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

The Cu(tet *a*)(red)$^{2+}$ complex has been assigned a square-planar configuration[12] and presumably has the same conformational structure as Ni(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(tet *a*)$^{2+}$ has been observed despite efforts to prepare others.[4] Therefore the existence of at least three isomers of Cu(tet *a*)$^{2+}$ is of special interest. In view of the large differences in the spectra, thermodynamic stability, and kinetic reactivity of Cu(tet *a*)(red)$^{2+}$ and Cu(tet *a*)(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(tet *a*)(red)$^{2+}$ complex.

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

(12) Reference 3, p 44.

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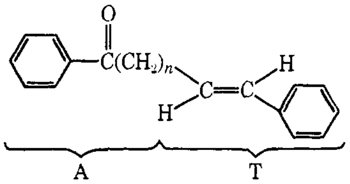
Received November 29, 1969

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.

Table I. Isomerization Quantum Yield Data[a]

Compd	$\Phi_{T\rightarrow C}$	$\Phi_{et}\Phi_{ISC}$[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 $\Phi_{T\rightarrow C}(1 + \alpha)$, 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.

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

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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.

(2) H. Morrison, *Tetrahedron Lett.*, 3653 (1964).

(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).

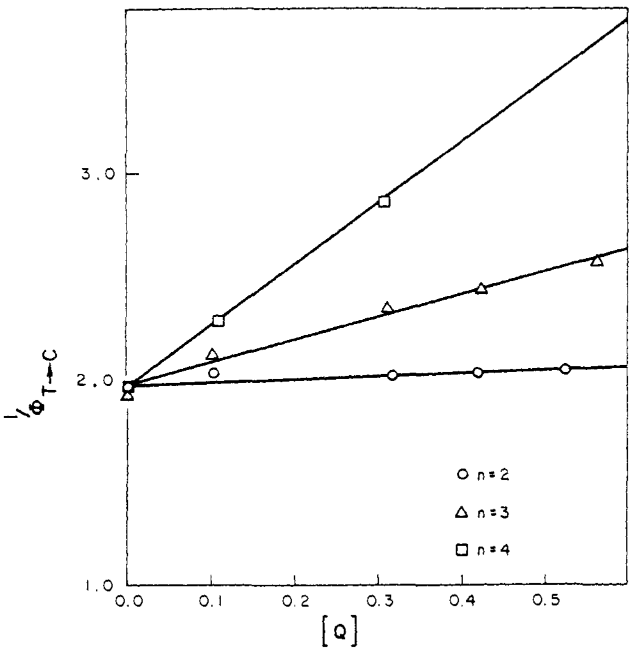

Figure 1. Quenching of *trans* → *cis* isomerization by *trans*-β-methylstyrene (benzene solution).

equilibration with low-energy sensitizers which are thought to operate *via* Schenck biradical intermediates produce mixtures where the *trans* isomer strongly predominates. This indicates that biradical intermediates are not involved in the direct photolysis of these compounds and that isomerization is the result of electronic energy transfer.[10,11]

Irradiation of solutions containing equimolar amounts of $n = 1, 2, 3$, or 4 and *trans*-β-methylstyrene as a quencher at concentrations comparable to those of the runs in Table I (0.01 *M*) indicated that intermolecular energy transfer cannot compete with intramolecular energy under these conditions.

We propose a mechanism to account for these findings (Chart I). Selective excitation of the acetophenone portion of these compounds results in formation of the n–π* singlet state of this chromophore (A^s). Singlet energy transfer from A^s to the olefin portion should be slow due to the large endothermicity involved.[12] Moreover, since intersystem crossing in phenyl ketones is known to be rapid,[13] the n–π* triplet state of the acetophenone chromophore should be formed (eq 2) with unit efficiency ($\Phi_{isc} = 1$). Our results indicate that this is the case (*vide infra*). Triplet energy transfer (eq 4) can now occur at an appreciable rate since the process is very exothermic.[12] In competition with energy transfer is any process emanating from A^t, as depicted in eq 3.[10] Excitation of the styryl group due to triplet energy transfer allows for *trans–cis* isomerization of this portion of the molecule (eq 5, 6). The above mechanism (eq 1–7) leads to the Stern–Volmer equation

Chart I.

