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Photooxidation of a Tetranuclear Cluster Complex in the Presence of Halocarbons:

Photochemistry of the Carbonyl- $\eta^5$ -cyclopentadienyliron(I) Tetramer

C. Randolph Bock and Mark S. Wrighton<sup>1\*</sup>

Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

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### Abstract

The photochemistry and electronic absorption spectra of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$  in the presence of halocarbons are reported. Irradiation of the complex at the appropriate wavelengths results in photooxidation, giving initially quantitative yields of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4^+$ . This is the only photoreaction observed for any irradiation wavelength longer than 300nm. In the absence of charge acceptor solvents no photooxidation is found: the complex is photoinert in either benzene or  $\text{CH}_3\text{CN}$ . The quantum efficiency in the presence of halocarbons depends on co-solvent, the halocarbon, and wavelength. For example, in 1/1  $\text{CH}_3\text{CN}/\text{CCl}_4$  (by volume) the initial quantum yields are: 0.21 at 313nm, 0.03 at 366 nm, 0.002 at 405 nm and  $\sim 0.0005$  at 436 nm. But in pure  $\text{CCl}_4$  the 313 nm quantum yield is only 0.05. The 313 nm yield for 1/1  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  is 0.0007. The absorption spectra reveal a halocarbon dependence in the near-uv, consistent with a charge-transfer-to-solvent excitation (CTTS). The CTTS maximum correlates with the ease of reduction of the halocarbons, and the wavelength dependence of the photooxidation substantiates the conclusion that the CTTS excitation is responsible for the photochemistry.

### Introduction

Photochemical reactions of metal-metal bonded complexes have only been extensively investigated for dinuclear complexes.<sup>2-6</sup> Some qualitative reports concern the trinuclear species  $\text{M}_3(\text{CO})_{12}$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ).<sup>6-10</sup> In all of the cases studied thus far, the dominant form of excited state chemical decay is rupture of the metal-metal bond(s) to ultimately yield mononuclear complexes. For larger clusters where one metal atom is bonded

to more than one or two other metal atoms one might expect that one-electron excited states may not result in enough labilization to give photodeclusterification. Thus, ligand photosubstitution and photoredox processes may be important and lead to new ways to modify clusters, while retaining the essential framework bonding associated with the metal-metal core.

In this report we describe the photochemical behavior of the tetranuclear cluster,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$ . This species has been known<sup>11</sup> for some time and is known<sup>12</sup> to undergo reversible reduction and oxidation, but no photochemical studies have been reported. We have examined the photochemical behavior of the complex in the presence of potential nucleophiles which could replace CO, but we found the complex to be essentially inert to ligand substitution. We do find that  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$  can undergo photooxidation in the presence of certain halocarbons, and we now report the main findings concerning this photochemistry. To interpret our results we draw on the rich precedence<sup>13</sup> associated with the photooxidation of  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$  in the presence of chlorocarbons.

### Results and Discussion

a. Photochemistry of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$ . Prolonged near-uv or visible ( $\lambda > 300\text{nm}$ ) irradiation of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$  in degassed  $\text{CH}_3\text{CN}$  solution at  $25^\circ$  results in no observable spectral changes, and the complex can be recovered unchanged from the solution. However, near-uv irradiation of degassed,  $25^\circ$   $\text{CCl}_4$  solutions of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$  rapidly yields precipitation of a dark green solid. The  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$  is thermally stable in  $\text{CCl}_4$  under the photoreaction conditions. Collection and identification of the product from the photoreaction shows that it is the one-electron oxidation product,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4^+$ . By comparison to a sample prepared by  $\text{Cl}_2$

oxidation of the  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_4]$  the chemical yield of the photoproduct is >90% based on the starting neutral complex. The photoproduct does not readily precipitate from more polar media so we have made quantitative measurements in  $\text{CH}_2\text{CN}/\text{CCl}_4$  1/1 by volume. Low energy visible absorption spectral changes accompanying 313nm irradiation are shown in Figure 1. Two isosbestic points are observed, 715 and 942 nm, and the same spectral changes with the same isosbestic points are found using  $\text{Br}_2$  chemical oxidation of the tetramer. Regeneration of the starting tetramer from the photooxidation product is possible by addition of the strong reducing agent  $\text{N}_2\text{H}_4$ .<sup>12</sup> Infrared spectral changes accompanying the photooxidation are included in Figure 1. Quantitative measures of the decline of the band at  $1640\text{ cm}^{-1}$  and the growth of the band at  $1705\text{ cm}^{-1}$  show nearly 100% initial yield of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_4]^+$  from the neutral tetramer. Representative data associated with the spectral changes in Figure 1 are given in Table 1. All spectral properties of the photooxidation product are in accord with those obtained on samples of the same ion generated chemically or electrochemically. The characteristic ir band at  $1705\text{ cm}^{-1}$  and the uv-vis spectral features show that the cationic tetramer is the product in the various halocarbon solvent systems to be described below.

We observed qualitatively that  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_4]$  is largely insensitive to visible light, even in the presence of  $\text{CCl}_4$  and despite its extensive near ir and visible absorption. A wavelength dependence of the quantum efficiency for photooxidation is shown by the data in Table II. The near-uv quantum efficiency of 0.21 at 313nm is very respectable, but the efficiency falls rapidly at the longer wavelengths, and at least for low energy visible irradiation we find no efficient photochemistry of any sort.

