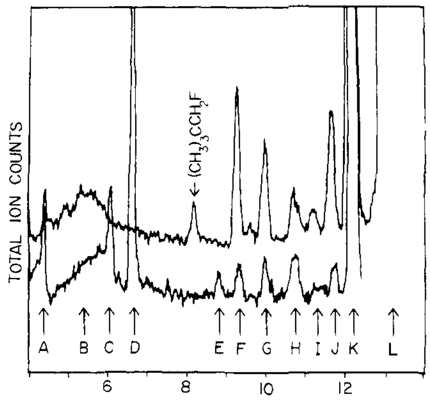

**Figure 1.** Desorption gas chromatograms from 1-h collections of flow tube gases. Lower trace: no ions present. Upper trace: ions present. All peaks were characterized by their mass spectrum and are identified as (A) $NF_3$; (B) $C_6H_5COOH$; (C) $CH_2Cl_2$; (D) $(CH_3)_2CO$; (E) $(CH_3)_2CHOH$; (F) $CHCl_3$; (G) $CF_2ClCCl_2F$; (H) $CH_2{=}CHCH_2CH_2Cl$; (I) $CH_3CCl_3$; (J) $CCl_4$; (K) $CH_3CHClCH_2CH_3$; (L) $(CH_3)_3CCH_2Cl$.

to the flow reactor. By addition of approximately 2 mtorr of $NH_3$ to the buffer gas, all positive ion reactions of **1** were suppressed.

The sampling port is 20 cm downstream from the neutral addition inlet. A 10-mm id borosilicate glass collection column was packed with glass wool that had been coated with 2,6-diphenyl-*p*-phenylene oxide–polymer (Tenax-GC[6]). This porous polymer is a relatively inert, reversible sorbent for collection of volatile, environmental samples.[7] Polymer-coated glass wool provides an inert surface for low-temperature condensation of volatile compounds. A small fraction ($1.5 \times 10^{-4}$) of the gases in the flow tube was diverted to the cooled (−198 °C) collection column. A fluoride ion density of $3 \times 10^8$ cm$^{-3}$ produces a like number of **2**, and, with 100% sampling efficiency, we should find about 8 ng of neopentyl fluoride in 1 h.

After collection (15 min to 1 h), the sampling column was removed and connected to the inlet port of a HP 5982A GC/MS/DS. The neutrals were then backflushed at 190 °C and focused at −78 °C onto the head of a $^1/_4$ in. × 6 ft chromatographic column (0.1% SP1000 on Carbopak C). Subsequent temperature-programmed elution coupled with full mass scanning detection by the MS allow unambiguous identification of collected species. Comparison with appropriate standards allows quantitative determination of the collected products.[8]

Figure 1 depicts the results of a typical GC/MS study for a 1-h collection. The lower trace shows neutrals collected with the ion source off (all reagents present but no ions). The upper trace shows a sample collected in the presence of $F^-$; the only additional peak is due to 6 ng of neopentyl fluoride. A full mass scan of the new peak at 8.3 min absolutely identifies it as the reaction product. Methylene chloride, acetone, and 2-propanol (peaks C, D, and E) are ubiquitous solvents, and all other peaks are due to trace-level impurities in the starting material (**1**). This proves that **2** has been produced by a chemical reaction in our flow tube.

Some serious objections remain. How can we be sure that surface reactions (either on the walls of the flow tube or on the collection column) were not responsible for **2**? Can we say that **2** is produced by a negative ion reaction such as in eq 1 and not an atom or radical reaction? We certainly produce F and $NF_2$ at the ion source as well as $F^-$.

