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Effects of Formal Charge on the Heterogeneous Electron Transfer Rate at a Mercury–Dimethylformamide Interface for a Series of Organic Salts

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Abstract: The heterogeneous electron transfer rate at a mercury–dimethylformamide interface was determined by ac polarography for a series of organic salts with a variety of formal charges. Several orders of magnitude difference in electron transfer rates were noted on going from +2 ions to −1 ions with the negatively charged ions having the higher electron transfer rate. These results were interpreted within the Marcus theory as arising primarily from solvation effects.

Since Hoijtink's original report, several papers have appeared regarding the heterogeneous electrochemical electron transfer rates to a wide variety of organic and organometallic compounds in aprotic media.[2-18] In the majority of cases, the results can be explained in terms of Marcus's theories for heterogeneous electron transfer.[19,20] In some cases, comparison with homogeneous electron transfer rates has also been made.[11,22] In the reduction of a series of nitrobenzene derivatives, a remarkably successful correlation has been obtained between kinetic parameters and predictions of the Marcus theory.[19] The results were interpretable in terms of the activation free energy for the heterogeneous electron transfer process coming mainly from reorganization of solvent molecules around the reacting species. Similar tendency has also been shown in the electrochemical kinetics of some quinone derivatives[7] and porphyrin derivatives.[12] Slow electron transfer rates due to major geometrical changes of the molecule being reduced have been observed for cyclooctatetraene,[3,8] phenyl-substituted cyclooctatetraenes,[41,42] stilbene derivatives,[5] and azocines.[9]

The majority of previous data has been limited to the one-electron reduction of neutral molecules (e.g., from neutral compound to anion radical) and anion radicals (e.g., from anion radical to dianion), and only a few papers have been published involving kinetic data for the systems containing a positively charged molecule as a reductant or an oxidant.[13,15,21]

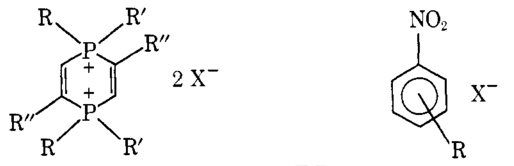
We have applied the ac polarographic method to determine the kinetic parameters for one-electron reduction of some 1,4-diphosphoniacyclohexa-2,5-diene salts, nitrophenyltriphenylphosphonium salts, nitrophenyltrimethylammonium salts, and potassium *p*-nitrophenylacetate at a dropping mercury electrode in *N*,*N*′-dimethylformamide (DMF). We were particularly interested in determining the effect of formal charge on the electron transfer rate. The recent report that some of the diphosphoniacyclohex-2,5-diene salts show antileukemia activity made the elucidation of their redox properties much more urgent.[43]

Recent electrochemical and ESR studies[23-27] have revealed that in aprotic media the first reduction of the above-mentioned salts can occur in a one-electron step (e.g., from dication to cation radical or from monocation to radical product) and that the reduction product, cation radical, or radical is highly stable in the solvent. Thus the kinetic data on the first reduction of these compounds were obtained by the ac polarographic method. The results are presented here.

Experimental Section

Chemicals. All 1,4-diphosphoniacyclohexa-2,5-diene salts were

Chart I. Compounds under Investigation



	R	R''	X⁻	R'		R	X⁻
I	Ph	Ph	ClO_4^-	Ph	VII	*p*-P^+Ph_3	I^-
II	*p*-MeO-Ph	Ph	Br^-	*p*-MeO-Ph	VIII	*m*-P^+Ph_3	I^-
III	Ph	Me	Br^-	Ph	IX	*m*-N^+Me_3	Cl^-
IV	Ph	*t*-Bu	Br^-	Ph	X	*p*-N^+Me_3	Cl^-
V	Ph	Ph	Cl^-	*n*-Bu	XI	*p*-$CH_2CO_2^-K^+$	
VI	Et	Ph	Cl^-	Et			

kindly supplied by Professor A. M. Aguiar. *p*- and *m*-nitrophenyltriphenylphosphonium iodides were prepared by the method of Horner and Hoffman,[28] mp 228.5°C (lit.[28] 228°C) and 208-209°C (lit.[28] 215°C), respectively. *p*- and *m*-nitrophenyltrimethylammonium chlorides were prepared by the method of Zaki and Fahin,[29] and recrystallized three times from absolute ethanol-ether, mp 180-182°C (lit.[29] 183-184°C) and 235-235.5°C (lit.[29] 230-235°C), respectively.

