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Electron Donor and Acceptor Induced Fluorescence Quenching and Charge Carrier Photogeneration in X-Metal-Free Phthalocyanine

Rafik O. Loutfy*[1a] and E. Roland Menzel[1b]

Contribution from the Xerox Research Centre of Canada, Mississauga, Ontario, Canada, L5L 1J9, and the Department of Physics, Texas Tech University, Lubbock, Texas 79409. *Received October 15, 1979*

Abstract: Fluorescence and charge carrier photogeneration efficiency of X-metal-free phthalocyanine (X-H_2Pc) surface doped with 2,4,7-trinitrofluorenone (TNF) have been examined. The carrier generation efficiency increased with an increase in TNF concentration, while the fluorescence was quenched. The data are interpreted in terms of singlet exciton diffusion to the surface of X-H_2Pc particles followed by exciplex formation at the electron-acceptor site. Subsequent exciplex dissociation into charge carriers increases the carrier photogeneration efficiency by as much as a factor of 3. Light was converted into useful work by a photoinduced electron transfer reaction at the surface of an organic semiconductor, S, such as $S^* + Q \rightarrow S^+ + Q^-$. Charge separation at the semiconductor surface under the influence of a photovoltaic barrier potential prevented the usually fast back-reaction (charge recombination). Changes in the photogeneration efficiency and fluorescence of X-H_2Pc were found also on doping with electron acceptors such as *o*-chloranil, tetracyanoethylene, and tetracyanodimethane as well as with electron donors such as tetramethyl-*p*-phenylenediamine and *N,N'*-diphenyl-*N,N'*-di(*m*-tolyl)-*p*-benzidine.

Introduction

A number of studies have indicated that the conductivity of organic semiconductors may be significantly altered by the presence of impurity materials.[2a] For example, Calvin, Kearns, and Tollin[2b] have shown that the addition of *o*-chloranil to the surface of films of metal-free phthalocyanine (H_2Pc) increases the dark conductivity by as much as 10^7 and increases the steady-state photoconductivity by 10^5. Similarly, the effects of oxygen, chlorine, and many other oxidizing agents (electron acceptors) on the conductivity of a number of aromatic hydrocarbons, including phthalocyanines, have been examined. These effects have been interpreted as due to an increase in the mobility of charge carriers caused by the oxidizing agent.

The interest in the effect of electron acceptors on the photoconductivity of organic semiconductors stems from the fact that aggregates of porphyrin-like molecules (i.e., chlorophyll) and oxidizing agents, such as quinones, coenzyme Q, etc., as well as reducing agents (e.g., carotenoids), occur together in photosynthetic systems, and their interaction may be of importance in the primary quantum conversion process.

The fluorescence emission of polycrystalline powders of metal-free phthalocyanine (analogue of chlorophyll) has recently been reported.[3] The observation of luminescence of solid H_2Pc can be a useful probe of charge carrier photogeneration.[4] The polycrystalline X form of H_2Pc exhibits unique electrical and photoelectrical properties.[5] A charge carrier photogeneration efficiency of 0.25 at an internal field of 30 V/μm has been observed in X-H_2Pc Schottky barrier sandwich cells.[6]

Based on electric-field-induced fluorescence quenching measurements on X-H_2Pc, it has been suggested that the first excited singlet state of H_2Pc is the direct precursor of photogenerated charge carriers.[4] A mechanism in which singlet excitons form geminate electron–hole pairs which dissociate into free carriers has been proposed.[7] In this model, both the geminate ion pair generation and its dissociation into free carriers are assumed to be electric field dependent.

In this paper we report luminescence spectroscopic and photoelectric measurements on a series of X-H_2Pc samples to which several oxidizing or reducing agents (electron acceptors or donors) were added. The objective of this work was to gain further understanding of the mechanisms of charge carrier photogeneration in metal-free phthalocyanine. The combination of fluorescence quenching and photoconductivity measurements should yield insight which neither fluorescence quenching alone nor photoconductivity alone can provide unambiguously.

