β-CH_3 and α-H are *positive.* Because $Q_{CH} \cong 23$ gauss and Q_{CCH_3} ranges from +5 to +30 gauss,[31] it is quite likely that in general $|Q_{CCH_3}| \leqslant |Q_{CH}|$.[41] Experimentally, $|A_{\alpha,\gamma}| > |A_\beta|$ so that it follows that $|\rho_{C_{\alpha,\gamma}}| > |\rho_{C_\beta}|$. These results are consistent only with the *predominant* mode of delocalization being metal-to-ligand parallel spin transfer, *i.e.*, partial α-spin transfer from the metal e orbitals to appropriate linear combinations of the LUMO's.[42] This conclusion conforms to Eaton's model of spin delocalization in tris acetylacetonates.[3]

Finally, one other observation is worth noting. From the signals of a *trans* isomer it is not generally possible to find constant ratios of $\Delta\nu_\alpha/\Delta\nu_\beta$ and/or $\Delta\nu_\gamma/\Delta\nu_\beta$. This indicates that the spin density distribution conforms to the full molecular asymmetry and not to the simpler situation in which a different total amount of spin is delocalized in each ring but the relative spin densities within each ring are the same.

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[41] For a complex with structurally related ligands, bis(4-isopropylamino-3-penten-2-onato)nickel(II), Q_{CCH_3} values at the α and γ positions have been estimated as +15 to +20 gauss.[29c]

[42] It is evident that in some cases the data indicate contributions to the total isotropic shifts from other mechanisms as well. In $V(mhh)_3$ and $V(mmh)_3$ the contact shifts of α-H are too large to be accommodated only by π delocalization in the ring LUMO's. For these complexes it is expected that $\rho_{C\alpha} \sim \rho_{C\gamma}$ and, therefore, that $|\Delta\nu_{\alpha-H}| \sim |\Delta\nu_{\gamma-CH_3}|$ for π delocalization.[41] The observed $|\Delta\nu_{\alpha-H}| \sim 3|\Delta\nu_{\gamma\text{-}CH_3}|$ is not consistent with this expectation. Furthermore, the apparent Q_{CCH_3} value calculated for the β position in $V(mmm)_3$ is only +3.3 gauss, taking $\rho_{C\beta}$ as that calculated from the β-H shift in $V(acac)_3$, an unusually low value to be obtained by substituting CH_3 for H in a π radical. Possibly spin imbalance in the chelate ring systems, produced by actual delocalization and/or spin polarization, and pseudo-contact interactions also make contributions of as yet undetermined magnitudes.

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An Electrochemical Study of π-Cyclopentadienyl-π-cycloheptatrienylvanadium(0)

BY WILSON M. GULICK, JR.,[1a] AND DAVID H. GESKE[1b]

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Electrochemical and spectrophotometric properties of π-cyclopentadienyl-π-cycloheptatrienylvanadium(0) (CpVTr) have been studied. CpVTr was found to undergo electrooxidation in acetonitrile solution on mercury and platinum electrodes at about 0.19 v *vs.* aqueous saturated calomel electrode. The electron-transfer step of the electrooxidation is reversible, but the cation, $CpVTr^+$, decomposes slowly, even in the temperature range −25 to −40°. The decomposition reaction appears to involve 2 moles of cation which react to regenerate 1 mole of CpVTr. Other decomposition products remain unidentified. Macroscopic electrolyses were employed to generate solutions of the cation, and ultraviolet and visible spectra of this species were secured. Observation of the time dependence of these spectra permitted differentiation of absorbance due to $CpVTr^+$ from that due to decomposition products.

Introduction

The mixed sandwich complex, π-cyclopentadienyl-π-cycloheptatrienylvanadium(0), $C_5H_5VC_7H_7$ (hereafter abbreviated CpVTr), reported by King and Stone[2] is one of the relatively few organometallic complexes which contain a π-C_7H_7 group.[3] Although an infrared study[4] of CpVTr prompted reexamination of the structure of the complex, X-ray crystallography[5] confirmed unequivocally a structure in which both rings are planar, parallel, and symmetrically bound to vanadium as depicted approximately in Figure 1.

We report here an examination of the electrooxidation of CpVTr to $CpVTr^+$ in acetonitrile solution. Since the course of the electrochemical experiments was followed spectrophotometrically, electronic spectra of both CpVTr and $CpVTr^+$ were secured. The relative instability of $CpVTr^+$ required low-temperature electrochemical and spectrophotometric techniques. We regard the acquisition of accurate spectral data for these molecules as of potential use in testing the molecular orbital theory of transition metal π complexes.

Experimental Section

Reagents.—Acetonitrile for use in ultraviolet spectrophotometry (Eastman Spectro Grade) was dried by stirring at ambient temperature with calcium hydride for 12 hr followed by filtration through sintered glass. Such solvent had useful transmission characteristics in the far-ultraviolet region, showing an absorbance of 0.85 at 210 mμ and 1.29 at 200 mμ when observed in a 1-cm cell *vs.* an empty cell. This solvent was considered satisfactory for use to 200 mμ in 0.1-cm cells. For experiments in which ultraviolet transparency was not a critical criterion, acetonitrile (Union Carbide Co.) purified by method E of Coetzee, *et al.*,[6] was employed. 2,2,4-Trimethylpentane (Eastman

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[1] (a) Abstracted in part from the Ph.D. thesis of W. M. G., Cornell University, 1965; (b) Alfred P. Sloan Foundation Fellow.

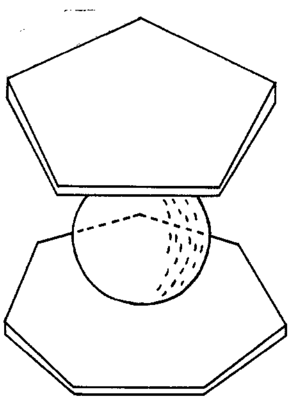
[2] R. King and F. Stone, *J. Am. Chem. Soc*, **81**, 5263 (1959). Despite the name chosen by these authors, we regard CpVTr as a more euphonious abbreviation than CpVCh.

[3] The analogous chromium complex, CpCrTr, has been reported by: (a) E. Fischer and S. Breitshaft, *Angew. Chem.*, **75**, 94 (1963); *Chem. Ber.*, **99**, 2905 (1966); (b) R. King and M. Bisnette, *Tetrahedron Letters*, 1137 (1963); (c) R. King and M. Bisnette, *Inorg. Chem.*, **3**, 785 (1964).

[4] H. Fritz and R. Schneider, *Chem. Ber.*, **93**, 1171 (1960).

[5] R. Rundle and G. Engebretson, *J. Am. Chem. Soc.*, **85**, 487 (1963).

[6] J. F. Coetzee, G. Cunningham, D. McGuire, and G. Padmanabhan, *Anal. Chem.*, **34**, 1139 (1962).



CpVTr

Figure 1.—Approximate representation of the structure of π-cyclopentadienyl-π-cycloheptatrienylvanadium(0).

Spectro Grade) was used as received. All solvents were degassed under vacuum and stored in sealed ampoules until used.