Spectro grade *N,N'*-dimethylformamide (MCB) was stirred with dried 4A molecular sieves (MCB) overnight and distilled under vacuum (1 mm) with ice-water circulated through the condenser. The central 60% fraction was collected and stored under dried nitrogen gas at room temperature. The water content of the solvent was below the detectability limit, less than 0.2 m*M*, but that of the electrolyte solution was about 10 m*M*. Water analysis was done using the method of Hogan et al.[39]

Tetraethylammonium perchlorate (TEAP) was prepared by equimolar addition of perchloric acid to an aqueous solution of tetraethylammonium bromide, purified by repeated recrystallization from water, and dried. The salt was vacuum dried at 100°C for two or more hours just before use.

Electrochemical Measurements. Dc polarograms were measured with a three-electrode polarograph, PAR Model 174. Ac polarographic measurements were performed with a lock-in amplifier, PAR Model 129A, equipped with a polarographic, PAR Model 174, and ac polarography interface, PAR Model 50. A lock-in amplifier, PAR Model H-8, was used as an ac signal generator. This instrumental system has a positive feedback circuit for ir compensation and sample-and-hold readout mode using mechanically controlled drop life (usually 2 sec), and allows simultaneous measurement of in-phase and quadrature components of ac polarographic current. The amplitude and frequency of the ac signal applied to the electrode were measured with a cathode ray oscilloscope, Tektronix type R564B. Ac polarographic data were obtained at eight frequencies in the range 50-1000 Hz. The system employed here was 0.5-1 m*M* depolarizer and 0.2 *M* TEAP in DMF. The electrochemical cell has been described elsewhere.[30] The cell electrode consisted of a dropping mercury working electrode, a coiled platinum wire auxiliary electrode, and an aqueous saturated sodium chloride calomel electrode (aqueous SCE) with a nonaqueous salt bridge. The capillary characteristics of the DME (at open circuit) were $m = 0.787$ mg/sec and $t = 10.2$ sec at $h = 52$ cm in 0.2 *M* TEAP-DMF solution. Measurements were performed at room temperature (22 ± 1°C) under a dried nitrogen atmosphere.

Results and Discussion

All compounds studied here (Chart I) gave two or more reduction waves in DMF. Dc polarographic and cyclic voltammetric (CV) data[23,24,26,27] showed that the first reduction steps of these compounds were uncomplicated one-electron processes. Many observables were consistent with reversible, diffusion-controlled behavior such as dc polarographic $E_{1/4} - E_{3/4}$ values (Tomes criterion of reversibility[31]) of about 58 mV, CV anodic-cathodic peak separation of about 60 mV,[32] CV anodic to cathodic peak current ratio of about unity, etc. ESR studies[23,25,26] also showed that the reduction product was highly stable in this solvent. Furthermore, the linear cot $\phi - \omega^{1/2}$ curves observed for all the compounds studied here (Figure 2) strongly suggested that the electrode behavior of these compounds shows little or no specific absorption phenomena.[40] In compound III the first and second waves were not completely resolved (the potential difference between the ac peaks was about 140 mV). However, since the second ac peak current was less than ⅕ of the first at all frequencies, this overlap did not make it difficult to determine the kinetic parameters of the first wave from the following ac data analysis. Some typical ac polarographic data are shown in Figures 1 and 2.

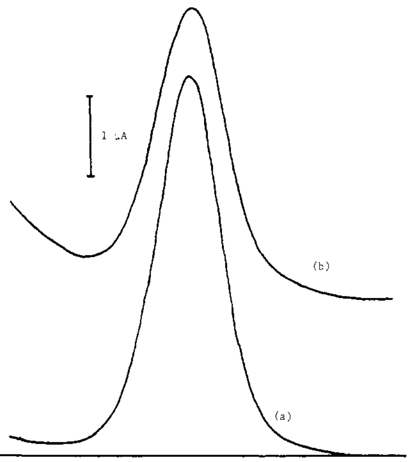


Figure 1. The (a) in phase and (b) quadrature components of the ac polarogram of 1.0 m*M* compound IV in DMF containing 0.2 *M* TEAP and 0.5% water.

