ligand deuteration is mitigated in the complex; but now a large isotope effect is observed for the solvent. *Deuteration of the solvent causes the radiationless lifetime to almost double while deuteration of the ligand causes only a 20–25% increase in $\tau_{nr}$ for the complex.* Quantum yield measurements indicate that the radiative lifetime, $\tau_m/Q$, is invariant, within experimental error, for all the 25° measurements. The measured lifetimes of the complexes were found to be independent of pH or pD; thus structures involving base hydrolysis of the ligand[30] seem unlikely as possible explanations of the large solvent deuterium effect.

The effect of solvent deuteration may be explained in terms of an excited state model involving partial charge transfer to solvent (CTTS) when viewed in the light of the "active H-atom" theory of Robbins and Thomson.[31] These authors point out that the electronic part of the expression for the radiationless decay rate, $J^{ko}(m,n)$, may be expressed as

$$J^{ko}(m,n) \propto \int \zeta_{mn}(r) \frac{dV}{dQ_k} dr \qquad (1)$$

where $dQ_k$ refers to the nuclear coordinates of the promoting mode, $V$ is the one-electron nuclear-electron interaction and $\zeta_{mn}(r)$ is the electric transition density ($\psi_m \rightarrow \psi_n$). They go on to show that this integral will be significant only when $\zeta_{mn}(r)$ is large in the region of the vibrating nuclei responsible for the perturbing force. They argue that increased electron density in the region of the atoms whose vibrations act as promoting modes should lead to greater efficiency of radiationless relaxation. These conclusions are supported with data on a variety of systems, including: a series of ammine complexes and β-diketone complexes of Cr(III), ligand-substituted bipyridyl and phenanthroline complexes of Ru(II) and Os(II), and solvent deuterium effects in aqueous solutions of rare earth chelates.

The interpretation of the present work in terms of a CTTS model is a logical extension of the work of Robbins and Thomson. If the excited state of $[Ru(bipy)_3]^{2+}$ were purely charge transfer to ligand (CTTL), as is commonly assumed, then one would expect a larger increase in $\tau_{nr}$ upon deuteration of the ligand. The fact that the most pronounced effect is observed upon deuteration of the solvent is strong evidence for increased electron density in the region of the solvent. Thus the luminescent state of $[Ru(bipy)_3]^{2+}$ may be thought of as having some CTTS character, which may be important in electron-transfer quenching mechanisms.

We have noticed that both the lifetime and quantum yield are sensitive to the temperature of the solution and we are presently conducting a study of this temperature dependence in order to determine activation parameters for the system.[32] We also plan to further test the "active H-atom" theory by using mixtures of $H_2O$–$D_2O$ and other appropriate solvent systems.

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## A Kinetic Investigation of the Reaction of 2-Bromooctane with Silver Perchlorate, a Second-Order Dependence in Silver Ion

*Sir:*

Nucleophilic substitution reactions of alkyl halides are known to be markedly accelerated by electrophilic metal ions such as silver ion. The stereochemical course of the reaction of optically active 2-iodooctane with silver nitrite[1a] and 2-bromooctane with silver nitrate has been shown by Pocker[1b] and Kornblum[1c] to proceed with inversion of configuration regardless of the solvent. A solvent dependency on the stereochemistry of the reaction of silver salts with α-phenylethyl chloride was observed.[1a] On the basis of salt effects, the fact that silver nitrate was more reactive than silver perchlorate, and the relatively low reactivity of neopentyl iodide, Hammond also suggested that these reactions had significant $S_N2$ character.[2]

Since the initial kinetic investigation[3] of the reaction between alkyl halides and silver salts, there have been numerous attempts to define the rate law for this reaction.[4] It has been established that the contribution of the alkyl halide to the order of the reaction is always close to unity. However, all attempts to elucidate the contribution of the $Ag^+$ and its counterion have led to fractional orders. For example, the reaction of $AgNO_3$ with ethyl iodide, isopropyl iodide, and neopentyl iodide in acetonitrile solvent at 25° did not fit a constant integral order but fell between second and third order.[2] Similar kinetic behavior was observed for the reaction of 2-bromooctane with $AgNO_3$ and $AgClO_4$ in acetonitrile.[1b] The stereochemical[1] and kinetic evidence[1b,2] prompted the suggestion that both silver cation and its accompanying anion participated in the rate limiting step (eq 1). Our interest in the kinetic behavior of these reactions was stimulated by the observation that we found it necessary to

$$NO_3^- + RI + Ag^+ \longrightarrow \underset{\text{transition state}}{[NO_3\text{-}RIAg]} \longrightarrow \text{products} \qquad (1)$$