Seaford grade nitrogen gas further purified by passage through heated copper turnings was used for degassing purposes. The supporting electrolyte employed, except as specifically noted, was tetraethylammonium perchlorate at a concentration of 0.1 M. The preparation of this material has been described previously.[7] CpVTr was a gift from Professors F. G. A. Stone and R. B. King.

Precautions in Handling CpVTr.—Solid CpVTr decomposes slowly in air. Rapid destruction of CpVTr in solutions containing oxygen is evidenced by a change in color from pale purple to brown. The utility of the procedure adopted for handling these materials (*vide infra*) was demonstrated by observing that CpVTr in solution did not suffer appreciable decomposition over many hours.

Solid CpTVr was handled in a glove box under dry nitrogen where it was placed in tared, thin-walled glass ampoules. These ampoules were made to fit into an all-glass apparatus in which they were crushed and their contents were dissolved in a known volume of solvent entirely under nitrogen atmosphere. Nitrogen pressure was then employed to dispense these solutions into nitrogen-flushed spectrophotometric or electrochemical cells.

Ultraviolet and Visible Spectroscopy.—All ultraviolet and visible spectrophotometric studies were carried out on a Cary Model 14 recording spectrophotometer. Room temperature ultraviolet spectra of CpVTr were obtained using a 0.10-cm quartz cell equipped with two microstopcocks. Visible spectra were secured using a standard 10.0-cm cylindrical cell with one ground joint in conjunction with an adapter made to connect the joint to the dissolution apparatus. The reference cell was filled with pure solvent.

Low-Temperature Spectrophotometry.—Low-temperature ultraviolet and visible spectrophotometric measurements were made in a quartz spectrophotometry dewar fabricated according to the design of Hirshberg and Fischer.[8] Special cells of 0.965- and 0.114-cm path lengths were used. (The dewar and cells were obtained from the Thermal-American Fused Quartz Co.) The cells were each equipped with two 12/2 socket jonts which served both for suspending them in the dewar and for providing sample entrance. Microstopcocks were employed to seal the cells. The reference cell for the low-temperature spectrophotometry of electrolyzed solutions contained acetonitrile 0.1 M in supporting electrolyte and was maintained at room temperature.

Temperature Control.—Low temperatures were obtained by passing cold, dry air into the spectrophotometry dewar. Cold air was produced and controlled by a thermostat employing a paint-spraying compressor (All State Model 102.89981) and a heat exchanger immersed in a slush of Dry Ice and trichloroethylene. Temperature control was achieved by the use of a Thermistemp Model 63RB temperature controller (Yellow Springs Instrument Co.) operating a solenoid valve which vented most of the cold air when the temperature in the dewar decreased below a preselected value.[9] A copper–constantan thermocouple taped directly to the spectrophotometric cell served to monitor the temperature. Ultraviolet and visible spectra described below were carried out at one of three temperatures as measured by the thermocouple: -25.6 ± 0.3, -30.8 ± 0.2, or $-40.5 \pm 0.6°$.

Electrochemistry.—Polarography and voltammetry at a rotating platinum microelectrode (rpe) were carried out using the ORNL three-electrode polarograph described previously.[10] The platinum electrode was rotated by a Sargent 600-rpm synchronous rotator. Under identical experimental conditions this same electrode has been shown to give a limiting current constant, i_l, of 4.81 μa/mM for the one-electron oxidation of iodide ion to iodine in acetonitrile.[11]

Cyclic voltammetry was carried out at a shielded, horizontal platinum-disk electrode of about 5-mm diameter. A Hewlett-Packard Model 202A function generator provided a triangular potential sweep which was recorded *vs.* current by a Houston Instruments X-Y recorder. All voltammetry was carried out at 25 ± 1° except as specifically noted.

Controlled-potential electrolyses were carried out in a standard three-compartment cell. The working electrode was a spiral of platinum wire rotated at about 800 rpm. In one experiment only a mercury pool of about 35-mm diameter was employed and the solution was stirred with a magnetic stirrer. The sample compartment was fitted with a jacket through which ethanol was pumped from a mechanically refrigerated reservoir. Sample temperature was monitored by a thermometer in the coolant return line.

Electrolyses were carried out using a voltage source which was controlled manually while the potential of the working electrode was monitored with a pH meter (Leeds and Northrup Model 7664). The electrolysis current was passed through a 100-ohm precision resistor (General Radio Type 500-D) and the resulting potential was recorded *vs.* time on a Varian G-14 recorder. These current–time curves were integrated graphically. Potentials throughout these experiments are referred to the aqueous saturated calomel electrode (sce) under conditions of "long" immersion.[12] Concentrations of CpVTr in solutions for electrochemical experiments were determined by measurement of their absorbance at the ultraviolet maximum.

In all controlled-potential electrolyses the current, i, decreased exponentially with time up to the point that approximately 90% of the theoretical number of coulombs had passed. During further electrolysis, i decreased less rapidly, resulting in a positive deviation from linearity in a log i *vs.* time plot. Since it was our objective to obtain solutions containing CpVTr$^+$ free of decomposition products, we did not attempt to obtain "total" oxidative electrolysis in the usual sense of reducing the current to 1% or less of its initial value, but rather terminated the oxidation soon after the current no longer decreased exponentially. Immediately after terminating the oxidation, a measured volume of the solution was removed for spectrophotometric examination. Transfer of the oxidized solution was accomplished using a Dry Ice jacketed, nitrogen-flushed hypodermic syringe. The remaining oxidized solution, still at low temperature, was, in several cases, electrolytically *reduced* as soon as possible after the termination of the oxidative electrolysis. This approach is essentially the technique of "reversal coulometry" described by Bard.[13] The working-electrode potential was 0.3–0.4 v for the oxidations and −0.2 v for the subsequent reductions.

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(7) D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960).

(8) Y. Hirshberg and E. Fischer, *Rev. Sci. Instr.*, **30**, 197 (1959).

(9) A more detailed description of this apparatus as well as other experimental details may be found in the Ph.D. thesis of W. M. G.

(10) K. Kuwata and D. H. Geske, *J. Am. Chem. Soc.*, **86**, 2101 (1964).

(11) D. H. Geske, *J. Phys. Chem.*, **63**, 1062 (1959).

(12) J. F. Coetzee and G. Padmanabhan, *ibid.*, **66**, 1709 (1962).

(13) A. J. Bard and S. V. Tatwawadi, *ibid.*, **68**, 2676 (1964).

