

dark or irradiation of **3** in the absence of the sensitizer or in the presence of equimolar 1,4-diazabicyclo[2.2.2]octane (DABCO), a singlet oxygen quencher,⁸ yielded no detectable dioxetane or epoxide. Addition of 2,6-di-*tert*-butyl-*p*-cresol, a free radical inhibitor, has no effect on the rate of oxidation of **3** nor on the ratio of **4** and **6**. **4** and **6** are both stable under photooxidation conditions and are not interconverted, nor is the epoxide formed from the irradiation of **3** + **6** + TPP in the absence of oxygen. Neither **4** nor **6** is produced from the vpc standard, 7,7'-binorbornyl, under the conditions of the photooxidations.

The extent of formation of epoxide in the experiments of Table I varies from 40% in methylene chloride (0.0037 *M* **3**) to 95% in benzene (0.00019 *M* **3**). This is a 28.5-fold range in the ratio of epoxide to dioxetane. Though concentration and solvent dependent, this ratio is not parallel to the polarity of the solvent, and certainly not to its capability as a substrate for the Baeyer-Villiger reaction,^{2a,c} since more epoxide was formed in benzene than in pinacolone. Hypotheses suggested by these results are under active investigation in this laboratory.

Acknowledgment. We gratefully acknowledge support of this research by the National Science Foundation and the National Institutes of Health.

(8) J. C. Ouannès and T. Wilson, *J. Amer. Chem. Soc.*, **90**, 6527 (1968).

Paul D. Bartlett,* Margaret S. Ho

Converse Memorial Laboratory, Harvard University
Cambridge, Massachusetts 02138

Received August 31, 1973

On the Appropriateness of Assigning Spin Labels to Excited States of Inorganic Complexes¹

Sir:

Recently there has been a surge of interest in the photochemistry and spectroscopy of transition metal complexes of the heavier transition elements. The tris(2,2'-bipyridine)ruthenium(II) ion is playing a key role because of its unusual luminescence properties. In most of these studies it is either explicitly stated or tacitly assumed that the excited state(s) responsible for the luminescence, energy transfer, or photochemistry possesses a well-defined multiplicity.²⁻⁶ The purpose of this communication is to point out that reliance upon a spin-based language may lead to erroneous conclusions regarding excited-state properties, mechanisms of energy transfer, and photochemical reactivity in inorganic systems.

A spin labeled state is defined theoretically as a state whose eigenket satisfies the equation $S^2|\psi\rangle = S(S +$

$1)\hbar^2|\psi\rangle$, and the existence of states with this property is contingent upon the commutation of S^2 with \mathcal{H} , the total Hamiltonian of the system. Such states are found (to a high degree of approximation) in organic molecules. The total Hamiltonian always contains terms of the form $\sum(\xi r_{ij})_i \cdot s_j$, however. Such terms are relatively unimportant for systems containing only light atoms but may become dominant for states of molecules containing even a single atom with high atomic number. Spin-orbit ξ values (cm^{-1})⁷ are high for atoms such as cobalt (517), rhodium (968), and ruthenium (878) and become enormous for 5d elements (Os, 3500; Ir, 3600; W, 2089; Pt, 4052). In contrast, that for carbon is only 30. Thus for compounds containing 4d or 5d elements and also some 3d elements, certain state eigenkets may not satisfy the above equation, even approximately, and a spin label is no longer meaningful.

Studies of luminescent transition metal complexes containing metals of (nd)⁶ configurations have led to a correlation between the orbital nature of an excited state and the degree of appropriateness of a singlet or triplet designation. For the well-studied complexes containing π -conjugated ligands, we recognize three main classifications of excited states.

First, there are $\pi\pi^*$ states that have properties approximating those observed for organic molecules. When such an excited state lies lowest, one usually observes (77°K) a long-lived phosphorescence (>msec) and an emission band structure closely resembling that of the phosphorescence of the ligand itself. The emitting manifold spans a narrow energy range (<10 cm^{-1}). States of this nature have been observed for the tris(2,2'-bipyridine)rhodium(III), tris(1,10-phenanthroline)rhodium(III), and *cis*-dichlorobis(5,6-dimethyl-1,10-phenanthroline)iridium(III) ions.^{8,9} Their low-lying $\pi\pi^*$ states can be described, to first order, as triplets, although the emitting levels of the latter species are approaching an intermediate character (*vide infra*).

Second, we observe dd states that possess an intermediate character. An example is the low-lying (emitting) excited state of $[\text{Co}(\text{CN})_6]^{3-}$, formally a 3T_1 .^{10,11} The emission displays (77°K) a broad structureless band and has an intermediate decay time (~ 700 μsec). The excited manifold spans a wide energy range (~ 600 cm^{-1}). For this "state" it is useful to use the 3T_1 formalism only as a starting point. To fit the observed level manifold theoretically we have been forced to resort to perturbation theory involving higher excited states of various multiplicities.^{12,13} For molecules containing metals of higher atomic number the situation will be worse.

