$^{12}C/^{13}C$ would correspond in our models to a tunneling contribution to k_H/k_D of ca. 1.5–2.0.[15]

Our results indicate that the Bell, Sachs, and Tranter[8] model is right in predicting substantial tunnel corrections. It does not seem to be right, however, in making the tunnel effect primarily or wholly responsible for variations in the isotope effect.

References and Notes

(1) This work was supported by the National Science Foundation.
(2) L. Melander, "Isotope Effects on Reaction Rates", Ronald Press, New York, N.Y., 1960, pp 24–32.
(3) F. H. Westheimer, *Chem. Rev.*, **61,** 265 (1961).
(4) R. P. Bell and D. M. Goodall, *Proc. R. Soc. London, Ser. A*, **294,** 273 (1966).
(5) R. P. Bell and B. G. Cox, *J. Chem. Soc. B*, 194 (1970); 783 (1971).
(6) A. F. Cockerill, *J. Chem. Soc. B*, 964 (1967).
(7) K. C. Brown and W. H. Saunders, Jr., unpublished results.
(8) R. P. Bell, W. H. Sachs, and R. L. Tranter, *Trans. Faraday Soc.*, **67,** 1995 (1971).
(9) W. H. Saunders Jr., *Chem. Scr.*, **8,** 27 (1975).
(10) W. H. Saunders Jr., unpublished results.
(11) An Atlas CH-4 mass spectrometer equipped with dual Faraday cup collectors.
(12) W. H. Saunders, Jr., "Investigation of Rates and Mechanisms of Reactions", 3rd ed, Part I, E. S. Lewis, Ed., Wiley-Interscience, New York, N.Y., 1974, Chapter V.
(13) It seems very likely that any tunnel effects in both cases would be of the same origin, for the $^{12}C/^{13}C$ tunnel effect probably reflects the effect of carbon mass on the tendency of *hydrogen* to tunnel.
(14) The form of the predicted dependence of the semiclassical $^{12}C/^{13}C$ effect on extent of hydrogen transfer is qualitatively similar to the observed dependencies on mole percent water in Figures 1 and 2.
(15) A referee has asked us to comment on the relation of our data to available A_H/A_D values. Values calculated from data in ref 6 show considerable scatter, but with one exception are 0.5 or below. Other elimination reactions of 2-phenylethyl derivatives give A_H/A_D near 0.5.[16,17] Model calculations[10] giving a $^{12}C/^{13}C$ tunnel correction of 1.5% predict an A_H/A_D of about 0.5, so our carbon isotope effects are qualitatively consistent with available data on the temperature dependence of k_H/k_D.[18]
(16) W. H. Saunders, Jr., and D. H. Edison, *J. Am. Chem. Soc.*, **82,** 138 (1960).
(17) A. F. Cockerill, S. Rottschaefer, and W. H. Saunders Jr., *J. Am. Chem. Soc.*, **89,** 901 (1967).
(18) R. P. Bell, "The Proton in Chemistry", 2nd ed, Cornell University Press, Ithaca, N.Y. 1973, Chapter 12, discusses the expected relation of A_H/A_D to tunneling.

John Banger, Annette Jaffe
An-Chung Lin, William H. Saunders, Jr.*
Department of Chemistry, University of Rochester
Rochester, New York 14627

Received July 7, 1975

Optically Detected Zero-Field Magnetic Resonance Studies of the Photoexcited Triplet State of the Photosynthetic Bacterium *Rhodospirillum rubrum*

Sir:

There has been much interest in the triplet states which are observed in fully reduced reaction center preparations and intact cells of photosynthetic bacteria.[1] Optical[2] and high field EPR studies[3-5] have led to renewed speculation concerning the role of a triplet state in the mechanism of bacterial photosynthesis and the structure of the reaction center which gives rise to the observed optical and triplet EPR spectra.

