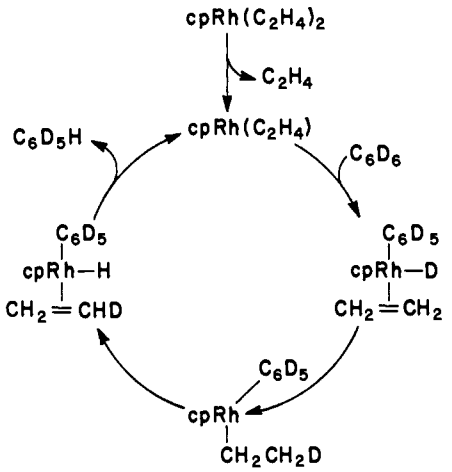
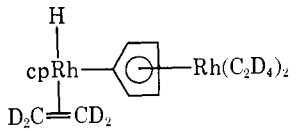


Figure 1. Proposed mechanism for exchange between benzene-d_6 and coordinated ethylene in η^5-$C_5H_5Rh(C_2H_4)_2$.

Other rhodium–olefin complexes which were observed to exchange hydrogen with benzene after 1 hr at 130° include acacRh$(C_2H_4)_2$, η^5-$C_5(CH_3)_5Rh(C_2H_4)_2$, and η^5-$C_5H_5Rh(C_2H_3CN)_2$. The amount of exchange with η^5-$C_5(CH_3)_5Rh(C_2H_4)_2$ is comparable to the amount with η^5-$C_5H_5Rh(C_2H_4)_2$, based on exchangeable hydrogen. The methyl hydrogens do not exchange. Much less exchange is observed with acacRh$(C_2H_4)_2$ and η^5-$C_5H_5Rh(C_2H_3CN)_2$. Only a trace of exchange was observed with η^5-$C_5H_4CNRh(C_2H_4)_2$ and η^5-C_5H_5Rh-(1,5-COD) under the same conditions.

A mechanism by which exchange between arenes and coordinated ethylene on η^5-$C_5H_5Rh(C_2H_4)_2$ could occur is suggested in Figure 1. While this mechanism has not been substantiated, there is precedence for the individual steps. Ethylene dissociation from η^5-C_5H_5Rh-$(C_2H_4)_2$ provides entry into the exchange cycle.[5] Oxidative addition of benzene then generates a phenylrhodium deuteride.[6] Insertion of ethylene into the Rh–D bond gives an ethylrhodium species. Collapse of the ethylrhodium species followed by reductive elimination of benzene results in one exchange.[7]

An analogous scheme for transferring D from coordinated ethylene to cyclopentadiene can be envisioned. In this scheme a coordinated cyclopentadienyl reacts as does benzene in Figure 1 *via* oxidative addition to rhodium to give



1

Evidence for **1** was obtained by heating for 10–20 min at 130° η^5-$C_5H_5Rh(C_2D_4)_2$ and η^5-$C_5H_5RhC_8H_{12}$ in cyclohexane-d_{12}. Deuterium appeared on the cyclopentadienyl ligands of both complexes. It is not likely that the 1,5-cyclooctadiene ligand is involved in this exchange because η^5-$C_5H_5RhC_8H_{12}$ showed very little exchange with benzene-d_6, even after 2 hr at 130°. In a similar experiment using η^5-$C_5H_5Rh(C_2D_4)_2$ and ferrocene, deuterium again appeared on the cyclopentadienyl ligands of both complexes. Ferrocene does not, however, exchange hydrogen with benzene under similar conditions.

(6) M. L. H. Green and P. J. Knowles, *J. Chem. Soc. A*, 1508 (1971).
(7) R. D. Cramer, *Accounts Chem. Res.*, 1, 186 (1968).

According to the mechanism of Figure 1, the extent of exchange might be affected by the ease of both ethylene dissociation and benzene addition. The amounts of exchange observed with different rhodium complexes suggest this is true. For example, ethylene dissociates from acacRh$(C_2H_4)_2$ and η^5-$C_5H_5Rh(C_2H_4)_2$ at comparable rates,[5] yet acacRh$(C_2H_4)_2$ gives much less exchange with benzene. A study of the kinetics of exchange is in progress.

