ture of the beneficial effect of $NaOCH_3$ on the substitution reaction is summarized by curve C. The initial concentrations of I, $NaSC_6H_5$, and $NaOCH_3$ are the same as those giving rise to curve B. Now, 0.2 M azobenzene is present as well, and the $NaOCH_3$ promoted reaction is inhibited. Inhibition is not complete because the formation of II still is faster than in the absence of $NaOCH_3$, curve A. Similarly, the formation of III also is inhibited. A control experiment involving a mixture of $NaSC_6H_5$, $NaOCH_3$, and azobenzene but not I shows that these materials do not react. A second control indicates that 0.3 M azobenzene does not influence the rate of formation of II in the absence of $NaOCH_3$.

The formation of II in the absence of $NaOCH_3$ very likely proceeds by the well-known ionic route involving attack of $C_6H_5S^-$ on I to give an intermediate σ complex.[12] A new pathway must be followed in the presence of $NaOCH_3$. The induction period and the rate retarding effect of a material known to be a good electron acceptor[13-15] strongly suggests that substitution in the presence of $NaOCH_3$ involves electron transfer and a radical chain mechanism.

We speculate that the propagation steps of the chain reaction may involve the formation of the radical anion of I which then eliminates bromide ion to give the 4-isoquinolyl radical ($Ar\cdot$), eq 2. This radical may react with $C_6H_5S^-$ to give the radical anion of II, eq 3, which then donates an electron to I to give II and to continue the chain, eq 4. The 4-isoquinolyl radical also can abstract a hydrogen atom from CH_3OH or CH_3O^- to give III, eq 5. The radical ion $\dot{C}H_2O^-$ formed by the reduction process can also continue the chain, eq 6.[16] Such an electron transfer scheme is not unprecedented.[1,17,18] The identity of initiation and termination steps is unknown.

$$\mathrm{I}\cdot^- \longrightarrow Br^- + Ar\cdot \tag{2}$$

$$Ar\cdot + C_6H_5S^- \longrightarrow \mathrm{II}\cdot^- \tag{3}$$

$$\mathrm{II}\cdot^- + \mathrm{I} \longrightarrow \mathrm{II} + \mathrm{I}\cdot^- \tag{4}$$

$$Ar\cdot + CH_3O^- \longrightarrow \mathrm{III} + \dot{C}H_2O^- \tag{5}$$

$$\mathrm{I} + \dot{C}H_2O^- \longrightarrow CH_2{=}O + \mathrm{I}\cdot^- \tag{6}$$

Our results have significant implications. Thus, it is a common practice when studying substitution reactions involving $R'S^-$ nucleophiles in ROH solvent to suppress the concentration of RO^-. This is done to avoid the possibility of a competing substitution reaction involving RO^-. In our case the addition of RO^- brings about an entirely new mechanism of substitution. It seems likely that a similar change in mechanism may be observed in other instances as well. Indeed, it may prove rewarding to deliberately add RO^-. Certainly, the suppression of RO^- should not always be the rule.

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Oxygen Quenching of Charge-Transfer Excited States of Ruthenum(II) Complexes. Evidence for Singlet Oxygen Production

Sir:

Ground-state oxygen is a good energy-transfer quencher of organic triplets[1,2] and a good catalytic deactivator of organic singlet states.[3] Little is known, however, about the excited-state interactions of metal complexes and oxygen. Oxygen efficiently quenches doublet states of Cr(III) complexes,[4] and Co(II) and Ni(II) complexes efficiently deactivate singlet oxygen;[5] the mechanisms remain uncertain. Because d–d and charge-transfer (CT) excited states of metal complexes have no direct organic counterpart and since spin–orbit coupling is much greater in complexes than in organics, different rules may well apply. We report here evidence for the efficient production of singlet oxygen on deactivation of CT-triplet states of ruthenium(II) complexes.

$Ru(bipy)_3Cl_2$ (G. Frederick Smith), $Ru(bipy)_2(CN)_2$,[6] $Ru(phen)_3(ClO_4)_3$, $Ru(phen)_2(CN)_2$[7] (bipy = 2,2′-bipyridine; phen = 1,10-phenanthroline), and Fisher Rose Bengal were used as sensitizers. Aldrich 2,3-dimethyl-2-butene (TME) and 1,3-cyclohexadiene (CHD) were used as oxygen scavengers.

Stern–Volmer quenching constants, K_{sv}'s, were computed from $[(\phi_0/\phi) - 1]/[O_2]$ and $[(\tau_0/\tau) - 1]/[O_2]$; ϕ's and τ's represent emission intensities and mean lifetimes, respectively. K_{sv}'s and bimolecular quenching constants, k_2's, are summarized in Table I.

That O_2 quenching involved more than just catalytic deactivation of the complexes was demonstrated by

Table I. Oxygen Quenching of Metal Complexes at ~21°

Complex–solvent	K_{sv}, M^{-1} ϕ method[a]	 τ method[b]	$k_2 \times 10^9$,[c] $M^{-1}\ sec^{-1}$
$Ru(phen)_2(CN)_2$–H_2O	3900	3900	5.5
$Ru(phen)_2(CN)_2$–CH_3OH	8500	9900	5.0
$Ru(phen)_3{}^{2+}$–H_2O	4900		4.7
$Ru(phen)_3{}^{2+}$–CH_3OH	1010		3.2
$Ru(bipy)_2(CN_2)$–H_2O	1180		4.5
$Ru(bipy)_2(CN)_2$–CH_3OH	1910		4.5
$Ru(bipy)_3{}^{2+}$–H_2O	2060	1890	3.3
$Ru(bipy)_3{}^{2+}$–CH_3OH	1380	1470	1.7

[a] ±5%. [b] ±10%. [c] Calculated from K_{sv} by ϕ method.