The third type of state is that for which any spin label at all is apparently not justified either experimentally or

(7) Value for carbon (zerovalent) calculated from ground term [C. E. Moore, *Nat. Bur. Stand. (U. S.) Circ.*, No. 467 (1949)]; osmium estimated for Os^{3+} [R. Dingle, *J. Mol. Spectrosc.*, **18**, 276 (1965)]; iridium (zerovalent) estimated [J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, England, 1971, p 113]; all others (zerovalent metal) [J. S. Griffith, *ibid.*, Appendix 6].

(8) D. H. W. Carstens and G. A. Crosby, *J. Mol. Spectrosc.*, **34**, 113 (1970).

(9) R. J. Watts, G. A. Crosby, and J. L. Sansregret, *Inorg. Chem.*, **11**, 1474 (1972).

(10) G. A. Crosby, *J. Chim. Phys. Physicochim. Biol.*, **46**, 160 (1967).

(11) M. Mingardi and G. B. Porter, *J. Chem. Phys.*, **44**, 4354 (1966).

(12) K. W. Hipps and G. A. Crosby, unpublished work.

(13) M. L. Ellzey, private communication.

(1) Research supported by AFOSR (NC)-OAR, USAF Grant No. 72-2207.

(2) (a) J. N. Demas and G. A. Crosby, *J. Amer. Chem. Soc.*, **93**, 2841 (1971); (b) M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Amer. Chem. Soc.*, **93**, 4336 (1971).

(3) H. D. Gafney and A. W. Adamson, *J. Amer. Chem. Soc.*, **94**, 8238 (1972).

(4) P. Natarajan and J. F. Endicott, *J. Amer. Chem. Soc.*, **94**, 3635 (1972); **95**, 2470 (1973).

(5) D. A. Chaisson, R. E. Hintze, D. H. Stuermer, J. D. Petersen, D. P. McDonald, and P. C. Ford, *J. Amer. Chem. Soc.*, **94**, 6665 (1972).

(6) J. N. Demas, D. Diemente, and E. W. Harris, *J. Amer. Chem. Soc.*, **95**, 6864 (1973).

theoretically. The lowest $d\pi^*$ excited levels of the tris-(2,2'-bipyridine)ruthenium(II) cation are the prototypes. This "state," once considered to be a triplet state by us and others,^{14,15} has been shown experimentally to be a manifold of four decaying levels spanning $\sim 60\text{ cm}^{-1}$.¹⁶ Theoretical studies have corroborated the experimental results and have led to a description of $d\pi^*$ excited states in which spin-orbit coupling plays a dominant role.¹⁷ Application of S^2 on the final state function for a level not only scatters the eigenket among the four-dimensional manifold but also into other levels $\sim 2000\text{ cm}^{-1}$ removed from it. The spin-operator equation is not even approximately obeyed. Thus, a spin labeling for the states is not appropriate at all. The experimental manifestations of this high degree of spin-orbit coupling in $d\pi^*$ states are fast relaxation among the levels even at very low temperatures ($< 2^\circ\text{K}$), radiative lives of the individual levels in the manifold that range from microseconds to milliseconds, and magnetic properties of the excited levels that reflect a high degree of metal orbital contribution to the g values.¹⁸ States having these characteristics have been observed for a series of ruthenium(II) molecules,^{16,17} analogous osmium(II) species,¹⁹ and some systems containing iridium(III).²⁰ For such states the term "intersystem crossing" also has no well-defined meaning.¹⁵

We wish to emphasize that the same complex may possess excited states of all three classes. In the tris-(2,2'-bipyridine)ruthenium(II) cation, one can, we believe, classify the $\pi\pi^*$ excited states meaningfully as singlets or triplets. The dd excited states undoubtedly possess an intermediate character, whereas the $d\pi^*$ states are, as described above, not subject to spin labeling. We believe there are important implications for mechanistic photochemistry contained in this statement. For instance, molecules possessing $\pi\pi^*$ states relatively isolated from lower and higher dd or $d\pi^*$ states might show slow relaxation to the others. Wavelength-dependent photochemical quantum yields could ensue. What types of states lie lowest will certainly affect the photochemistry.²¹

It is possible to modify the degree of spin-orbit coupling in excited states by both chemical and physical means. A system possessing a well-defined low-lying manifold of $d\pi^*$ excited states, the *cis*-dichlorobis(1,10-phenanthroline)iridium(III) cation, can be converted by methyl substitution of the ligand to a cation whose lowest excited state is reasonably described as $^3(\pi\pi^*)$ in highly polar glasses at 77°K .⁹ Reduction of the

polarity of the glass leads to increased $d\pi^*-\pi\pi^*$ configurational mixing and a progressive failure of the triplet labeling. For other molecules, such as *cis*-dichlorobis(4,7-diphenyl-1,10-phenanthroline)iridium(III) chloride, the lowest excited (emitting) state contains large components of both $\pi\pi^*$ and $d\pi^*$ parentages, and one can assign neither a unique spin nor a unique configurational label to an emitting state.⁹ The state (spin + orbit) is only accurately described by the symmetry label corresponding to an irreducible representation of the molecular point group.