The efficient 313nm reaction in the presence of  $\text{CCl}_4$  and the low reactivity in pure  $\text{CH}_3\text{CN}$  parallels earlier observations for  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$  which undergoes photooxidation in the presence of halocarbons but is essentially photoinert in solvents such as benzene,  $\text{CH}_3\text{CN}$ , alkanes, etc. We have carried out additional studies of the photoreactivity of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$  in the presence of various halocarbon donors, Table III. The quantum yields are ordered in the chloro-carbon series:  $\text{CH}_2\text{Cl}_2 < \text{CHCl}_3 < \text{CCl}_4$ . Additionally,  $\text{CH}_2\text{Br}_2$  is significantly more reactive than  $\text{CH}_2\text{Cl}_2$ . These reactivity patterns can be correlated with the ease of reduction of the halocarbon.

One final set of results is important, regarding the photochemistry of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$ . Table IV shows the effect of solvent on the quantum yields for photooxidation using  $\text{CCl}_4$  as the halocarbon. Not unexpectedly, we find that the more polar solvents give larger quantum yields for the photooxidation process. This result seems to be consistent with the charge-transfer nature of the overall chemical process. Perhaps surprisingly, we find no evidence for photosubstitution in the cyclopentadienyl ring as reported<sup>14</sup> for  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$  in halocarbon-EtOH mixtures. It is likely, though, that cyclopentadienyl substitution is a secondary process, in any event.

b. Electronic Spectra and the Nature of the Reactive Excited State. The spectra of the  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$  and the photooxidation product are shown in Figure 2 for  $\text{CH}_3\text{CN}$  solution at 25°. For both the neutral and the cationic tetramer the spectra consist of a low energy, low intensity vis-nir band system and a near-uv high intensity band. The similarity of the two spectra likely reflects the importance of the common  $\text{Fe}_4$  core in each species. We do not

make a detailed assignment here, but the absorptions are logically associated with electronic transitions between orbitals delocalized over the  $Fe_4$  core. As shown by the data in Table V the positions and intensities of the main features of the spectrum of the neutral tetramer are independent of solvent. As described below, however, careful comparisons in the near-uv show some small, but important solvent dependencies.

With respect to the photochemistry described above, the crucial result concerning the electronic spectrum of  $[(\eta^5-C_5H_5)Fe(CO)]_4$  is that the near-uv spectrum is slightly perturbed in the presence of halocarbons. A comparison of the spectra of the neutral tetramer in  $CH_3CN$  and in  $CCl_4/CH_3CN$  9/1 by volume is shown in Figure 3. In the difference spectrum maxima are observed at  $\sim 315$  nm and  $\sim 400$  nm. Generally, two maxima are found in the difference spectra involving other halocarbon/ $CH_3CN$  solvents. The higher energy peak maximum and its intensity depend on the halocarbon, while the lower energy maximum is constant in position but varies in intensity.

We propose that the increased absorptivity associated with the high energy peak in the difference spectrum is due to charge-transfer-to-solvent (CTTS) excitation. Data in Table VI list the CTTS maximum and intensity for a number of halocarbons. The CTTS assignment gains support from the correlation of CTTS maximum and ease of reduction of the halocarbon, Figure 4. Consistently, we find that the more easily reduced halocarbon exhibits the lower energy CTTS maximum. The CTTS assignment is further substantiated by the wavelength dependence of the photooxidation efficiency (cf. Table II and Figure 3). Similar arguments have been used in interpreting both the spectra and photochemistry of  $Fe(\eta^5-C_5H_5)_2$  in  $CCl_4$ .<sup>13</sup> Additionally, it is worth noting that the CTTS intensities found here for the tetramer are very similar

to those for  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ .<sup>13</sup> Unfortunately, in the tetramer there exists a band of molar absorptivity of  $\sim 2 \times 10^4$  in the vicinity of the CTTS which tends to obscure the CTTS band. In  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$  the nearby transitions have molar absorptivities of  $< 10^2$ . We draw attention to one final similarity in the tetramer and  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ : the oxidation  $E_{1/2}$  values for the two are very similar.<sup>12</sup> This fact is consistent with the comparable CTTS maximum for the two complexes.

The low energy peak near 400 nm typically observed in the difference spectra is apparently not of the CTTS type. We draw this conclusion largely from the fact that we observe relatively little photooxidation at 405 nm. We ascribe the difference peak near 400 nm to "solvent effects". In fact, we find support for this interpretation from the intensity of the difference spectra of the neutral tetramer in various solvent/ $\text{CCl}_4$  mixtures. The intensity of the maximum varies linearly with the empirical Kosower Z values<sup>15</sup> for a large number of solvents, Figure 5. For the same set of data points the intensity is constant for the difference peak at  $\sim 315$  nm associated with the CTTS transition. We offer no explanation for the lack of a solvent effect on the CTTS intensity, but the empirical result clearly distinguishes the high and low energy difference peaks. Importantly, the lack of a solvent dependence on the  $\text{CT} \rightarrow \text{CCl}_4$  band lends credence to the interpretation of the data in Table IV. That is, the difference in quantum efficiency can not be ascribed to differences in the fraction of light giving rise to CTTS excitation.

Summary

The  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$  species can be photooxidized to  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4^+$  by near-uv irradiation in the presence of halocarbons. Wavelength dependent quantum yields can be correlated with a spectral feature attributed to a charge-transfer-to-solvent (halocarbon) excitation. These results parallel those for  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ . The photooxidation represents new photochemistry for clusters, but it is not clear whether the process offers any potential advantages compared to mononuclear complex photooxidations. Studies directed towards using the cluster as a photoassistance agent for driving redox processes are underway.

Acknowledgment

We thank the Office of Naval Research for support of this research.

## EXPERIMENTAL

Materials. All solvents used for spectroscopy and photochemistry were transparent over the wavelength range of interest and were commercially available spectroscopic grade. The various halocarbons are commercially available and were either chromatographed or distilled prior to use. The  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$  used in the synthesis of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$  was used as received from commercial sources.