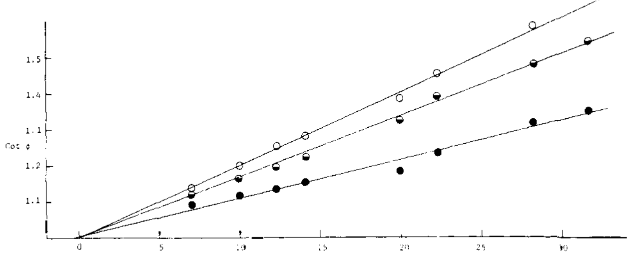


Figure 2. Frequency dependence of the cotangent of the phase angle for selected compounds: ●, III; ⊖, V; ○, VIII.

The diffusion coefficients, which are required to calculate the rate parameters of interest, were evaluated from dc polarographic limiting currents and the Ilkovic equation.[33] In all instances, it was assumed that the oxidized and reduced forms possessed equal diffusion coefficients.

The apparent rate constant of electron transfer at the standard redox potential, k_{sap}, and transfer coefficient, α, were determined from analysis of phase angle ϕ. In this study cot ϕ was obtained from the ratio I_{in}/I_q, where I_{in} and I_q are in phase and quadrature components of ac faradaic current, respectively. Apparent k_s values were calculated from the slope of the cot $\phi - \omega^{1/2}$ profiles (Figure 2), using the well-known relationship[34] where

$$\cot \phi = 1 + (2\omega)^{1/2}/\lambda \tag{1}$$

$$\lambda = (k_{sap}/D^{1/2})(e^{-\alpha j} + e^{(1-\alpha)j}) \tag{2}$$

$$D = D_O^{1-\alpha} D_R^{\alpha} \tag{3}$$

$$j = (nF/RT)(E_{dc} - E_{1/2}{}^r) \tag{4}$$

$$E_{1/2}{}^r = E^0 - (RT/nF) \ln (D_O/D_R)^{1/2} \tag{5}$$

Table I. Electrochemical Parameters for Reduction of Some 1,4-Diphosphoniacyclohexa-2,5-diene Salts and Nitrobenzene Derivatives in DMF Containing 0.2 *M* TEAP at 22°C

Compd	$-E_{1/2}$, V vs. SCE	$D^{1/2}$, (cm²/sec)$^{1/2}$	k_{sap},[a] cm/sec	$-\phi_O$,[b] mV	k_{scor},[c] cm/sec	α
I	0.515	1.53×10^{-3}	0.23	48	1.4×10^{-2}	0.50
II	0.592	1.44×10^{-3}	0.22	58	7.4×10^{-3}	0.50
III	0.772	1.27×10^{-3}	0.4	72	3.1×10^{-3}	0.50
IV	0.720	1.77×10^{-3}	0.17	68	3.2×10^{-3}	0.50
V	0.635	1.57×10^{-3}	0.16	62	4.3×10^{-3}	0.45
VI	0.765	2.16×10^{-3}	0.14	72	2.1×10^{-3}	0.50
VII	0.660	2.52×10^{-3}	0.15	64	4.3×10^{-2}	0.50
VIII	0.790	2.52×10^{-3}	0.18	73	4.3×10^{-2}	0.50
IX	0.850	2.09×10^{-3}	0.17	77	4.2×10^{-2}	0.50
X	0.860	2.30×10^{-3}	0.19	77	3.8×10^{-2}	0.50
XI[d]	1.143	4.89×10^{-3}	0.07	91	14	0.50

[a] Apparent rate constant at standard redox potential. [b] Outer Helmholtz plane potential calculated assuming no specific adsorption of supporting electrolyte. [c] Rate constant at standard redox potential corrected with Frumkin double layer correction. [d] These data are essentially the same in the presence or absence of dicyclohexyl-18-crown-6.

Table II. Effect of Water on Half-Wave Potential and Kinetic Parameters of Compounds IV and VIII in DMF Containing 0.2 *M* TEAP at 22°C

Compd	Added water, %	$-E_{1/2}$	k_{sap}	α
IV	0	0.720	0.17	0.50
	0.5	0.725	0.16	0.50
	1	0.725	0.16	0.50
VIII	0	0.798	0.18	0.50
	1	0.788	0.17	0.50

ω is the angular frequency of the applied ac voltage, E^0 is the standard redox potential. D_O and D_R are the diffusion coefficients of the oxidized and reduced forms, respectively. We used the cot ϕ values at the half-wave potential in the above relations. The α values were evaluated from the following equation[34]

$$E_{\cot\phi m} = E_{1/2}{}^{r} + (RT/nF)\ln(\alpha(1-\alpha)) \qquad (6)$$

where $E_{\cot\phi m}$ is the potential of the maximum on the cot ϕ − E_{dc} plot. The polarographic data and kinetic parameters of the first reduction step are summarized in Table I. The tables also provide the outer Helmholtz plane potential, Ψ_O, relative to the bulk of solution at the half-wave potential. The Ψ_O values, which were calculated from the differential capacity data using the Gouy-Chapman theory[35] on assumption of no specific adsorption of the supporting electrolyte, were used to apply the Frumkin double layer correction[35,36] to the apparent k_s values. The corrected rate constants, k_{scor}, are also given in Tables I and II.

