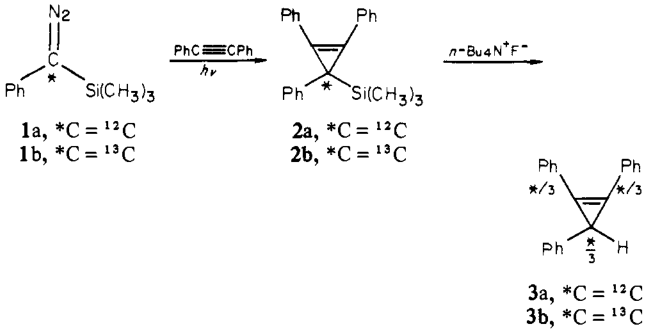
(**1a**)[11] in molten diphenylacetylene. After chromatography on silica gel and recrystallization from pentane at −20 °C, **2a**, mp 106.0–107.0 °C, was obtained in 78% yield.[12] Fluorodesilylation was carried out by heating 100 mg of **2a** in 3 mL of THF at 65 °C for 2 days with 0.6 mL (2.0 equiv) of 1 M tetra-*n*-butylammonium fluoride (Aldrich). An ^{1}H NMR spectrum of the crude reaction mixture after workup showed 1,2,3-triphenylcyclopropene (**3a**) to be the only detectable product. After recrystallization from pentane, **3a**, mp 111.0–112.0 °C (lit.[6] 112–113 °C), was isolated in 74% yield.



1a, *C = ^{12}C
1b, *C = ^{13}C

2a, *C = ^{12}C
2b, *C = ^{13}C

3a, *C = ^{12}C
3b, *C = ^{13}C

Proton abstraction by the putative triphenylcyclopropenyl anion formed in this reaction presumably occurred from the 5% H_2O present in the tetra-*n*-butylammonium fluoride solution. In order to verify that this was the case and to show that hydrogen atoms were not being abstracted from the THF solvent by a radical or diradical species, 0.6 mL of the tetra-*n*-butylammonium fluoride solution was evaporated and dried for 30 min at 0.1 torr. Then 1 mL of D_2O was added, the solution evaporated, and the salt dried again in the same way. The residue was dissolved in 3 mL of THF, and the fluorodesilylation reaction was carried out as before. The ^{1}H NMR and mass spectrum of the triphenylcyclopropene that was isolated showed the incorporation of 0.8 atoms of deuterium at C-3.

In order to probe the symmetry of the putative triphenylcyclopropenyl anion intermediate, ^{13}C-labeled 1,2,3-triphenyl-1-(trimethylsilyl)cyclopropene (**2b**) was prepared by addition of labeled phenyl(trimethylsilyl)diazomethane (**1b**) to diphenylacetylene. The diazo compound was synthesized starting with $^{13}CO_2$ (90% ^{13}C), which was allowed to react with phenylmagnesium bromide. The labeled benzoic acid was reduced to benzyl alcohol, which was converted to benzyl chloride. Formation of the Grignard reagent, reaction with trimethylsilyl chloride,[13] oxidation of the benzyltrimethylsilane product to benzyl trimethylsilyl ketone in two steps,[14] and pyrolysis of the lithium salt of the tosylhydrazone[11] resulted in the production of **1b** in an overall yield of 10% for the eight steps.

When Pyrex-filtered light from a 550-W Hanovia high-pressure mercury arc or from a 300-W General Electric quartz slide projector lamp was used to decompose the diazo compound **1b** in molten diphenylacetylene, the ^{13}C label in the resulting triphenyl(trimethylsilyl)cyclopropene was found by ^{13}C NMR to be totally scrambled. Although thermally induced 1,2 shifts of trimethylsilyl groups in cyclopropenes are known,[15] the modest temperature (65 °C) at which the addition reaction was conducted made such a rearrangement in **2b** unlikely under these conditions. Instead, it seemed probable that photoexcitation of **2b**, whose UV absorption extends out to 400 nm, was responsible for the observed scrambling of the ^{13}C label. Indeed, when a KV 470-nm filter was used with the quartz lamp, decomposition of the diazo compound (λ_{max} = 450 nm) again occurred; but **2b** was obtained with all of the ^{13}C label at C-3.