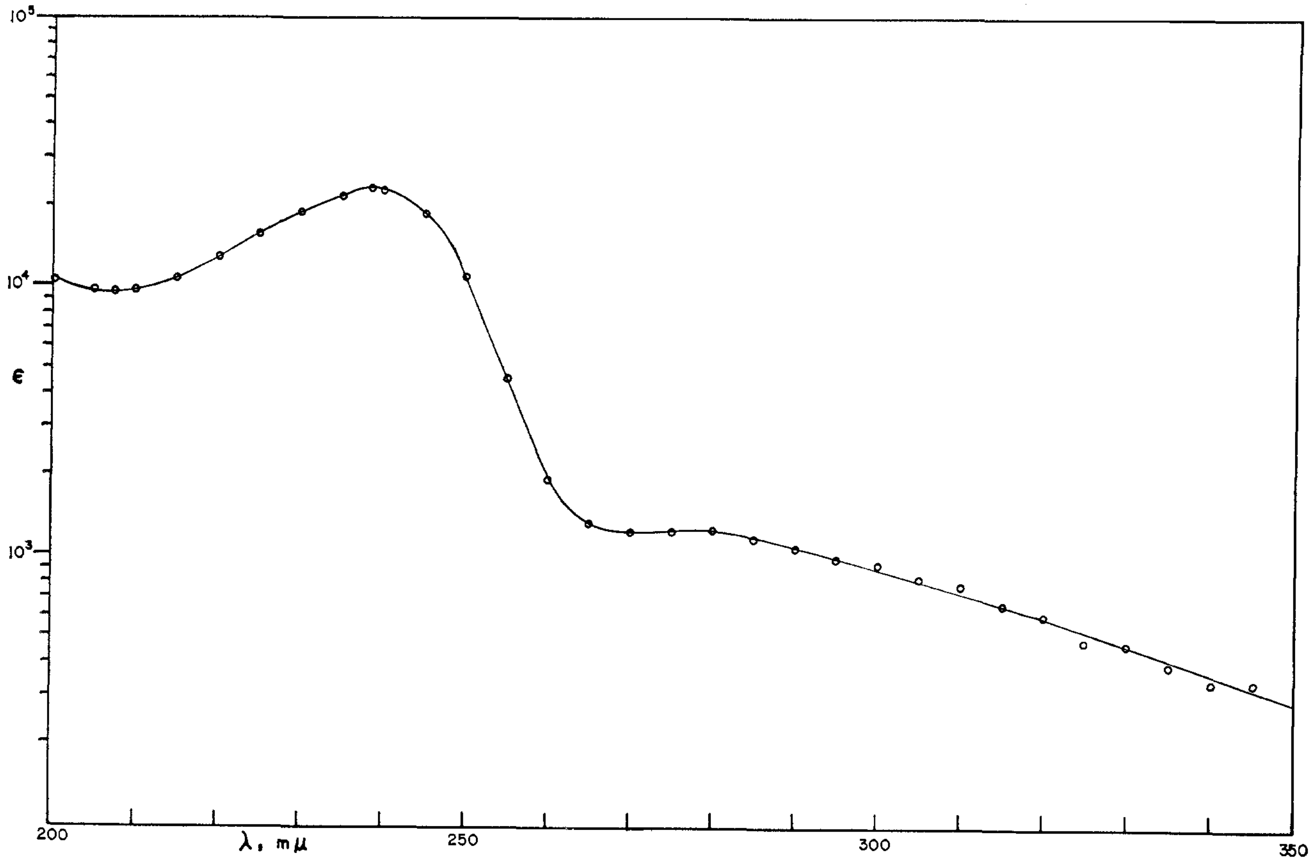

Figure 2.—Ultraviolet absorption spectrum of CpVTr in acetonitrile solution.

Results

Ultraviolet and Visible Spectra of CpVTr.—Two solutions of CpVTr in acetonitrile, 0.518 and 0.390 mM, respectively, were prepared with great care in order to determine precisely the ultraviolet and visible spectra of CpVTr. The agreement between the observed molar absorptivities for these two solutions was better than 1% in the ultraviolet region and within 2% in the visible region.

The ultraviolet spectrum of CpVTr as given in Figure 2 is characterized by a broad absorption band with a shoulder at 280 mμ with molar absorptivity 1.23×10^3 cm^{-1} M^{-1} and a maximum at 238.5 mμ with molar absorptivity 2.25×10^4 cm^{-1} M^{-1}. In the visible region a very broad absorption occurs with a maximum at 563 mμ with molar absorptivity 32.6 cm^{-1} M^{-1}. A minimum occurs at 454 mμ followed by a steep rise in absorption at shorter wavelengths. CpVTr yields similar spectra in 2,2,4-trimethylpentane solution. At a concentration of 0.43 mM, maxima at 559 and 240 mμ were obtained with molar absorptivities of 42 cm^{-1} M^{-1} and 2.75×10^4 cm^{-1} M^{-1}, respectively.

Careful observation of these solutions during the dissolution process revealed no trace of discoloration. A fresh CpVTr solution showed an absorbance of 0.690 at 238.5 mμ in a 0.1-cm stoppered cell, and after 56 hr this absorbance had decreased to 0.650, or less than 6%. These observations, in conjunction with the reproducible values of the molar absorptivities, led us to conclude that air oxidation of CpVTr had been prevented and that accurate results could be achieved if measurements were made shortly after filling the cells. The ultraviolet spectrum of a solution was observed after the CpVTr had been fully decomposed by air. This spectrum consists of a nearly featureless straight line with molar absorptivity (calculated from the initial concentration of CpVTr) increasing from about 10^3 cm^{-1} M^{-1} at 350 mμ to 10^4 cm^{-1} M^{-1} at 210 mμ.

Voltammetry.—CpVTr in acetonitrile solution undergoes oxidation at both a dropping mercury electrode (dme) and at the rpe with a half-wave potential of about 0.19 v *vs* sce. On both electrodes, the current–voltage curve is well defined.[14] Values of the diffusion current constant, I, the limiting current constant, i_l/C, and $E_{3/4} - E_{1/4}$ are characteristic of a reversible, one-electron oxidation. On platinum a second oxidation occurs with a half-wave potential of 0.839 v *vs.* sce. This wave, which is drawn out and clearly not reversible, has a value of i_l/C of about 120% of that for the first oxidation wave. On the dme, no *reduction* of CpVTr occurs within the potential limit of acetonitrile, −2.3 v *vs.* sce. Voltammetric data are summarized in Table I. Cyclic voltammetry of an exploratory nature was run on a 1.62 mM CpVTr solution in acetonitrile. When the sweep rate was varied

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(14) Preliminary experiments performed by J. Gandebouef indicated that similar voltammetric behavior is observed in dimethylformamide and in acetone.

TABLE I

VOLTAMMETRIC DATA FOR CpVTr[a]

Dropping Mercury Electrode

Concn, mM	$-i_d/C$[b]	I[c]	$E_{1/2}$, v	$E_{3/4} - E_{1/4}$, mv
1.51	4.37	3.4	0.184	...
1.62	4.79	3.7	0.185	56
1.04	5.66	4.5	0.196	54
1.62 (−20°)	3.41	2.7	0.168	...

Rotating Platinum Microelectrode

Concn, mM	$-i_l/C$[b]	$E_{1/2}$,v	$E_{3/4} - E_{1/4}$, mv
1.62	4.70	0.196	58
1.04	5.75	0.192	56
(second oxidn)	7.04	0.839	113

[a] Values reported are averages of two scans for each solution; maximum, not average currents are reported. [b] Anodic currents are designated as negative. Units are μa/mM. [c] $I = i_d/m^{2/3}t^{1/6}C$.

from 8 to 80 mv sec^{-1}, the peak potential changed from 0.237 to 0.293 v *vs.* sce. At all sweep rates investigated, the ratio of the cathodic (reverse) current to the anodic (forward) current remained somewhat less than unity.

