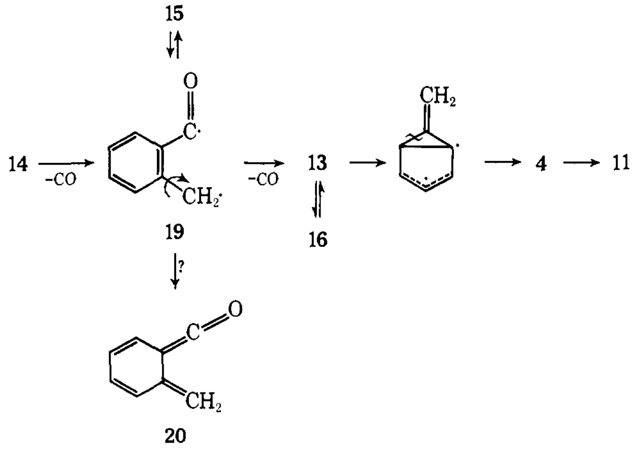
ground state on the basis of esr spectroscopy;[13a,b] the corresponding benzocyclopropenes have been obtained and decompose at room temperature to styrenes most likely through the 1,3-biradical intermediate.[13a] In our case the multiplicity of the various biradical intermediates remains to be determined. Significantly, no evidence for the singlet species **20**, which has been postulated as a photochemical intermediate from benzocyclobutenones,[12,14] was obtained. Finally, we have found that benzocyclobutenone (**15**) undergoes FVP to the triad of C_7H_6 products (**4**, **16**, and **11**) as implied by the scheme; similarly **4** is converted to **11** at temperatures ≥1000°.



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(14) M. P. Cava and R. J. Spangler, *J. Amer. Chem. Soc.*, **89**, 4550 (1967).

E. Hedaya, M. E. Kent
Union Carbide Research Institute
Tarrytown, New York 10591

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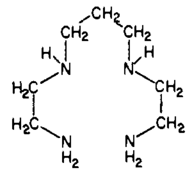
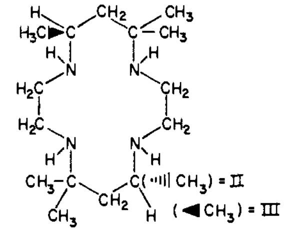
Effect of Macrocyclic Structures on the Rate of Formation and Dissociation of Copper(II) Complexes

Sir:

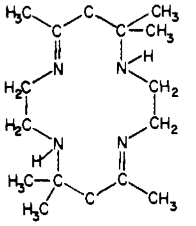
The kinetics of formation of copper(II) complexes with ligands containing four nitrogen donor groups are measured for the somewhat flexible 14-membered macrocyclic ligands[1-4] shown in structures II, III, and IV as well as for an open-chain polyamine, 2,3,2-tet (I), and a porphyrin ligand (V). In acid solutions the aliphatic macrocyclic ligands react much slower with $Cu(aquo)^{2+}$ than do the porphyrins. Furthermore, with tet *a* (II) and tet *b* (III) the initial products have a different structure than the final products, and the rearrangements to give their more stable products are very slow. Because acid has such a large effect on the kinetics, the formation reactions with the unprotonated ligands also are examined in 0.5 *M* NaOH where copper is present in the form of the soluble hydroxide complexes, $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$.[5] Under these conditions the 14-membered macrocycles II, III, IV react more slowly than the open-chain ligand I by factors of 10^3–10^4 (Table I).



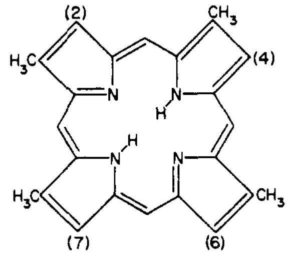
I, 2,3,2-tet



II, tet *a* or *meso* -1,7-CTH
III, tet *b* or *rac* -1,7-CTH



IV, *trans* [14]diene or 1,7-CT



V, hematoporphyrin IX
(2),(4) = $CHOHCH_3$
(6),(7) = CH_2CH_2COOH
VI, deuteroporphyrin-2,4-disulfonic acid dimethylester
(2),(4) = SO_3H
(6),(7) = $CH_2CH_2COOCH_3$