The presence of water in a nonaqueous system can cause variation of the electrochemical kinetic data through the preferential hydrogen bonding (solvation) of the parent molecule or reduction product even when the effect of the coupling chemical reaction (protonation) is negligible. In fact, a significant decrease in homogeneous and heterogeneous (electrode) electron transfer rates with the addition of water has been observed with some aromatic molecules.[11] Accordingly, we examined the effect of water on the half-wave potential and kinetic parameters for the first reduction steps of 1,1,4,4-tetraphenyl-1,4-diphosphonia-2,5-di-*tert*-butylcyclohexadiene dichloride (compound IV) and *p*-nitrophenyltriphenylphosphonium iodide (compound VII). The results are summarized in Table II. No appreciable variation in both the half-wave potential and kinetic parameters was observed with the addition of up to 1% water. It also has been confirmed by Rieke and coworkers[23,24,27] that the polarographic results for the first wave of the former compound are essentially unchanged upon the addition of up to 10% water. These results show that the reduction products are highly stable in DMF and that the preferential solvation effect of water is negligible for these compounds. Therefore, it may be concluded that the presence of a trace of water (ca. 10 m*M*) in the electrolytic systems will not make the electrochemical kinetic data unreliable.

The kinetic data tabulated in Table I are characterized as follows. (1) The transfer coefficients, α, are very close to 0.5 regardless of the half-wave potentials and k_s values for all compounds. (2) Introduction of a positively charged substituent into nitrobenzene makes the electron transfer rate remarkably slower than with neutral nitrobenzene derivatives; the apparent k_s value for compound VIII is 0.18 cm/sec and that for *p*-nitrotoluene is 2.7[6] or 7 cm/sec.[14] (3) The presence of positively charged atoms in the molecule has an effect similar to the introduction of a positively charged group on the electron transfer kinetics; the apparent k_s values for the 1,4-diphosphoniacyclohexa-2,5-diene dications are about an order of magnitude smaller than those reported to date for planar aromatic compounds. The feature mentioned in (2) and (3) becomes much more pronounced when the apparent rate constants are corrected with the Frumkin theory for the double layer effect; the corrected rate constants for these salts are three or more orders of magnitude smaller than those for planar aromatic molecules. Although the double layer correction involves some uncertainties and inexactness (especially the preelectrode site), this will not alter the above statements qualitatively. (4) In the series of the 1,4-diphosphoniacyclohexa-2,5-diene salts, introduction of alkyl groups instead of phenyl groups on the 1,4-phosphorus atoms or 2,5-carbon atoms results in smaller rate constants. For example, compare compounds I, V, and VI or I, III, and IV. This tendency is significant even when the apparent rate constants are compared.

A more critical discussion for these kinetic data can be achieved by consideration of the Marcus theory[19] for the electron transfer process. According to the theory, the free energy of activation can be expressed with two terms, namely the work term and the reorganization term. The work term, the work required to transport the reactant from the bulk of the solution to the plane at which electron transfer occurs, can be approximated with the Frumkin type double layer correction.[13,17] The reorganization term consists of two contributions, the work associated with the reorganization of solvent molecules around the reacting species and the work of internal reorganization in the reactants involving changes in bond lengths and angles. For the one-electron reduction of a series of neutral nitrobenzene derivatives, it has been found by Peover and Powell[6] that the change in the rate constant can be interpreted in terms of the solvent reorganization energy based on the Marcus theory.

It would appear that the kinetic data for the reduction of the nitrobenzene salts can be explained also in terms of the Marcus theory. The reduction process does not cause the rupture of the onium group and would seemingly be accompanied with no significant geometric change. The EPR spectra show the neutral radicals to be quite stable and very similar to that of nitrobenzene radical anion. The nitrogen hyperfine coupling constant is smaller due to the electron attracting onium group. On this ground, the onium salts should have a higher heterogeneous electron transfer rate than nitrobenzene. Peover and Powell found that in the reduction of their neutral nitrobenzene derivatives the com-

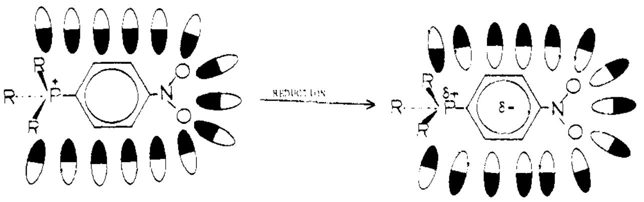


Figure 3. Qualitative pictorial representation of solvent orientation around onium ions and reduced products.