The **2b** thus prepared was subjected to the fluorodesilylation reaction described above. The upfield portion of the ^{1}H NMR spectrum of the product consisted of two doublets centered at δ 3.23, one with J = 168 Hz and the other with J = 2 Hz. The former corresponds to **3b** with the ^{13}C label at C-3 and the latter to **3b** with the ^{13}C label at C-1 and C-2. Correcting the integral of the central peak for the 10% of unlabeled **3a** hidden under it, gave a ratio of 1:1.8 ± 0.1 for the two integrals. Integration of the ^{13}C NMR spectrum in the presence of $Cr(acac)_3$, a paramagnetic relaxation reagent, gave essentially the same result.

The distribution of ^{13}C label in **3b** is close to the statistical ratio of 1:2.0. Substantial scrambling of the label thus occurs in the transformation of **2b** into **3b** by fluorodesilylation, although the scrambling does not appear to be quite complete. When the fluorodesilylation reaction of **2b** was interrupted after 75% completion and the unreacted **2b** examined by ^{13}C NMR, no scrambling of the label in **2b** was detected. Therefore, scrambling does not take place in the starting material under the reaction conditions. Since trimethylsilyl groups are known to undergo sigmatropic migrations with considerably greater facility than do protons,[16] the absence of detectable scrambling in **2b** renders it highly unlikely that the labeling pattern that is observed in **3b** is the result of scrambling that occurs after proton capture.

The nearly statistical distribution of ^{13}C in **3b** argues against proton capture occurring in an intermediate in which a pentavalent silicon remains bonded to C-3 of the three-membered ring. It would be quite surprising if this type of intermediate reacted with water in such a nonregioselective fashion. Moreover, we have found that 1,2-dimethyl-3-phenyl-3-(trimethylsilyl)cyclopropene[15] fails to undergo fluorodesilylation under the above reaction conditions. This provides further evidence against the rate-determining step involving a transition state that is not substantially stabilized by phenyl substituents on the double bond of the reactant.

We believe that the most economical interpretation of our data is in terms of the formation of a singlet triphenylcyclopropenyl carbanion. Although such a carbanion could conceivably undergo intersystem crossing to the triplet, the fact that proton capture rather than hydrogen atom abstraction apparently occurs suggests that singlet–triplet crossing is not competitive with protonation under our reaction conditions. If a singlet cyclopropenyl anion is, in fact, the reactive species, the nearly statistical distribution of the label in **3b** indicates that pseudorotation must occur faster than protonation. This in turn implies that the barriers to pseudorotation in the anion are small and/or that tunneling[17] makes an important contribution to the pseudorotation process.

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Formation of Photoactive Charge-Transfer Complexes between Methylviologen and Sacrificial Electron Donors. EDTA and Triethanolamine

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In recent years, model systems have been extensively studied that promote the photoreduction of H_2O to H_2 through the use

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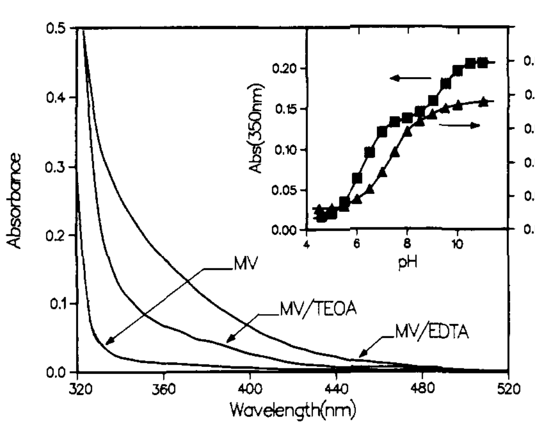

Figure 1. Absorption spectrum (1-cm cell) of 20 mM MV^{2+}, 20 mM MV^{2+} + 350 mM TEOA, and 20 mM MV^{2+} + 100 mM EDTA at pH 10.0. Inset: Absorbance (1-cm cell) at 350 nm as a function of pH for 20 mM MV^{2+} in 100 mM EDTA (■) or TEOA (▲).

of a photosensitizer (such as $Ru(bpy)_3{}^{2+}$), an electron relay (such as methylviologen; 1,1′-dimethyl-4,4′-bipyridinium ion, MV^{2+}), and a sacrificial electron donor (such as EDTA or triethanolamine, TEOA).[1-7] Although complexation of MV^{2+} with a variety of organic electron donors has been known for some time,[8,9] photolysis of the MV^{2+} complexes has only recently received attention.[10-15] We wish to report here the formation of photoactive complexes between MV^{2+} and EDTA or TEOA; upon photolysis, the stable reduced methylviologen cation ($MV^{+}\cdot$) is generated. The formation of charge-transfer complexes between viologen relays and amine-based sacrificial donors could have serious implications for the full understanding of the water-splitting model systems.

