ethylene C–H bonds in competition with reaction at the double bond is consistent with the liquid phase experiments of Closs, et al.[3] The isomerization of cyclopropane formed by the addition of CH_2 to C_2H_4 is readily observed, and, at these pressures, would account for more than half of the original cyclopropane formed. The kinetic parameters, including especially the energies of activation, are not very different for monohalocyclopropanes from those of the pure hydrocarbon. Consequently, the lack of isomerization following CTCl addition to ethylene must result from a considerably lower excitation energy in the excited molecule, reflecting a lower heat of addition to the double bond for monochlorocarbene than in the corresponding CH_2.

An additional major radioactive product was observed from the CH_2ClF–C_2H_4–O_2 samples, with a relative yield compared to the parent of 0.36 ± 0.02. This compound corresponds to a monofluoro C_3 compound, and probably is cyclopropyl-t fluoride, from the reaction with ethylene of CTF formed by the expected elimination of HCl from CHTClF*. Further experiments are being carried out since monofluorocarbene has not yet been reported in the literature.

Pyrolytic decomposition of the molecules CH_2Cl_2 and CH_2ClF presumably will also result in the formation of monohalocarbenes. The recoil tritium method of excitation has the advantage that all of the other molecules in the system except those specifically excited by tritium reaction have a much lower state of excitation, determined by the ambient temperature of irradiation, and are not expected to undergo subsequent pyrolytic reactions. This is particularly useful and important when the observations are based on molecules (e.g., monohalocyclopropane) whose kinetic parameters indicate comparable or more rapid rates of decomposition than the dihalomethane molecules themselves. The recoil tritium has in addition both the advantages and disadvantages of being a radioactive tracer method: the products have the asset of containing radioactive atoms, and hence can easily be traced; on the other hand, they are formed in negligible quantities unsuitable for further experiments (synthetic, spectroscopic, etc.) requiring macroscopic quantities of the compound.

Yi-Noo Tang,[13] F. S. Rowland[13]

Department of Chemistry, University of Kansas,
Lawrence, Kansas
Department of Chemistry, University of California,
Irvine, California

Photosensitization by Ferrocene.
Photochemistry of Higher Electronic Excited States

Sir:

We wish to report that ferrocene catalyzes the photochemical cis–trans isomerization of piperylene and the dimerization of isoprene. The evidence leads us to suggest that the mechanism for these reactions involves a complex of ferrocene and olefin which absorbs light and is excited to an electronic state considerably higher than the first excited singlet. This excited state dissociates to ferrocene in a triplet state and to a triplet olefin which then isomerizes or adds to a ground-state olefin.

Much recent work has demonstrated the capacity of various substances, called photosensitizers, to promote the isomerization and dimerization of various olefins.[1-4] In many of these cases the mechanism of photosensitization has been shown to involve transfer of energy and multiplicity from the sensitizer to the olefin with resultant excitation of the olefin to its lowest triplet state. In some other cases, e.g., the photoaddition of maleic anhydride to benzene, the reaction proceeds via the triplet state of the complex.[5] The addition of maleic anhydride to cyclohexene has been reported to involve formation of an intermediate complex.[6] Also, recent reports indicate that cuprous chloride and rhodium chloride catalyze photocyclization of 1,5-cyclooctadiene.[7]

We have observed that ferrocene accelerates the photoisomerization of trans-piperylene by a factor of at least five and catalyzes the photodimerization of both piperylene and isoprene. The photolyses were carried out in sealed, degassed Pyrex tubes. A Hanovia 450-watt medium-pressure mercury lamp in a quartz immersion well provided the necessary irradiation. The dimerization reactions were studied using neat olefin solutions; the isomerizations were accomplished using various concentrations of piperylene in solvents such as benzene, decalin, and trans-1,2-dimethylcyclohexane. In a typical isomerization experiment a solution of 1.0 M ferrocene and 0.2 M trans-piperylene in benzene was isomerized 9.3% (corrected for back reaction) in 3 hr. while a similar solution without ferrocene was isomerized 2.0% after 4 hr. The dimerization of isoprene was studied in neat solutions of isoprene that contained 0.05 M ferrocene. If a Pyrex immersion well housed the lamp (minimum wave length 2800 Å.) the reactions were markedly slowed. A uranyl glass filter (minimum wave length 3300 Å.) completely stopped the ferrocene-induced isomerization of piperylene. On the other hand, substitution of quartz for Pyrex tubes accelerated the isomerization reaction by increasing the intensity of the light in the 2800 Å. region.