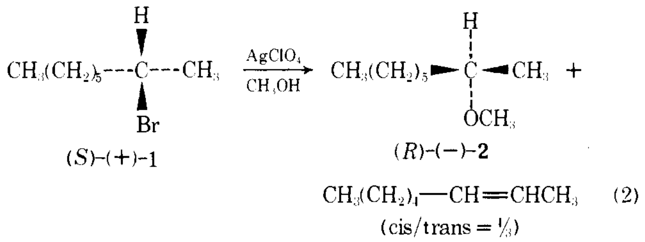
Table I. Rates of Reaction of 1 with $AgClO_4$ in $CH_3OH$[a]

| Initial Concn of $AgClO_4$[b] | Initial Concn of 1[b] | $k_1'$, $sec^{-1}$ [c] | $k_3$, $M^{-2}$ $sec^{-1}$ [d] | $t_{1/2}$, sec |
|---|---|---|---|---|
| 0.350[e] | 0.005 | $2.51 \times 10^{-2}$ | 0.21 | 28 |
| 0.175 | 0.005 | $6.39 \times 10^{-3}$ | 0.22 | 108 |
| 0.090 | 0.005 | $1.73 \times 10^{-3}$ | 0.22 | 401 |
| 0.048 | 0.005 | $5.18 \times 10^{-4}$ | 0.24 | 1338 |

[a] Reaction temperature was maintained at 25 ± 0.2°. [b] Concentration given in moles/liter. [c] Calculated assuming rate = $k_1'$ [RBr]. [d] A correlation coefficient of >0.996 was obtained for each kinetic run. [e] A constant ionic strength of 0.35 $M$ in $ClO_4^-$ was maintained by assuming $[AgClO_4] + [NaClO_4] = [ClO_4^-]$. Implicit in this assumption is that both of these salts are completely dissociated. Although the percent dissociation in $CH_3OH$ is not known, their conductivities[13] in ethanol are comparable, suggesting that the ionic strength should remain fairly constant as the relative proportions of the two salts are varied.

use an excess of silver salt in synthetic applications in order to get reasonable reaction times, and that an increase in the amount of silver used gave a marked increase in rate, suggesting that these reactions were more than first order in silver. Despite the generality of this well-known reaction, the kinetic role of silver ion has apparently never been subjected to close scrutiny by varying the $Ag^+$ concentration at a constant ionic strength. We now report our findings that the reaction of 2-bromooctane (**1**) with an excess of $AgClO_4$ in methanol solvent exhibits reproducible kinetic behavior and is second order in silver ion. Our kinetic studies differ from those previously reported in two respects: (a) we have maintained a constant perchlorate ion concentration while varying the silver ion concentration by addition of sufficient $NaClO_4$ to maintain the desired ionic strength; and (b) we have studied the reaction under pseudo-first-order conditions in **1** with a ratio of silver ion to **1** greater than 10.

The reaction of 2-bromooctane (**1**) with a homogeneous solution of $AgClO_4$ in methanol at 25° afforded 2-methoxyoctane (**2**) and 2-octene in a 1:1 ratio (eq 2). The progress of the reaction was followed by measuring the depletion in concentration of **1** by gas chromotography (6 ft, 10% SE-30) using cyclodecane as an internal standard. Under pseudo-first-order conditions in halide, the $AgClO_4$ concentration was varied (Table I) while maintaining the concentration of **1** constant (0.005 $M$). The total perchlorate anion concentration was maintained essentially constant at 0.35 $M$ by addition of $NaClO_4$. A plot of the pseudo-first-order rate constant $k_1'$ (rate = $k_1'$ [RBr] where $k_1' = k_3[Ag^+]^2$) vs. the square of the silver concentration was linear (least-squares correlation coefficient = 0.9999) with a slope $k_3 = 2.03 \times 10^{-1}$ $M^{-2}$ $sec^{-1}$. These data establish the reaction of **1** with excess $AgClO_4$ in methanol to be cleanly second order in silver ion, $-d[RBr]/dt = k_3[Ag^+]^2[RBr]$.