We have studied triplet state species of the photosynthetic bacterium *Rhodospirillum rubrum* in chemically reduced preparations[6] by zero-field optical detection of magnetic resonance at 2 K. An approximately 3×10^{-2} *M* solution of sodium dithionite in 50% (by volume) glycerol and 0.1 *M* Tris-Cl^- buffer, pH 7.4 (deoxygenated with nitrogen), was used to volume dilute packed whole cells of *R. rubrum*[7] by approximately six times forming a stock solution of dithionite treated whole cells. In practice a further dilution without dithionite of this stock solution by a factor 50 appeared to provide the best samples for optical detection experiments. Using CW dye laser excitation at 590 nm (Spectra-Physics Model 375 dye laser pumped by a Spectra-Physics Model 164 argon-ion laser) strong, structureless fluorescence with a maximum at 920 nm is observed from the cell preparations at 2 K. Using fluorescence-microwave techniques previously described,[8] two sharp zero field EPR transitions at 467 and at 668 MHz are observed, both as a microwave-induced decrease in fluorescence intensity monitored at 920 nm. The 467-MHz transition, shown in Figure 1, is approximately five times as intense as the transition at 668 MHz and corresponds to a change of <1% of the fluorescence intensity; the third transition (2E transition) could not be observed after extensive signal averaging. The line widths of the 467 and 668 MHz transitions are remarkably sharp (width at half-height of 7 and 15 MHz, respectively) and reproducibly symmetrical. The zero-field splitting parameters calculated from our optical detection measurements are in excellent agreement with the zero-field splitting parameters, $|D| = 0.0187\ \text{cm}^{-1}$, $|E| = 0.0034\ \text{cm}^{-1}$, reported for *R. rubrum* in X-band high field EPR experiments.[9] From the $|D|$ and $|E|$ values we conclude that we are observing optically detected triplet state transitions originating in the reaction center.

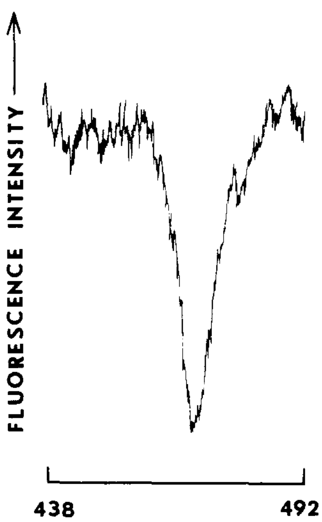

Figure 1. Fluorescence-detected zero field EPR transition in *R. rubrum* cell suspensions at 2 K. Excitation of fluorescence is at 590 nm with dye laser, and detection wavelength for optical–microwave double resonance experiment is 920 nm. Frequency scale is in megahertz.

The time dependence of the population changes among the zero field triplet spin sublevels was determined by monitoring the fluorescence response to square-wave microwave modulation, as described previously.[8] These experiments measure the rates at which each of the triplet spin sublevels undergo intersystem crossing into the ground state. Using the arbitrary designation (including the assumption that the sign of D is positive) of x for the top energy spin sublevel, y for the middle, and z for the lowest energy spin sublevel, we find the decay rate constants, k_i, for the triplet spin levels to be $k_x = 2105 \pm 182\ \text{sec}^{-1}$, $k_y = 2885 \pm 400\ \text{sec}^{-1}$, and $k_z = 1335 \pm 58\ \text{sec}^{-1}$. From the observed intensity ratios of the zero field transitions, and relative populating-rates of the spin sublevels must also be of the same relative magnitude as the decay rates.

It is of interest to compare the depopulating rates measured at zero field for *R. rubrum* preparations with those measured in high field EPR and flash photolysis experiments. Dutton, Leigh et al. report triplet EPR signals at 10 K with transient times on the order of 6 μsec in *R. spheroides* preparations.[5] Parson et al. have measured transient optical absorbance changes in *R. spheroides* at 15 K with

$\tau_{1/2}$ of 120 μsec which are speculated to correspond to the absorption of the metastable triplet state.[1,2] Taking into account the differences in temperature and the fact that the different cell environments may influence the detailed triplet dynamics, our dynamic data, with decay times on the order of 500 μsec, are consistent with the optical measurements of Parson et al.[2] The measurements of Dutton and Leigh would seem to best be explained as due to processes other than those associated with triplet intersystem crossing kinetics.