The photostationary state observed in ferrocene-sensitized piperylene isomerization and the product distribution for the ferrocene-sensitized dimerization of isoprene are the same as those reported in cases where the energy of the triplet state of the sensitizer exceeds the triplet-state energy of the olefin so that olefin triplet states are easily generated from both isomers ("high energy" sensitizers).[1,2,8] Thus, we find that ferrocene-

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(6) R. Robson, P. W. Grubb, and J. A. Barltrop, J. Chem. Soc., 2153 (1964).
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(8) The value for the percentage cyclobutanes and cyclooctadienes reported in ref. 5 is incorrect. The correct value of the dimer composition for a high-energy sensitizer is 92% cyclobutanes and cyclooctadienes (R. S. H. Liu, personal communication).

induced isomerization of piperylene gives a photostationary state that contains 54–55% *trans*-piperylene, and ferrocene-sensitized dimerization of isoprene produces a mixture of dimers that contains 92% cyclobutanes and cyclooctadienes; the remaining dimers are cyclohexenes.

The evidence for the existence of complexes between ferrocene and olefin is twofold. The ultraviolet absorption spectra of mixtures of piperylene and ferrocene in *n*-heptane and *n*-hexane show new absorption between 2200 and 3000 Å. At higher wave lengths no deviation from Beer's law is observed. In the n.m.r. spectrum of *trans*-piperylene, a new methyl doublet appears on the addition of ferrocene. The new methyl doublet is at τ 8.03 ± 0.02, $J = 13 \pm 1$ c.p.s., while the methyl doublet of *trans*-piperylene is at τ 8.25 ± 0.02, $J = 13 \pm 1$ c.p.s.

Ferrocene quenches anthracene triplets ($T_1 \leftarrow S_0$ energy = 43 kcal./mole[9]) at a diffusion-controlled rate[10] which suggests that the lowest triplet state of ferrocene itself does not possess sufficient energy to effect the observed reactions.

Nor do we feel that the ferrocene–olefin complex functions as a sensitizer which excites an uncomplexed olefin molecule to its triplet state. The observation that solutions of ferrocene and olefin obey Beer's law above 3000 Å. implies that the $S_1 \leftarrow S_0$ transitions of ferrocene and complex are isoenergetic in this region. Molecular orbital calculations for ferrocene by Moffitt[11] and Dunitz and Orgel[12] suggest that the $S_1 \leftarrow S_0$ transition of ferrocene requires 45–55 kcal./mole. Experimentally, the longest wave length band of ferrocene is a broad band centered at 4500 Å. (64 kcal./mole).[13] Since the $S_1 \leftarrow S_0$ transitions of ferrocene and complex are probably isoenergetic (involving metal electrons that are not perturbed by complexation), neither the lowest singlet nor its associated triplet, lying at a yet lower energy level, should have sufficient energy to catalyze the observed reactions. It seems unlikely that a higher triplet state of the ferrocene–olefin complex acts as a sensitizer for another olefin molecule since a higher triplet would decay[14] before encountering a free piperylene molecule.

Another possibility is that ferrocene acts as a sensitizer because the heavy iron atom facilitates intersystem crossing of a neighboring piperylene. We have eliminated this possibility because the excitation of *trans*-piperylene to its triplet state requires only 58.8 kcal./mole (4860 Å.)[15] whereas light of much higher energy (*e.g.*, 2800–3300 Å.) is required for reaction.