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adding TME or CHD. Irradiation than caused rapid oxygen uptake. Also, luminescence behavior clearly demonstrated O_2 consumption, especially with the cyanide complexes. With O_2 present, emission was not visible; but if stirring was stopped, within ~5 sec a bright deep orange emission grew in as O_2 was consumed.

Quantitative photooxygenations at 0° used stirred methanol solutions containing a fixed amount of olefin (~3 mmol) and either 3 mg of Rose Bengal or 5 mg (5–10 μmol) of complex in ~30 ml. Oxygen uptakes (initially ~3-5 ml/min) ceased rather abruptly after ~15-30 min. Methanol was then removed by two flash evaporations with CCl_4. The oil, redissolved in CCl_4 and filtered, was characterized by ir.

Table II summarizes O_2 uptakes. Infrared spectra for a given olefin with all three sensitizers were indistinguishable and exhibited the same bands as the singlet oxygen–olefin reaction products.[1] $Ru(phen)_3^{2+}$ and $Ru(bipy)_2(CN)_2$ sensitizations exhibited similar uptakes; no quantitative data were taken.

The K_{SV}'s by the τ and ϕ methods for each $Ru(phen)_2(CN)_2$ and $Ru(bipy)_3^{2+}$ complex–solvent system are experimentally equal. Thus, O_2 quenching in these cases is principally diffusional and not from ground-state association. The k_2's which are all near the diffusion controlled limit indicate that a large fraction of encounters result in deactivation. We infer from the great structural similarity that the same conclusions hold for the remaining complexes.

Irradiation of Rose Bengal in the presence of oxygen is a clean, efficient source of singlet oxygen.[1,2] The Rose Bengal sensitized photooxygenations of TME and CHD proceed stoichiometrically (1:1) to yield unique and easily characterized products, a hydroperoxide and an *endo*-peroxide, respectively.[1] Thus, the Rose Bengal runs serve as analytical tests for the exact amount of olefin used and as an authentic source of the singlet oxygen addition products.

Table II shows that 1 mol of oxygen combines with 1 mol of TME or CHD for both metal complexes, the same as if singlet oxygen were the reactive species. This fact, coupled with the identification of the complex sensitized organic products as the singlet oxygen ones, leads to the conclusion that *singlet oxygen production is a significant pathway for oxygen deactivation of CT-triplet states of metal complexes.* This conclusion is based on the results for $Ru(bipy)_3^{2+}$ and $Ru(phen)_2(CN)_2$ in methanol. Since these two types of complexes are spectroscopically representative of a wide range of Ir(III),[8] Os(II),[9] and Ru(II)[10] complexes having lowest lying CT excited states, however, the phenomenon is probably a general one. One cannot necessarily generalize to d-d excited states. We have no quantitative data on the fraction of quenching events leading to energy transfer, but the similar rates of O_2 uptake for Rose Bengal and complex sensitization suggest that the efficiencies are high.

Metal complexes, because of their great resistance to uv photodestruction, may be useful as singlet oxygen generators for uv-rich sources or as sensitized actinometers. Further work on transfer efficiencies, olefins yielding multiple products, and other metal complexes is in progress.

Table II. Sensitized Oxygen Uptakes in Methanol at 0°

Sensitizer	Oxygen uptake (mmol)[a] 2,3-Dimethyl-2-butene	1,3-Cyclohexadiene
Rose Bengal[b]	3.09	3.12
$Ru(phen)_2(CN)_2$[c]	3.11	3.12
$Ru(bipy)_3^{2+}$[c]	3.08	3.17

[a] ~±1%. [b] With a 500-W DEK projection lamp, 5-cm water filter. [c] With a 1000-W Hg–Xe arc, 5-cm aqueous $CuSO_4 \cdot 5H_2O$ (100 g/l.).

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Synthesis of β-Hexa-, β-Hepta-, and β-Octaketones

Sir:

Recent interest in β-polycarbonyl compounds stems from their involvement in the biosynthesis of polyketide-type aromatic metabolites.[1] Numerous β-tetra- and two β-pentacarbonyl compounds have been synthesized, principally by stepwise acylation of the next smaller member.[2] This linear approach cannot, as yet, be carried beyond five carbonyl groups; a major problem being the difficulty of acetylating strongly basic anions.

A recent communication from this laboratory described a novel approach to β-polyketones; β-tetra- and β-pentaketones were prepared by acylation of the polyanions of di- and triketones with β-keto ester monoanions.[3] These condensations, in effect, extend the ketide chains by two carbonyl groups. We now wish to describe the use of this β-ketoacylation reaction in the synthesis of higher polycarbonyl compounds, namely, 1,3,5,7,9,11-hexaketone **1**, 1,3,5,7,9,11,13-heptaketone **2**, and 1,3,5,7,9,11,13,15-octaketone **3**.

The initial approach to hexaketone **1** involved β-ketoacylation of 1-phenyl-1,3,5,7-octanetetraone with ethyl benzoylacetate (Scheme I). The tetraketone was treated with 4 equiv of lithium diisopropylamide in tetrahydrofuran (THF) at 0° under nitrogen, converting it into red tetraanion **4**. The sodium salt of the keto ester (formed with sodium hydride) was added in THF and the mixture was heated at 35°. After 2 hr, and again after 4, 8, and 10 hr, the mixture was cooled in an ice bath and 0.25 equiv of lithium diisopropylamide was

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