The more rigid porphyrin V is less reactive than I by a factor of 10^9. All the reactions are second order and the products are believed to be square-planar complexes of copper. However, the microscopic mechanisms of formation must differ greatly. The porphyrin structure has the greatest tendency to force a mechanism of simultaneous multiple desolvation of the metal ion while the open-chain polyamine can readily react by the stepwise replacement of coordinated solvent (H_2O and OH^-). In the case of the 14-membered macrocycles both paths must be considered. It is difficult for these ligands to twist and fold in order to maintain a stepwise desolvation path. Models indicate that some degree of multiple desolvation is necessary in the coordination of the third and fourth nitrogens. However, the rate-determining steps may be earlier in the coordination process. Three factors which suggest that twisting or folding of these cyclic ligands is important are (1) their much greater reactivity compared to the porphyrin molecule, (2) the formation of intermediate structural isomers, and (3) the fact that subtle changes in structure, as in tet *a* compared to tet *b*, cause noticeable changes in the rate constants.

Table I also gives the observed rate constants for the reaction of $Cu(aquo)^{2+}$ with tet *a*, tet *b*, and the *trans*-[14]-diene at pH 4.7 in comparison to data recently available for a sulfonated deuteroporphyrin (VI)[6] and for an open-chain pentadentate polyamine, tetraethylenepentamine (tetren).[7] The hematoporphyrin (V) was not used because of its limited solubility in acidic solutions. At pH 4.7 copper(II) is incorporated into the porphyrin ring more rapidly by several orders of

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(1) The macrocyclic ligands in structures II, III, and IV were prepared by the procedures of Curtis,[2,3] and his abbreviations are given along with those of Busch and coworkers.[4]

(2) N. F. Curtis, *J. Chem. Soc.*, 2644 (1964).

(3) N. F. Curtis, *Coord. Chem. Rev.*, 3, 3 (1968).

(4) L. G. Warner and D. H. Busch, *J. Amer. Chem. Soc.*, **91**, 4092 (1969).

(5) L. A. McDowell and H. L. Johnston, *ibid.*, **58**, 2009 (1936).

(6) J. Weaver and P. Hambright, *Inorg. Chem.*, **8**, 167 (1969).

(7) R. E. Shephard, G. M. Hodgson, and D. W. Margerum, to be submitted for publication.

Table I. Second-Order Rate Constants for the Reaction of Cu(II) with Various Ligands at 25.0°

Ligand	Obsd rate constant, M^{-1} sec^{-1} In 0.5 *M* NaOH	 At pH 4.7
2,3,2-tet (I)	$\sim 10^7$	
tetren		8.9×10^4 ($\mu = 0.1$ *M*)
tet *a* (II)	1.6×10^3	5.8×10^{-2} ($\mu = 1.0$ *M*)[a,b]
		2.0×10^{-2} ($\mu = 0.1$ *M*)[b]
tet *b* (III)	3.6×10^3	2.7×10^{-2} ($\mu = 1.0$ *M*)[a,b]
trans-[14]-diene (IV)	5.6×10^3	2.8×10^{-1} ($\mu = 1.0$ *M*)[a]
Hematoporphyrin (V)	2.0×10^{-2}	
Deuteroporphyrin (VI)		3.2 ($\mu = 0.5$ *M*)[c]

[a] In 0.5 *M* acetic acid–sodium acetate buffer. [b] With tet *a* (and tet *b*) the reaction product in acidic solutions is the blue complex of copper and is not the more stable red complex formed in base. The rate of conversion of blue to red is extremely slow at this pH. [c] In 0.1 *M* acetic acid–sodium acetate buffer.

