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(10) Postdoctoral Research Associate.

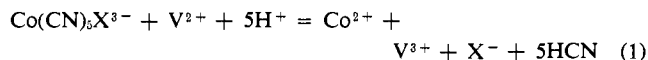
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Electron-Transfer Reactions of Vanadium(II) and Some Monosubstituted Pentacyanocobaltate(III) Ions¹

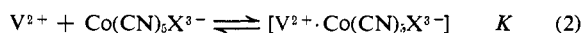
Sir:

Previous studies have shown that the reactions of the type in eq 1 generate $\text{Co}(\text{CN})_5^{3-}$ as a metastable inter-



mediate.² The finding of $\text{Co}(\text{CN})_5^{3-}$ does not in itself establish all the details of the mechanism, however, for it might have resulted as the primary product of an inner-sphere reaction ($\rightarrow \text{Co}(\text{CN})_5^{3-} + \text{V}(\text{H}_2\text{O})_6^{2+}$), and it would also be the likely substance formed in an outer-sphere reaction, resulting from the rapid decomposition of the low-spin six-coordinate Co(II) complex $\text{Co}(\text{CN})_5\text{X}^{4-}$. Whereas the mechanism of electron transfer has been classified unambiguously³⁻⁶ as inner sphere or outer sphere for the reactions of many oxidizing agents with Cr^{2+} , $\text{Co}(\text{CN})_5^{3-}$, and $\text{Ru}(\text{NH}_3)_6^{2+}$, the question remains unresolved for but a few reactions of $\text{V}(\text{H}_2\text{O})_6^{2+}$.⁷⁻¹⁰ Evidence has been obtained in this study that the reactions in eq 1 proceed by inner-sphere (ligand bridged) mechanisms.

Rate studies have been carried out on the initial oxidation-reduction stage of the reactions in eq 1 for $\text{X} = \text{Cl}^-$, Br^- , I^- , $-\text{SCN}^-$, N_3^- , and H_2O . The reactions were measured at wavelengths permitting the following of both the loss of the complex, $\text{Co}(\text{CN})_5\text{X}$ ($\text{X} = \text{Br}^-$, I^- , $-\text{SCN}^-$, and N_3^-), and the formation of the intermediate ($\text{X} = \text{Br}^-$, Cl^- , H_2O) with time. The rates which were evaluated by both stopped-flow and conventional spectrophotometric methods were found not to follow a simple second-order rate law. The second-order rate constants calculated from kinetic data taken with V^{2+} in considerable excess were found to decrease with increasing V^{2+} concentration. The reactions appeared to proceed with ion-pair formation according to the mechanism



(1) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2494.

(2) K. M. Davies and J. H. Espenson, *Chem. Commun.*, 111 (1969).

(3) N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966), and references therein.

(4) J. Candlin, J. Halpern, and S. Nakamura, *J. Am. Chem. Soc.*, **85**, 2517 (1963).

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(7) B. R. Baker, M. Orhanović, and N. Sutin, *ibid.*, **89**, 722 (1967).

(8) J. H. Espenson, *ibid.*, **89**, 1276 (1967).

(9) H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968).

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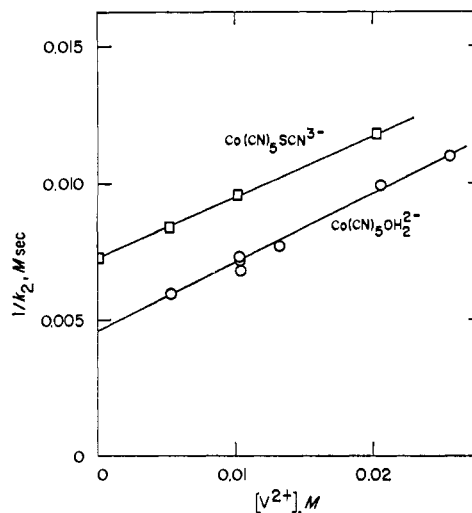


Figure 1. Illustrating the dependence of the apparent second-order rate constant on $[\text{V}^{2+}]$ at 25.0° and $\mu = 1.00 M$: upper line, $\text{Co}(\text{CN})_5\text{SCN}^{3-}$; lower line, $\text{Co}(\text{CN})_5\text{OH}_2^{2-}$.