TABLE II

			Electrooxidation					Electroreduction				
				Coulombs					Coulombs			
Expt	Absorbance of initial soln at 238.5 mμ in 0.1-cm cell	Concn, mM	Vol oxidized, ml	Theoret, for n = 1	Obsd	% completion	Temp range, °C	Vol. reduced, ml	Theoret[g]	Obsd	% completion	Temp range, °C
A	0.671	0.299	47.6	1.37	1.20	87.3	−29 to −24	41.6	1.05	0.74	70.6	−24 to −22
B[a]	0.609	0.271	31.1	0.81	0.82	101.0	−31 to −26	25.1	0.66	0.44	66.7	−28 to −25
C	0.620	0.276	46.8	1.25	1.19	95.1	−31 to −26	39.8	1.01	0.78	77.4	−30 to −28
D	2.070	0.921	47.3	4.20	3.89	92.6	−30 to −29	...[e]	...	...	...	...
E	0.933	0.415	47.9	1.92	1.80	93.8	−30 to −28	41.9	1.57	1.06	67.6	−29 to −27
F	...[b]	...	∼40	4.89	4.33	88.6	−30 to −24	...[c]	...	...	...	...
G	2.497	1.111	47.9	5.13	4.04	78.7[d]	−33 to −31	...[e]	...	...	...	...
H	...[c]	1.510	46.6	6.80	6.40	94.1	−36 to −35	40.6	5.57	3.81	68.5	−37 to −34
I	...[f]	0.703	53.4	3.64	3.36	92.3	−40 to −38	...[f]	...	...	...	....

[a] Mercury-pool anode in this experiment only. [b] Theoretical number of coulombs calculated from weight of CpVTr; entire solution electrolyzed. Sodium perchlorate supporting electrolyte was employed. [c] Concentration too high for spectrophotometric measurement; calculated from weight of CpVTr taken. [d] Ratio of final current to initial current indicated >90% complete; in all other experiments this ratio was in substantial agreement with the coulometry. [e] These solutions were not reduced; the oxidized solutions instead were used for other experiments. [f] Concentration computed from weight of CpVTr taken; solution not reduced. [g] Computed assuming that only previously oxidized material would be reduced.

Controlled-Potential Electrolyses.—In order to provide a more detailed characterization of CpVTr$^+$, the product of the electrooxidation of CpVTr, eight macroscopic controlled-potential oxidations were carried out as described in the Experimental Section. The numbers of coulombs computed from the recorded current–time curves are compared (Table II) with the theoretical values calculated assuming a one-electron oxidative process. The *gross* reversibility of the electrode process was investigated by *reducing* several of these oxidized solutions and comparing theoretical and experimental coulometry (Table II). Specific experimental procedures are given in the footnotes to Table II.

Properties of the Oxidized Solutions. Ultraviolet and Visible Spectra of CpVTr$^+$.—In experiments A, B, C, E, and I a sample of the solution after electrooxidation was transferred to the ultraviolet cell (0.114-cm path) in the optical dewar described above.

Obtaining molar absorptivities from these spectra is complicated by the dependence of solvent density on temperature; the molarity of the solution increases as the temperature is lowered. Molarities were corrected approximately using the calculated[15] ratios of the density of acetonitrile at the low temperatures to that at 25°. Since even at reduced temperatures the cation, CpVTr$^+$, has a limited lifetime, spectra were further complicated by decomposition products which showed strong ultraviolet absorption. Therefore data from the spectrophotometric investigation of the cation were treated in the following manner. The first spectrum obtained after completion of each electrolysis was assumed to contain no decomposition products. The concentration of absorbing species (CpVTr$^+$) at the reduced temperatures was calculated from the original concentration of CpVTr in the solution, the electrochemical completeness of the oxidation, and the temperature correction. The observed absorbance was corrected, as necessary, for residual CpVTr by manually subtracting an appropriate percentage of the spectrum of that material. Using these corrected values of concentration and absorbance, molar absorptivities were calculated for CpVTr$^+$. Data from these "first" spectra are summarized in Table III.

Because the assumption that all "first" spectra were unaffected by decomposition products of CpVTr$^+$ is not strictly valid, we examined the changes in the spectra with time to differentiate absorbance due to

(15) Densities were computed from data available for very pure acetonitrile: "International Critical Tables," Vol. III, The Kynoch Press, Birmingham, England, pp 27, 33. It is likely, therefore, that the densities calculated are only approximately correct for acetonitrile decimolar in supporting electrolyte. Although this difficulty could have been obviated by use of molality throughout, we felt that the inconvenience of doing so was unwarranted in view of the limitations imposed upon the accuracy of these spectral data by the instability of CpVTr$^+$.

TABLE III

ELECTRONIC SPECTRAL DATA FOR $CpVTr^+$

Ultraviolet

Expt	Temp at which spectrum was obsd, °C	λ (max), mμ	Molar absorptivity[a] (max)	λ (shoulder), mμ	Molar absorptivity[a] (shoulder)
A	−25	225.9	2.71×10^4	240	0.51×10^4
B	−25	225.6	2.33×10^4	240	0.70×10^4
C	−25	225.5	2.40×10^4	245	0.42×10^4
E	−30	225.8	2.11×10^4	245	0.27×10^4
I	−40	226.8	2.36×10^4	248	0.35×10^4
			Visible		
		λ[b]		λ[b]	
D	−30	470	3.44×10^2 [a]	440	3.46×10^2 [a]
G	−30	470	4.91×10^2	440	5.17×10^2

[a] Molar absorptivities obtained from the absorbance observed in "first" spectra and corrected as outlined in text. [b] These are not maxima; numerical data are given as a calibration for Figure 4.

$CpVTr^+$ from that of its decomposition products. The most pronounced changes in the spectra on long standing are a marked increase in absorbance in the region of 260–280 mμ and both an increase in absorbance and a shift to shorter wavelength of the peak initially at 225 mμ.