Preparation and Characterization of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4^{0,+}$ . The  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$  was prepared according to the procedure of King.<sup>11c</sup> The complex was purified by recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane, and the resulting material has ir and uv-vis absorption spectral properties (Tables and Figures) in accord with those in the literature,<sup>11c,12</sup> including molar absorptivities within 10%. The cationic cluster was prepared by passing  $\text{Cl}_2$  through a  $\text{CH}_2\text{Cl}_2$  solution of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$ . The  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4\text{Cl}$  salt precipitated, and the  $\text{PF}_6^-$  salt was prepared by dropwise addition of a saturated aqueous solution of  $\text{NH}_4\text{PF}_6$  to an aqueous solution of the  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4\text{Cl}$ . The  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4\text{PF}_6$  precipitated and was collected by filtration. The solid was washed with cold water, cold EtOH and then dried. Spectral properties (Tables and Figures) are in accord with literature values.<sup>12</sup>

Spectra. All uv-visible-near ir spectra were obtained with a Cary 17 uv-vis-nir spectrophotometer. Ir spectra were recorded on a Perkin-Elmer 180 grating infrared spectrometer using matched 1.0mm path length cells.

Difference spectra were accurately recorded with the following exemplary procedure: solutions of the tetramer in 9/1 halocarbon/ $\text{CH}_3\text{CN}$  mixture were obtained by halocarbon dilution of 1.0ml aliquots of a stock  $\text{CH}_3\text{CN}$  solution containing  $5 \times 10^{-4}$  M tetramer. A reference solution was made by similarly diluting the stock solution with  $\text{CH}_3\text{CN}$ . Using matched 1.0cm path length quartz cells, and scanning slowly to allow for slit width equilibration, the difference spectra were recorded with the halocarbon solution in the sample beam and the  $\text{CH}_3\text{CN}$  solution in the reference beam. Base lines were also recorded by scanning mixed solvent vs.  $\text{CH}_3\text{CN}$ . When the solvent mixture absorbed appreciably in the region of interest, this could be automatically subtracted out by placing a second cell containing pure mixed solvent in the reference beam. In these cases the spectra and base lines were recorded with the additional cell in the reference beam. In all cases we were certain to assure that the optical density did not exceed 2.0 in either the reference or sample compartment.

Photolyses. In a typical experiment, 3.0ml samples of a solution containing  $2 \times 10^{-4}$  M complex were placed in 13 x 100 mm Pyrex test tubes with constrictions. These were degassed in at least three freeze-pump-thaw cycles and were then hermetically sealed. Photolyses were performed with a merry-go-round<sup>16</sup> apparatus equipped with either a 450W or 550W Hanovia medium pressure mercury lamp, and appropriate Corning glass filters and filter solutions to isolate the 313-, 366-, 405-, and 436 nm Hg emissions. Spectra-Physics He-Ne and Ar ion lasers

equipped with 6X beam expanders were used for the 632.8 and 514.5 nm irradiations, respectively. Actinometry was accomplished with ferrioxalate<sup>17</sup> or Reinecke's salt.<sup>18</sup> Progress of the photooxidation was monitored by uv-vis-near-ir or ir spectral measurements. For the quantum yield determinations, the conversions were kept below 10%, and over this period plots of conversion against irradiation time are linear.

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Table I. Stoichiometry for Photooxidation of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$  in 1/1  $\text{CH}_3\text{CN}/\text{CCl}_4$ .<sup>a</sup>

Irrdn. Time, hr.	Change in Concentration, $\text{M} \times 10^4$	
	$\text{Fe}_4$	$\text{Fe}_4^+$
0.5	-3.3	+2.6
1.0	-4.8	+4.5
2.0	-5.9	+6.6

<sup>a</sup> 313 nm irradiation of  $1.0 \times 10^{-3} \text{M}$   $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$  in  $\text{CH}_3\text{CN}/\text{CCl}_4$ , 1/1 by volume, at  $25^\circ$ . Spectral data for this experiment are given in Figure 1.

Table II Quantum Yields for Disappearance of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$  in the Presence of  $\text{CCl}_4$ .<sup>a</sup>

<u>Irradiation Wavelength, nm</u>	<u><math>\phi \pm 0.10 \phi</math></u>
313	0.21
366	0.03
405	0.002
436	-0.0005
514.5	<0.0001
632.8	<0.0001

<sup>a</sup>Degassed 1/1 (v/v)  $\text{CH}_3\text{CN}/\text{CCl}_4$  solutions of  $2 \times 10^{-4} \text{ M}$   $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$  irradiated at 25°.

**Table III.** Photooxidation Quantum Yields for  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$  as a Function of Halocarbon.<sup>a</sup>

<u>Solvent</u>	<u><math>\phi_{366\text{nm}}</math></u>	<u><math>\phi_{313\text{nm}}</math></u>
$\text{CCl}_4/\text{CH}_3\text{CN}$ (1/1)	0.03	0.21
$\text{HCCl}_3/\text{CH}_3\text{CN}$ (1/1)	0.003	0.05
$\text{H}_2\text{CCl}_2/\text{CH}_3\text{CN}$ (1/1)	—	-0.0007 <sup>b</sup>
$\text{H}_2\text{CBr}_2/\text{CH}_3\text{CN}$ (1/1)	$\leq 0.005^b$	0.15
$\text{CH}_3\text{CN}$	—	$< 0.001^b$

<sup>a</sup>Irradiation at indicated wavelength in degassed solvent systems at 25°. Quantum yields are  $\pm 10\%$ .

<sup>b</sup>Quantum yield is for disappearance of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$ .