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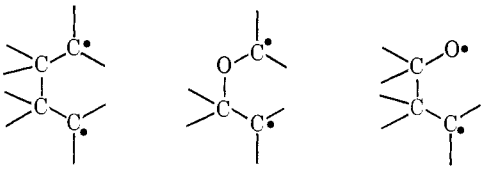
Intervention of the 1,4-Diradical 1-Oxatetramethylene in the Thermodecarboxylation of γ-Peroxylactones[1]

Sir:

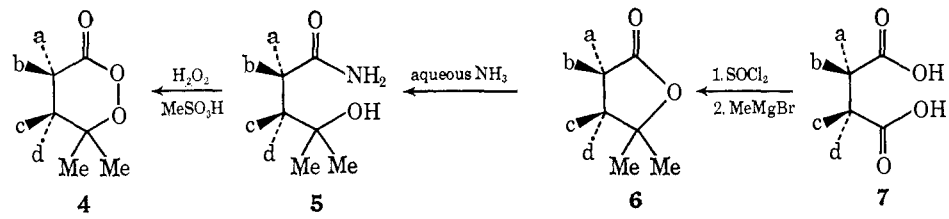
While tetramethylene diradicals **1**, a controversial class of reaction intermediates of current theoretical



1 2 3

and mechanistic dispute,[2] are implicated in such diverse reactions as cyclobutane pyrolysis,[3] Norrish type II photolysis of alkanones,[4] or thermocycloaddition of olefins,[5] the only well-documented oxygen heteroanalogs are the 2-oxatetramethylenes **2**, generated in the Paterno–Büchi[6] photocycloaddition of ketones and olefins. Oxetanes are potential precursors to 1-oxaheteroanalogs **3** of tetramethylenes; yet competitive C–C fission leading to **2** can render mechanistic conclusions ambiguous.[7] Similarly, the oxadi-π-methane rearrangement may involve such 1,4-diradical inter-

(1) Paper XXXIV in the cyclic peroxide series. For Paper XXXIII *cf.* W. Adam, G. A. Simpson, and F. Yany, *J. Phys. Chem.*, in press.
(2) (a) G. Jones, II, *J. Chem. Educ.*, **51**, 175 (1974); (b) R. G. Bergman in "Free Radicals," Vol. 1, J. K. Kochi, Ed., Wiley-Interscience, New York, N. Y., 1973, Chapter 5; (c) L. M. Stephenson, T. A. Gibson, and J. I. Brauman, *J. Amer. Chem. Soc.*, **95**, 2489 (1973); (d) L. Salem, *Pure Appl. Chem.*, **33**, 317 (1973); L. Salem and C. Rowland, *Angew. Chem.*, **84**, 86 (1972).
(3) (a) G. Jones II, and M. F. Fatina, *J. Chem. Soc., Chem. Commun.*, 375 (1973); (b) P. C. Beadle, D. M. Golden, K. D. King, and S. W. Benson, *J. Amer. Chem. Soc.*, **94**, 2943 (1972).
(4) (a) H. E. O'Neal, R. G. Miller, and E. Gunderson, *J. Amer. Chem. Soc.*, **96**, 3351 (1974); (b) P. J. Wagner, A. E. Kemppainen, and E. Gunderson, *ibid.*, **95**, 5604 (1973); P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971).
(5) P. D. Bartlett and G. M. Cohen, *J. Amer. Chem. Soc.*, **95**, 7923 (1973).
(6) (a) N. C. Yang, M. Kimura, and W. Eisenhardt, *J. Amer. Chem. Soc.*, **95**, 5068 (1973); (b) T. R. Darling, N. J. Turro, R. H. Hirsch, and F. D. Lewis, *ibid.*, **96**, 434 (1974); N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Schore, *Accounts Chem. Res.*, **5**, 92 (1972).
(7) G. Jones II, S. B. Schwartz, and M. T. Marton, *J. Chem. Soc., Chem. Commun.*, 374 (1973).



i, a = b = c = d = H
j, a = b = c = d = D
k, a = d = H; b = c = D
l, a = c = H; b = d = D

mediates, but stereolabeling also supports a concerted $_{\sigma}2_S + {}_{\pi}2_S$ process.[8] Presently we are fortunate in providing kinetic and stereochemical evidence that the unprecedented 1-oxatetramethylene intermediate **3** serves as precursor to the decarboxylation products of γ-peroxylactones **4**.