Mixtures of MV^{2+} (as the Cl^- salt) and EDTA or TEOA in aqueous solution exhibit a new absorption band, not shown to any degree by these species alone, with a tail extending to 500 nm (Figure 1).[16] The absorbance is a function of pH with a profile consistent with the requirement that the deprotonated amine function for TEOA (and/or carboxylate function for EDTA) is involved in the complexation. A Benesi–Hildebrand analysis (plot of $1/\Delta$Abs vs. 1/[donor])[17] for the absorbance at pH 11.2 for EDTA and pH 10.2 for TEOA (assuming a 1:1 complex stoichiometry) yields the following estimates for K_{eq} and ϵ_{350}: 68 M^{-1} and 11 M^{-1} cm^{-1} for the EDTA system and 0.3 M^{-1} and 50 M^{-1} cm^{-1} for the TEOA system.[18] The value of K_{eq} is significantly reduced in less alkaline solution; for the EDTA system, K_{eq} = 5.3 M^{-1} at pH 4.6.

Table I. Quantum Yields for the Formation of $MV^{+}\cdot$ from the Photolysis of Charge-Transfer Complexes of MV^{2+} with EDTA and TEOA[a]

$[MV^{2+}]$, M	[donor], M	pH	Φ[b]
	EDTA[c]		
0.020	0.10	4.6	0.086
0.020	0.10	8.0	0.032
0.020	0.10	10.0	0.035
0.010	0.10	10.0	0.023
0.0050	0.10	10.0	0.012
	TEOA[d]		
0.020	0.10	10.0	0.018[c]
0.16	0.17	8.7	0.010
0.16	1.40	8.7	0.0045
0.19	3.50	8.7	0.0018

[a] Excitation at 366 nm. [b] Average (±15%) of 3–4 determinations. [c] T = 22 °C. [d] T = 30 °C except where otherwise noted.

Photolysis of deaerated (freeze–pump–thaw or argon purged) solutions of MV^{2+} and EDTA or TEOA at 366 nm yields $MV^{+}\cdot$, which persists for hours. After an induction period corresponding to the formation and disappearance of 1–3 μM $MV^{+}\cdot$ ascribed to the presence of an adventitious quencher, the generation of $MV^{+}\cdot$ is linear with irradiation time; $[MV^{+}\cdot]$ was measured at 395 and 605 nm by using molar absorptivities of 4.21×10^4 and 1.37×10^4 M^{-1} cm^{-1}, respectively.[20] From these data, quantum yields of formation of $MV^{+}\cdot(\Phi)$, relative to ferrioxalate actinometry, were determined as a function of pH and substrate concentration and are summarized in Table I.

The photoactive complexes formed between MV^{2+} and EDTA or TEOA are clearly charge transfer in nature. The low value of K_{eq} for TEOA (pK_a 7.9) in alkaline solution is of the order of magnitude seen for complexes in which at least one of the partners is neutral.[8] Complexation of MV^{2+} with EDTA is enhanced due to ion pair formation; the pK_a values for successive deprotonation of EDTA are 2.0, 2.8, 6.1, and 10.2.[21] Thus, in alkaline solution, EDTA is present as −3/−4 anions.

The values of Φ at 366 nm are a complex function of pH and the composition of the solution. As might be expected, the various protonated and deprotonated forms of the complexes, having different propensities for oxidation–reduction and complexation, exhibit different efficiencies of release of the radicals from the solvent cage within which they were created. Most interesting is the general observation that, at constant pH, the quantum yield exhibits a marked decrease as the [donor]/[acceptor] ratio is increased, suggesting that excess donor can quench the excited state(s) of the complex and/or that a series of complexes are formed, each with its own photoactivity. In the TEOA case, the effect of medium viscosity in the high-concentration regime may alter the efficiency of radical pair separation into the bulk solution. It should be noted that the photoreduction yield for MV^{2+}/TEOA is temperature dependent: Φ = 0.0014 for 0.16 M MV^{2+} and 1.4 M TEOA at 6 °C.