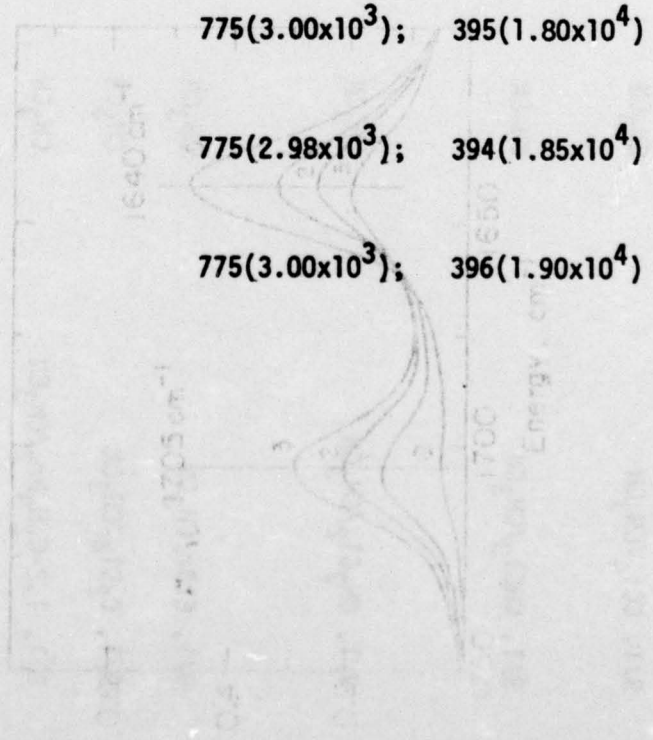
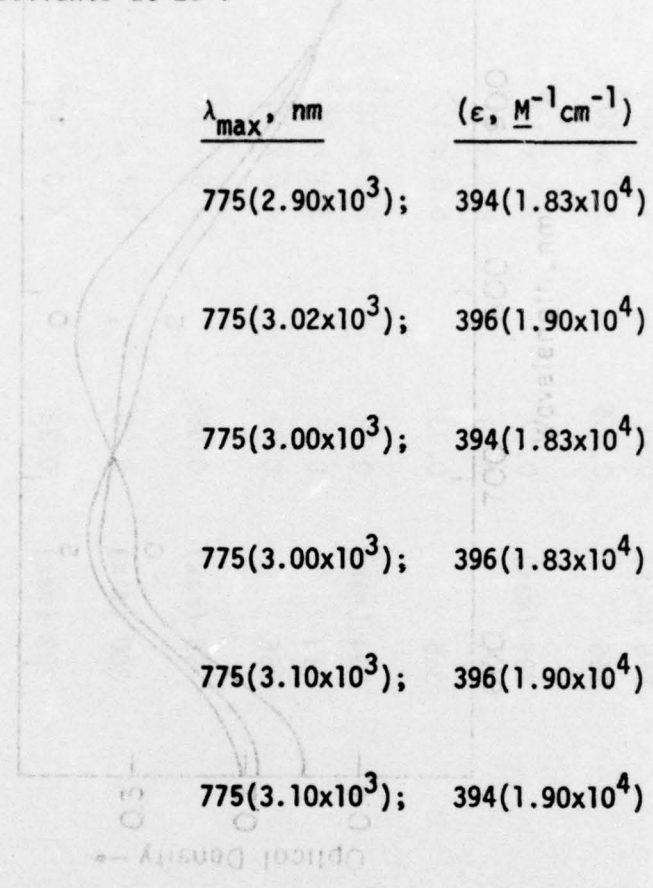
Table IV. Solvent Dependence of Quantum Yields for Photooxidation of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$ .<sup>a</sup>

<u>S/CCl<sub>4</sub> (1/1, v/v)</u>	<u><math>\phi_{313\text{nm}}</math></u>
CH <sub>3</sub> CN/CCl <sub>4</sub>	0.21
MeOH/CCl <sub>4</sub>	0.19
EtOH/CCl <sub>4</sub>	0.21
isoPrOH/CCl <sub>4</sub>	0.19
CH <sub>2</sub> Cl <sub>2</sub> /CCl <sub>4</sub>	0.07
C <sub>6</sub> H <sub>6</sub> /CCl <sub>4</sub>	0.10
CCl <sub>4</sub>	0.05

<sup>a</sup>Degassed S/CCl<sub>4</sub> (1/1, v/v) solutions containing  $2 \times 10^{-4} \text{ M } [(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$  irradiated at 313nm.

**Table V.** Optical Absorption Spectral Data for  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$  in Several Solvents at 25°.

<u>Solvent</u>	<u><math>\lambda_{\text{max}}</math>, nm</u>	<u><math>(\epsilon, \text{M}^{-1}\text{cm}^{-1})</math></u>
CH <sub>3</sub> CN	775(2.90x10 <sup>3</sup> );	394(1.83x10 <sup>4</sup> )
CCl <sub>4</sub>	775(3.02x10 <sup>3</sup> );	396(1.90x10 <sup>4</sup> )
CHCl <sub>3</sub>	775(3.00x10 <sup>3</sup> );	394(1.83x10 <sup>4</sup> )
CH <sub>2</sub> Br <sub>2</sub>	775(3.00x10 <sup>3</sup> );	396(1.83x10 <sup>4</sup> )
CHBr <sub>3</sub>	775(3.10x10 <sup>3</sup> );	396(1.90x10 <sup>4</sup> )
CH <sub>2</sub> Cl <sub>2</sub>	775(3.10x10 <sup>3</sup> );	394(1.90x10 <sup>4</sup> )
EtBr	775(3.00x10 <sup>3</sup> );	395(1.80x10 <sup>4</sup> )
THF	775(2.98x10 <sup>3</sup> );	394(1.85x10 <sup>4</sup> )
Benzene	775(3.00x10 <sup>3</sup> );	396(1.90x10 <sup>4</sup> )