(*S*)-(+)-1

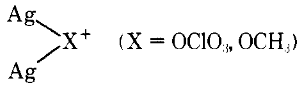
(*R*)-(−)-**2**

$CH_3(CH_2)_4—CH=CHCH_3$ (cis/trans = ⅓)

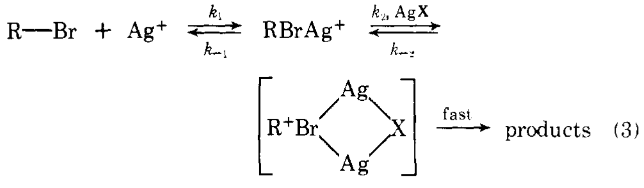
3

The reaction of (*S*)-(+)-2-bromooctane[5] with $AgClO_4$ in $CH_3OH$ at 25° afforded (*R*)-(−)-2-methoxyoctane. Thus, as noted previously in other solvents,[1,6] the reaction in methanol also proceeds with net inversion of configuration. The overall retention of optical activity (ROH → RBr → ROMe) was 67%.[9] This suggests that the reaction in methanol with $AgClO_4$ was less stereospecific than the reaction of **1** with $AgNO_2$[1c] or $AgNO_3$[1b] in acetonitrile where 83 and 87% retention of optical activity was reported. A stereospecific inversion of configuration was suggested in both cases.[10]

The second-order dependence in silver ion for this reaction is surprising since it had been generally assumed that only one silver cation was involved in consummation of carbon-bromine bond cleavage. It is difficult to envisage a mechanism involving two positively charged silver cations unless one invokes a termolecular process. It is, therefore, likely that at least one of the silver atoms involved is closely associated with a negatively charged counterion. Unfortunately the order of the reaction in perchlorate ion cannot be documented, because variations in ionic strength are not controllable; the addition of $NaClO_4$ accelerates the reaction because of electrolyte effects. Although the nature of the intermediate and the steps involved are not yet clear, we propose a tentative mechanism consistent with the kinetic data that involves a rapid equilibrium between the halide and silver ion with subsequent attack on this positively charged intermediate by a neutral molecule of $AgClO_4$ or perhaps $AgOCH_3$[12] (eq 3). Alternatively, the same transition state may be formed by the bimolecular collision of RBr and



(X = $OClO_3$, $OCH_3$)



intimate ion pair

Both pathways are tenable but certainly not compelling. The formation of **2** by inversion is consistent with backside attack at carbon by solvent on an intimate ion pair. This type of graded SN1–SN2 mechanism has been invoked previously.[1,2] Furthermore, if dissociation of the silver aggregate (eq 3) were required *prior* to precipitation of AgBr, this would provide an attractive explanation for the racemization[9,10] of **1** by silver salts in acetonitrile. More detailed studies are in progress that will examine the kinetic behavior of this reaction as a function of the $[RBr]/[Ag^+]$ ratio in $CH_3OH$ and hopefully further delineate the overall reaction mechanism.

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(9) Reaction of (*S*)-(+)-**1** ($[\alpha]^{25}\text{D}$ +29.1° (*c* 6.37, $CCl_4$)) with $AgClO_4$ in $CH_3OH$ at 25° afforded **2** having $[\alpha]^{25}\text{D}$ −6.9° (*c* 3.60, $CCl_4$) after purification by GLC. At one-half reaction, the starting bromide **1** was collected by GLC and had lost only ~1% of its optical activity having $[\alpha]^{25}\text{D}$ 28.7° (*c* 8.25, $CCl_4$).

(10) Kornblum reported[11] that conversion of (+)-2-octanol to (−)-**1** by $PBr_3$ is accompanied by 18% racemization and, at one-half reaction with $AgNO_2$–$CH_3CN$, **1** had racemized 19–21%.

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## Electronic Structure of Dioxygen in Cobalt(II) Oxygen Carriers, Singlet Oxygen or $O_2^-$?

*Sir:*

In a recent communication,[1] evidence was presented supporting the existence of magnetically equivalent oxygen atoms in the mononuclear cobalt complex Co(bzacen)py$O_2$. The experimental results consisted of the solution ESR spectrum of the $^{17}O$-enriched complex, which was interpreted in terms of two equal isotropic $^{17}O$ splittings of 21.6 G. The value is in the range to be expected for $a_O$ in an $O_2^-$ ion, and we implicitly assumed the oxygen molecule to be a modified $O_2^-$ ion. This assumption is in line with that of most previous workers in the field. The previous ESR evidence in support of the $O_2^-$ formulation has been summarized by Hoffman et al.[2]

Recently Tovrog and Drago[3] have brought forward experimental data which they use to argue against the $O_2^-$ formulation. They suggest that there is very little electron transfer from metal to oxygen on complex formation, and that the oxygen molecule is best regarded as being in a singlet state. Their explanation of our $^{17}O$ results is that the $O_2$ molecule is jumping between two σ-bonded bent structures, the observed $a_O$ being accounted for by overlap between cobalt $d_{z^2}$ and oxygen $sp^2$ hybrids. In addition they dismiss the report of the ESR spectra of $^{17}O$-labeled $O_2$ coordinated to a cobalt(II)-ammonia complex in a γ-Zeolite. The spectra of this system were interpreted by Vansant and Lunsford[4] in terms of an $O_2^-$-type structure for oxygen. In support of an $O_2$ formulation they claim that CO, certainly a very weak electron acceptor, combines with their cobalt complexes to give ESR spectra indistinguishable from those in the presence of oxygen.