One of the most interesting features of the zero field spectra is that a single dominant set of triplet signals are observed with narrow, symmetrical line widths. Whatever models of cooperativity or delocalization among bacteriochlorophyll and bacteriopheophytin are used to describe the photochemical reaction center in the photosynthetic cells, the models must include the fact that the zero field triplet spectra are unique, sharp, and structureless at low temperatures. Further studies on other cells, as well as on isolated bacteriochlorophyll and bacteriopheophytin molecules, are presently underway to determine the influence of temperature and local cell structure on the triplet intersystem crossing rates for in vivo systems.

Acknowledgment. We wish to thank Dr. H. L. Crespi for providing us with *R. rubrum*.

References and Notes

(1) For a recent review see W. W. Parson and R. J. Cogdell, *Biochim. Biophys. Acta*, **416**, 105 (1975).

(2) W. W. Parson, R. K. Clayton, and R. J. Cogdell, *Biochim. Biophys. Acta*, **387**, 265 (1975).

(3) P. L. Dutton, J. S. Leigh, and M. Siebert, *Biochim. Biophys. Res. Commun.*, **46**, 406 (1972).

(4) P. L. Dutton, J. S. Leigh, and D. W. Reed, *Biochim. Biophys. Acta*, **292**, 654 (1973).

(5) J. S. Leigh and P. L. Dutton, *Biochim. Biophys. Acta*, **357**, 67 (1974).

(6) C. A. Wraight, J. S. Leigh, P. L. Dutton, and R. K. Clayton, *Biochim. Biophys. Acta*, **333**, 401 (1974).

(7) *R. rubrum* was grown in an ordinary water medium (J. G. Ormerod, K. S. Ormerod, and H. Gest, *Arch. Biochim. Biophys.*, **94**, 449 (1961).

(8) R. H. Clarke and R. H. Hofeldt, *J. Chem. Phys.*, **61**, 4582 (1974).

(9) R. A. Uphaus, J. R. Norris, and J. J. Katz, *Biochem. Biophys. Res. Commun.*, **61**, 1057 (1974).

(10) Alfred P. Sloan Research Fellow.

(11) Supported in part by the Energy Research and Development Administration under Contract No. E(11-1)-2570 and by the U.S. Army Research Office-Durham.

(12) Work performed under the auspices of the Energy Research and Development Administration.

Richard H. Clarke,* [10] **Robert E. Connors**
Department of Chemistry, Boston University
Boston, Massachusetts 02215[11]

J. R. Norris, M. C. Thurnauer
Chemistry Division, Argonne National Laboratory
Argonne, Illinois 60439[12]

Received July 31, 1975

The Tetrakis(*N,N*-dimethyldithiocarbamato)tantalum(V) Cation. A Stereochemically Rigid Eight-Coordinate Complex

Sir:

Stereochemical nonrigidity is a pervasive feature of the chemistry of eight-coordinate complexes and, despite several low-temperature studies,[1-6] no tetrakis chelates have been reported which are stereochemically rigid on the NMR time scale.[7-9] We have now identified several tetrakis chelates which exhibit inequivalent site environments in low-temperature ^{1}H NMR spectra.[10] We present herein a preliminary account of our ^{1}H NMR and x-ray crystallographic studies of the eight-coordinate, dodecahedral tetrakis(*N,N*-dimethyldithiocarbamato)tantalum(V) cation, $[\mathrm{Ta(S_2CN(CH_3)_2)_4}]^+$.

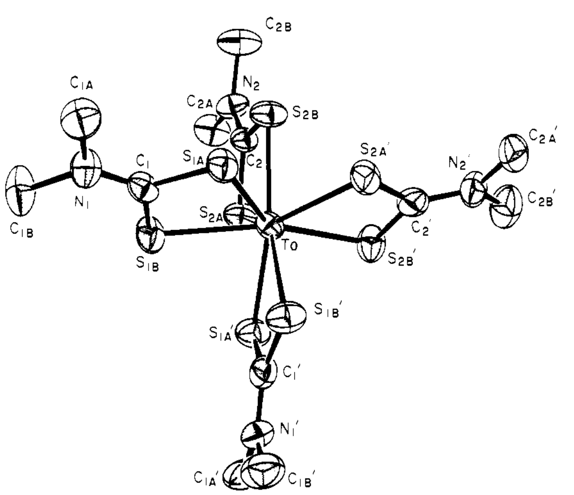

Figure 1. A view of the $[\mathrm{Ta(S_2CN(CH_3)_2)_4}]^+$ cation in crystals of $[\mathrm{Ta(S_2CN(CH_3)_2)_4]Cl\cdot CH_2Cl_2}$.