**Table VI.** Difference Spectral Data for  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}(\text{CO})]_4$ .

5.50 x 10 <sup>-5</sup> M in Solvent Indicated, 1 cm Pathlength				
Sample Compartment	Reference Compartment	$\lambda, \text{nm}^a$	$\Delta OD^b$	$\Delta \epsilon^c$
9/1, CCl <sub>4</sub> /CH <sub>3</sub> CN	CH <sub>3</sub> CN	316 (max) 366	0.22 0.055	4.0 x 10 <sup>3</sup> 1.0 x 10 <sup>3</sup>
9/1, CHCl <sub>3</sub> /CH <sub>3</sub> CN	CH <sub>3</sub> CN	299 (max) 313 366	0.17 0.13 0.03	3.1 x 10 <sup>4</sup> 2.4 x 10 <sup>3</sup> 5.0 x 10 <sup>2</sup>
9/1, CH <sub>2</sub> Cl <sub>2</sub> /CH <sub>3</sub> CN	CH <sub>3</sub> CN	294 (max) 313 366	0.12 0.06 0.02	2.2 x 10 <sup>3</sup> 1.1 x 10 <sup>3</sup> 4.0 x 10 <sup>2</sup>
9/1, EtBr/CH <sub>3</sub> CN	CH <sub>3</sub> CN	296 (max)	0.085	1.6 x 10 <sup>3</sup>
9/1, C <sub>2</sub> Cl <sub>4</sub> /CH <sub>3</sub> CN	CH <sub>3</sub> CN	300 (max)	0.20	3.7 x 10 <sup>3</sup>
9/1, 1,2-C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub> /CH <sub>3</sub> CN	CH <sub>3</sub> CN	299 (max)	0.22	4.0 x 10 <sup>3</sup>

<sup>a</sup> (max) indicates maximum of CTTS transition, cf. text and Figures.

<sup>b</sup> Observed optical density at  $\lambda$ .

<sup>c</sup> Change in molar absorptivity associated with CTTS.

## Figure Captions

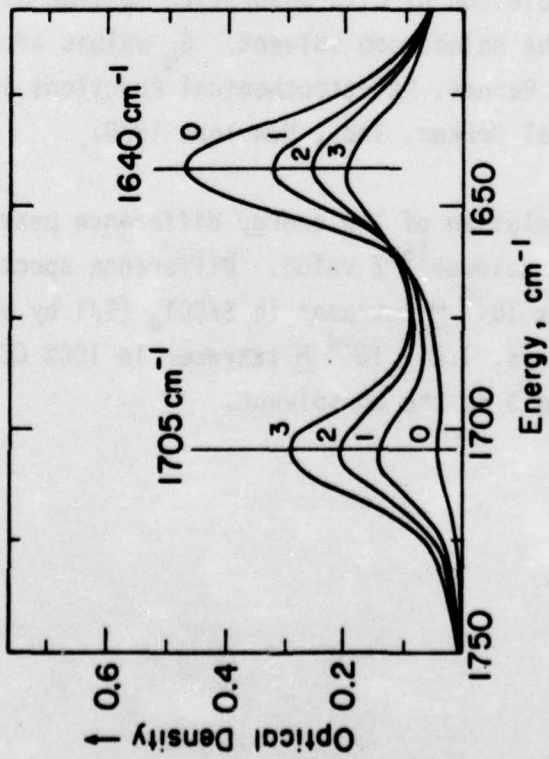
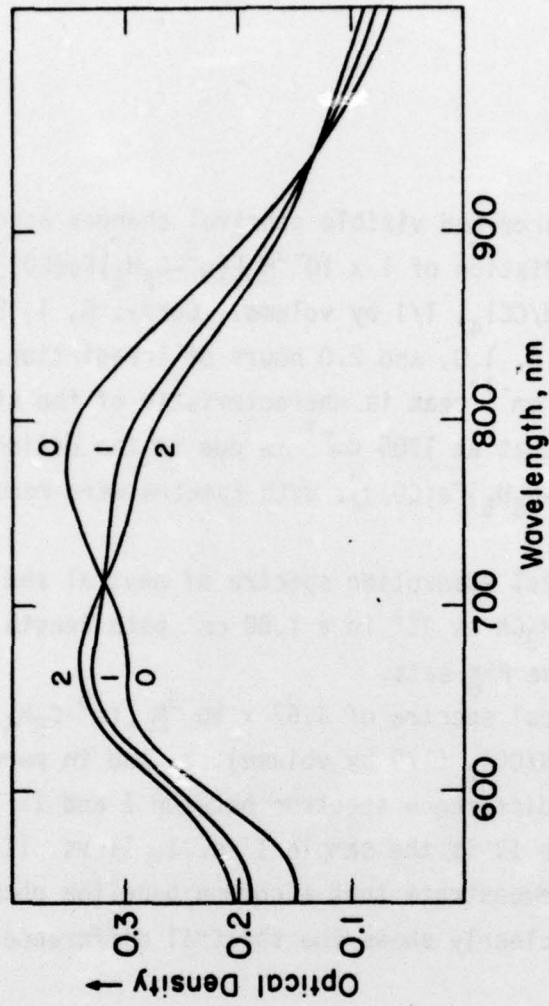
Figure 1. Infrared and visible spectral changes accompanying 313 nm irradiation of  $1 \times 10^{-3} \text{ M } [(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$  at  $25^\circ$  in degassed  $\text{CH}_3\text{CN}/\text{CCl}_4$ , 1/1 by volume. Curves 0, 1, 2, 3 correspond to 0, 0.5, 1.0, and 2.0 hours of irradiation, respectively. The  $1640 \text{ cm}^{-1}$  peak is characteristic of the starting material and that at  $1705 \text{ cm}^{-1}$  is due to the cationic tetramer,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4^+$ . Both spectra were recorded with 1.0mm cells.