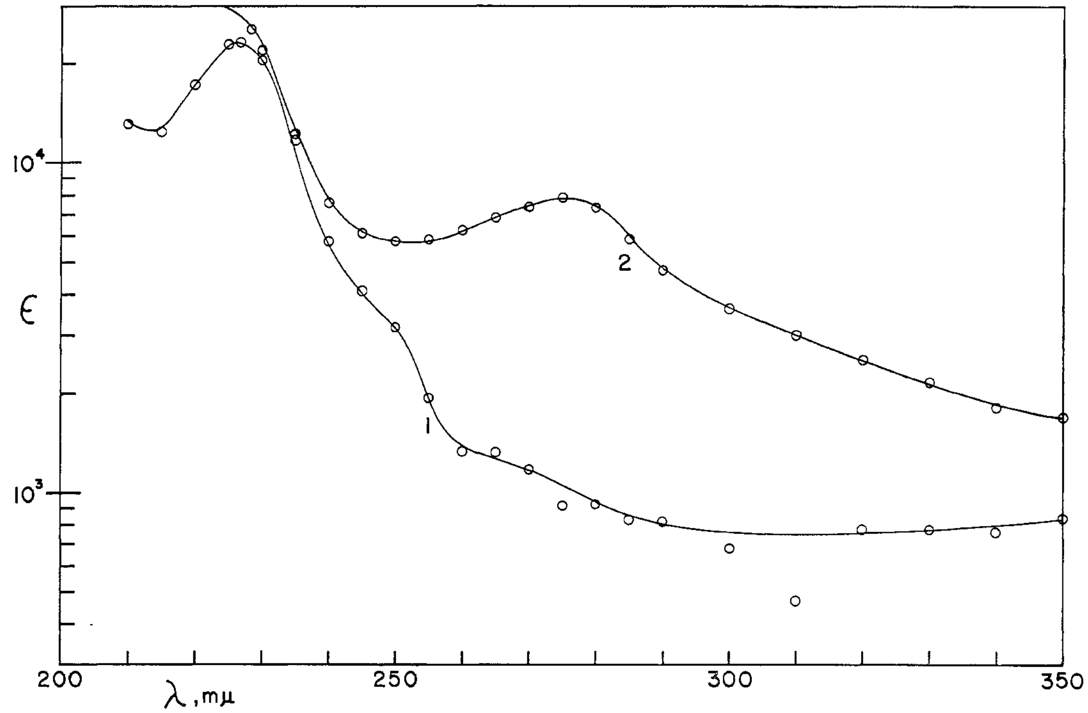

Figure 3.—Ultraviolet absorption spectra of $CpVTr^+$ obtained from electrooxidation of CpVTr in acetonitrile, experiment I: (1) "first" spectrum obtained at −40° within 0.25 hr after termination of the electrooxidation; (2) spectrum obtained at room temperature 11 hr after spectrum 1. Since concentrations of decomposition products were not known, the molar absorptivity values presented in (2) were calculated from the observed absorbance and the initial CpVTr concentration.

In experiment I a spectrum obtained at −40° 0.7 hr after the "first" spectrum was, within the estimated experimental uncertainty, identical with the initial result and successive spectra obtained up to 2.3 hr after the "first" spectrum showed only small increases in absorbance. Figure 3 shows the "first" spectrum from experiment I as well as one obtained much later after warming the sample to room temperature. The second spectrum is typical of the limit of the observed changes in these spectra. Decomposition of CpVTr as manifested by spectral changes is appreciably faster at −30° (experiment E) than at −40° and sufficiently rapid at −25° (experiments A, B, and C) that quantitative spectral data cannot be secured with confidence.

In experiments D and G the visible spectrum of $CpVTr^+$ was examined by the same method described for the ultraviolet spectra, using the cell of longer path length (0.965 cm). Spectra in both experiments were obtained at −30°. The extremely weak absorbance of CpVTr in the visible region made correction for incomplete oxidation unnecessary. The visible spectra of $CpVTr^+$ appear in Figure 4. Since there are no real maxima, molar absorptivities at 440 and 470 mμ are given in Table III. As in the case of ultraviolet spectra, we examined the changes in the visible spectra with time. On standing at −30°, the absorbance increased somewhat with time but the general shape of the spectra remained the same.

Electrochemistry of $CpVTr^+$.—The portions of the oxidized solutions D and G remaining in the electrolysis cell were investigated polarographically as the solutions were warmed from approximately −30° to room temperature over a period of about 2 hr. Voltage scans were begun at 0.4 v *vs.* sce and run toward more reducing potentials. Both experiments produced qualitatively identical results. A small oxidizing current was observed, followed by a reducing current about 10 times as large. This wave, which corresponds to the CpVTr–$CpVTr^+$ couple, appeared at a potential close

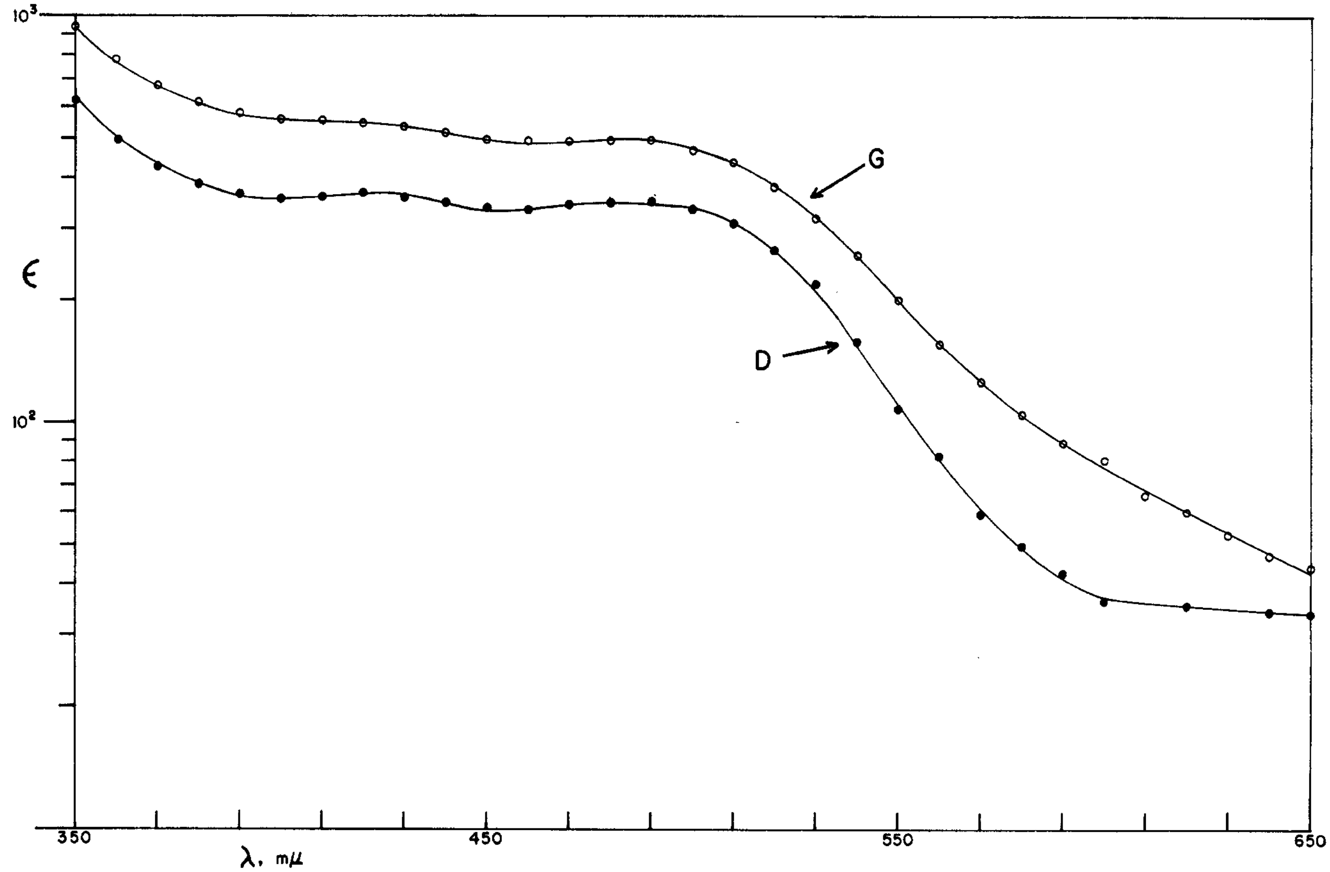

Figure 4.—Visible spectra of CpVTr$^+$ obtained by electrooxidation of CpVTr in acetonitrile, experiments D and G. Both spectra at −30°.

to that for the room-temperature oxidation of CpVTr. The ratios of CpVTr to CpVTr$^+$ estimated from the diffusion currents were in substantial agreement with coulometric data (Table II).