$$\text{A–T} \xrightarrow{I_a} \text{A}^s\text{–T} \qquad \text{A–C} \xrightarrow{I_a} \text{A}^s\text{–C} \tag{1}$$

$$\text{A}^s\text{–T} \xrightarrow{\Phi_{isc}} \text{A}^t\text{–T} \qquad \text{A}^s\text{–C} \xrightarrow{\Phi_{isc}} \text{A}^t\text{–C} \tag{2}$$

$$\text{A}^t\text{–T} \xrightarrow{k_d} \text{A–T} \qquad \text{A}^t\text{–C} \xrightarrow{k_d} \text{A–C} \tag{3}$$

$$\text{A}^t\text{–T} \xrightarrow{k_{et}} \text{A–P*} \qquad \text{A}^t\text{–C} \xrightarrow{k_{et}} \text{A–P*} \tag{4}$$

$$\text{A–P*} \xrightarrow{k_t} \text{A–T} \tag{5}$$

$$\text{A–P*} \xrightarrow{k_c} \text{A–C} \tag{6}$$

$$\text{A}^t\text{–T} + \text{Q} \xrightarrow{k_q} \text{A–T} + \text{Q}^t \tag{7}$$

$$\frac{1}{\Phi_{T \to C}} = \frac{1}{F\Phi_{isc}}\left\{\left(1 + \frac{k_d}{k_{et}}\right) + \frac{k_q}{k_{et}}[Q]\right\} \tag{8}$$

$$F = k_c/k_c + k_t$$

The results of quenching studies using *trans*-β-methylstyrene as a quencher (Figure 1) show that the behavior of $n = 2$, 3, and 4 is consistent with the proposed mechanism while the situation for $n = 1$ is more complicated.[14] In all four cases the fact that $\Phi_{T \to C}$ (Table I) is within experimental error of the percentage of *cis* isomer present at the photostationary state which is in turn equal to the rate ratio (*F*) for β-methylstyryl triplets[15] indicates that each photon absorbed by the phenone moiety is transferred to the styryl group. In the case of $n = 2$–4 this implies that $\Phi_{isc}\Phi_{et} = 1$ (see Table I).[14]

Since $\Phi_{isc}\Phi_{et} = 1$, eq 8 can be rewritten for $n =$

$$\frac{1}{\Phi_{T \to C}} = \frac{1}{F}\left(1 + \frac{k_q}{k_{et}}[Q]\right) \tag{9}$$

2–4. The slope divided by the intercept for a plot of $1/\Phi_{T \to C}$ *vs.* [Q] gives the rate ratio k_q/k_{et}. Table II shows the results for compounds $n = 2$–4.

Table II. Rate Constants for Intramolecular Triplet Energy Transfer

Compd	k_q/k_{et}	k_{et},[a] sec^{-1}
$n = 2$	0.069	7.2×10^{10}
$n = 3$	0.55	1.0×10^{10}
$n = 4$	1.5	3.3×10^{9} sec

[a] Assuming $k_q = 5 \times 10^9\ M^{-1}\ sec^{-1}$.

The detailed mechanism of energy transfer must be able to account for the 20-fold decrease in k_{et} in going from $n = 2$ to $n = 4$. Inspection of molecular models shows that the average distance between the two chromophores remains nearly constant in the compounds in question. However, the number of conformations in

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[10] J. Saltiel, K. R. Newberger, and M. Wrighton, *J. Amer. Chem. Soc.*, **91**, 3658 (1969).

[11] In the case of $n = 3$ and 4, isomerization was accompanied by very inefficient ($\Phi < 0.005$) type II elimination to give acetophenone and the corresponding diene. Though quantitatively unimportant this process is interesting since it corresponds to a photoreaction from T_2 (*i.e.*, the n–π* triplet) in these systems.

[12] The energy of acetophenone $S^1 = 78.5$ kcal/mol; *trans*-β-methylstyrene $S^1 \approx 95$ kcal/mol; acetophenone $T^1 = 73.6$ kcal/mol; *trans*-β-methylstyrene $T^1 = 59.8$ kcal/mol. These values were obtained from J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 297; A. A. Lamola, Ph.D. Thesis, California Institute of Technology, Pasadena, Calif., 1965, p 28.

[13] M. A. El-Sayed, *Accounts Chem. Res.*, **1**, 8 (1968).

[14] Some interaction between the two chromophores in the $n = 2$ compound is indicated by the minor spectral effects noted. This may make the mechanism of the "energy transfer" process in this compound different from that proposed; however, our kinetic results indicate that the $n = 2$ compound behaves like the $n = 3$ and 4 compounds and not like the $n = 1$ compound.

[15] This number can be obtained from the data in the paper by A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

which the two ends of the molecule are nearly in contact decreases greatly with increasing number of methylene groups. In addition, the rate ratio for $n = 3$ in *t*-butyl alcohol is 0.75 as compared to the value of 0.55 in benzene. Since the solvent properties of *t*-butyl alcohol are quite different from those for benzene (for example, the viscosities at 23° are a factor of 10 different[16]), this shows that k_{et} depends to the same extent on these properties, as does k_q. The logical conclusion to be drawn from both of these considerations is that in the $n = 2$–4 compounds intramolecular energy transfer occurs by the same mechanism as bimolecular quenching—namely the exchange mechanism which requires a collision between the donor and acceptor.

The quenching curve for the $n = 1$ compound is composed of two linear portions with differing slopes. These results imply that energy transfer occurs from two different excited states in this compound. Further work is in progress on this compound.