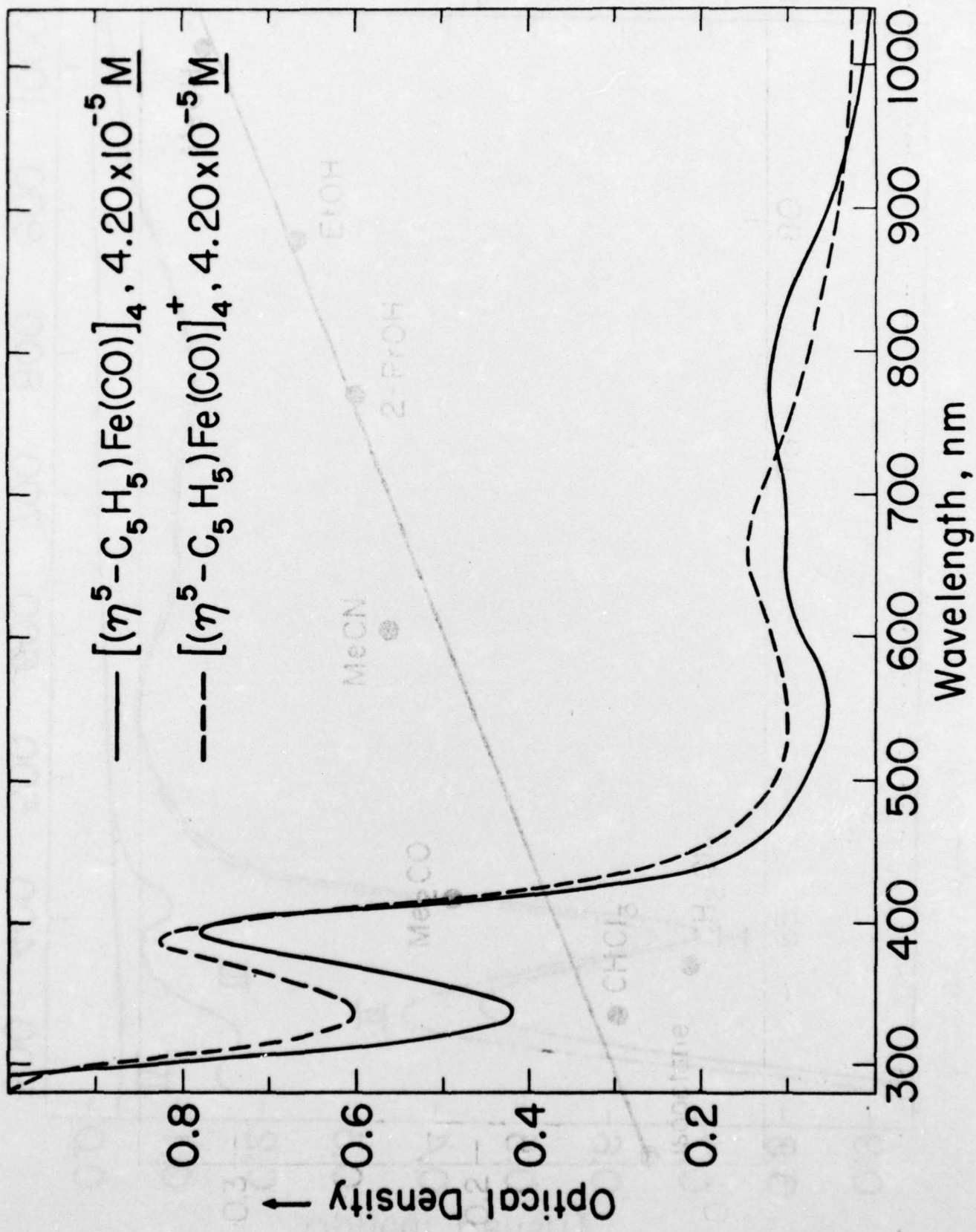
Figure 2. Optical absorption spectra of neutral and cationic cluster in  $\text{CH}_3\text{CN}$  at  $25^\circ$  in a 1.00 cm path length cell. The cation is as the  $\text{PF}_6^-$  salt.