In later polarograms the current due to reduction of CpVTr$^+$ diminished and a corresponding increase in the oxidizing current was observed. In addition, a second reduction at about −0.2 v appeared. In later scans at higher temperatures, the diffusion currents for the oxidizing wave and the second reduction grew to maximum values as the reduction of CpVTr$^+$ vanished. Still later, at room temperature, the oxidizing wave and the second reduction wave both decreased and a third reduction wave at −0.68 v appeared and increased. In addition to demonstrating the electrochemical reduction of CpVTr$^+$, these data indicate that one product of the low-temperature decomposition of CpVTr$^+$ is CpVTr.

Current Reversal Coulometry. Polarographic Investigation.—When several of the oxidized solutions, while still at low temperature (Table II), were *reduced* electrolytically, total electrolysis, in the usual sense, *was* obtained.

In experiment H we observed that the solution gave substantially identical polarographic behavior both before and after the oxidation–reduction coulometric cycle. Several polarograms for the oxidation of CpVTr were recorded at room temperature prior to the macroelectrooxidation. The half-wave potential was 0.184 v *vs.* sce and the maximum diffusion current was 6.60 μa. After reversal coulometry, the half-wave potential was also 0.184 v and the maximum diffusion current was 5.40 μa. These later polarograms revealed, in addition, two small reduction waves with, respectively, half-wave potentials of about −0.15 and −0.51 v and maximum diffusion currents of 0.16 and 0.53 μa.

The polarographic diffusion current for oxidation of CpVTr, 5.40 μa, observed after the current reversal cycle was *larger* than the value of 4.68 μa calculated from coulometric data. Since previous experiments indicated that CpVTr is regenerated by decomposition of CpVTr$^+$, an attempt to calculate the diffusion current for the system after reversal coulometry was made in the following manner. (1) The percentage unoxidized (6.2%) was assumed to remain CpVTr. (2) CpVTr was assumed to be the sole product of the electrochemical reduction. (3) All CpVTr$^+$ which was not reduced electrolytically was assumed to decompose according to a disproportionation reaction such as that represented by

$$2\text{CpVTr}^+ \longrightarrow \text{CpVTr} + \text{X} \qquad (1)$$

where X was assumed to be nonelectroactive. Such calculations yield 3.8 μequiv from (1), 39.5 μequiv from (2), and 9.1 μequiv from (3). The diffusion current thus predicted after reversal coulometry is 5.64 μa. The experimental value, 5.40 μa, is 96% of that calculated.

Current Reversal Coulometry. Spectrophotometric

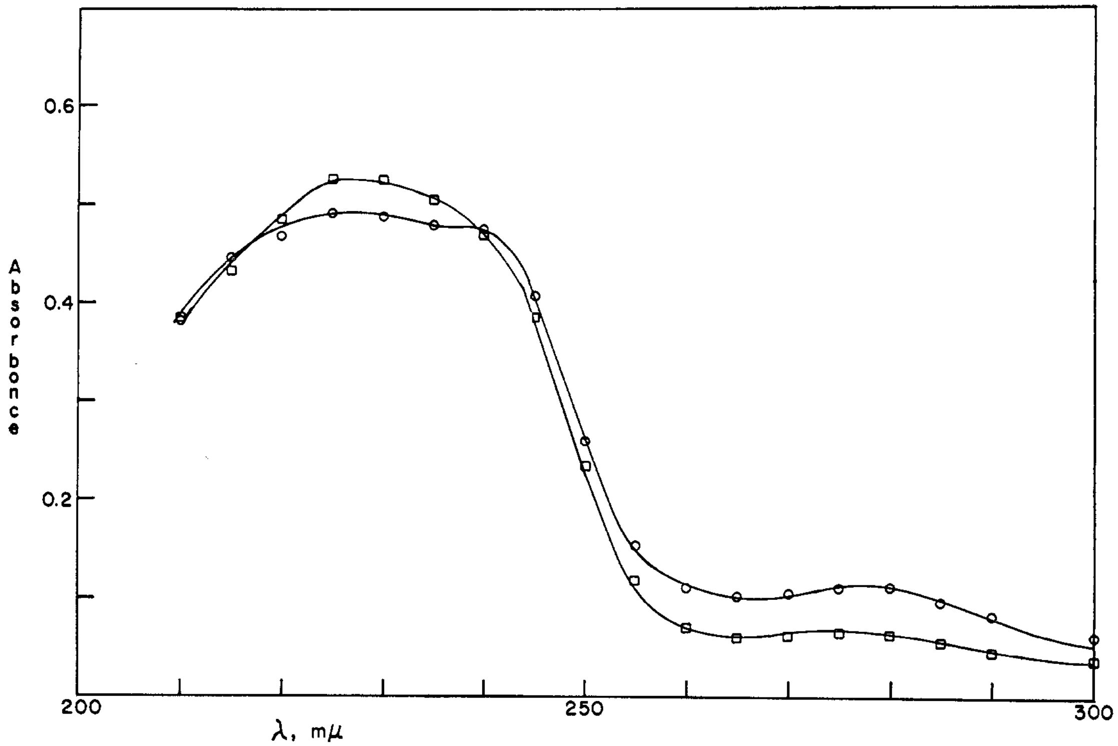

Figure 5.—Comparison of observed and calculated ultraviolet absorption spectra for the solution which had been cycled through the current-reversal coulometric process in experiment A. Circles indicate the experimental spectrum, and squares, the calculated spectrum.

Investigation.—Some cases have been reported[16] in which solutions of organometallic species gave identical polarograms before and after the reversal coulometry, but spectrophotometry showed that, in fact, starting material had not been regenerated by the reversal process. Therefore, after solutions A, B, C, and E had been subjected to the reversal coulometric procedure at reduced temperature (Table II), they were allowed to warm to room temperature and ultraviolet spectra were obtained. Comparison of ultraviolet spectra of these solutions with spectra of solutions of CpVTr indicated that both CpVTr and decomposition products of CpVTr$^+$ were present. This finding is in accord with the reductive coulometry which indicated that fewer equivalents were reduced than were originally oxidized.