magnitude than it is incorporated into the tet *a* and tet *b* macrocycles. The relative rates at higher acidities favor the porphyrin to an even greater extent. The rate constants for tet *a* at pH 4.7 are for the formation of Cu(tet *a*)(blue)$^{2+}$ rather than for the formation of the product in basic solution, Cu(tet *a*)(red)$^{2+}$. Perchlorate salts of the blue and red complexes give the same elemental analysis but their properties are quite different. In addition to the spectral differences the Cu(tet *a*)(red)$^{2+}$ complex is more stable thermodynamically than Cu(tet *a*)(blue)$^{2+}$ by a factor of 10^8,[8] and its dissociation in acid solution is much faster. The Cu(tet *a*)(blue)$^{2+}$ complex in solution converts to the Cu(tet *a*)(red)$^{2+}$ complex, but the reaction is extremely slow in acidic solutions. The rate of conversion increases with pH. The observed first-order rate constant is 10^{-3} sec^{-1} at pH 9 and increases to 5 sec^{-1} in 0.5 *M* NaOH. The formation of Cu(tet *a*)(red)$^{2+}$ in 0.5 *M* NaOH proceeds *via* the blue complex which can be observed as a reaction intermediate at higher concentrations of reactants. The data in Table I for 0.5 *M* NaOH are obtained under conditions where the blue intermediate is not observed.

The reaction of tet *b* with Cu(aquo)$^{2+}$ also gives an intermediate blue complex as the initial product.

The reason that tet *a* is slow to react with Cu(aquo)$^{2+}$ in acid to give Cu(tet *a*)(blue)$^{2+}$ is that the diprotonated ligand (pK_2 = 10.4)[8] is unreactive. Even at pH 1 only the monoprotonated ligand (pK_1 = 12.6) reacts. The resolved rate constant for the reaction of Cu(aquo)$^{2+}$ with H(tet *a*)$^+$ is 7.6×10^3 M^{-1} sec^{-1} and the value for the rate constant with H$_2$(tet *a*)$^{2+}$ must be less than 10^{-5} M^{-1} sec^{-1}. This is in marked contrast to the behavior of the open-chain polyamines. Thus with tetraethylenepentamine, H$_2$tetren^{2+}, H$_3$tetren^{3+}, and H$_4$tetren^{4+} all can react with Cu(aquo)$^{2+}$ and have rate constants of 4.2×10^7, 1.6×10^5, and 1.4×10^4 M^{-1} sec^{-1}, respectively.[7] The macrocyclic structure causes the two protons in H$_2$(tet *a*)$^{2+}$ to be nearer one another than would be the case in an open-chain molecule. The fact the pK_2 value is as large as 10.4 suggests that hydrogen bonding compensates for electrostatic repulsion of the two protons. Addition of a third proton is thermodynamically difficult and H$_3$(tet *a*)$^{3+}$ has a pK_3 value of only 0.8. For similar reasons (electrostatic repulsion and hydrogen bonding of the nitrogens), it is kinetically difficult for Cu(aquo)$^{2+}$ to react with H$_2$(tet *a*)$^{2+}$.

The porphyrins do not add protons in the ring until pH 4–5, and therefore their rates are less drastically affected by acid. Nevertheless, the two hydrogens on the porphyrin ring nitrogens, which are very weakly acidic (p$K_a \cong 16$),[9] must be transferred in forming the metal ion complexes. The rates of Mg(II)[10] and Zn(II)[11] incorporation into porphyrins are slow and are catalyzed by nitrogen bases. Despite this Cu(OH)$_3^-$ reacts slower than Cu(aquo)$^{2+}$ with the porphyrins. Some of the resolved rate constants for the formation reactions are given in Table II. In general Cu(OH)$_3^-$ is more reactive than Cu(OH)$_4^{2-}$ and less reactive than would be expected for Cu(aquo)$^{2+}$ with neutral polydentate ligands.

Table II. Formation Rate Constants Resolved for Individual Species at 25.0°

Reactants	Rate constant, M^{-1} sec^{-1}
Cu(OH)$_3^-$ + 2,3,2-tet	$\sim 10^7$ [a]
Cu(OH)$_3^-$ + tet *a*	5×10^3
Cu(OH)$_3^-$ + V	0.20
Cu^{2+} + H$_2$tetren^{2+} [7]	4.2×10^7
Cu^{2+} + H(tet *a*)$^+$	7.6×10^3
Cu^{2+} + VI	4.3

[a] The reactivities of Cu(OH)$_4^{2-}$ and Cu(OH)$_3^-$ are about the same for 2,3,2-tet.