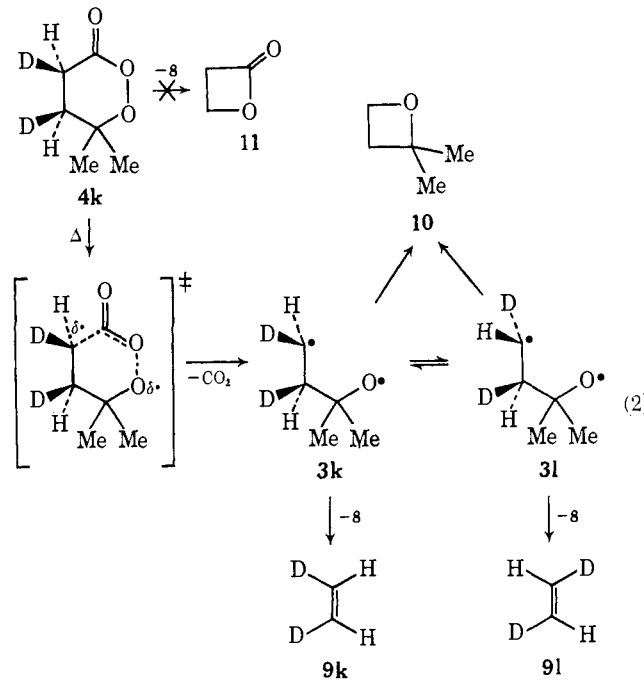
Analogous to **4i**, the deuterium labeled γ-peroxylactones **4j–l** were prepared (eq 1) by perhydrolysis of their respective γ-hydroxyamides **5**,[9] which were readily available by ammonolysis of the respective γ-lactones.[6] The required succinic acids **7** were prepared by deuteration of the respective dipotassium salts of acetylenedicarboxylic, maleic, and fumaric acids with dideuteriomide.[10] The extent of deuteration, determined by quantitative nmr using the γ-methyls as internal standard, was 90 ± 1% for **4j–l**.[11]

The rate of thermodecarboxylation of **4i** and **4j** in CCl_4 at 120° was assessed by quantitative infrared analysis, monitoring the characteristic 1780 cm^{-1} γ-peroxylactone carbonyl frequency. Both **4i** and **4j** followed first-order kinetics through better than 95% reaction, affording rate constants $k_H = (1.77 \pm 0.01) \times 10^{-5}$ and $k_D = (1.39 \pm 0.01) \times 10^{-5}$ sec^{-1}. Thus, the secondary isotope effect is $k_H/k_D = 1.27 \pm 0.02$ for the four deuteriums, implying multiple bond fission concurrent with O–O bond homolysis.[12]

The thermal decarboxylation products of **4** were *ca.* 90% acetone (**8**) and ethylene (**9**) and *ca.* 6% 2,2-dimethyloxetane (**10**). Even a very careful search for β-propiolactone (**11**) revealed the absence of this cyclization product, although the latter is stable toward the thermolysis conditions in the presence of γ-peroxylactone, **4**. A control experiment showed that oxetane **10** is also stable under the reaction conditions. Therefore, acetone and ethylene are formed directly from γ-peroxylactone **4** and not from oxetane **10**.

In case of the stereolabeled γ-peroxylactones *erythro*-**4k** and *threo*-**4l**, the deuterated olefin product was analyzed by quantitative infrared analysis[13] for the proportions of the *cis*- and *trans*-1,2-dideuterioethylenes **9k** and **9l**, respectively, in order to assess the stereochemical course of the decarboxylation. In both cases it was observed that the cis/trans product ratio was 0.95 ± 0.05. Since a control experiment revealed that *cis*-**9k** did not isomerize when heated in the presence of the γ-peroxylactone under the reaction conditions, it is clear that the γ-peroxylactones decarboxylate nonstereospecifically. Consequently, some species of sufficient lifetime capable of efficiently erasing stereomemory in the olefin product must be interposed.

A mechanism for the thermal decarboxylation consistent with the presented facts is detailed for the *erythro*-**4k** isomer in eq 2. The appreciable isotope effect[12,14] requires that O–O bond homolysis must be accompanied by Cα–CO bond breaking. Rupture of the Cβ–Cγ bond cannot be concurrent with O–O bond and Cα–CO bond scission, *i.e.*, a three-bond cleavage, since then *erythro*-**4k** must form stereospecifically *cis*-**9k**; yet, we have seen that the reaction is nonstereospecific. Thus, a two-bond cleavage transition state is required, generating first the 1-oxatetramethylene **3k**, which is sufficiently long-lived to equilibrate rotamerically with its **3l** isomer before the 1,4-diradical is annihilated. In their destruction the 1,4-diradicals **3k** and **3l** proceed principally (*ca.* 90%) by the fragmentation route into the respective ethylenes **9k** and **9l** and to a minor extent (*ca.* 6%) by cyclization into oxetane **10**.