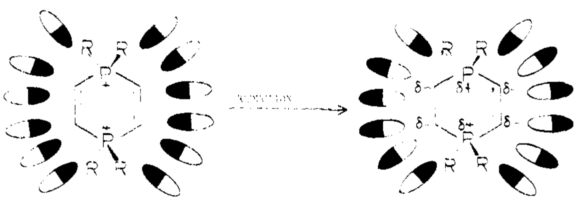


Figure 4. Qualitative pictorial representation of solvent orientation around diphosphoniacyclohexa-2,5-diene salts before and after reduction.

pounds with the smallest A_N had the highest k_{sap} values. The reduction of the positively charged onium salts, however, is much slower than that of the neutral nitrobenzene compounds. We attribute this to the fact that the positively charged onium ions will have the solvent molecules highly oriented around them with the negative end of the solvent dipoles directed toward the positive center. However, upon reduction the nitrobenzene portion of the onium salt will acquire a negative charge. This will necessitate an inversion of orientation of the solvent dipoles around the nitrobenzene portion. This is depicted qualitatively in Figure 3. Thus, this inversion of orientation of the solvent dipoles would make the reorganization energy substantially larger in comparison to the reduction of neutral nitrobenzene derivatives where the solvent orientation prior to reduction can be assumed to be much more random.

In order to gain additional evidence to support this model, we examined the first reduction step of *p*-nitrophenyl acetate anion. In this case, the anion molecule should have the solvent molecules highly oriented around it prior to the reduction step with the positive poles directed toward the anion. Thus, upon reduction to the dianion there will be less solvent reorganization than for the neutral nitrobenzene. This should manifest itself in a much higher rate constant for the anion than for the onium cationic molecules. The experimental results show good agreement with this prediction; the corrected rate constant for the anion is three orders of magnitude larger than those for the cations, although the apparent values are of the same order. It should be noted also that the perylene$^+$/perylene, perylene/perylene$^-$ and perylene$^-$/perylene^{2-} redox systems have apparent rate constants of the same order regardless of different charges of reactants.[10,15] This suggests that the slow rate observed for the reduction of our compounds could not be due to some specific solvation effect characteristic of a cation.

Similar discussions as described above also seem to be applicable to the kinetic data on the reduction of a series of 1,4-diphosphoniacyclohexa-2,5-diene salts. In this case, the onium salts are dipositively charged and are expected to have the solvent molecules highly oriented around them with the negative end of the solvent dipoles directed nearest to the onium salt. Reductions of the dications give species with an overall formal charge of plus one. However, EPR data indicate that a large portion of the extra odd electron is located on the four ethylene carbon atoms. Thus the radical cation is expected to have ylid character with negatively charged carbon atoms. This is also borne out by the chemistry of the radical cation, for bulk electrolysis in a protic medium yields the tetrahydro diphosphonium product.[44] Thus, we would expect that solvent orientation near the two ethylene double bonds must undergo inversion as in the nitrophenyl onium salts. This then would explain the very slow heterogeneous electron transfer rates for the diphosphoniacyclohexa-2,5-diene salts. Figure 4 shows graphically this solvent reorientation upon reduction. The fact that the rate constant of compound I is larger than that of compound VI can be also explained by consideration of the solvent reorganization term. Namely, this may be due to the following. (1) The charge density on the four ethylene carbon atoms can be assumed to be larger for compound VI$\cdot^+$ than for compound I$\cdot^+$, as indicated by the fact that the ring vinyl proton coupling constants, a^H, determined by ESR are 4.8 G for compound VI and 3.8 G for compound I,[25] which would make the solvent inversion effect for compound VI larger than for compound I. (2) Introduction of small ethyl groups instead of bulky phenyl groups into 1,4-phosphorus atoms could make the solvation at the phosphorus atoms easier.