Experimental Section

The organic semiconductor used in the present studies was X-metal-free phthalocyanine powder (Figure 1A) which was obtained as described by Byrne and Kurz.[8] The additives were applied to X-H_2Pc powder by adding a known quantity of X-H_2Pc to a methylene chloride solution of the additive. The slurry was ground in a mortar until all the solvent evaporated. The additive is thus distributed over the surface of the particles. The remaining solid was gently ground to a fine powder.

The fluorescence spectra of powders placed in 2-mm-i.d. glass tubes were obtained using sample excitation with a 2.5-mW He–Ne laser (λ 6328 Å). The sample luminescence was admitted to a 0.5-m McPherson double monochromator (1-μm grating blaze) equipped with a cooled S-1 response photomultiplier. The signal at 8150 Å was measured with a photon-counting apparatus. Measurements were made at room temperature.

The photoelectrical measurements were carried out on cells shown in Figure 1B, in which a thin (1 μm) film of X-H_2Pc particles (60% by weight) dispersed in poly(vinyl acetate) was sandwiched between NESA (SnO_2/Sb, Pittsburgh Glass) and a semitransparent aluminum electrode (60–100 Å), *T* 40–10%). The electron-acceptor additives were added to the polymer matrix during the organic film fabrication process. Details of the device fabrication are described in ref 6. The samples were illuminated from the aluminum side with 620-nm light. The light source was a 500-W Oriel Xe lamp equipped with a Ditric optics band-pass filter. A thin photoactive Schottky barrier region (~320 Å) is formed at the Al/H_2Pc interface, generating an internal field of about 35 V/μm. No external bias potential was applied to the cells. The photocurrents, J_{ph}, were measured with a Keithley Model 616 electrometer. The incident light intensity and the transmission of the Al electrode were measured using an Alphametrics Model 1010 radiometer equipped with a PS1100 calibrated light probe.

The photogeneration efficiencies were calculated according to

$$\eta = \frac{J_{ph}\ (\mathrm{A/cm^2})}{I_T\ (\mathrm{W/cm^2})}\ \frac{1}{0.499}$$

(1 W of 620-nm light/cm^2 generates 0.499 A/cm^2) where I_T is the

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[1] (a) Xerox Research Centre of Canada; (b) Texas Tech University.

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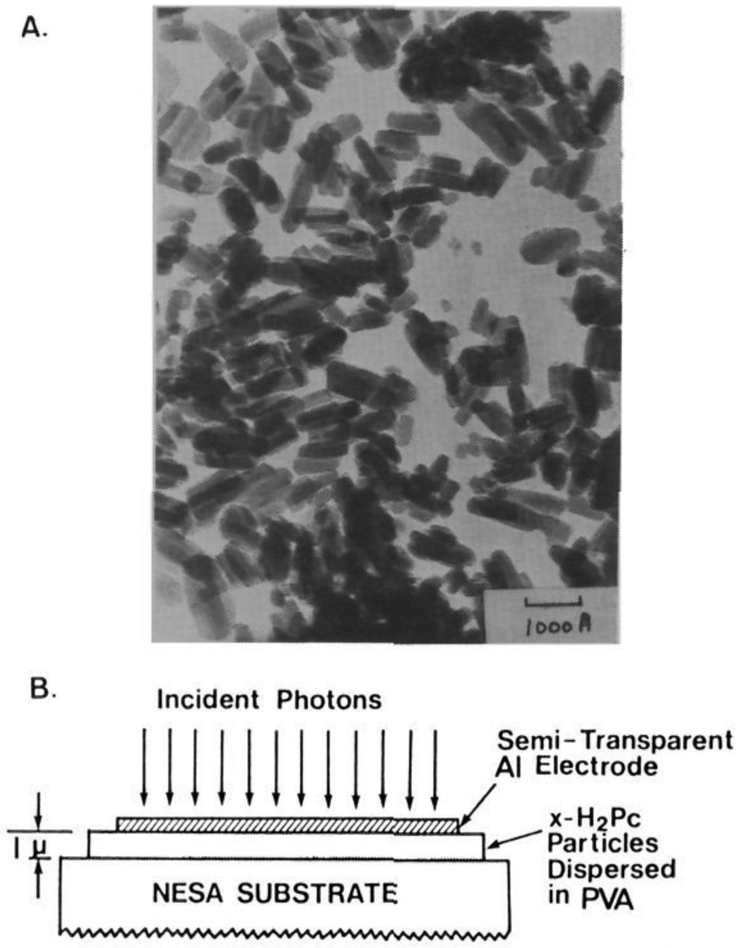

Figure 1. (A) Electron micrograph of X-H_2Pc particles. (B) Side view of a NESA/X-H_2Pc, PVA/Al photovoltaic cell.