We do not accept Tovrog and Drago's conclusions. Before presenting further experimental evidence for the $O_2^-$ picture, we wish to make some preliminary comments.

If the $O_2$ molecule is effectively in a singlet state carrying very little unpaired spin, it becomes difficult, if not impossible, to explain Vansant and Lunsford's spectra.[4] It is true, as Tovrog and Drago state, that the resolution is poor, as expected for a powder spectrum. However, the important point is the *spread* of the spectrum in the $^{17}O$-labeled complex and the approximate values of the oxygen splittings ($A_O$). The minimum value that can be assigned to the sum of the splittings for the two oxygens is ~140 G, based on the total spread and the values of $A_{Co}$. Secondly, the values of ~60 and ~80 G for the two coupling constants are close to the figures of 60 and 88 G measured in a single crystal study of an unimpeachable bent peroxy group carrying one unpaired electron.[5] Incidentally, our value of 21.6 for $a_O$ is almost exactly that to be predicted for the isotropic splitting due to an electron density of 0.5 in a pπ atomic orbital on oxygen,[6] and it would be an extraordinary coincidence if the same splitting were due to the mechanism that Tovrog and Drago propose.

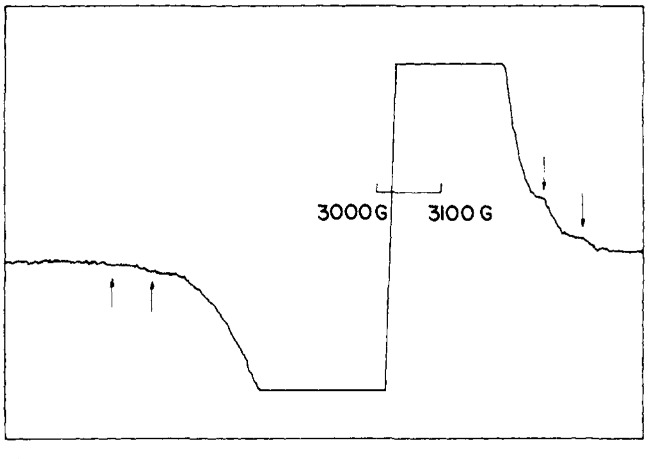

**Figure 1.** First derivative X-band ESR spectrum of a frozen solution of Co(bzacen)py-$^{17}O_2$ (~40 atom %) complex in $CH_2Cl_2$ at −100°. The two extreme $^{17}O$ satellites at high and low field are indicated by arrows.

In the present report, we describe the frozen solution ESR spectrum of $^{17}O$-enriched Co(bzacen)py$O_2$ complex. The results show unambiguously that the bound oxygen molecule is effectively an $O_2^-$ ion, *at least in this complex.*

Co(bzacen)py$O_2$ was synthesized with $O_2$ gas enriched to 40 atom % $^{17}O$. Solutions in methylene chloride were frozen and the ESR spectra recorded at −100°. The first and second derivative spectra respectively are shown in Figures 1 and 2. Despite the heavy overlapping in the central part of the spectrum there are easily distinguishable $^{17}O$ satellites at the two extremes of the first derivative spectrum. The second derivative spectrum shows considerably better resolution, and the $^{17}O$ satellites are clearly visible. The separation between the outermost satellites is ~60 G. The total spread of the spectrum is ~740 Gauss which implies that $\Sigma A_O \sim 148$ G, and therefore that the two oxygen hyperfine splittings are ~60 and ~88 G. Despite the probable error of ±10 G in these figures, there is absolutely no doubt that they arise from the combined isotropic and anisotropic contributions due to a single unpaired electron in the π system of an unsymmetrically bound $O_2^-$ group. The observed splittings can be simply rationalized in terms of pπ-spin densities of approximately 0.40 and 0.60 on the two oxygens, as explained previously.[5]

The addition of carefully purified oxygen-free CO had no detectable effect on the solution or ESR spectrum of Co(bzacen)py.

The complex studied here differs from that used by Tovrog and Drago, both in the nature of the Schiff base and in the fact that their Co(II) complexes are high spin. The relevance of our results to their complexes might therefore be questioned. After the submission of our original manu-