fitted by this mechanism[17] with $k_7 = 1 \times 10^{-4}\ M^{-1}$ sec^{-1}.[18] When reaction 7 is included G is found to be only approximately 50 times more efficient than PBN in trapping BzO· radicals[19] (see Table II).

Table II. Initial Rate Ratios for Competitive Benzoyloxy Radical Scavenging by Substituted Phenyl *N-tert*-Butylnitrones and $10^{-4}\ M$ Galvinoxyl

R	[R-PBN], M	$(100)k_2/k_6$
p-CH$_3$O	1×10^{-3}	4.4
p-CH$_3$	5×10^{-3}	3.0
H	5×10^{-3}	1.9
p-Cl	5×10^{-3}	1.4
p-NO$_2$	1×10^{-2}	0.86

An estimate of $2 \times 10^7\ M^{-1}$ sec^{-1} for the rate constant of the reaction of methyl radicals with galvinoxyl is available.[20] If the same rate constant is assumed for the reaction of BzO· with G, the rate constant for PBN spin trapping of BzO· is $4 \times 10^5\ M^{-1}$ sec^{-1}. This value compares well with the previous estimate of 10^5–$10^6\ M^{-1}$ sec^{-1} based on different considerations.

Since the effect of structure and substituents on the rate of reaction 2 is of some interest in spin trapping, data for four para-substituted PBN's have been obtained (see Table II). It is found that electron donation enhances and electron withdrawal hinders the rate of BzO· addition to PBN but the effect is not large. A Hammett plot fits σ^+ better than σ with a slope of -0.47. For benzoyloxy radicals one concludes that the transition state has some polar character with PBN the electron donor, since the Hammett slope would be expected to be positive if the substituent effect mainly influences the energy of PBN in the ground state. This result is not unexpected for an electrophilic radical. One might anticipate a less negative slope (maybe positive) for a nucleophilic radical (*e.g.*, hydroxy or alkoxyalkyl radicals) and a negligible substituent effect for phenyl radical additions. Studies of such systems are in progress.

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(17) $-\mathrm{d[G]/d}t = 2[\mathrm{Bz_2O_2}](k_1 + k_7[\mathrm{G}])$ integrates to $[\mathrm{G}\cdot] = (k_1/k_7 + [\mathrm{G}\cdot]_0)\exp(-2k_7[\mathrm{Bz_2O_2}]t) - (k_1/k_7)$.

(18) This value is considerably lower than that for triphenylmethyl radical induced decomposition of Bz$_2$O$_2$: $k = 1.2\ M^{-1}$ sec^{-1} at 25°;[16] in fact the induced decomposition of Bz$_2$O$_2$ by G is slow enough that G has been used[9] to suppress the "ordinary" induced decomposition of Bz$_2$O$_2$ in benzene which always accompanies the simple homolysis in the absence of inhibitors (see K. U. Ingold and B. P. Roberts, "Free Radical Substitution Reactions," Wiley, New York, N. Y., 1971, p 151).

(19) The initial rate ratio was obtained at 40° with $10^{-1}\ M$ Bz$_2$O$_2$, $10^{-2}\ M$ PBN, and $10^{-4}\ M$ G; $k_2/k_6 = 0.0193$ was extracted from the following expression where $k_1 = 6.4 \times 10^{-8}$ sec^{-1} (see Table I).

$$\frac{-\mathrm{d[G]/d}t}{\mathrm{d[BzO\text{-}SA]/d}t} = \frac{[\mathrm{G}](2k_1k_6/k_2 + 2[\mathrm{G}]k_7k_6/k_2 + k_7[\mathrm{PBN}])}{[\mathrm{PBN}](2k_1 + k_7[\mathrm{G}])}$$

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Excited State Ru(bipyr)$_3{}^{2+}$ as an Electron-Transfer Reductant

Sir:

It was reported recently that the first triplet charge-transfer state of Ru(bipyr)$_3{}^{2+}$, where bipyr denotes 2,2′-bipyridine, can sensitize substitution reactions of coordination compounds.[1] We describe here results which indicate that this state can also function as an electron-transfer reductant, the complex being oxidized to ground-state Ru(bipyr)$_3{}^{3+}$.

Our first experiments were carried out with solutions buffered with acetate to pH 4 and $1.25 \times 10^{-4}\ M$ in [Ru(bipyr)$_3$]Cl$_2$ and $1 \times 10^{-3}\ M$ in [Co(NH$_3$)$_5$Br](NO$_3$)$_2$; such solutions show negligible reaction in the dark. Irradiation at 410 nm led to Co^{2+} production with a quantum yield, ϕ, of 0.1. There was formed no detectable Co(NH$_3$)$_5$(H$_2$O)$^{3+}$ ($\phi \leq 0.001$), free bipyridyl ($\phi \leq 0.001$), or free pyridine ($\phi \leq 0.003$). In fact, no consumption of Ru(bipyr)$_3{}^{2+}$ occurred, and the process at this point appeared to be one of ordinary photosensitization such as previously reported for cobalt(III) ammines.[2] We were concerned, however, that a chemical mechanism might still be involved, since at pH 4 Ru(bipyr)$_3{}^{3+}$ is rapidly reduced by solvent. The standard oxidation potential for the Ru(bipyr)$_3{}^{2-}$–Ru(bipyr)$_3{}^{3-}$ couple is -1.23 V.[3]