Table I. Fluorescence Quenching of X-H_2Pc by Electron Acceptors and Donors

additive[a]	$\Delta F/F^0$ [b]	η, %
Electron Acceptors		
o-chloranil (*o*-Ch)	0.92	87
tetracyanoethylene (TCNE)	0.88	
2,4,7-trinitrofluorenone (TNF)	0.86	61
tetracyanoquinodimethane (TCQM)	0.77	
2,4-dinitrophenol (DNP)	0.73	
Electron Donors		
tetramethylphenylenediamine (TMPD)	0.90	
N,N'-diphenyl-*N,N'*-di(*m*-tolyl)-*p*-benzidine (*m*-TBD)	0.48	32

[a] The additive concentration corresponds approximately to a one monolayer surface coverage. [b] F^0 is the fluorescence intensity of X-H_2Pc and ΔF is the decrease in fluorescence due to the presence of a monolayer of the additive.

Table II. Dependence of X-H_2Pc Charge Carrier Photogeneration Efficiency, η, Fluorescence Intensity, *F*, Exciplex Formation Probability, ϕ_{CT}, and Exciplex Dissociation Efficiency to Free Carriers, ϕ(E), on TNF Concentration

TNF, mg/g	η, %[a]	F[b]	ϕ_{CT}	ϕ(E)
0	27	3.9	0.00	0.00
33	54	0.70	0.82	0.33
67	66	0.86	0.86	0.45
133	75	0.47	0.88	0.55
267	82	0.40	0.90	0.72

[a] Reproducibility was better than ±5%. [b] From the solid line, Figure 2.

intensity of the light transmitted through the electrode. In arriving at the above equation we assumed that all the light is absorbed within the barrier region. This is a good assumption in view of the high molar extinction coefficient of the material. At the low light levels used in the photoconductivity measurements, and consequently low current density, the current flow is not significantly impeded by the device series resistance.

The fluorescence of X-H_2Pc doped with the electron acceptors 2,4,7-trinitrofluorenone (TNF), *o*-chloranil, tetracyanoquinodimethane, tetracyanoethylene (TCNE), and 2,4-dinitrophenol and the electron donors tetramethyl-*p*-phenylenediamine and *N,N'*-diphenyl-*N,N'*-di(*m*-tolyl)-*p*-benzidine were examined. In all cases the concentration of the additives was that required to give a monolayer coverage of the surface of phthalocyanine particles. This was estimated assuming the additive molecules to be flat and covering an area of X-H_2Pc particles surface equivalent to their molecular dimensions. The molecular dimensions of the additives were estimated using molecular models and the surface area of X-H_2Pc was measured to be 69 m^2/g by gas adsorption techniques.[9]