The kinetics of dissociation of the more stable macrocyclic ligands require high acidities to force the reaction. Table III compares rate constants observed in 6.1 *M* HCl where the half-life for Cu(tet *a*)(red)$^{2+}$ is shortened to 22 days. Data are included for a second red complex of copper(II) with tet *a* which is prepared from oxalate solutions. This compex, Cu(tet *a*)(unstable red)$^{2+}$, converts to the stable red com-

Table III. Observed First-Order Dissociation Rate Constants in 6.1 *M* HCl at 25°

Complex	k_d, sec^{-1}
Cu(tet *a*)$^{2+}$ (red)	3.6×10^{-7}
Cu(tet *a*)$^{2+}$ (unstable red)	4.3×10^{-6}
Cu(tet *a*)$^{2+}$ (blue)	3.8×10^{-3}
Cu(*trans*-[14]-diene)$^{2+}$	1.2×10^{-3}
Cu(2,3,2-tet)$^{2+}$	4.1

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(8) D. K. Cabbiness and D. W. Margerum, *J. Amer. Chem. Soc.*, **91**, 6540 (1969).

(9) J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier Publishing Co., New York, N. Y., 1964, p 27.

(10) S. J. Baum and R. A. Plane, *J. Amer. Chem. Soc.*, **88**, 910 (1966).

(11) T. P. Stein and R. A. Plane, *ibid.*, **91**, 607 (1969).

plex in base. The factor of 10^7 in the relative reactivity of $Cu(2,3,2\text{-tet})^{2+}$ and $Cu(\text{tet } a)(\text{red})^{2+}$ gives an indication of the large effects which macrocyclic structures have on the dissociation kinetics.

The $Cu(\text{tet } a)(\text{red})^{2+}$ complex has been assigned a square-planar configuration[12] and presumably has the same conformational structure as $Ni(\text{tet } a)^{2+}$ in regard to the orientation of the four secondary amine protons.[4] Curtis assumed that tet *a* could coordinate only with its four donor atoms arranged in a single plane while tet *b* could fold. Only one conformational isomer of $Ni(\text{tet } a)^{2+}$ has been observed despite efforts to prepare others.[4] Therefore the existence of at least three isomers of $Cu(\text{tet } a)^{2+}$ is of special interest. In view of the large differences in the spectra, thermodynamic stability, and kinetic reactivity of $Cu(\text{tet } a)(\text{red})^{2+}$ and $Cu(\text{tet } a)(\text{blue})^{2+}$, there must be major differences in their structures. The blue complex could be a folded form with one nitrogen donor in an axial position or a complex distorted in some other way, for example, with the copper ion out of the plane of the four nitrogens. In any case some degree of ligand twisting or folding is needed to form the blue complex and additional base is necessary to bring about the necessary hydrogen inversions on the nitrogen donor groups in order to give the stable $Cu(\text{tet } a)(\text{red})^{2+}$ complex.

Acknowledgment. This investigation was supported by National Science Foundation Grant GP-6725X.

(12) Reference 3, p 44.

Dale K. Cabbiness, Dale W. Margerum
Department of Chemistry, Purdue University
Lafayette, Indiana 47907

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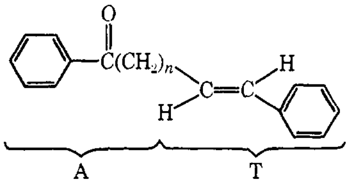
Intramolecular Triplet Energy Transfer[1]

Sir:

Although reports of intramolecular carbonyl "sensitized" olefin isomerizations have appeared in the literature,[2–4] it has not been demonstrated that such isomerizations were the result of prior electronic energy transfer. In two cases[2,4] spectral results indicate that the chromophores involved interact to the extent that they can no longer be considered isolated; consequently the process is probably best described as an internal conversion.[5] In other cases,[2,3,6] biradical intermediates which either form new compounds (oxetanes, cleavage products) or return to starting material with concomitant isomerization have been implicated.[6] In addition to the questions regarding carbonyl–olefin intramolecular triplet energy transfer, very little rate data have been published[7] to help understand the intimate details of intramolecular triplet energy transfer between any two nonconjugated chromophores. We therefore wish to report several unambiguous cases of intramolecular triplet energy transfer between carbonyl and olefin chromophores and to provide the first set of rate constants for this process in a series of structurally related compounds.