Reduction of Ru(bipyr)$_3{}^{3+}$ by solvent is slow in 1 N H$_2$SO$_4$, and this medium was tested, using the above concentrations of Ru(bipyr)$_3{}^{2-}$ and of substrate. There is again no dark reaction, but now on irradiation at 410 nm the initial strong luminescence from ^{3}Ru(bipyr)$_3{}^{2+}$ fades and the solution changes from yellow to the light green color of Ru(bipyr)$_3{}^{3+}$. The amount of Ru(bipyr)$_3{}^{3+}$ formed was determined by following the increase in absorbance at 452 nm as the slow thermal reduction back to Ru(bipyr)$_3{}^{2+}$ took place following the irradiation. Thus, in one experiment, photolysis to 8% reduction of Co(NH$_3$)$_5$Br^{2+} was accompanied by 50% oxidation of the Ru(bipyr)$_3{}^{2+}$. If the irradiated solution was immediately brought to pH 4 by the addition of sodium acetate, the full original amount of Ru(bipyr)$_3{}^{2+}$ was regenerated. A series of experiments established the average stoichiometry to be 1.4 Co^{2+} produced per Ru(bipyr)$_3{}^{2+}$ oxidized. Since the reduction yields Br$^-$, an ion which rapidly reduces Ru(bipyr)$_3{}^{3+}$, the resulting Br may in part react with Co(NH$_3$)$_5$Br^{2+} to increase the apparent yield of Co^{2+}.

There seems to be no doubt that ^{3}Ru(bipyr)$_3{}^{2+}$ is implicated. Emission from this state is partially quenched on O$_2$ saturation of the solution; we find a concomitant reduction in $\phi_{\mathrm{Co}^{2+}}$ of about 60%. The triplet state is also quenched by Co(NH$_3$)$_5$Br^{2+}, as shown in Figure 1, which yields a Stern–Volmer constant, K_{SV}, of 255 M^{-1}, a value consistent with the diffusional encounter rate of two dipositive ions. The concentration dependence of $\phi_{\mathrm{Co}^{2+}}$ is given in Figure 2; the least-squares line yields a K_{SV} of 298 M^{-1}, a value not inconsistent with that from the quenching studies in view of the possibility that the stoichiometry of the reaction may change with concentration.

The mechanism of the reaction appears to be one of electron transfer from ^{3}Ru(bipyr)$_3{}^{2+}$ to Co(NH$_3$)$_5$Br^{2+} during an encounter. However, it is not possible at this stage to eliminate a mechanism of ordinary photosensitization followed by oxidation of Ru(bipyr)$_3{}^{2+}$ in

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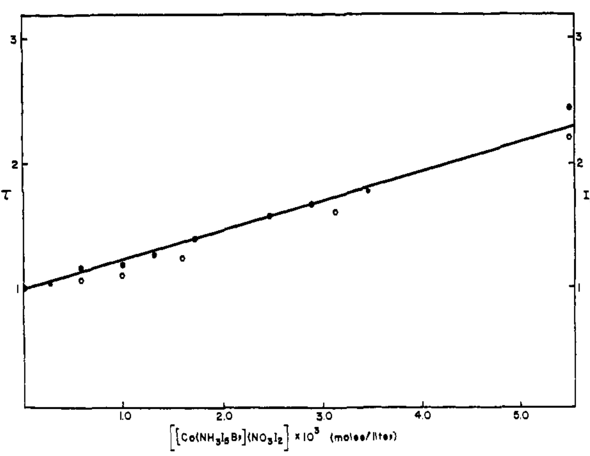

Figure 1. Quenching of $^3Ru(bipyr)_3{}^{2+}$ by $Co(NH_3)_5Br^{2+}$. ○: phosphorescence quenching, I_0/I, corrected for absorption of the exciting and the emitted light. ●: lifetime quenching, τ_0/τ, using the equipment cited in ref 1.