Theoretical ultraviolet spectra for these solutions were calculated for comparison with those obtained experimentally. Assuming that the only electroreduction product is CpVTr, its contribution to the absorbance is readily calculated from the coulometry of the electroreduction. The portions of *oxidized solution initially removed* from the electrolysis cell for low-temperature spectrophotometry were allowed to stand at room temperature for several hours in the sealed ultraviolet cell. It was assumed that spectra of these solutions would be representative of the decomposition products of CpVTr$^+$. Appropriate percentages of these spectra were added to the contribution from CpVTr. In Figure 5 the observed and calculated spectra of the reduced solution from experiment A are compared. Similar results were obtained for B, C, and E.

Discussion

Voltammetry.—Polarographic and rpe voltammetric data show conclusively that the primary electrode reaction of CpVTr is a one-electron reversible oxidation. Values of the limiting current constant, i_l, for rpe voltammetry were compared to that for the oxidation of iodide and found to be in accord with a one-electron oxidation. Values of the polarographic diffusion current constant, I, compare favorably with the value for the reduction of silver ion in acetonitrile, 3.10.[17] The quantity $E_{3/4} - E_{1/4}$ for both electrode systems is within experimental error of 56 mv, the value predicted for a reversible, one-electron process.[18] We conclude that the nature of the primary electrode process is clearly established as

$$\mathrm{CpVTr} \rightleftharpoons \mathrm{CpVTr}^+ + e^- \qquad (2)$$

For comparison, the half-wave potential for the oxidation of CpVTr is somewhat less anodic than that for the oxidation of ferrocene in acetonitrile, 0.307 v *vs.* sce.[19] It is of interest that despite the highly touted stability 18-electron systems, this 17-electron compound could not be reduced in the potential region accessible in acetonitrile.

Properties of Oxidized Solutions.—Although the

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[16] R. E. Dessy, F. E. Stary, R. B. King, and M. Waldrop, *J. Am. Chem. Soc.*, **88**, 471 (1966).

[17] A. I. Popov and D. H. Geske, *ibid.*, **79**, 2074 (1957); **80**, 1340, 5346 (1958).

[18] J. Tomes, *Collection Czech. Chem. Commun.*, **9**, 12, 18, 150 (1937).

[19] T. Kuwana, T. Bublitz, and D. Hoh, *J. Am. Chem. Soc.*, **82**, 5811 (1960); also compare $E_{1/2}$ for the reversible couple CpCrTr$^+$–CpCrTr,[16] −1.2 v *vs.* Ag–AgClO$_4$ in dimethoxyethane.

primary electrode process is clearly established, it is of interest to consider the fate of $CpVTr^+$ on a somewhat longer time scale.[20] Attention is focused on the question of whether solutions of $CpVTr^+$ are, in fact, sufficiently stable at −30° to yield meaningful electronic spectra. As a matter of ancillary interest, we shall examine the evidence which supports the use of eq 1 to describe the decomposition of the cation.

The most direct evidence showing that the lifetime of the cation is not excessively short is that current reversal coulometry (Table II) resulted in regeneration of CpVTr to the extent of nearly 70%. Both polarography and spectrophotometry indicate that these solutions contain CpVTr after the oxidation–reduction cycle. We regard the agreement obtained between the observed and calculated spectra (Figure 5) as proof that we have, in fact, regenerated this material and done so in *approximately* the quantities given by coulometry.

In the current reversal experiments, about 1 hr was required for the oxidation, a second hour for the reduction, and as much as 0.25 hr between the electrolyses when samples were withdrawn for spectrophotometry. Since no other species can reasonably be formulated which would yield CpVTr upon one-electron reduction, we conclude that the oxidized solutions contained, predominantly, $CpVTr^+$, at the time when their spectra were obtained. Additional evidence comes from the polarographic investigation of oxidized solutions in which we found coincidence of the half-wave potential for the reduction of $CpVTr^+$ with that for the oxidation of CpVTr. The half-life of $CpVTr^+$, as estimated semiquantitatively from polarograms, is greater than 0.5 hr at −30°.

Polarography of electrooxidized solutions indicates that CpVTr is regenerated as the cation decomposes at low temperatures. This is substantiated by the upward deviation of log i *vs.* time plots for the macroelectrooxidations and by the quantitative agreement of the polarographic diffusion current in experiment H with that calculated using eq 1.

We have not specified products from the decomposition of $CpVTr^+$, other than CpVTr. It is known[21] that $C_7H_7^+$ in acetonitrile solution is reducible at −0.12 v *vs.* sce to yield bitropyl. If $C_7H_7^+$ were a product of the decomposition of $CpVTr^+$, the reductive coulometry of these experiments would not be valid. If, however, $C_7H_7^+$ were produced in appreciable amounts, we would expect to (1) observe the reduction of tropylium ion in cyclic voltammetry and (2) observe spectrophotometric evidence for the presence of bitropyl ($\lambda_{\min}$ 277 mμ, log ϵ 2.82; $\lambda_{\max}$ 255 mμ, log ϵ 3.85[22]). Reduction of tropylium ion is not observed on a time scale of approximately 100 sec in slow-sweep cyclic voltammetry.

Inspection of the *experimental* spectra of solutions which have been cycled through the current reversal process reveals that, in addition to CpVTr, a species is present which absorbs *strongly* only at wavelengths shorter than the CpVTr maximum, 238.5 mμ. This observation is inconsistent with the presence of significant amounts of bitropyl. Further evidence for the absence of $C_7H_7^+$ is found in comparison of the experimental and calculated spectra of Figure 5. The agreement obtained in the 238-mμ region indicates that the concentration of CpVTr calculated assuming 100% current efficiency for the electroreduction of $CpVTr^+$ is approximately correct, thus precluding the presence of other electroreducible species in appreciable quantity.

Use of a disproportionation reaction such as suggested in eq 1 to rationalize the regeneration of CpVTr is not a new mechanism for the decomposition of sandwich compound cations. The monoacation bis-π-diphenylchromium(I) is known[23] to disproportionate slowly in water or methanol according to

$$2CrAr_2^+ \longrightarrow CrAr_2 + Cr^{2+} + 2Ar \tag{3}$$

More recently, Calderazzo[24] has shown that in neutral aqueous media the decomposition of the monocation dimesitylenevanadium(I) follows a similar course. We feel that the reaction indicated in eq 1 is, thus, quite reasonable for $CpVTr^+$,[25] at least at low temperature. No major effort was made to identify other decomposition products (X in eq 1) of $CpVTr^+$.

Spectra of $CpVTr^+$.—Spectra of $CpVTr^+$ changed[26] with time even at reduced temperatures. Observation of these changes indicated that the spectrum which exhibits both small absorbance near 260–280 mμ and the smallest change with time at low temperature is likely to be most accurate. The 260–280-mμ region is selected as a primary criterion since the change in that region appears to be more sensitive than the change at shorter wavelengths. Application of these criteria leads to selection of the spectrum from experiment I (Figure 5) as the best representation of the ultraviolet spectrum of the cation. It is perhaps noteworthy that

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(20) Cyclic votammetry gave some indication that, on a longer time scale, we were not dealing with an ideally reversible system. Nicholson and Shain [*Anal. Chem.*, **36**, 706 (1964)] have shown that for an ideally reversible process E_{peak} should not change with the rate of voltage scan and that $i_{\text{reverse}}/i_{\text{forward}}$ should equal unity. These criteria were not fulfilled.