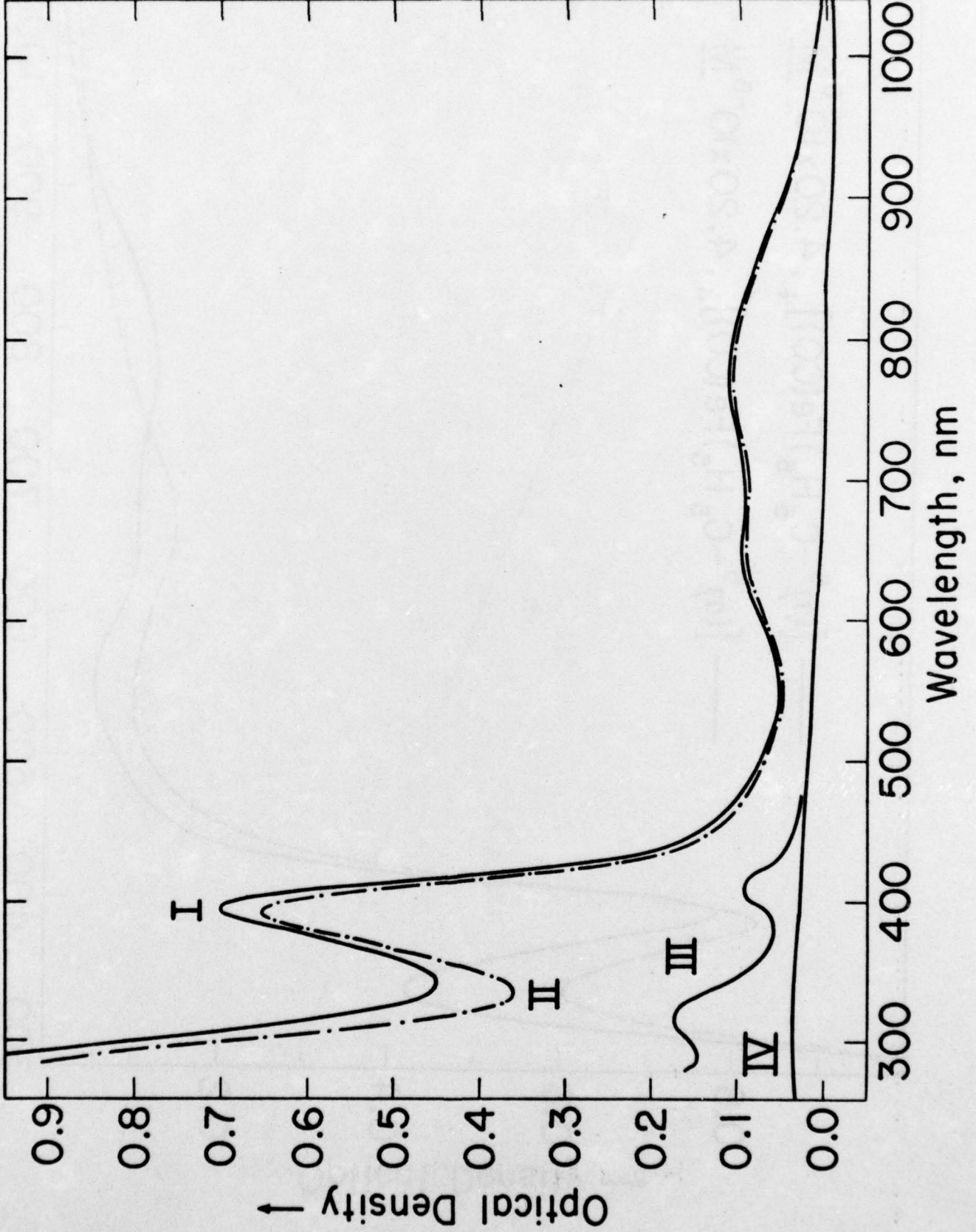
Figure 3. Optical spectra of  $3.67 \times 10^{-5} \text{ M } [(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$  in  $\text{CH}_3\text{CN}/\text{CCl}_4$  (1/9 by volume), I, and in pure  $\text{CH}_3\text{CN}$ , II, and the difference spectrum between I and II is curve III. Curve IV is the sample I vs. I, II vs. II, or air vs. air to demonstrate that a common baseline obtains. Thus, curve III clearly shows the spectral differences with  $\text{CCl}_4$  present.

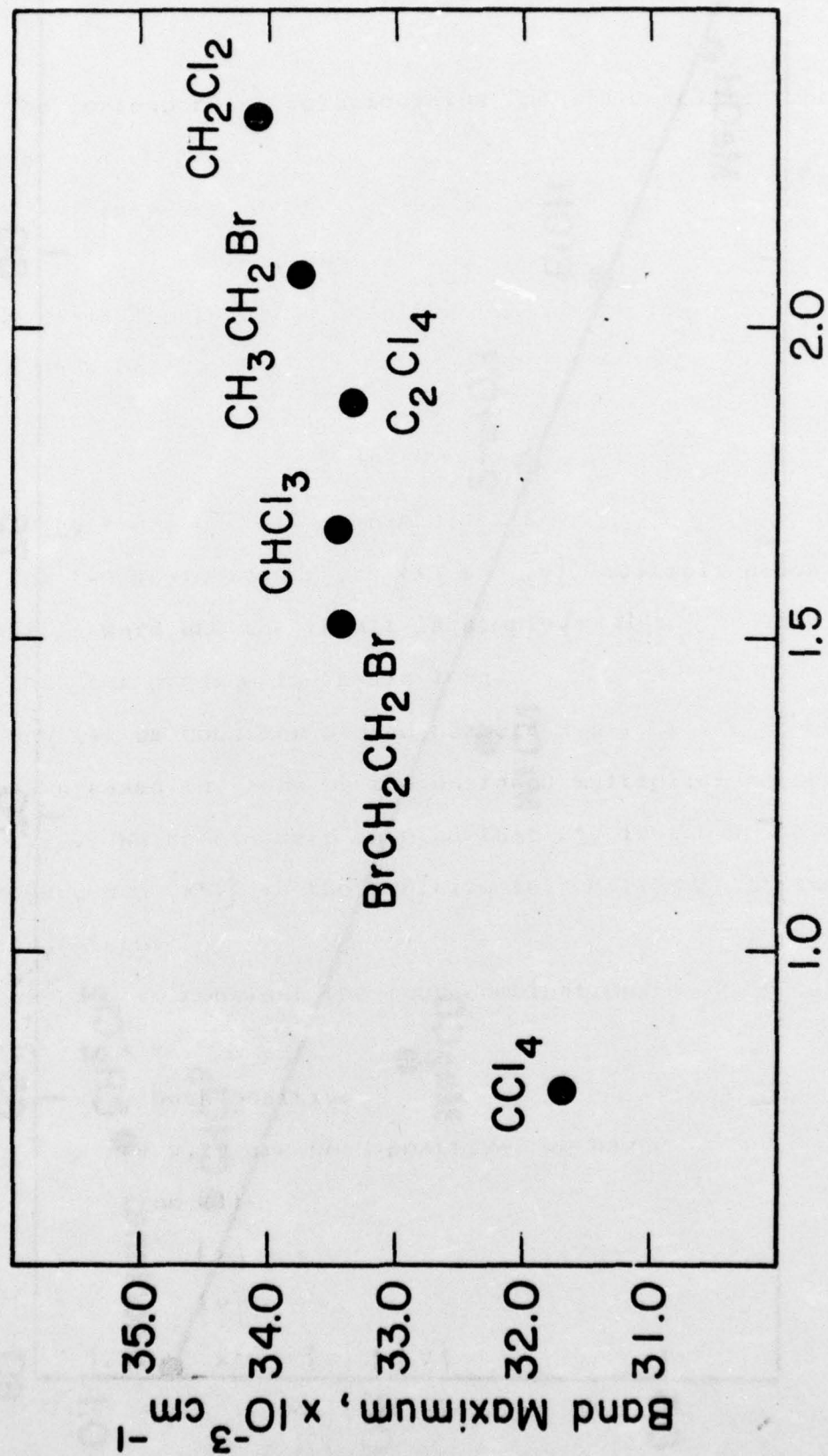
Figure 4. Correlation of CTTS absorption maximum with ease of reduction of the halocarbon solvent.  $E_{1/2}$  values are from: C.K. Mann and K.K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, Inc., New York 1970.