Air sensitive, yellow crystals of composition $\mathrm{Ta(S_2CN(CH_3)_2)_4Cl\cdot CH_2Cl_2}$ (**1**) and orange crystals of composition $\mathrm{Ta(S_2CN(CH_3)_2)_2Cl_3\cdot 0.25CH_2Cl_2}$ (**2**) have been isolated following reaction of tantalum(V) chloride with anhydrous sodium *N,N*-dimethyldithiocarbamate (1:5.1 molar ratio) in refluxing dichloromethane. Both new compounds are 1:1 electrolytes in dichloromethane, and both exhibit a single methyl resonance at τ 6.60 in ^{1}H NMR spectra of dichloromethane solutions at 37°. Compound **1** shows the following characteristic ir bands: $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ 1557, $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ 992, and $\nu(\mathrm{Ta}\overset{\cdots}{-}\mathrm{S})$ 358 cm^{-1} (Nujol mull). The ir spectrum of compound **2** is closely similar except that additional strong bands attributable to $\mathrm{TaCl_6}^-$ are observed at 316 and 328 cm^{-1}. These data suggest that compounds **1** and **2** should be formulated as $[\mathrm{Ta(S_2CN(CH_3)_2)_4]Cl\cdot CH_2Cl_2}$ and $[\mathrm{Ta(S_2CN(CH_3)_2)_4}][\mathrm{TaCl_6}]\cdot 0.5\mathrm{CH_2Cl_2}$, respectively, in accord with a previous study of the analogous *N,N*-diethyldithiocarbamate complexes.[11]

The presence of the $[\mathrm{Ta(S_2CN(CH_3)_2)_4}]^+$ cation in both crystalline salts has been confirmed by x-ray diffraction. Crystal data: $[\mathrm{Ta(S_2CN(CH_3)_2)_4]Cl\cdot CH_2Cl_2}$ (**1**), M = 782.2; monoclinic, space group $C2/c$ ($C_{2h}{}^6$, No. 15); a = 12.055 (5), b = 18.473 (8), c = 12.794 (5) Å; β = 94.71 (3)°; d_{measd} = 1.83 g cm^{-3}, Z = 4, d_{calcd} = 1.829 g cm^{-3}; $[\mathrm{Ta(S_2CN(CH_3)_2)_4}][\mathrm{TaCl_6}]\cdot 0.5\mathrm{CH_2Cl_2}$ (**2**), M = 1098.0; monoclinic, space group $C2/c$; a = 30.97 (1), b = 9.537 (4), c = 25.95 (1) Å; β = 117.17 (3)°; d_{measd} = 2.11 g cm^{-3}, Z = 8, d_{calcd} = 2.139 g cm^{-3}. The structures have been solved by straightforward application of the heavy-atom technique using data (Mo Kα radiation) collected with a Picker FACS-I automated diffractometer. The structure of **1** has been refined (anisotropically for the atoms in the cation) to an unweighted R_1 value of 0.063 for the 2458 observed reflections. For compound **2**, refinement (anisotropic for the heavy atoms Ta, S, and Cl) has resulted in an R_1 value of 0.096 for the 3317 observed reflections.

A perspective view of the eight-coordinate $[\mathrm{Ta(S_2CN(CH_3)_2)_4}]^+$ cation in the more accurately determined structure (compound **1**) is shown in Figure 1. The bidentate dithiocarbamate ligands span the *m* edges of an idealized D_{2d}-$\bar{4}2m$ dodecahedron to give the *mmmm*-D_{2d} stereoisomer.[12,13] The cation is located on a crystallographic twofold axis which passes through the midpoints of the opposite dodecahedral *b* edges defined by atoms $\mathrm{S_{1B}}$ and