(2)

(8) J. I. Seeman and H. Ziffer, *Tetrahedron Lett.*, 4413 (1973).
(9) W. Adam and L. M. Szendrey, *Chem. Commun.*, 1299 (1971).
(10) S. Hünig, H. R. Miller, and W. Thier, *Angew. Chem., Int. Ed. Engl.*, 9, 27, 271 (1965).
(11) Authentic samples of **7k** and **7l** with known per cent deuteration for comparison were generously supplied by Professor Dr. J. Retey of the University of Karlsruhe.
(12) T. W. Koenig and W. D. Brewer, *Tetrahedron Lett.*, 2773 (1965).
(13) (a) P. D. Bartlett, G. M. Cohen, S. P. Elliott, K. Hummel, R. A. Minns, C. M. Sharts, and J. Y. Fukunaga, *J. Amer. Chem. Soc.*, **94**, 2899 (1972); (b) J. E. Baldwin and P. W. Ford, *ibid.*, **91**, 7192 (1969). (c) Infrared spectra of the pure *cis*- and *trans*-1,2-dideuterioethylenes and of a 1:1 mixture were kindly supplied by Professor Bartlett of the Harvard University and Professor Baldwin of the University of Oregon which enabled calibration of our results.
(14) M. Taagepera and E. R. Thornton, *J. Amer. Chem. Soc.*, **94**, 1168 (1972).

At least initially the 1-oxatetramethylene **3** must be created as a singlet and the lifetime of this species might be enhanced by efficient intersystem crossing to its triplet. In this respect our 1,4-diradical may reflect the behavior of the 2-oxatetramethylene **2**.[15] However, our present data cannot shed light on this mechanistically relevant point.

An alternative mechanism which considers fast and reversible simple homolysis of the O–O bond, followed by a rate-determining decarboxylation and/or deketonation is unlikely in view of the appreciable secondary isotope effect and the lack of production of β-lactone **11**. Such a mechanism would require that fragmentation and not generation of the intermediary 1,6-diradical is rate-determining, analogous to the thermal isomerization of cyclopropane into propene for which rearrangement and not generation of the trimethylene diradical is rate determining.[2b] Although the fragmentation of diradicals can exhibit small secondary isotope effects, *e.g.*, the concerted double deketonation of the 1,6-dioxahexamethylene diradical produced in the thermolysis of 1,2-dioxanes,[16] the isotope effect is expected to be negligible for the considerably more exothermic decarboxylation compared to ketonation.[17] However, it seems pertinent to prove this question rigorously by determining the secondary isotope effects separately for α- and β-deuteration. Also chemical trapping experiments of the 1-oxatrimethylene **3** seem feasible in view of their lifetime.[4a] Both mechanistic questions are currently under scrutiny.

Acknowledgments. Financial support by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, are gratefully appreciated.

(15) L. Salem, *J. Amer. Chem. Soc.*, **96**, 3486 (1974).
(16) W. Adam and J. Sanabia, *Angew. Chem.*, **85**, 914 (1973).
(17) T. Koenig, ref 2b, Chapter 3. (b) Deketonation of the *tert*-butoxy radical into acetone and the methyl radical has an activation energy of ~13 kcal/mol and a reaction enthalpy of *ca.* +2 kcal. On other hand, decarboxylation of the acetoxy radical into carbon dioxide and the methyl radical has an activation energy of ~6.6 kcal/mol and a reaction enthalpy of *ca.* −10 kcal (*cf.* J. K. Kochi, ref 2b, Vol 2, Chapter 23).
(18) A. P. Sloan Fellow 1968–1972; J. S. Guggenheim Fellow 1972–1973.
(19) Western Fher Fellow 1971–1972; taken in part from the doctoral dissertation.

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Dynamics and Thermodynamics of Axial Ligation in Metalloporphyrins. III. Effects of Molecular Interaction of Ferric Porphyrins with an Aromatic Acceptor

Sir:

The presently available X-ray crystallographic data on a variety of homoproteins[1,2] provide strong evidence for the ubiquitous nature of molecular interaction between porphyrin π system[3] and certain aromatic side chains of the protein. The importance of these aromatic interactions is evidenced by the invariance with genetic origin of the participating aromatic amino acids.[1] Similar π complexes between chlorophyll and quinones[4] have been postulated in the initial stages of the photosynthetic process.