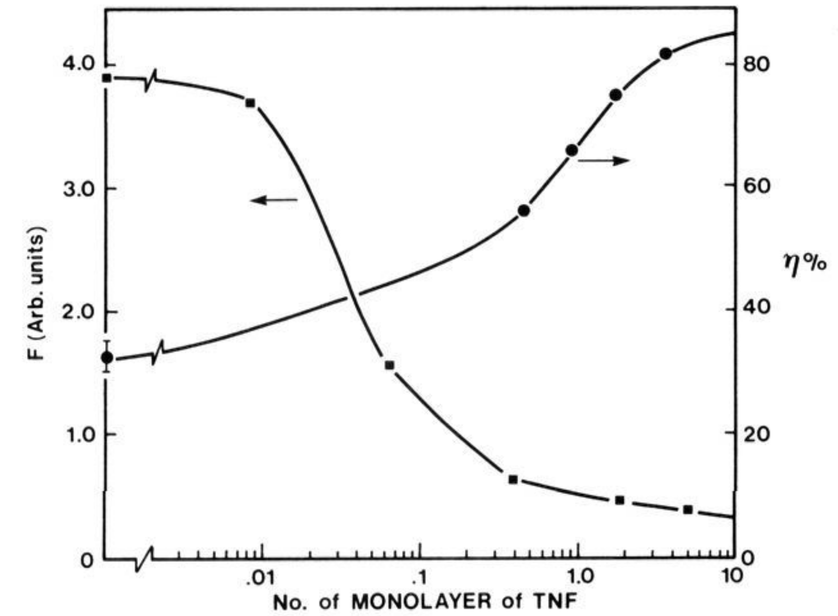

Figure 2. The dependence of X-H_2Pc fluorescence intensity and photogeneration efficiency on TNF concentration.

In one experiment a series of samples of X-H_2Pc containing various concentrations of TNF were prepared and both the fluorescence and photocurrent were measured as a function of TNF concentration. Photocurrents were measured also for X-H_2Pc doped with *o*-chloranil and *N,N'*-diphenyl-*N,N'*-di(*m*-tolyl)-*p*-benzidine.

In X-H_2Pc samples to which different oxidizing and reducing agents were added, the presence of the additives quenched the fluorescence of X-H_2Pc in all cases, but to different degrees depending on the nature of the additive. The relative decrease in the fluorescence of X-H_2Pc ($\Delta F/F^0$) as a function of the nature of the additives is given in Table I. The most effective fluorescence quencher was *o*-chloranil followed by TCNE and TNF.

The dependence of the fluorescence intensity of X-H_2Pc on trinitrofluorenone (TNF) concentration is given Table II and shown in Figure 2. The fluorescence decreased with TNF concentration at concentrations ≤135 mg of TNF/g of X-H_2Pc. At higher TNF concentrations (greater than one monolayer surface coverage, assuming homogeneous coverage) the fluorescence quenching leveled off.

The variation of the room-temperature steady-state photocurrent, J_{ph}, and photogeneration efficiency, η, of TNF-doped X-H_2Pc with TNF concentration is also shown in Figure 2 and the data are listed in Table II. The charge carrier photogeneration efficiency increased with increase of TNF concentration. The increase in η leveled off at high dopant concentration. The spectral response of photoconductivity in doped samples followed the absorption spectrum of pure phthalocyanine. This indicates that no spectral sensitization by the dopant takes place.

The photogeneration efficiencies of X-H_2Pc samples doped with *o*-chloranil and *N,N'*-dipenyl-*N,N'*-di(*m*-tolyl)-*p*-benzidine are also given in Table I for comparison.

Disucssion

Perhaps the most salient feature of the obtained results is the increase in charge carrier photogeneration efficiency on addition of electron donors or acceptors *concomitant* with a decrease in H_2Pc fluorescence in all samples subjected to both measurements. This correlation indicates that the fluorescence quenching is not simply a matter of quenching by energy transfer. Instead, the correlation suggests that the fluorescence quenching is intimately connected with photogeneration of charge carriers.

In the ensuing discussion we propose a mechanism to account for this correlation. It should be recognized at the outset that the correlation between photogeneration of carriers and fluorescence data for TNF-doped X-H_2Pc is only semiquantitative because fluorescence quenching and photogeneration efficiency at high dopant levels lead to saturation. This is not surprising since at high concentration greater than one monolayer surface coverage

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(9) J. Harbour, Xerox Research Centre of Canada, private communication.

of H_2Pc particles occurs. On the other hand, low dopant levels could not be assessed by photoconductivity measurements because at the high "built-in" Schottky barrier field the carrier generation efficiency for undoped H_2Pc is already high. Thus only a small quantitatively useful concentration range overlap for the two sets of data exists. The ensuing model is thus necessarily a simplified one.