Two control experiments answered these questions. Neopentyl chloride alone was injected into the flowing afterglow with no ions present. After deposition of **1** onto the cooled collection column for 30 min, the neopentyl chloride was turned off; $F^-$ was then generated from $NF_3$, and sampling was continued for 1 h. A chromatogram of this sample shows that **2** is not present. Therefore, our neopentyl fluoride was not produced by surface reactions. Our afterglow is equipped with an ion shutter.[5c] This is a tungsten mesh astride the flow tube. When biased at −100 V, the quadrupole MS indicated that all negative ions were blocked, and yet all neutrals ($NF_3$, F, $NF_2$, etc.) were free to pass. We then added **1** downstream from the shutter and collected as before. Again, we could not detect the presence of **2** with our GC/MS/DS (sensitivity for **2** around 100 pg). Both $F^-$ and **1** must interact in the flow tube to produce neopentyl fluoride; radical reactions do not produce our product. These experiments establish that eq 1 is correct as written by Olmstead and Brauman.[3]

Neutral product analysis uniquely characterizes the chemistry of gas-phase ions. This powerful new technique now clears the way for a more complete understanding of ion–molecule reactions in the absence of solvent.

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[6] Tenax-GC porous polymer adsorbent was obtained from Applied Science, State College, PA (manufactured by ENKA N.V., The Netherlands).

[7] E. D. Pellizzari, J. E. Bunch, B. H. Carpenter, and E. Sawicki, *Environ. Sci. Technol.*, **9**, 552, (1975).

[8] Neopentyl chloride (**1**) was obtained from MCB, Norwood, OH. Neopentyl fluoride (**2**) was prepared from neopentyl alcohol according to P. H. Anderson, B. Stephenson, and H. S. Mosher, *J. Am. Chem. Soc.*, **96**, 3171 (1974).

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## Facile Syntheses of Tetraalkylchlorin and Tetraalkylporphyrin Complexes and Comparison of the Structures of the Tetramethylchlorin and Tetramethylporphyrin Complexes of Nickel(II)

*Sir:*

We report facile syntheses of meso-substituted tetraalkylchlorin and tetraalkylporphyrin complexes of some first-row transition metals and provide a comparison of the structures of Ni(TMC) and Ni(TMP), where TMC = 5,10,15,20-tetramethylchlorinato and TMP = 5,10,15,20-tetramethylporphyrinato. The use of metalloporphyrins as models for coordination sites in metallobiomolecules is now of recognized importance.[1] That reduced hemes occur in certain biological systems[2,3] has led to interest in the synthesis of model systems[4,5] involving reduced porphyrins, e.g., chlorins, bacteriochlorins, and isobacteriochlorins. In no instance has there been available an easy route to analytically and isomerically pure samples of metal complexes of reduced porphyrins. To this end, we have turned our attention to the synthesis of the simple TMP and TMC and related tetraalkyl systems.

All suggested syntheses for $H_2TMP$[6-8] report problems with "contamination" by $H_2TMC$, probably because $H_2TMC$ has a higher oxidation potential than tetraphenyl- or octaethylchlorin. We find that a template synthesis increases the "contamination" of TMP by TMC to make it the major product. Reaction 1 with R = Me affords different M(TMC)/M(TMP) ratios, depending upon the metal M and the amount of anhydride present. In the presence of 2% acetic anhydride, the following products[9] were

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[1] For a recent review, see: Ibers, J. A.; Holm, R. H. *Science (Washington, D.C.)* **1980**, *209*, 223-235.

[2] Scott, A. I.; Irwin, A. J.; Siegel, L. M.; Shoolery, J. N. *J. Am. Chem. Soc.* **1978**, *100*, 316-318; *Ibid.* **1978**, *100*, 7987-7994.

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[8] Tabushi, I.; Sakai, K.; Yamamura, K. *Tetrahedron Lett.* **1978**, 1821-1824.