The mechanism of irreversible photogeneration of MV^{+} in alkaline solution follows the pattern of the popular photosensitization system (designating EDTA or TEOA as R_2NCH_2–).[3,4,6,22]

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$$\mathrm{MV^{2+} + R_2NCH_2{-}} \rightleftarrows \mathrm{[MV^{2+},R_2NCH_2{-}]} \qquad (1)$$

$$\mathrm{[MV^{2+},R_2NCH_2{-}]} \overset{h\nu}{\rightleftarrows} \mathrm{[MV^{+\cdot},R_2\dot{N}^+CH_2{-}]} \qquad (2)$$

$$\mathrm{[MV^{+\cdot},R_2\dot{N}^+CH_2{-}]} \rightarrow \mathrm{MV^{+\cdot} + R_2\dot{N}^+CH_2{-}} \qquad (3)$$

$$\mathrm{MV^{+\cdot} + R_2\dot{N}^+CH_2{-}} \rightarrow \mathrm{MV^{2+} + R_2NCH_2{-}} \qquad (4)$$

$$\mathrm{R_2\dot{N}^+CH_2{-}} \rightarrow \mathrm{R_2N\dot{C}H{-} + H^+} \qquad (5)$$

$$\mathrm{MV^{2+} + R_2N\dot{C}H{-}} \rightarrow \mathrm{M\overset{+}{V}^{+\cdot} + R_2N{=}CH{-}} \qquad (6)$$

$$\mathrm{R_2\overset{+}{N}{=}CH{-}} \rightarrow \text{products} \qquad (7)$$

In alkaline solution, where reaction 5 is believed to be faster than reaction 4,[22,23] the observed quantum yield is twice the yield of primary photoinduced electron transfer (reaction 3). Although the absolute yields of electron transfer are low, it is clear that they are a sensitive function of solution medium. Where complexation is important in the photosensitized system, one would also expect the yield of radicals to be a function of solution medium. Indeed, we have found that to be the case in the $\mathrm{Ru(bpy)_3^{2+}/MV^{2+}/EDTA}$ system at high ionic concentrations.[24] We have also found that photoactive charge-transfer complexes are formed between $\mathrm{MV^{2+}}$ and cysteine, mercaptoethanol, and carboxylic acids.

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(24) Mandal, K.; Hoffman, M. Z., manuscript in preparation.

*Book Reviews**

Advances in Chemical Physics. Volume XLIV. Edited by I. Prigogine (University of Brussels and University of Texas, Austin) and S. A. Rice (University of Chicago). John Wiley and Sons, New York. 1980. 671 pp. $65.00.

It is simply a matter of routine to review an established series such as this. There are five chapters in this review volume.

The text begins with a chapter by L. Englebrecht and J. Hinze, titled Molecular Properties Observed and Computed. The article details formulas derived through ab initio methods for the computation of various molecular properties analogous to different spectroscopic constants leading to quantitative studies of coupling effects which are useful in the interpretation of spectroscopic results. Rightly, little emphasis is placed on spectroscopic quantities that are readily accessible from experiment.

The second chapter is on Generalized Langevin Equation and Many-Body Problems in Chemical Dynamics by S. A. Adelman. New theoretical methods largely developed by the author and addressed to problems pertaining to many-body dynamics applicable to the liquid-state and solid-state chemical phenomena are reviewed. The methods are developed within the regime of continuum mechanics and formulated along linear response theory with a harmonic perturbing force utilizing, as usual, correlation functions. Despite the continuum approach, the method is capable of generating results related to chemical dynamics on molecular time scales. The simplicity of the new approach is contrasted with the complex conventional classical trajectory approaches of Liouvillean mechanics in appendices. The article provides an impressive review which will prove useful to beginners in the field of non-equilibrium statistical mechanics. The heavy reliance on established mathematical techniques (e.g., Fourier and Laplace transforms) and the generous inclusion of intermediate results give increased clarity. There are, of course, parts where the urge to maintain uniformity has been realized at some expense. For example in Section C, the relations (II.43 and II.44) between the Einstein frequency ω_e (the short-time approximation), the adiabatic frequency Ω (the long-time approximation), and the Debye frequency ω_D can readily be generated by the simple equation:

$$\omega^n = \frac{\int_0^{\omega_D} \omega^n \rho(\omega)\, \mathrm{d}\omega}{\int_0^{\omega_D} \rho(\omega)\, \mathrm{d}\omega}$$

$$\omega = \omega_e,\ n = 2;\ \omega = \Omega,\ n = -2$$

where the spectral density $\rho(\omega) \propto \omega^2$ without the need to use correlation functions. However, the latter approach would appear indispensible for the solution of the intermediate case. Fairly complex applications of the theory are discussed.

An article titled Experimental and Theoretical Studies of Roto-translational Correlation Functions by M. Evans, G. Evans, and R. Davies occupies the third chapter. This review provides another treatment of non-equilibrium statistical mechanics of condensed phases, but this time specializing on molecular dynamics associated with mesophases such as plastic and liquid crystals. The approach is essentially conventional via Liouville and Fokker–Planck equations. The strength of the models developed is demonstrated by the remarkable agreement between results from theory and experiment pertaining to far infrared absorption spectroscopy.

The fourth chapter, On a Theoretical Description of Solvated Electrons, by A. M. Brodsky and A. V. Tsarevsky discusses the theoretical treatment of thermalized excess electrons in disordered condensed phases which do not exhibit intrinsic electron conductivity.

The final chapter, by A. E. Hansen and T. D. Bouman, is titled Natural Chiroptical Spectroscopy: Theory and Computations. The theoretical approach in this review, which is essentially spectroscopic (predominantly electronic), covers only ordinary absorption and circular dichroism (CD) and the relation of these quantities to the structure of organic and biological chiral molecules.

In conclusion, all the articles contributed have maintained the high standard expected of these series and the reviews strongly reflect the influence of contributions by their authors in the field.

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Topics in Current Chemistry. Volume 102. Inorganic Ring Systems. Edited by F. L. Boschke et al. Springer-Verlag, Berlin, Heidelberg, and New York. 1982. 237 pp. $41.00.

This book contains six major review articles on various aspects of the chemistry of non-metal inorganic ring systems. Each contribution is based on a plenary lecture of the third Inorganic Ring Systems (IRIS) meeting held in Graz, Austria, in August of 1981. The contents include: Up-to-date Improvements in Inorganic Ring Systems as Anticancer Agents, by J.-F. Labarre (87 pages, 83 references); Phosphorus(III)–Nitrogen Ring Compounds, by R. Keat (27 pages, 121 references); Sulfur–Nitrogen Anions and Related Compound, by T. Chivers and R. T. Oakley (30 pages, 114 references); Homocyclic Sulfur Molecules, by R. Steudel (27 pages, 96 references); Cyclic Selenium Sulfides, by R. Stendel and R. Laitinen (20 pages, 80 references); and Polyhedral Oligosilsesquioxanes and Their Homo Derivatives, by M. G. Voronkov and V. I. Lavrent'yev (37 pages, 98 references). An author index for Volumes 101 and 102 is also included.

Each of the articles is written by a recognized authority in the area. Consequently, the content accurately reflects the nature and direction of the research in the subjects under consideration. However, as one might expect, the emphasis is often on work from the authors' own laboratories. The review of sulfur–nitrogen anions is a particularly welcome addition. In recent years, there has been a rapid growth in information on sulfur–nitrogen rings which has been, in part, stimulated by interest in polysulfur nitride. This review contains a concise summary of information on reactions of sulfur–nitrides and of molecular orbital models which allow for the introduction of a certain amount of logical organization into the bewildering array of observations in this area. The chemistry of phosphorus(III)–nitrogen rings with particular emphasis on the complex conformational possibilities inherent in these systems is well presented. A summary of information and approaches to the development of inorganic rings as anticancer agents is concerned primary with the aziridino phosphosphazenes and phosphathiazenes. Subjects range from synthetic,

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*Unsigned book reviews are by the Book Review Editor.