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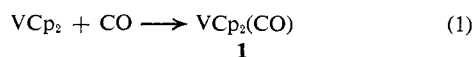
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**Carbonyl Complexes of
Bis(cyclopentadienyl)vanadium(II) and
Bis(cyclopentadienyl)vanadium(III).
Bis(cyclopentadienyl)iodovanadium(III), a Model
Compound for the Quantitative Assessment of the
Reversible Carbon Monoxide Coordinative Addition**

Sir:

Bis(cyclopentadienyl)vanadium(II), VCp_2 , was reported to react with carbon monoxide¹ or, better, with CO-H_2 ² to give $\text{VCp}(\text{CO})_4$. The reaction³ between VCp_2 and $\text{V}(\text{CO})_6$ in the presence of CO at atmospheric pressure yields the salt-like compound $[\text{VCp}_2(\text{CO})_2][\text{V}(\text{CO})_6]$, containing the cation $[\text{VCp}_2(\text{CO})_2]^+$, isoelectronic with $\text{TiCp}_2(\text{CO})_2$.^{4,5}

We have now found that VCp_2 reacts with carbon monoxide under mild conditions.



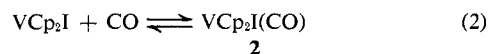
Gas volumetric measurements have shown that reaction 1 is fast (about 10 min for a $5.34 \times 10^{-2} M$ solution of VCp_2 in toluene at 25° at atmospheric pressure of CO) and substantially quantitative. For preparative purposes, $\text{VCp}_2(\text{CO})$ can be obtained by carbonylation of VCp_2 in heptane at 25° for about 10 min, followed by cooling at -10° (80.9% yield). The monocarbonyl of vanadium(II) is a deep brown solid, very sensitive to air.

Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{OV}$ (209.14 g/mol): C, 63.17; H, 4.82. Found: C, 63.50; H, 5.02; mol wt 202 (cryoscopy in benzene). The infrared spectrum has one single C-O stretching vibration at 1881 cm^{-1} (toluene), consistent with the formulation of this compound as a monomeric monocarbonyl. The magnetic susceptibility is 1330×10^{-6} cgs (including the diamagnetic correction = 159×10^{-6} cgs) corresponding to $\mu_{\text{eff}} = 1.76$ BM. This value is consistent with the fact that the number of valence electrons⁶ is 17 in this mononuclear compound. The low value of the C-O stretching vibration is quite common for bent bis-cyclopentadienyl systems of d^2 - d^4 configurations. For example, the following infrared absorptions were reported: $\text{TiCp}_2(\text{CO})_2$ ⁵ (1975 and 1897 cm^{-1}), $\text{MoCp}_2(\text{CO})_2$ ⁷ (1905 cm^{-1}), and $\text{WCp}_2(\text{CO})_2$ ⁸ (1864 cm^{-1}). The considerable amount of back-donation suggested by these low wave

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number values is in agreement with the basic properties of the metal center which are now well substantiated in these systems both experimentally⁹ and theoretically.¹⁰

Bis(cyclopentadienyl)iodovanadium(III),¹¹ VCp_2I ($\mu_{\text{eff}} = 2.81$ BM at room temperature, mol wt = 311, calcd 308.04 g/mol, by cryoscopy in benzene), reacts with CO



The iodo carbonyl derivative has one single C-O stretching vibration at 1953 cm^{-1} (toluene solution), corresponding to a 72 cm^{-1} increase with respect to $\text{VCp}_2(\text{CO})$, which is consistent with the increased oxidation state of the central metal atom. Compound 2 is monomeric in benzene solution as shown by the fact that, all else being equal, the freezing point depression observed for VCp_2I in benzene under nitrogen¹² was the same as that under carbon monoxide. Equilibrium 2 is rapidly established, and the equilibrium constants were measured gas volumetrically at temperatures between 272 and 316°K. The results are in Table I and the following thermodynamic values were obtained:

Table I. Equilibrium Data^a for the Reaction
 $\text{VCp}_2\text{I} + \text{CO} \rightleftharpoons \text{VCp}_2\text{I}(\text{CO})$

$T, ^\circ\text{K}$	$10^3[\text{CO}], M$	$10^{-2}K, M^{-1}$
272	7.28	8.46
282	7.39	4.06
295	7.47	1.49
308	7.44	0.56
316	7.31	0.30

^a In toluene as solvent at the total (CO + vapor of the solvent) constant pressure of 1 atm. The concentration of CO was experimentally determined from 286 to 314°K and extrapolated to the other temperatures.