Fluorescence Quenching. Both direct energy transfer and radiation reabsorption mechanisms can be eliminated as responsible for the observed fluorescence quenching of X-H_2Pc by the dopants used. In all cases, the singlet energy of the dopant is much higher than that of X-H_2Pc. Fluorescence quenching may be explained in the following manner. The oxidizing and reducing power of phthalocyanine increases significantly on excitation and therefore it may form exciplexes with electron donors and electron acceptors, respectively. The relative ease of exciplex formation between excited H_2Pc and electron acceptors would be, among other things, a function of the electron affinity of the acceptor and the ionization energy of the excited H_2Pc.[10] Similarly, the probability of exciplex formation between excited H_2Pc and electron donors would depend on the ionization energy of the donor and the electron affinity of excited H_2Pc. The fluorescence quenching data in Table I show that different additives quench H_2Pc fluorescence with different efficiencies. This is in part due to differences in their oxidizing and reducing power. However, factors such as orientation and aggregation cannot be ignored. The mechanism proposed above postulates that the decrease in fluorescence intensity of excited H_2Pc is due to the annihilation of singlet excitons at the surface of the particles at the dopant sites to give excited charge-transfer complexes (exciplexes). Competing singlet deactivation routes are

$$S_1 \xrightarrow{\phi_F} S_0 + h\nu \tag{1}$$

$$S_1 + Q \xrightarrow{\phi_{CT}} (S^{\mp}{\cdot}Q^{\pm})^*(\text{exciplex}) \tag{2}$$

where Q is the quencher and S_0 and S_1 are the ground and first excited singlet state of H_2Pc. The observed fluorescence quenching dependence on TNF concentration is readily understood qualitatively in terms of the surface coverage by the electron acceptor. Excitons diffuse from the site of absorption (the bulk) in H_2Pc particles to the surface. Quenching at the surface depends on the distance an exciton has to migrate along the surface to encounter a TNF molecule. We envisage the exciplex formed according to relation 2 to dissociate either to form free charge carriers or to regenerate S_0. Dissociation to regenerate S_1 cannot be significant because of the large fluorescence quenching. To account for this quenching (as much as 90% in some cases), the above interpretation requires that the exciton migration range be large. Let us examine whether this is to be expected in H_2Pc.

Because of the structural and spectral similarity between H_2Pc and chlorophyll, the critical distance for singlet energy transfer in H_2Pc is likely very similar to that in chlorophyll, estimated to be 80 Å.[11] (Explicit calculation for H_2Pc yields a value of about 85 Å.) For solid H_2Pc the distance between molecules is some 6–11 Å; i.e., the concentration is about a factor of 10^3 higher than the critical concentration for energy transfer. Forster's theory[11] of energy transfer (dipole–dipole energy transfer) predicts that the production of fluorescence from the primary molecules, i.e., those which acquired energy by light absorption rather than energy transfer, is proportional to $(C_0/C)^2$, where C_0 is the critical concentration. This ratio is thus roughly 10^{-6}; i.e., only one in 10^6 excited molecules emits from the primary site. We can estimate an exciton migration range of 400 Å for solid H_2Pc. Exciton diffusion lengths of 200 Å have been reported for thin-film H_2Pc cells.[12,13] We have obtained estimates of the exciton diffusion length of 300 ± 100 Å from computer fitting of photoconductivity action spectra[14] using expressions similar to those given by Fan and Faulkner.[12] In view of the size of the H_2Pc particles (1000 × 300 × 300 Å, Figure 1A) this is a large migration range, as required for our interpretation. One might consider a role of quenchers less direct than that implied by reaction 2 by supposing that electron donors or acceptors form ground-state charge-transfer complexes at the H_2Pc particles surface.

$$S_0 + Q \rightleftharpoons S^{\pm}{\cdot}Q^{\mp}\ (\text{ground-state charge-transfer complex}) \tag{3}$$

Such complexes would act as electric dipoles with local fields which could be as large as 300 V/μm in their vicinity. Excitons migrating to molecules within such large fields would directly dissociate into free carriers.