$n = 1–4$

In this series of compounds the acetophenone and *trans*-β-methylstyryl chromophores are separated by one to four methylene groups.[8] The ultraviolet spectra of these compounds indicate that, while the chromophores in the $n = 1$ compound interact strongly ($\epsilon_{\max}^{n-\pi^*}$ enhanced by a factor of 6 relative to an equal molar solution of acetophenone and *trans*-β-methylstyrene; the n–π* band shows vibrational fine structure with $\Delta\bar{\nu} = 1500$ cm^{-1}, no shift in $\lambda_{\max}$), there is very little interaction in the $n = 2$ compound and none in the $n = 3$ or $n = 4$ compound. Consequently, the $n = 2$, 3, and 4 compounds represent ideal systems for the study of intramolecular energy transfer.

Selective excitation of the acetophenone portion (A) of these compounds with 3660-Å light[9] results in efficient isomerization of the *trans*-β-methylstyryl group (T) as shown in Table I. For each compound ($n = 1–4$) the photostationary isomer ratio, $([A–T]/[A–C])_{pss}$, was 0.91. Radical equilibration of $n = 1–4$ and

Table I. Isomerization Quantum Yield Data[a]

Compd	$\Phi_{T\to C}$	$\Phi_{et}\Phi_{ISC}$[b]
$n = 1$	0.53 ± 0.02	1.01[c]
$n = 2$	0.52 ± 0.02	0.99
$n = 3$	0.52 ± 0.02	0.99
$n = 4$	0.51 ± 0.01	0.98

[a] Irradiations were performed at 25° in benzene solution; wavelength of exciting light was 3660 Å. [b] Calculated from $\Phi_{T\to C}(1 + \alpha)$, where $\alpha = k_T/k_C = 0.909$. The decay ratio, α, was determined from the photoequilibrium $[trans]/[cis]_{pss} = \alpha$. [c] Since the equations in Chart I do not apply to $n = 1$, this number (1.01) only indicates that every photon absorbed produces an excited state from which isomerization can occur.

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(1) Photochemical Reactions. III; for part II see D. O. Cowan and R. L. Drisko, *J. Amer. Chem. Soc.*, **89**, 3068 (1967); for part I see D. O. Cowan and R. L. Drisko, *Tetrahedron Lett.*, 1255 (1967). This work was presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

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(3) H. Morrison, *J. Amer. Chem. Soc.*, **87**, 932 (1965).

(4) P. A. Leermakers, J. Montillier, and R. D. Rauh, *Mol. Photochem.*, **1**, 57 (1969).

(5) A. A. Lamola, *J. Amer. Chem. Soc.*, **91**, 4786 (1969).

(6) H. Morrison and S. Kurowsky, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, Abstract No. ORGN 142.

(7) $k^t_{et} > 10^{10}$ sec^{-1} for energy transfer from a benzophenone moiety to a naphthylene chromophore separated by one to three methylene groups; A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 2322 (1965). $k^t_{et} = 25$ sec^{-1} and 0.04 sec^{-1} for energy transfer from benzophenone and carbazole to naphthylene separated by steroid ring; R. A. Keller and L. J. Dolby, *ibid.*, **91**, 1293 (1969). $k^t_{et} = 2.0 \times 10^8$ sec^{-1} for energy transfer from benzene to butene: H. Morrison and R. Peiffer, *ibid.*, **90**, 3428 (1968). Morrison has recently[6] indicated that this value is incorrect inasmuch as singlet quenching of the phenyl group by piperylene was not corrected for.

(8) The synthesis and characterization of compounds $n = 1–4$ will be described in our full paper along with other details.

(9) All quantum yield measurements were performed on a "good geometry" optical bench using a Hanovia 1KW short arc Hg–Xe lamp, Corning CS-052 and CS-7-37 filters, a quartz cell with optically flat windows masked so that the entire cell, but not the cell edge, was illuminated, and a RCA-935 phototube to monitor transmitted light. The light intensity was determined by ferrioxalate actinometry and the amount of isomerization was followed by either glpc ($n = 2–4$) or ir and nmr ($n = 1$).