$\Delta H^\circ = -13.1 \pm 1.0$ kcal/mol; $\Delta S^\circ = -34.6 \pm 3.4$ eu.

It is interesting to compare our values with the corresponding thermodynamic quantities reported by Vaska¹³ for the addition of CO to $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ ($\Delta H^\circ = -10.8$ kcal/mol; $\Delta S^\circ = -22$ eu). The two systems are, however, largely different since in our case spin pairing has to take place upon carbonylation, contrary to the iridium(I) system. This may be compensated by the lower amount of molecular rearrangement required in our case, thus yielding similar ΔH° values.

Bis(cyclopentadienyl)iodocarbonylvanadium(III) was isolated in admixtures with VCp_2I , since partial decarbonylation always occurred. However, a mixture of $\text{VCp}_2\text{I}(\text{CO})$ and VCp_2I of known composition (91:9% by weight, respectively) was isolated and eq 2 was also verified by decarbonylation of $\text{VCp}_2\text{I}(\text{CO})$. The magnetic susceptibility of this mixture could satisfactorily be explained by assuming that $\text{VCp}_2\text{I}(\text{CO})$ is diamagnetic, as expected.

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No formation of the slightly soluble salt-like $[\text{VCp}_2(\text{CO})_2]\text{I}$ was observed under the conditions specified for reaction 2. Formation of $[\text{VCp}_2(\text{CO})_2]\text{I}$ occurs only in the presence of VCp_2 , which is, as said above, the precursor to $\text{VCp}_2(\text{CO})$ under carbon monoxide. For preparative purposes, $[\text{VCp}_2(\text{CO})_2]\text{I}$ was obtained at atmospheric pressure of CO from VCp_2I in the presence of a catalytic amount (about 10% by weight) of VCp_2 in toluene. *Anal.* Calcd for $\text{C}_{12}\text{H}_{10}\text{IO}_2\text{V}$: C, 39.59; H, 2.77. Found: C, 39.52; H, 2.51. This compound has two infrared C–O stretching vibrations at 2036 and 1988 cm^{-1} (Nujol), to be compared with the bands at 2050 and 2010 cm^{-1} reported³ for the $[\text{VCp}_2(\text{CO})_2]^+$ cation of the triiodide or tetraphenylborate salts.

All the compounds reported in this paper have similar infrared spectra (as Nujol mulls) suggestive¹⁴ of symmetrically bonded η^5 -cyclopentadienyl ligands, at least in the solid state.

The data presented in this paper may be of value for a better understanding of the energetics involved in the combination of CO with iron(II), both in natural and synthetic complexes.^{15–18}

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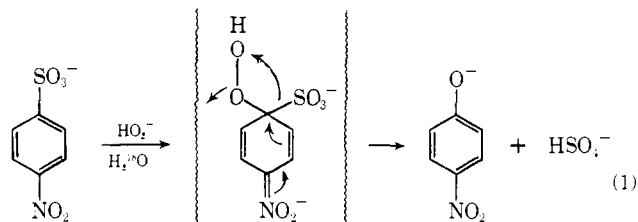
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Electrophilicity of the 8 Position of the Isoalloxazine (Flavine) Ring System. Comment on the Mechanism of Oxidation of Dihydroisoalloxazine

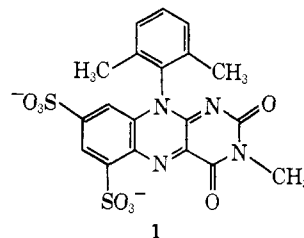
Sir:

Bullock and Jardetsky¹ have shown that the CH_3 group substituted at the 8 position of the isoalloxazine ring system of FMN exchanges $-\text{H}$ for $-\text{D}$ in D_2O at pH 6.8 (90–95°) with a rate constant of $2.4 \times 10^{-4} \text{ sec}^{-1}$. This observation may be compared to that of Bowden and Stewart² showing lack of hydrogen exchange when TNT is treated with NaOD in D_2O (with minimum volume of DMSO to ensure solubility) for 5–15 min. From these results it becomes obvious that the 8 position of the isoalloxazine ring system must be unusually electrophilic. We wish to report herein a quantitative evaluation of the electrophilicity of the 8 position of the isoalloxazine ring.