We have measured room-temperature solution absorption and fluorescence spectra of pure H_2Pc and H_2Pc mixed with TNF at various concentrations. While the H_2Pc fluorescence decreased with addition of TNF, no change at all was found in the H_2Pc absorption spectra. These findings are consistent with exciplex formation, but not with substantial ground-state charge-transfer complex formation, unless the ground-state charge-transfer complex has an absorption spectrum essentially indistinguishable from that of H_2Pc and is essentially nonfluorescent. If this were the case, then the fluorescence lifetime of H_2Pc in the pure and mixed solutions should be the same. We have measured such lifetimes using a phase fluorimetric technique reported earlier.[15] The observed ratio between the lifetimes of H_2Pc in the pure solution (τ_0) and in the mixed solution (τ) was $\tau_0/\tau = 1.4$, with $\tau_0 = 5.5$ ns. The corresponding ratio of fluorescence intensities was 1.6. We deduce that no significant ground-state charge-transfer complex formation occurs.

Effect of Oxidizing and Reducing Agents on X-H_2Pc Charge Carrier Photogeneration Efficiency. As described earlier, the fluorescence quenching of X-H_2Pc upon the addition of dopant is accompanied by an increase in the charge carrier photogeneration efficiency. The photoelectric measurements were carried out under high internal electric field (35 V/μm), which facilitates dissociation of ion pairs into free carriers. This fixed field arises from Schottky barrier formation at the Al/H_2Pc interface.

In the absence of dopant, an H_2Pc molecule in the first excited singlet state, S_1, may either decay to a geminate ion pair or relax through radiative or nonradiative decay to the ground state. The geminate ion pair may dissociate to form free charge carriers, to regenerate S_1, or to S_0.

In the presence of surface dopant, excitons diffuse to the surface and are captured by the quencher with a probability ϕ_{CT}. ϕ_{CT} depends on the dopant concentration.

We have

$$S_1 + Q \xrightarrow{\phi_{CT}} (S^{\pm}{\cdot}Q^{\mp})^* \tag{4}$$

$$(S^{\pm}{\cdot}Q^{\mp})^* \xrightarrow{\phi(E)} \text{free carriers} \tag{5}$$

$$(S^{\pm}{\cdot}Q^{\mp})^* \xrightarrow{1 - \phi(E)} S_0 + Q \tag{6}$$

where $\phi(E)$ is the probability of exciplex dissociation into free charge carriers.

In the absence of quenchers we have a fluorescence intensity F^0 and carrier generation efficiency η^0. Addition of quencher to the system leads to a fluorescence F

$$F = F^0(1 - \phi_{CT}) \tag{7}$$

and carrier generation efficiency η:

$$\eta = \eta^0 + \phi_{CT}\phi(E) \tag{8}$$

ϕ_{CT} values for various dopant concentrations, obtained from eq

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[10] The ionization energy of an excited state is usually less than that of the ground state by an amount equivalent to the excitation energy.

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7 and Figure 2, are listed in Table II. Using these values of ϕ_{CT} and eq 8, values of $\phi(E)$ as a function of dopant concentration are obtained. These are listed in Table II also. The increase of $\phi(E)$ with increasing dopant level indicates that the dopant aids not only geminate ion pair formation but also ion-pair dissociation into free charge carriers. This is perhaps not surprising since TNF is known to be an electron transporting molecule.

In summary, the aforementioned results show that electron donors and acceptors strongly quench the fluorescence of solid metal-free phthalocyanine. The fluorescence quenching is attributed to the formation of exciplexes at the surface. The probability of exciplex formation with TNF at a monolayer coverage was found to be high, approaching 0.87. Photoconductivity and fluorescence measurements indicate that the exciplexes decay to regenerate the singlet ground state and in the presence of a field to form free charge carriers. The carrier photogeneration efficiency of X-H_2Pc increased by as much as a factor of 3 in the presence of TNF. Perhaps the principal mechanism of charge carrier photogeneration in X-H_2Pc is extrinsic, involving exciplexes with electron acceptors such as oxygen.