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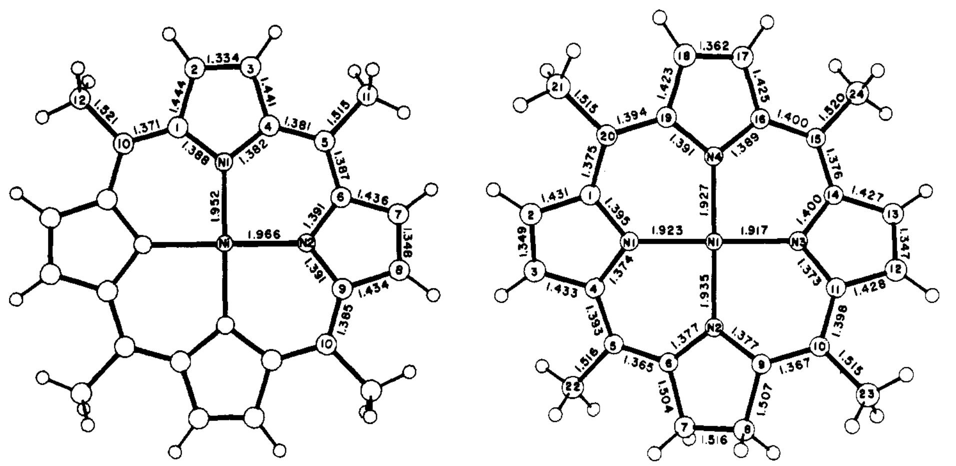
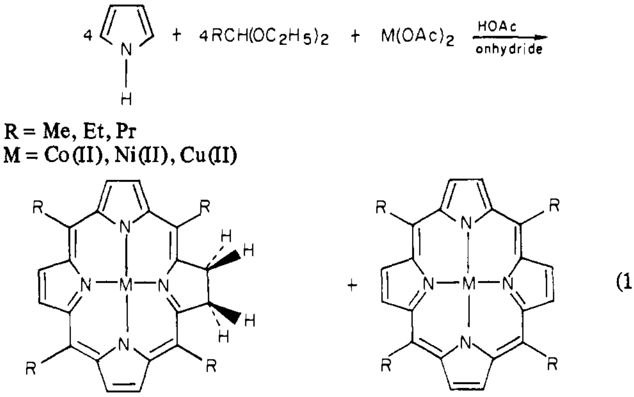


**Figure 1.** Projected views of Ni(TMP) (left) and Ni(TMC) (right), showing the labeling scheme and bond distances. The Ni(TMP) molecule has an inversion center. Estimated standard deviations on bond distances are 0.002–0.005 Å.



R = Me, Et, Pr
M = Co(II), Ni(II), Cu(II)

*meso*-tetraalkylmetallochlorin *meso*-tetraalkylmetalloporphyrin

obtained after workup: Ni, TMC/TMP 4:1 (total, 1.6%);[10] Co, TMP only; Cu, TMC only (2%). For Ni in the presence of 5% acetic anhydride, Ni(TMC) is the only product (1.9%). The dependence of the chlorin/porphyrin ratio on the transition metal can be rationalized on the basis of the different oxidations known from the electrochemistry of metal derivatives of tetraphenylporphyrin.[11]

Reaction 1 is also sensitive to the nature of R. Thus, with R = Et or Pr and Ni, only the (tetraalkylporphyrinato)nickel(II) complexes are obtained,[12] presumably because of steric interactions between the alkyl substituents on the resulting meso positions and the $\beta$-pyrrole hydrogen atoms. However, with Cu, no tetraethylporphyrin is observed, and only a minor amount of tetrapropylporphyrin is found; the tetraalkylchlorins remain the major products.[12]

Demetalation of both the porphyrins and chlorins has been achieved by the standard concentrated $H_2SO_4$ technique,[13] with care being taken to exclude $O_2$ for the demetalation of the chlorins. In this way, both free-base and other metal derivatives have been prepared. Reduction of Ni(TMC) in pyridine with *p*-toluenesulfonylhydrazine[14] yields the corresponding isomerically pure isobacteriochlorin.