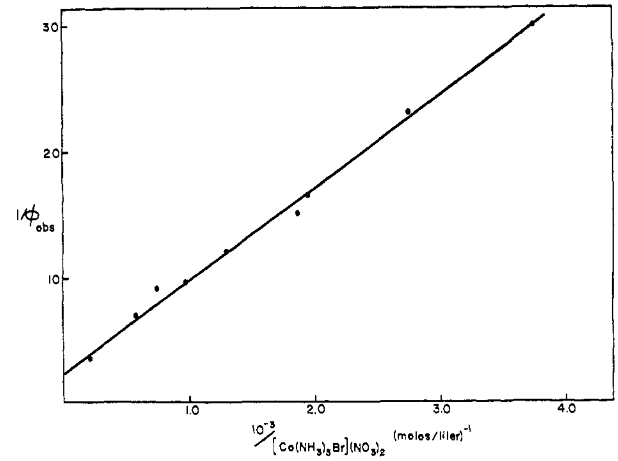

Figure 2. Effect of $Co(NH_3)_5Br^{2+}$ concentration on $\phi_{Co^{2+}}$.

secondary reactions with radicals produced in the reduction of $Co(NH_3)_5X^{2+}$. Reduction *via* photoelectron production can be ruled out, however. $Ru(bipyr)_3{}^{2+}$ is ordinarily quite stable toward irradiation even under circumstances such that scavenging of any produced $e_{aq}{}^-$ should occur. For example, no reaction occurs in solutions saturated with N_2O, nor did flash photolysis of $Ru(bipyr)_3{}^{2+}$ in water show any transient absorbing at 700 nm with a half-life greater than 50 μsec (using the equipment of ref 4). Also, it has been found that $Ru(bipyr)_3{}^{3+}$ efficiently captures $e_{aq}{}^-$ to produce $^3Ru(bipyr)_3{}^{2+}$ [5] so that the reverse process is not likely.

As noted above, the possibility that the reaction is one of sensitization producing, say, a ^{3}CT cobalt complex which decomposes to Co(II) and a radical capable of oxidizing $Ru(bipyr)_3{}^{2+}$ cannot be ruled out. Results of the key experiment of direct irradiation of $Co(NH_3)_5Br^{2+}$ in the presence of (nonabsorbing) $Ru(bipyr)_3{}^{2+}$ are inconclusive because only an extremely small concentration of Ru(II) can be used.

An interesting aspect of the electron-transfer mechanism which we propose is that in the process a good reductant, $^3Ru(bipyr)_3{}^{2+}$, is transformed into a strong oxidant, $Ru(bipyr)_3{}^{3+}$. A necessary condition for the reaction to be observed may, therefore, be that the reduction of the substrate be irreversible, as is the case here.

Other substrates were found, with results as summarized in Table I. Species whose standard reduction potential is less than about +0.0 V are not reduced. The inference of the mechanism is that the standard potential for $Ru(bipyr)_3{}^{2+} \rightarrow {}^3Ru(bipyr)_3{}^{2+}$ may be as low as 1.2 V. The above figure of 1.2 V is, of course, quite approximate; not only are the half-wave potentials irreversible, but possibly major Nernst corrections have not been made. The interesting point remains that with further investigation it may be possible to obtain an experimental entropy of formation of excited state $Ru(bipyr)_3{}^{2+}$.

Table I. Reduction of Various Substrates by $^3Ru(bipyr)_3{}^{2+}$

Substrate	$\phi_{Co^{2+}}$ [a]	K_{SV}, M^{-1}	$\epsilon_{1/2}$, V (*vs.* sce)[b]
$Co(NH_3)_6{}^{3+}$	Small		−0.44
$Co(NH_3)_5F^{2+}$	0.0003	0	−0.33
$Co(NH_3)_5Cl^{2+}$	0.063	100	0.28
$Co(NH_3)_5Br^{2+}$	0.104	225	0.38
$Co(HEDTA)Cl^-$	~0.2		
$Fe(C_2O_4)_3{}^{3-}$	0.1[c]		

[a] Determined for 1×10^{-3} *M* complex. [b] From A. A. Vlček, *Discuss. Faraday Soc.*, **26**, 164 (1958). [c] $\phi_{Fe^{2+}}$.

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Geometry and Solvolysis of *exo-anti*-Tricyclo[3.1.1.0^{2,4}]heptan-6-yl *p*-Nitrobenzoate[1]

Sir:

Only two examples (compounds **1** and **2**)[2] demonstrate that the cyclopropane ring incorporated in a system homoconjugates symmetrically with a developing carbonium center, causing an enormous enhancement in rate of solvolysis. The ground-state geometry of the system is evidently a decisive factor contributing to this rate acceleration. We have completed solvolytic studies of the title compound **3a** and an X-ray analysis of **3b** (R = *p*-BrC_6H_4CO). The system has now been shown to possess a geometry similar to the one predicted for the maximum delocalization of the positive charge of the bicyclo[3.1.0]hex-3-yl cation.[3]

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(1) The prefix anti denotes the anti orientation of the cyclopropane ring with respect to the substituted bridge.

(2) (a) J. S. Haywood-Farmer and R. E. Pincock, *J. Amer. Chem. Soc.*, **91**, 3020 (1969); H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **89**, 1953 (1967); M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967); (b) R. M. Coates and J. L. Kirkpatrick, *ibid.*, **92**, 4883 (1970), and references cited therein.

(3) R. Hoffmann, *Tetrahedron Lett.*, 3819 (1965). We assume the interplanar angle between the cyclopropane and the main cyclopentane ring (see text) is the same both for **3b** and the bicyclo[3.1.0]hexane system.