Crystallographic studies on the 1,1,4,4,2,5-hexaphenyl-1,4-diphosphoniacyclohexa-2,5-diene salt have shown that the molecule exists in a boat conformation.[37] On the other hand, the 1,1,4,4,-tetraethyl-2,5-dimethyl-1,4-diphosphoniacyclohexa-2,5-diene salt was found to be planar.[38] In addition, an unusually large temperature dependency of the phosphorus hyperfine coupling constants observed with these salts suggests that rocking motion of the phosphorus atoms relative to the four ethylene carbon atoms is likely.[25] Therefore, the possibility that the conformational change such as ring flattening occurs during an electron transfer cannot be excluded in this series. However, considering that the transfer coefficients, α, for these salts are very close to 0.5[5,8] and that the change of three orders of magnitude in the rate constant observed with nitro compounds could be satisfactorily explained with the solvent reorganization term only,[6] it is quite likely that contribution of such internal reorganization to the activation free energy is minor.

In summary, it is clear that formal charge has a significant influence on the heterogeneous electron transfer rate with the solvent reorganization being of critical importance. It is expected that similar effects will be seen in homogeneous electron transfer processes.

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The Crystal and Molecular Structure and Absolute Configuration of Ethyl Chlorophyllide *a* Dihydrate. A Model for the Different Spectral Forms of Chlorophyll *a*

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Abstract: A single crystal x-ray structural determination of ethyl chlorophyllide *a* has provided the first detailed structural data for a magnesium-containing chlorophyll derivative. It has also furnished a model for chlorophyll aggregation in vivo. Ethyl chlorophyllide *a*, prepared by the chlorophyllase catalyzed transesterification of chlorophyll *a*, crystallizes from acetone-water mixtures in the form of the dihydrate. The crystals are trigonal with space group $P3_1$ and unit cell parameters $a = 8.859$ (1), $c = 38.119$ (5) Å, $Z = 3$, $d_{\text{calcd}} = 1.31$, $d_{\text{obsd}} = 1.28$ (3). The crystal structure was determined by standard methods and refined to a conventional R of 0.053. Refinement of the complete data set, including Friedel pairs, in space groups $P3_1$ and $P3_2$ provided an absolute configuration consistent with that determined chemically for chlorophyll *a*. The magnesium atom in this structure is five coordinate with a water molecule in the fifth coordination site. The second water molecule is hydrogen bonded to the coordinated water molecule and to the methyl ester carbonyl oxygen atom of one chlorophyllide molecule and to the carbonyl oxygen atom of the ethyl ester of another. A layered crystal structure is formed in which the two-dimensional aggregate that makes up each layer is composed of cross-linked one-dimensional polymers. These one-dimensional polymers provide the basis for a model of chlorophyll aggregation in photosynthetic organisms. Estimates of the positions of the red absorption maxima of short one-dimensional polymers show a striking correspondence to those observed for chlorophyll in vivo.

Chlorophyll *a* is the principal photosynthetic pigment in algae and higher plants. In the process of photosynthesis this pigment serves both as a collector of photoexcitation and as the electron donor in the primary photosynthetic reaction. A knowledge of the molecular structure of the photosynthetic apparatus depends upon the detailed elucidation of the distribution and organization of this pigment in the cell.

As a basis for such an elucidation, x-ray structural studies of a number of chlorophylls and chlorophyll derivatives have been undertaken in this laboratory. The structure of ethyl chlorophyllide *a* dihydrate reported herein provides the first detailed structural data for a magnesium-containing chlorophyll derivative. The mode of aggregation observed in this structure furnishes a reasonable model for chlorophyll aggregates in vivo. Detailed structural parameters of both the isolated molecule and the aggregate provide a basis for further theoretical studies. A preliminary report of this work has appeared.[1]

Experimental Section

Preparation of Ethyl Chlorophyllides *a* and *b*. The chlorophyllides were prepared by a modified version of the procedure described by Holt and Jacobs.[2] Fresh leaves (1 kg) of a plant rich in chlorophyllase, *Ailanthus altissima*, were blended in a Waring blender with 3 l. of 95% ethanol. The mixture was allowed to stand for 4-5 hr in the dark under a nitrogen atmosphere. The course of the conversion to the chlorophyllides was followed with the basicity test described by Willstätter and Stoll.[3] After filtration under vacuum, the leaf meal was washed with 1 l. of acetone. Fifty grams of talc was then added to the combined filtrate and it was diluted with 4 l. of distilled water. This mixture was allowed to stand for several hours at 5°C and then filtered under vacuum. The layer of talc containing the crystalline chlorophyllide was washed alternately with petroleum ether and 50% aqueous acetone until it had