According to this sequence, the second-order rate constant k_2 is $kK/(1 + K[\text{V}^{2+}])$. Linear plots of $1/k_2$ vs. $[\text{V}^{2+}]$ were obtained in accord with this formulation; typical data are shown in Figure 1. Table I summarizes

Table I. Rate Parameters for the Reactions of V^{2+} and $\text{Co}(\text{CN})_5\text{X}^{3-}$ at 25.0° and $\mu = 1.00 M^b$

X	λ , nm	kK , $M^{-1} \text{sec}^{-1}$	k , sec^{-1}	K , M^{-1}
Cl^-	280	278	6.4	44
Br^-	280-300-050	168	<i>c</i>	<i>c</i>
Br^-^a	280	363	3.4	107
I^-	500	121	5.7	21
$-\text{SCN}^-$	264	138	4.5	31
$-\text{SCN}^-^a$	264	256	3.3	78
N_3^-	383	112	<i>c</i>	<i>c</i>
H_2O	280	218	4.1	53

^a $\mu = 0.200 M$. ^b $[\text{H}^+] \sim \mu$, except for $\text{Co}(\text{CN})_5\text{N}_3^{3-}$, where $[\text{H}^+]$ was $0.100 M$ at $\mu = 1.00 M$. ^c Under the conditions employed $K[\text{V}^{2+}]$ was very small compared to unity; hence only the product kK and not the separate values were obtained.

the values of the rate parameters for each complex.

The similarity in the values of k found for the different complexes suggests that the rate is controlled primarily by the loss of a water molecule coordinated to V^{2+} . Similar effects have been noted in earlier studies.⁹ The range of values of the limiting second-order rate constant kK (120-260 $M^{-1} \text{sec}^{-1}$) is somewhat higher than the values¹⁰ noted for other reactions (8-45 $M^{-1} \text{sec}^{-1}$). This is not surprising considering the charge types in the present reaction give rise to more favorable ion-pair formation.

For the complexes $\text{Co}(\text{CN})_5\text{N}_3^{3-}$ and $\text{Co}(\text{CN})_5\text{SCN}^{3-}$ direct proof of an inner-sphere mechanism was obtained in studies carried out at 350-360 nm where the V(III) complexes VN_3^{2+} and VNCS^{2+} have absorption maxima.¹¹ At these wavelengths the transmittance-time oscillograms indicated not only the presence of the usual $\text{Co}(\text{CN})_5^{3-}$ intermediate² and its slow decom-

(11) B. R. Baker, N. Sutin, and T. J. Welch, *Inorg. Chem.*, **6**, 1948 (1967).

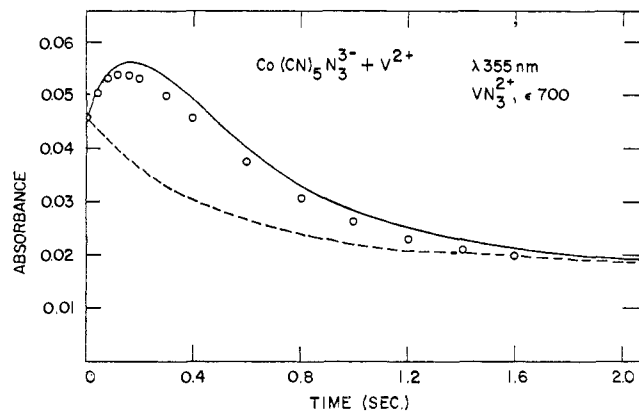
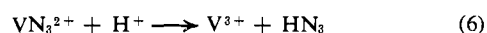
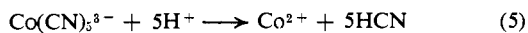
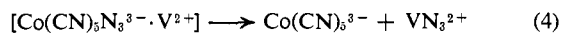


Figure 2. Comparison of the observed absorbance-time values in the reaction of $\text{Co}(\text{CN})_5\text{N}_3^{3-}$ and V^{2+} with those calculated for the inner-sphere (solid) and outer-sphere (dashed) mechanisms.

position,^{2,12} but the V(III) complex $\text{V}(\text{H}_2\text{O})_6\text{X}^{2+}$ as well. Consideration of the various known values of the molar absorptivities and rate constants in the scheme shown in eq 4-6 reproduced the experimental data



quite well. The agreement of the observed absorbance-time trace and that calculated for an inner-sphere mechanism is shown in Figure 2. Along with this comparison, the pattern predicted had the reaction followed an outer-sphere mechanism is also shown. The results indicate that VN_3^{2+} is formed in eq 4 at a concentration in great excess over that dictated by the eventual equilibrium in eq 6, thus providing direct "product criterion" evidence for an inner-sphere mechanism is support of the conclusions based on the rate constants cited above.