(21) D. H. Geske, *J. Am. Chem. Soc.*, **81**, 4145 (1959).

(22) W. von E. Doering and L. H. Knox, *ibid.*, **79**, 352 (1957).

(23) F. Hein and H. Scheel, *Z. Anorg. Allgem. Chem.*, **307**, 52 (1960).

(24) F. Calderazzo, *Inorg. Chem.*, **3**, 810 (1964).

(25) While this reaction is consistent with the available data, we do not assert that it is a proven mechanism. Since all experiments have been carried out a low concentrations of CpVTr (it is not very soluble) and thus at low concentrations of $CpVTr^+$, reaction of the latter with trace impurities in the solvent cannot be excluded from consideration. A reaction of the form $CpVTr^+ + Y \rightarrow CpVTr + Z$ would cause the polarographic diffusion current observed for oxidation of CpVTr in the solution which was cycled through the current-reversal process in experiment H (*vide supra*) to be *larger* than that predicted using eq 1. Since this is not the case, there is no evidence which favors reaction of $CpVTr^+$ with impurities as an alternative to disproportionation. Polarography indicates that further reactions occur and/or decomposition of $CpVTr^+$ may follow a different course at room temperature.

(26) The observed changes in these ultraviolet spectra could be explained by assuming that tropylium ion ($\lambda_{\max}$ 274 mμ, ϵ 4.42 × 10^3; $\lambda_{\max}$ 217 mμ, ϵ 4.29 × 10^4)[21] is produced by the decomposition of $CpVTr^+$. Such an assumption, however, is not supported by the electrochemical and spectrophotometric data given previously. Once decomposition of $CpVTr^+$ has proceeded significantly, the observed spectra consist of two or more overlapping absorptions and assignment of real band positions is no longer possible. Hence the observation of peaks apparently similar to those of tropylium may be accidental and misleading. The possibility of a decomposition product which has an absorption spectrum similar to tropylium ion deserves consideration. For example, the dication *p*-phenylenebis(cycloheptatrienylium) shows very similar absorptions ($\lambda_{\max}$ 225 mμ, log ϵ 4.69; $\lambda_{\max}$ 271 mμ, log ϵ 4.40) in acetonitrile: R. W. Murray and M. L. Kaplan, *Tetrahedron Letters*, 2903 (1965).

the electrolysis and spectrophotometry in experiment I were performed at lower temperatures than in preceding experiments.

There are not such discrete criteria to establish the validity of the visible spectrum of the cation, since the only change on standing is an initial general increase in absorbance. We feel, however, that the spectrum showing the smaller absorbance, that from experiment D (Figure 4), is probably the more accurate of the two.

Spectra of CpVTr.—Preparation and manipulation of solutions of CpVTr were carried out with the utmost care to exclude atmospheric oxygen. Since such solutions neither discolored nor changed absorbance over many hours, it is likely that the largest experimental errors occurred in measuring the volumes of the solutions. These errors are almost certainly no larger than 2%. We believe, therefore, that the peak positions and molar absorptivities for CpVTr are accurate in both the ultraviolet and the visible regions.

Spectra of CpVTr and CpVTr$^+$.—The electronic spectra of relatively few sandwich complexes are available in the literature. Presumably this paucity arises from the air sensitivity of many of these compounds and the difficulty involved in obtaining spectra of solutions free of decomposition products. Unfortunately, no quantitative data for the related molecules CpCrTr and CpCrTr$^+$ are available for comparison with the present work. (CpCrTr$^+$ is isoelectronic with CpVTr.) King and Bisnette[3c] do describe solutions of CpCrTr as deep blue and those of the corresponding cation as yellow; solutions of CpVTr are pale purple, while those of the cation are bright orange.

King and Stone[2] proposed that contributing resonance structures for CpVTr involved considerable separation of charge between the two rings. Hence, it might be tempting to regard the intense absorption in the ultraviolet region as an intramolecular charge-transfer band. Such a transition, however, would result in rather different dipole moments for the ground and excited states and should, therefore, be sensitive to solvent polarity.[27] The observation that CpVTr shows so nearly the same spectrum in acetonitrile and in isooctane seems to preclude such an assignment.

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[27] See, for example, J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Methuen and Co., Ltd., London, 1963, p 272.

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Chemistry of the Cyclopentadienylmetal Carbonyls. VII.[1] Nucleophilic Substitution Reactions of Cyclopentadienyliron, -tungsten, and -molybdenum Carbonyl Cations

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Reactions of pentafluorophenyllithium and phenyllithium with the cationic species $C_5H_5Fe(CO)_3{}^+$, $C_5H_5Fe(CO)_2[(C_6H_5)_3P]^+$, $C_5H_5Fe(CO)_2py^+$, $C_5H_5Fe(CO)_2(CH_3CN)^+$, $C_5H_5M(CO)_4{}^+$, and $C_5H_5M(CO)_3L^+$ (M = Mo, W; $L = (C_6H_5)_3P$, $(C_6H_5)_3As$) have been studied. Depending on the nature of the metal and the ligands substituted on the metal, the reaction that occurs is: (a) reaction at a carbonyl to give an acyl metal derivative, (b) displacement of a ligand to give an aryl metal compound, (c) reaction at the cyclopentadienyl ring to give a 1-arylcyclopentadiene complex, and/or (d) reduction to give the corresponding biaryl and a dimeric cyclopentadienylmetal carbonyl. The reaction of $NaBH_4$ and $C_5H_5M(CO)_4{}^+$ gives $C_5H_5M(CO)_3H$ (M = Mo, W), in a reaction analogous to (b) above. The reaction of $NaBH_4$ and $C_5H_5M(CO)_3[(C_6H_5)_3P]^+$ surprisingly gives $C_5H_5M(CO)_2[(C_6H_5)_3P]CH_3$ (M = Mo, W) in high yield. A possible mechanism for this reaction is suggested.

Introduction

Reactions of nucleophilic reagents such as alkyl- or aryllithium compounds, or sodium borohydride, with low-valency transition metal complexes bearing a positive charge have been reported. These reactions proceed in three general pathways determined by the nature of the metal–ligand complex. The types of reactions observed are listed below.

(1) Reactions which Proceed with Attack on a Ligand.—These reactions vary widely; one general subclassification includes reaction on a delocalized hydrocarbon bonded to the metal. This category includes $NaBH_4$ or RLi reactions with $(C_5H_5)_2M^+$ (M = Co,[2] Rh[3]), $C_6H_6M(CO)_3{}^+$ (M = Mn,[4] Re[5]), $C_7H_7Cr(CO)_3{}^+$,[6]

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