In view of these considerations, we propose the following mechanism for reactions of dienes sensitized by ferrocene

$$\text{ferrocene} + \text{diene} \rightleftharpoons \text{complex} \qquad (1)$$

$$\text{complex} + h\nu \longrightarrow \text{complex}^{Sn} \qquad (2)$$

$$\text{complex}^{Sn} \longrightarrow \text{ferrocene}^{Tn} + \text{diene}^{Tn} \qquad (3)$$

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$$\text{diene}^{Tn} \longrightarrow \text{diene}^{T_1} \qquad (4)$$

$$\text{diene}^{T_1} \longrightarrow \text{products} \qquad (5)$$

Reaction 2 is included for the reasons discussed previously. Reaction 3 is proposed to give both ferrocene and the diene in triplet states to conserve multiplicity and because it is the reverse of the observed process of triplet–triplet annihilation.[16,17] Whether these triplets are in higher excited states is a completely open question; reaction 4 may be, therefore, unnecessary. Reaction 5 represents the known reactions of triplet dienes which lead either to isomerization or dimerization, depending on the circumstances.

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J. J. Dannenberg, J. H. Richards
Contribution No. 3183, Gates and Crellin Laboratories of Chemistry
California Institute of Technology, Pasadena California
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Spectroscopic and Kinetic Observation of a Pepsin–Inhibitor Complex

Sir:

We wish to report on the interaction of pepsin (E) with N-(α-acetaminocinnamoyl)-L-diiodotyrosine (N-acetyldehydrophenylalanyl-L-diiodotyrosine) (I). Compound I, a close analog of the excellent pepsin substrate[1] N-acetyl-L-phenylalanyl-L-diiodotyrosine, was prepared from L-diiodotyrosine and the azlactone of α-acetaminocinnamic acid,[2] m.p. 193–195° dec., $[\alpha]^{29}D$ $-38°$ (c 3, 5% ammonia). *Anal.* Calcd. for $C_{20}H_{18}N_2O_5I_2$: C, 38.73; H, 2.93; I, 40.92; mol. wt., 620. Found: C, 38.94; H, 3.31; I, 40.38; mol. wt., 585 (osmometric, in ethanol). The ultraviolet absorption spectrum of I at pH 2, in 3% methanol, showed (mμ) λ_{max} 282 (ϵ 20,550), λ_{min} 252 (ϵ 10,810), λ 315 (ϵ 2770 ± 25).

CH$_3$CONH — C — CONH — CH — COOH
‖
CH   CH$_2$
|
C$_6$H$_5$

X   X

OH

I, X = iodine
II, X = H

The apparent ϵ of I in pepsin-containing solutions is greater than 2770 at 315 mμ.[3,4] Forty-three determinations of the optical density (O.D.$_0$) of such solutions have been made, with [E]$_0$ = 2.42–50.8 × 10^{-5} M and [I]$_0$ = 1.01–19.4 × 10^{-5} M. The experimental data

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(2) The procedure was essentially that of M. Bergmann, F. Stern, and C. Witte, *Ann.*, 449, 277 (1926), for the synthesis of II.
(3) (a) All subsequent data refer to pH 2, 35°, 315 mμ (chosen for experimental convenience). (b) In some runs a very slow change of O.D. with time occurred. The O.D. at $t = 0$ was used in the calculations.
(4) The environment of the cinnamoyl chromophore in cinnamoyl-α-chymotrypsin and -trypsin is such as to produce an enhanced ϵ_{315}, if simple cinnamoyl analogs in dilute aqueous solution are used as reference compounds. See M. L. Bender, G. R. Schonbaum, and B. Zerner, *J. Am. Chem. Soc.*, 84, 2540 (1962), and M. L. Bender and E. T. Kaiser, *ibid.*, 84, 2556 (1962).