Vainstein, *et al.*,³ have reported a synthetic technique whereby electron deficient sulfonic acids may be converted to the corresponding phenols by treatment with alkaline hydrogen peroxide (eq 1). The reaction of **1**⁴



and 2,4-dinitrobenzenesulfonic acid with excess hydrogen peroxide was compared. In the pH range of 10.0–11.25 (30°, $\mu = 1.0$ with KCl, H_2O solvent) it was found that the first-order rate constants (k_{obsd}) at a particular pH value for **1** ($k_{\text{obsd}}/[\text{H}_2\text{O}_2]_T = 8.4 \times$



$10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$ at pH 10) exceeded the k_{obsd} values obtained with 2,4-dinitrobenzenesulfonate by *ca.* 10^2 . The product (**2**) obtained from **1** possesses a pK_a of 4.45. The conjugate base of **2** exhibits a λ_{max} value of 480 nm. Based on the value of ϵ ($1.85 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) obtained from the isolated product⁵ yields of 85–90% of **2** were obtained at the completion of the kinetic run at pH 10.0 where hydrolysis of **1** is unimportant. Isolation and analysis⁵ of the product of the reaction of **1** with H_2O_2 indicated one SO_3H substituent of **1** to have been replaced. The spectra and pK_a of **2** closely resemble those of the 8-hydroxyisoalloxazines (**3**) whose structures have been established by alternate synthesis and analysis.⁶ Compound **4**, the 8-dimethylaminoisoalloxazine, whose structure has been solved by X-ray diffraction,⁷ also has a spectrum similar to that of

(5) **2** was synthesized and isolated by the following procedure. **1** (0.85 g) was dissolved in 200 ml of aqueous 0.1 M H_2O_2 buffered to pH 9.5 with 0.5 M ($\text{HCO}_3^- + \text{CO}_3^{2-}$). The reaction (6 hr at 25°) was followed by the appearance of λ_{max} 480 nm. At completion, the reaction solution was adjusted to pH 7.0 with HCl and 0.5 g of Pd on asbestos was added to decompose excess H_2O_2 . After 12 hr at 25° the Pd on asbestos was removed by filtration, the filtrate was acidified to pH 6.0 and evaporated *in vacuo*, and the residue was crushed and extracted three times with 100-ml volumes of 1-propanol saturated with dry hydrogen chloride. The remaining salt residue was dissolved in a minimum volume of hot water, 1-propanol was added, and the suspension was filtered. The 1-propanol solutions were combined and reduced to dryness *in vacuo*; the residue was taken up in a minimum volume of water and adjusted to pH 7.0 with a small amount of K_2CO_3 . The aqueous solution of the reaction products was loaded on a $1.8 \times 25 \text{ cm}$ water washed Bio-Rex 5 anion exchange column and eluted with a 0–1 M (potassium chloride) gradient. The fraction which eluted at about 0.8 M KCl or after about 500 ml contained **2**. This was taken to dryness, *in vacuo*, extracted with 1-propanol saturated with hydrogen chloride, and filtered and the filtrate was evaporated to dryness. The dissolution in 1-propanol, filtration, and evaporation was repeated two times to ensure the elimination of inorganic salt. Finally, pure **2** (6–26% yield) was obtained by crystallization from 2 M HCl in water–ethanol (1:1 v/v). The uv–visible spectra of **2** in water at 30°, $\mu = 1.0$ KCl, gives the following values: at pH 10.0, λ_{max} 's 252.5, 302, and 480 nm; ϵ 's 2.60×10^4 , 5.50×10^3 , and $1.85 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, respectively; at pH 2.0 λ_{max} 's 234, 262, 432, and 445 nm; ϵ 's 1.92×10^4 , 1.49×10^4 , 1.19×10^4 , and $1.13 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, respectively. The 100-MHz nmr of **2** in 3 M DCl–DMSO- d_6 solution exhibited singlets at 188 and 323 Hz of six and three protons, respectively, a degenerate multiplet at 738 Hz of three protons and a doublet of doublets at 600, 602.5, 762, and 764.5 Hz of two protons, TMS was used as an internal standard. *Anal.* Calcd for $\text{C}_{21}\text{H}_{21}\text{N}_4\text{O}_7\text{S}_2\text{K}$: C, 49.21; H, 4.10; N, 10.94; S, 6.25. Found: C, 49.88; H, 4.14; N, 11.29; S, 6.75.

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