/(k_{11}[\text{RTS}] + k_8[O_2])$$

where $G_{e_{aq}^{-}} = 2.7$ molecules per 100 eV, $[O_2] = 1.2 \times 10^{-3}$ M, and $k_8 = 2.10^{10}$ M^{-1} s^{-1}. The observed linear variation of $1/G(\text{-RTS})$ vs. $1/[\text{RTS}]$ led to the experimental value $k_{11} = (2.5 \pm 0.5)10^9$ M^{-1} s^{-1}; this rate constant is in agreement with results obtained by pulse radiolysis.

In conclusion, the slow disappearance of RTS during γ radiolysis of oxygen saturated solutions is not due to the reaction between $^1O_2$ and RTS but to a side reaction between the substrate and e_{aq}^{-}. Therefore, noncatalyzed disproportionation of $O_2^{-}\cdot$ in neutral solutions does not yield $^1O_2$.

Supplementary Material Available: $1/G(\text{-RTS})$ vs. $1/[\text{RTS}]$ for γ radiolysis and high-performance liquid chromatograms (5 pages). Ordering information is given on any current masthead page.

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Rh(I)–Cu(II) Catalyzed Oxidation of 1-Hexene by O_2 Using Immobilized, Site-Separated Organosulfide Complexes

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A new class of catalytic oxidations involving metal centered oxygen atom transfer to terminal olefins from dioxygen has been discovered in the past seven years.[1] Most recently Mimoun has reported a homogeneous system involving Rh(I), Cu(I) or Cu(II), and H^+ as cocatalysts for the oxidation of terminal olefins to methyl ketones with >98% specificity and unusually high turnovers (110 in 4 h).[1a] Several workers have proposed the sequential coordination of O_2 and terminal olefin, followed by the formation of a five-membered peroxy metallocycle,[1a–c,2] as the first steps in their oxidation reaction mechanisms. The relatively short lifetimes of the homogeneous catalysts active in this class of oxidations encouraged us to seek a functionalized solid support to site isolate the rhodium complexes, on the assumption that the catalyst deactivation process was multiordered in rhodium. The presumed need to coordinate both O_2 and olefin to rhodium led us to consider the use of immobilized monodentate,[3] anionic[4] ligands which would be stable to oxidation[5] and form strong bonds with group 8 transition metals. We report here (1) the preparation of novel monomeric organosulfide–rhodium carbonyl complexes which do not have a counterpart in solution chemistry and (2) the effectiveness of the organosulfide supported Rh(I)–Cu(II) system in the catalytic oxidation of 1-hexene to 2-hexanone using dioxygen.

A series of silica gel bound organosulfide samples ([SG]–SH) were produced varying only in their sulfide concentrations (0.20, 0.10, 0.050 and 0.025 mmol of S per gram of [SG]) by reacting

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[3] Our use of a bidentate polystyrene-2,2′-bipyridine supported rhodium complex [[P]–bpyRhXCl (where X denotes μ-Cl, $P(C_6H_5)_3$, or monodentate [P]–bpy)] resulted in an inactive system for the catalytic oxidation reported by Mimoun. The preparation and characterization of [P]–bpyRhXCl is described in a paper to be published in *Inorg. Chem.* ([P] represents a polymer support.)

[4] Mimoun reported, and we have further investigated, the role of chloride in improving the catalyst lifetimes. The homogeneous system's activity (used for comparison in this report) may be improved to 193 turnovers in 24 h simply by adding 3 equiv of chloride. The reaction in this case proceeded identical with that when using Mimoun's precursors: $RhCl_3 \cdot 3H_2O$ and $Cu(NO_3)_2 \cdot 2.5H_2O$. We feel this is a result of chloride coordination inhibiting rhodium complex aggregation. Indeed, this effect is maximized at 5 equiv of chloride, resulting in 343 turnovers in 24 h, with all the improvement coming from much slower catalyst deactivation (the initial rates with 3 and 5 equiv of Cl^- were identical).

[5] For example, a polystyrene–diphenylphosphine support [[P]–$P(C_6H_5)_2$] was unsuitable due to the facile oxidation of the phosphine to phosphine oxide.[1c]

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