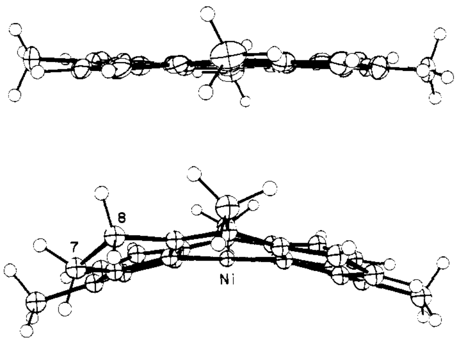


**Figure 2.** Views of the Ni(TMP) molecule (top) and Ni(TMC) molecule (bottom) along the N2–Ni–N3 plane. The nonhydrogen atoms are drawn at the 50% probability level while hydrogen atoms are drawn on an arbitrary scale.

In view of the important role played by the structural features of the porphyrin ring system in various biological systems,[15] and the emerging importance of the chlorin ring system in related systems,[2,3] detailed comparisons of metallochlorins with metalloporphyrins seem especially desirable. Figure 1 compares some of the structural features of Ni(TMP) and Ni(TMC)[16] on projected views of each molecule. A striking feature of Figure 1 is the lack of symmetry of the Ni(TMC) molecule compared with the expected symmetry of the Ni(TMP) molecule. With respect to bond distances, there is left–right symmetry to the Ni(TMC) molecule, but even neglecting the saturated dihydropyrrole ring there is not top–bottom symmetry. Some average distances in the TMP vs. TMC complexes are Ni–N,[17] 1.959 (10)[18] vs. 1.920 (3) and 1.931 (4) Å; $N-C_a$, 1.388 (4) vs. 1.375 (3) and 1.394 (3) Å; $C_a-C_b$, 1.439 (5) vs. 1.428 (4) Å; $C_b-C_b$, 1.341 (10) vs. 1.348 (4) and 1.362 (4) Å; $C_a-C_m$, 1.381 (7) vs. 1.371 (4) and 1.396 (4) Å. In Ni(TMC), usually one set of bond distances is shorter

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(9) All products analyze satisfactorily (C, H, N, metal). Representative NMR spectra ($CDCl_3$, $Me_4Si$ internal reference) for Ni(TMP) are $\delta$ 3.90 (s, 12 H), 9.00 (s, 8 H); Ni(TMC) $\delta$ 3.08 (s, 6 H), 3.73 (s, 6 H), 3.93 (s, 4 H), 8.4 (d, $J$ = 4.9 Hz, 2 H), 8.64 (s, 2 H), 8.82 (d, $J$ = 4.9 Hz, 2 H).

(10) Yields reported here are of crystalline material. Bulk materials were chromatographed twice on $Al_2O_3$ (neutral, Baker) with benzene/chloroform 1:1 as eluent, followed by final chromatography on silica gel (Grace, grade 62) with benzene/chloroform 2:1 as eluent. Crystallization was achieved through vapor diffusion of pentane into concentrated benzene solutions of the chromatographed materials. Although Tabushi et al.[8] report an isolated yield of $H_2TMP$ of 8.7%, we could get no more than an isolated yield of 2% by his method.

(11) Wolberg, A.; Manassen, J. *J. Am. Chem. Soc.* **1970**, *92*, 2982–2991.

(12) Yields: Ni(TEtP), 3.9%; Ni(TPrP), 5.4%; Cu(TEtC), 4.4%.

(13) Buchler, J. W. In "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: New York, 1975; pp 199–201.

(14) Whitlock, H. W.; Hanauer, R.; Oester, M. Y.; Bower, B. K. *J. Am. Chem. Soc.* **1969**, *91*, 7485–7489.

(15) Baldwin, J.; Chothia, C. *J. Mol. Biol.* **1979**, *129*, 175–220.