Figure 5. Correlation of low energy difference peak intensity at 395 nm with Kosower<sup>15</sup> Z value. Difference spectra were recorded for  $1.2 \times 10^{-4} \text{ M}$  tetramer in  $\text{S}/\text{CCl}_4$  (9/1 by volume) in reference beam vs.  $1.2 \times 10^{-4} \text{ M}$  tetramer in 100%  $\text{CCl}_4$  in sample beam where S is the co-solvent.

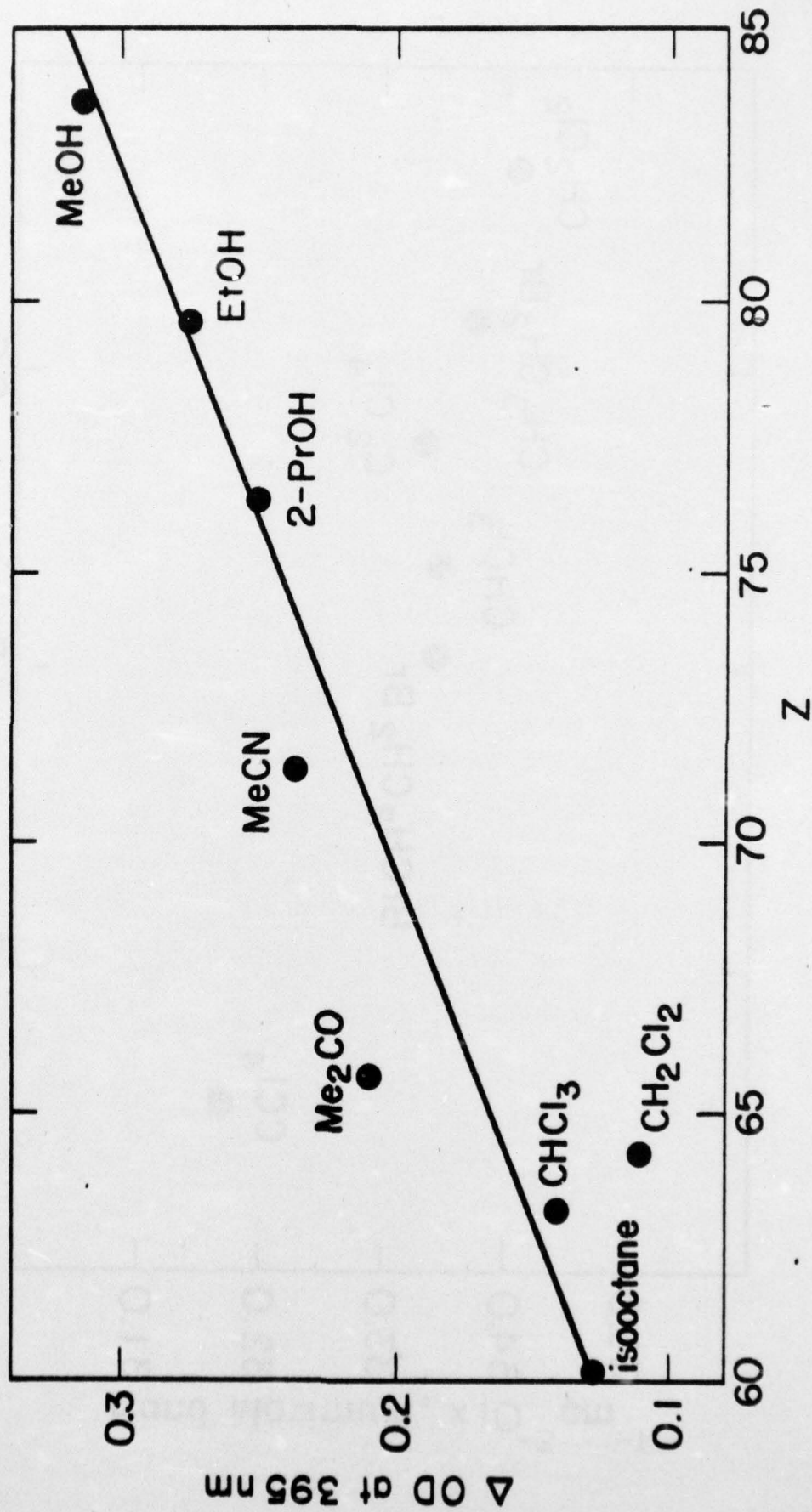








$-E_{1/2}$ , volts vs. SCE



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