In the myoglobins and hemoglobins[1] the prominent function of these molecular interactions appears to be to position the noncovalently held protoporphyrin in the heme cavity. In the cytochromes, in addition, changes in the molecular interactions[2] are tied to the structural changes accompanying the redox process.

Although it has been demonstrated[5–7] that model porphyrin complexes may interact with a variety of aromatic residues, ostensibly yielding π complexes, previous studies have shed little light on the effect of molecular interactions on the function of the iron in the heme group.

We report here on a proton nmr investigation of the molecular interaction between ferric complexes of tetraphenylporphine, TPP, or octaethylporphyrin, OEP, with the organic π acceptor trinitrobenzene, TNB, in $CDCl_3$, with the objective of determining the effects of this interaction on the thermodynamics and kinetics[8] of axial ligation in both high-spin, HS, and low-spin, LS, porphyrins. We explored the effect of TNB on the following two recently characterized reactions[9,10]

$$\text{TPPFeCl} + 2\text{L} \rightleftharpoons \text{TPPFeL}_2^+\text{Cl}^- \quad (1)$$

$$\text{OEPFeCl} + \text{Cl}^{-*} \rightleftharpoons \text{OEPFeCl}^* + \text{Cl}^- \quad (2)$$

(where L = *N*-methylimidazole).

K_{eq} for reaction 1 is given by $K_{eq} = [\text{TPPFeL}_2^+\text{Cl}^-]/(\text{TPPFeCl})[\text{L}]^2$, and can be conveniently determined[11] by integration of the nmr spectrum. Table I illustrates the effect on the apparent K_{eq} in eq 1 upon the addition of TNB; the decrease in K_{eq} indicates that

Table I. Effect of Trinitrobenzene on the Apparent Equilibrium Constant for the Axial Coordination of *N*-Methylimidazole to Ferric Porphyrins[a]

$[\text{TNB}]^b/[\text{Fe}]_{total}$	$K_{eq} \times 10^{-3}$	$[\text{TNB}]^b/[\text{Fe}]_{total}$	$K_{eq} \times 10^{-3}$
0.00	1.43	1.95	0.38
0.23	0.91	3.28	0.27
0.44	0.77	5.82	0.17
0.98	0.55	7.80	0.14

[a] $K = [\text{TPPFeL}_2^+\text{Cl}^-]/(\text{TPPFeCl})[\text{L}]^2$, when L = *N*-methylimidazole; $CDCl_3$ solvent at 25°. [b] Mole ratio of TNB to total ferric porphyrin complex.

(1) E. Antonini and M. Brunori, "Hemoglobin and Myoglobin in their Reactions with Ligands," North Holland Publishing Co., Amsterdam, 1971, Chapter 4; M. F. Perutz and L. F. TenEyck, *Cold Spring Harbor Symp. Quant. Biol.*, **36**, 295 (1971), and references therein; J. C. Kendrew, *Brookhaven Symp. Biol.*, **15**, 28 (1962).
(2) R. E. Dickerson, *Advan. Biochem.*, 72, 815 (1972); T. Takano, R. Swanson, O. B. Kallai, and R. E. Dickerson, *Cold Spring Harbor Symp. Quant. Biol.*, **36**, 397 (1971).
(3) M. F. Slifkin, "Charge Transfer Interaction of Biomolecules," Academic Press, London, 1971, Chapter 6.
(4) G. Tollin and G. Green, *Biochim. Biophys. Acta*, **60**, 524 (1962); **66**, 308 (1963).
(5) C. D. Barry, H. A. O. Hill, B. E. Mann, P. J. Sadler, and R. J. P. Williams, *J. Amer. Chem. Soc.*, **95**, 4545 (1973), and references therein.
(6) D. Mauzerall, *Biochemistry*, **4**, 1801 (1965).
(7) A. H. Siderov, *Teor. Eksp. Khim.*, **9**, 550 (1973).
(8) R. Foster, "Organic Charge-Transfer Complexes," Academic Press, London, 1969, Chapter 11.
(9) G. N. La Mar and F. A. Walker, *J. Amer. Chem. Soc.*, **94**, 8607 (1972).
(10) G. N. La Mar, *J. Amer. Chem. Soc.*, **95**, 1663 (1973).
(11) ^{1}H nmr spectra were run on a Jeol PS-100 FT spectrometer using a Digilab nmr-3 data system; solutions were ~0.02 *M* in complex.