(16) Ni(TMP) crystallizes with $Z$ = 2 in space group $P2_1/c$ in a cell of dimensions $a$ = 11.338 (11), $b$ = 5.648 (6), $c$ = 14.212 (15) Å, $\beta$ = 104.80 (6)° (−150 °C). The current refinement on the 6351 $F_o^2$ values yields $R$ (on $F^2$) of 0.15 for the 135 variables (anisotropic thermal motion for nonhydrogen atoms; hydrogen atoms fixed). The molecule has a crystallographically imposed inversion center. Ni(TMC) crystallizes with $Z$ = 4 in space group $P2_1/n$ in a cell of dimensions $a$ = 12.593 (4), $b$ = 7.489 (3) $c$ = 19.296 (6) Å, $\beta$ = 94.08 (2)° (−150 °C). The current refinement on the 4194 $F_o$ values yields $R$ (on $F$) of 0.048 for the 117 variables (isotropic thermal motion for the nonhydrogen atoms; hydrogen atoms fixed).

(17) In the nomenclature of Hoard, J. L. In "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; pp 317–380.

(18) Standard deviations in parentheses are for a single observation.

and another set longer than the equivalent type in Ni(TMP). This asymmetry, particularly the unexpected alteration of the $C_a$–$C_m$ bond lengths, is indicative of a reduction in aromaticity of Ni(TMC) relative to Ni(TMP). This is dramatically illustrated in Figure 2, a view of each molecule down the N2–Ni–N3 plane. The extreme nonplanarity of the Ni(TMC) molecule is apparent. Deviations of the meso-carbon atoms from the least-squares plane through Ni, N1–N4, C1–C6, and C9–C20 are approximately 0.6 Å, far greater than in even the most puckered porphyrin skeletons. The present results are consistent with an asymmetric charge distribution, possibly resulting from charge transfer toward the reduced side of the chlorin. The nonplanarity here is to be contrasted with the essential planarity of the chlorin core in [2,3-dihydro-($\alpha,\beta,\gamma,\delta$-tetraphenylporphyrinato)pyridine]zinc(II),[19] the only other metallochlorin structure known, and the near planarity of the chlorin core in phyllochlorin ester.[20] It is thus clear that chlorin systems show far greater structural variations than do the porphyrin systems, a possibly important biological factor.

**Acknowledgments.** This work was kindly supported by the National Institutes of Health (HL 13157). In addition, A.U. thanks the Minna–James–Heineman–Stiftung for financial assistance.

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## Reality of Electron Transfer in Slow Organic Reactions

*Sir:*

The idea that single-electron transfer may be involved in the rate-determining step of a variety of bimolecular organic reactions is a popular one and guides many current experimental investigations. In cases where the transfer would be expected to be exergonic, and the reactions occur at or near diffusion-controlled rates, there is no difficulty with the concept, and it is supported by numerous experiments, mostly involving photoexcited states. However, when slow reactions of large activation energy are involved, in which the transfer would be expected to be endergonic, there is considerable confusion as to how transition states should be formulated and what experimental criteria can serve to detect electron transfer in the rate-determining step.

A common observation in such systems is that, when the potential electron donor is varied with a common acceptor (or vice versa), plots of $RT \ln k$ vs. the one-electron oxidation potential of the donor (or acceptor) are linear (as might be anticipated) but with slopes considerably less than unity.

In one of the most explicit recent discussions of the problem, Schuster[1] has argued that such small slopes are entirely consistent with a rate-determining, irreversible endergonic electron transfer in the reactions involved. The purpose of this communication is to show that the argument leads to difficulties but that an alternative interpretation, possible electron transfer *after* the rate-determining step, can account for the quite compelling evidence[2] that at some stage in the reaction electron transfer has in fact taken place.