α-Lithiosilanes. 4. Silaethylene Cycloadditions with Conjugated Dienes

Paul Ronald Jones,* Thomas F. O. Lim, and Richard A. Pierce

Contribution from the Department of Chemistry, North Texas State University, Denton, Texas 76203.
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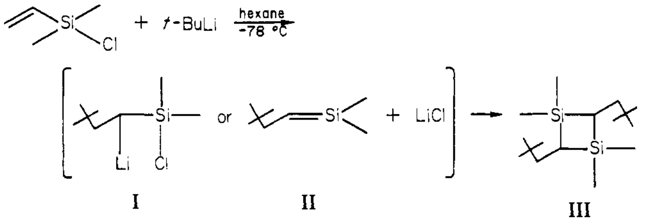
Abstract: The reaction of vinyldimethylchlorosilane with *tert*-butyllithium was investigated in the presence of several conjugated dienes. With 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, cyclopentadiene, and anthracene, cycloadducts of the silaethylene intermediate are obtained in hydrocarbon solvents. The presence of tetrahydrofuran in the reaction mixture suppresses the formation of cycloadducts in favor of 1,3-disilacyclobutane formation. No cycloadduct is obtained with 2,5-dimethylfuran. It is concluded that lithium chloride elimination to give silaethylene intermediates occurs in hydrocarbon solvents, while in THF or in the presence of strong Lewis bases the addition reaction to give α-lithiosilanes occurs and products arising from their coupling reactions are obtained.

Introduction

Recently, we reported the production of 1,3-disilacyclobutanes from vinyldimethylchlorosilane and *tert*-butyllithium in hydrocarbon solvent.[1] At that time, we proposed that the reaction went through an α-lithiochlorosilane (I) which eliminated LiCl to give the silaethylene II, which then dimerized to give the products.

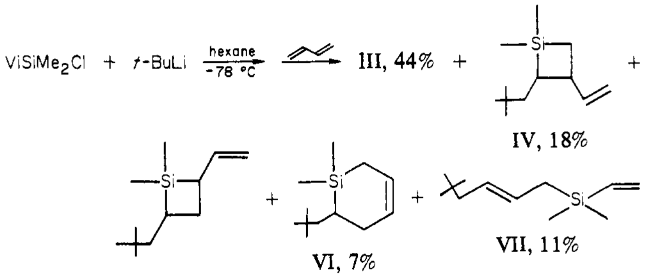


I II III

Other reports have also indicated that species such as I may be important low-temperature silaethylene precursors.[2-4] In as much as silaethylenes produced by high-temperature thermolysis have been trapped with conjugated dienes,[5,6] we were led to investigate similar reactions involving our low-temperature silaethylene. We report the results of our investigation here.

Results

When 1,3-butadiene was used as the trapping reagent, the products and percent yields obtained are shown below.



IV, 18%

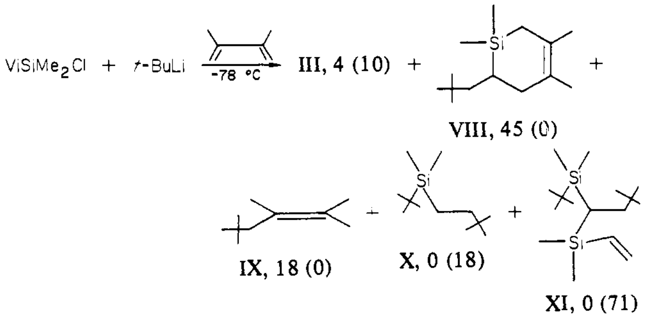
V, 22%

VI, 7%

VII, 11%

As we have noted elsewhere,[1] the ratio of [2 + 2] products IV and V to the [2 + 4] product VI is consistent with the cycloaddition of the highly reactive silaethylene II to the predominant s-trans conformer of butadiene. Product VII presumably arises from addition of *tert*-butyllithium to butadiene followed by coupling with vinyldimethylchlorosilane.

When 2,3-dimethyl-1,3-butadiene was used as the trapping reagent in hexane, the [2 + 4] cycloadduct was obtained. The products and yields shown below were obtained. The numbers in parentheses represent yields where THF was used as the solvent.



VIII, 45 (0)

IX, 18 (0)

X, 0 (18)

XI, 0 (71)

(% yield in THF)

It is of interest to note that only the [2 + 4] cycloadduct VIII

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