From the point of view expressed here the validity of a spin label depends on both the orbital nature of the excited state and the magnitude of the spin-orbit coupling terms of the atomic constituents. Thus a search for spin-conservation rules for energy transfer has meaning for some donor states but appears fruitless for others.²² In addition, the role of configuration interaction in dictating both the spectroscopic properties and the photochemistry may be dominant for certain systems.²³

(22) I. Fujita and H. Kobayashi, *J. Chem. Phys.*, **52**, 4904 (1970).

(23) J. I. Zink, *Inorg. Chem.*, **12**, 1957 (1973).

G. A. Crosby,* K. W. Hipps, W. H. Elfring, Jr.
Chemical Physics Program, Department of Chemistry
Washington State University
Pullman, Washington 99163
Received October 31, 1973

Abstraction of the Hydroxylic Hydrogen of Alcohols by Alkoxy Radicals¹

Sir:

Identity reactions in which a hydrogen atom is transferred between identical, or nearly identical, radicals are well documented. Particularly well-known examples



of such reactions involve H transfer between two oxygen atoms, for example, between two $\text{ArO}\cdot$,²⁻⁵ two $\text{R}_2\text{NO}\cdot$,² two $\text{ROO}\cdot$,⁶ and two $\text{R}_2\text{CNO}\cdot$ ⁷ radicals. It was therefore rather surprising to us to find that the alkoxy-alcohol identity reaction has not only been almost totally ignored⁸ but that when we have proposed it at meetings of free-radical chemists our proposal has drawn vigorous opposition. We wish to report experimental proof that not only can this reaction occur but that its rate is at least as great as the rate of abstraction of a primary alkyl hydrogen.

An alkoxy-alcohol reaction that would be significant in terms of reaction products could be identified in various ways. We chose to use epr spectroscopy to look at systems in which the relatively stable *tert*-butoxy radical, $\text{BO}\cdot$,⁹ could react with an alcohol to form an

(1) Issued as N.R.C.C. No. 13783.

(2) R. W. Kreilick and S. I. Weissman, *J. Amer. Chem. Soc.*, **84**, 306 (1962); **88**, 2645 (1966).

(3) M. R. Arick and S. I. Weissman, *J. Amer. Chem. Soc.*, **90**, 1654 (1968).

(4) M. A. DaRooge and L. R. Mahoney, *J. Org. Chem.*, **32**, 1 (1967).

(5) L. R. Mahoney and M. A. DaRooge, *J. Amer. Chem. Soc.*, **92**, 890 (1970); **94**, 7002 (1972).

(6) J. A. Howard, W. J. Schwalm, and K. U. Ingold, *Advan. Chem. Ser.*, No. 75, 6 (1968).

(7) G. D. Mendenhall and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 627 (1973).

(8) Or else it has been suggested to be a slow process, see, e.g., Y. Takezaki and C. Takeuchi, *J. Chem. Phys.*, **22**, 1527 (1954), and references cited therein.

(9) Throughout this paper B represents the $(\text{CH}_3)_3\text{C}$ group.

(14) J. N. Demas and G. A. Crosby, *J. Mol. Spectrosc.*, **26**, 72 (1968).

(15) F. E. Lytle and D. M. Hercules, *J. Amer. Chem. Soc.*, **91**, 253 (1969).

(16) R. W. Harrigan and G. A. Crosby, *J. Chem. Phys.*, **59**, 3468 (1973) [see note added in proof therein]; R. W. Harrigan, G. D. Hager, and G. A. Crosby, *Chem. Phys. Lett.*, **21**, 487 (1973). R. W. Harrigan and G. A. Crosby, Abstracts, 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972, PHYS 105; G. A. Crosby and G. D. Hager, Abstracts, 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973, PHYS 151.

(17) K. W. Hipps, G. D. Hager, and G. A. Crosby, Abstracts, 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1973, PHYS 081; D. C. Baker and G. A. Crosby, *ibid.*, PHYS 082; G. D. Hager and G. A. Crosby, *ibid.*, PHYS 083.

(18) D. C. Baker and G. A. Crosby, unpublished work.

(19) D. E. Lacky and G. A. Crosby, unpublished work.

(20) R. J. Watts and G. A. Crosby, unpublished work.

(21) G. A. Crosby, R. J. Watts, and D. H. W. Carstens, *Science*, **170**, 1195 (1970).