(12) J. H. Espenson and J. R. Pipal, *Inorg. Chem.*, **7**, 1463 (1968).

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Metalation Reactions. I. Formation and Charge Distribution in Conjugated Propargylic Dianions

Sir:

We wish to report the unusually easy formation of dicarbanions by the abstraction of two protons from the same carbon atom in hydrocarbons. These anions have unexpected spectral characteristics indicating increased electron localization on introduction of the second charge in the molecule.

trans-1-Phenylhex-4-en-1-yne (Ia), 1-phenyl-4-methylpent-4-en-1-yne (Ib), *trans*-1,5-diphenylpent-4-en-1-yne (Ic), and 1-phenylpent-4-en-1-yne (Id) were prepared by coupling phenylacetylenemagnesium bromide with the corresponding allyl bromide.¹ 2,7,7-Trimethylhept-1-en-4-yne (Ie) was prepared in a similar manner from *t*-butylacetylenemagnesium bromide and methallyl bromide.

(1) Correct analyses and spectra were obtained for these compounds.

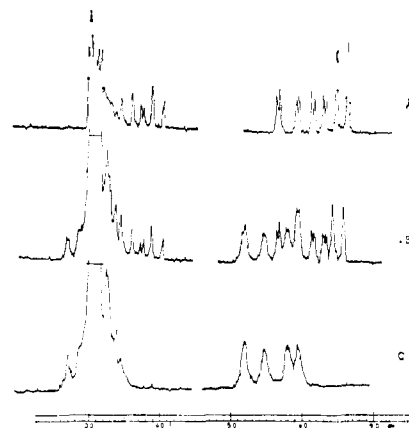
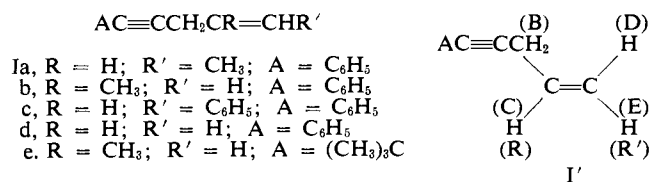
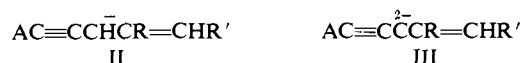


Figure 1. Nmr spectrum of a solution formed by addition at -90° of 100 mg of Id to 1 ml of 3.0 *F* butyllithium in deuterated ether. The spectrum was recorded at 38° : (A) 3 min after the addition of Id (monoanion II); (B) 30 min after the addition of Id; (C) 120 min after the addition of Id (dianion III).

Addition of the compounds Ia-d to an excess of a solution of butyllithium in ether or deuterated ether at -80° produces first a very fast, and then a second, change in their nmr spectra² (Figure 1, Table I). The reaction observed consists in consecutive abstractions of one and then a second proton from the propargylic methylene group, giving respectively the mono- (II) and dilithium (III) derivatives.³ The reaction of Ie is slower but proceeds smoothly to the dianion IIIe. The presence of a phenyl group in these molecules is therefore not a necessary condition for dianion formation.



No proton is abstracted from the vinyl group, as shown by integration and the invariance of the coupling constants in this group during the reaction. The nmr spectrum of III is not that of a product formed other than by transmetalation, since protonation yielded the starting material, conjugated enynes, and allenes con-



jugated to a double bond.⁵ Treatment with trimethylsilyl chloride gave the bis(trimethylsilyl) derivatives.⁵

Nmr spectra of charged molecules had been studied before, and a linear correlation was found between the π -electron density on aromatic carbon atoms and the chemical shifts of the aromatic protons attached to these carbons.^{6,7} This correlation was extended to ben-

(2) The chemical shifts were determined relatively to the low-field component of the CH₂ quartet of ether at τ 6.42. The position of this signal was not changed by the presence of butyllithium.

(3) These species are written in the form of anions for convenience sake. The ionic character of allyllithium was proved recently.⁴ Only one resonance form is written here.

(4) P. West, J. I. Purmort, and S. V. McKinley, *J. Am. Chem. Soc.*, **90**, 797 (1968).

(5) *cis* and *trans* enynes were obtained. The composition of the products changes with the conditions of the reaction and depends also on what is protonated or silylated: the mono- or the dianion. These results will be reported in a subsequent paper.