In Schuster's formulation, an endergonic irreversible electron transfer is written as

$$D + A \overset{K_{12}}{\rightleftharpoons} D...A \xrightarrow{k_{23}} D^{+}\cdot...A^{-}\cdot \xrightarrow{k_{30}} \text{products} \qquad (1)$$

and he proposes that

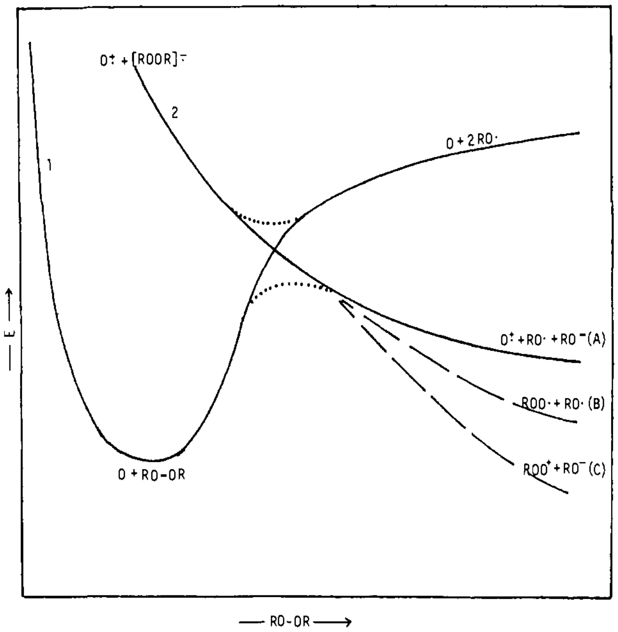

**Figure 1.** Plot of energy ($E$) vs. RO–OR bond length for reaction of a diacyl peroxide (RO–OR) with an electron donor (D).

$$k_p = K_{12}k_i e^{-\alpha\Delta G_{23}/RT} \qquad (2)$$

where $k_p$ is the observed rate constant, $k_i$ the rate constant for the electron transfer if it were isoergonic, $\Delta G_{23}$ the free energy change for the electron transfer, and $\alpha$ a proportionality constant which is also the slope of a $RT \ln k_p$ vs. oxidation potential plot.

Rewriting eq 2 in energy terms and simple algebra (eq 3) shows

$$\Delta G_p^{\ddagger} = \Delta G_{12} + \Delta G_i^{\ddagger} + \alpha\Delta G_{23} \qquad (3)$$

that, if $\Delta G_p^{\ddagger} > (\Delta G_{12} + \Delta G_i^{\ddagger})/(1 - \alpha)$, $\Delta G_p^{\ddagger} < \Delta G_{23}$, an obvious impossibility, which has also been noted, less explicitly, by Scandola and Balzani.[3] Since, as such reactions are usually considered, $\Delta G_i^{\ddagger}$ and $\Delta G_{12}$ should both be very small ($\Delta G_{12}$ might even be negative if any attractive forces exist between D and A), eq 2 and 3 should only be valid for very slightly endergonic processes. Indeed, this is in the region where the Marcus formulation already predicts $\alpha = 0.5$.

How then should we look at the rate-determining step in such processes when they are strongly endergonic and slow? Two approaches lead to a rather similar picture. First, we might assume that $\Delta G_{12}$ is really quite large, i.e., that D and A must be squeezed very tightly together, or that, if $k_{30}$ refers to some sort of bond scission in A, the bond is highly stretched. Alternatively, we might consider that charge transfer is only partial in the transition state, so a modest attractive force or mutual polarization, similar to that in charge-transfer complexes, is generated, lowering the energy barrier. This, of course, is a very old idea—it is essentially the picture proposed by Greene when he first described the reaction of phthaloyl peroxide with donor olefins,[4] and is similar to the structures proposed in the 1940's to account for polar effects in general in radical reactions.[5-7]

To develop these ideas further, I will consider a typical example, the accelerated decomposition of diacyl peroxides in the presence of electron donors.[2,4,8] Figure 1 is a plot of energy vs. peroxide bond length, RO–OR, for such systems. As such, it is a cross section through a multidimensional surface of which another important coordinate is certainly RO–OR–D separation. It is accordingly assumed that, for each value of RO–OR, the RO–OR–D separation is that resulting in the lowest energy for the

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