Acknowledgment. We are pleased to acknowledge the support (in part) of this work by National Institutes of Health Grant GM-12988.

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[16] For experimental estimates of diffusion rate constants in tertiary alcohols see P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, **90**, 2232 (1968). Wagner concludes that the diffusion rate constant in *t*-butyl alcohol is somewhat larger than would be calculated from the viscosity.

[17] Alfred P. Sloan Fellow.

[18] National Institutes of Health Predoctoral Fellow, 1965–1968.

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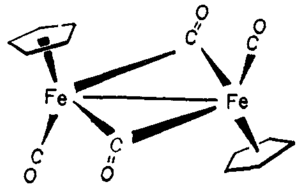
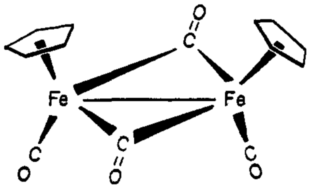
A Definitive Identification of the Structures of Dicyclopentadienyldiiron Tetracarbonyl in Solution

Sir:

It was shown in 1958 that $(C_5H_5)_2Fe_2(CO)_4$ has the molecular structure I in the only crystalline form then recognized.[1] Investigations of the vibrational spectra of solutions of this substance[2,3] showed that some kind and degree of rearrangement of I must occur in solution. Benzene and cyclohexane solutions were shown to contain polar molecules (apparent dipole moment, number averages, 3.1 and 2.4 D).[4] More recently, two new, detailed studies were published. Cotton and Yagupsky[5] studied the CO stretching fundamentals as well as overtones and combinations, by employing CS_2 and heptane solutions, and considered that all their data could be accounted for by assuming that the iron compound in CS_2 solution is almost entirely made up of molecules with structure II plus a trace of some noncentrosymmetric, nonbridged isomer (probably of C_{2v} or C_2 symmetry). The Ru analog was postulated to consist of a roughly equimolar mixture of the same two structures. Fischer, Vogler, and Noack[6] studied the CO stretching fundamentals as a function of temperature. They drew essentially the same conclusions as to the presence of two isomers in solution, and Noack[7] estimated that the *cis*-bridged isomer is more stable than the nonbridged isomer by ~4 and ~1.5 kcal/mol for the iron compound and its ruthenium analog, respectively. Bryan, *et al.*,[8] have recently confirmed the existence of structure II in a second crystal form obtainable at low temperatures from polar solvents.



I(C_{2h})



II(C_{2v})

The "two-structure" hypothesis for the solutions was soon challenged by Manning,[9] who studied solutions in more polar solvents. On the basis of various small effects (broadenings, occasional splittings, and variations in relative intensities), he was led to propose a "three-structure" model in which those spectral features attributed in the two-structure model to II (or its Ru analog) are now attributed to a mixture of I and II. In our view, Manning's observations fall short of proving the three-structure hypothesis; nevertheless, Manning makes a good case that such a hypothesis is plausible. It thus appeared that some independent and definitive experiment was required. We have carried out such an experiment and give here a preliminary account of the results.

Figure 1 shows the 100-MHz pmr spectrum of $(C_5H_5)_2Fe_2(CO)_4$ as a function of temperature and solvent dielectric constant. The upper four spectra, taken on a solution in $C_6D_5CD_3$–CS_2, show that the single peak observed at 25° collapses and finally separates into two peaks of similar but not equal intensities, which are sharp at ~−75°. These results prove that the solutions contain two species in *comparable* quantities which interconvert rapidly at temperatures above ~−40°. We can see no acceptable alternative to the view that the two interconverting species are I and II and presume that the nonbridged structure is an intermediate through which the interconversion is effected. The bottom spectrum is obtained in a solvent whose dielectric constant is raised by addition of CD_2Cl_2. This should displace the *cis–trans* equilibrium in favor of the *cis* species, and,

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[1] O. S. Mills, *Acta Cryst.*, **11**, 620 (1958).

[2] H. Stammreich, G. Wilkinson, and F. A. Cotton, *J. Inorg. Nucl. Chem.*, **9**, 3 (1959).

[3] K. Noack, *ibid.*, **25**, 1383 (1963).

[4] E. Weiss, H. Hubel, and R. Merenyi, *Chem. Ber.*, **95**, 1155 (1962).

[5] F. A. Cotton and G. Yagupsky, *Inorg. Chem.*, **6**, 15 (1967).

[6] R. D. Fischer, A. Vogler, and K. Noack, *J. Organometal. Chem.*, **7**, 135 (1967).

[7] K. Noack, *ibid.*, **7**, 151 (1967).

[8] R. F. Bryan, P. T. Greene, D. S. Field, and M. J. Newlands, *Chem. Commun.*, 1477 (1969).

[9] A. R. Manning, *J. Chem. Soc., A*, 1319 (1968); 1498 (1969).