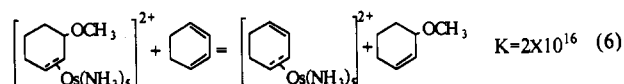
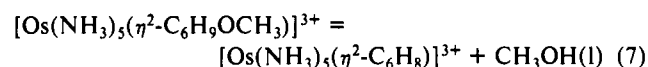


the conversion of 3-methoxycyclohexene to cyclohexadiene and methanol, all species in the gas phase, ΔG° at 20 °C is calculated as 2.1 kcal. We assume that ΔG° for transferring the two cyclic molecules to the liquid phase, CH₃OH, is the same, and then, on inclusion of ΔG° for converting CH₃OH(g) to CH₃OH(l), the equilibrium quotient [cyclohexene]/[3-methoxycyclohexene] for reaction 5 is calculated as 0.1. Even with allowance for an error of 10² in the estimation of K_5 , the comparison of K_4 with K_5 shows a profound effect of Os(NH₃)₅²⁺ in promoting the conversion of 3-methoxycyclohexene to the conjugated diene. Stated in another way, the addition of reaction 4 to the reverse of reaction 5 results in reaction 6 (methanolic solution) governed by an equilibrium



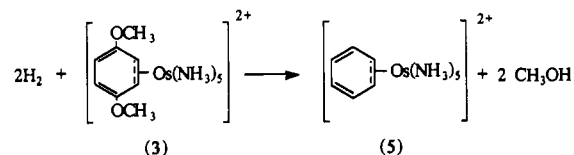
quotient of 2×10^{16} . Thus, we see an enormous increase in the affinity of Os(NH₃)₅²⁺ for the ligand when 3-methoxycyclohexene is converted to cyclohexadiene by elimination of CH₃OH. The effect can in part be attributed to the greater back-bonding interaction with the conjugated diene compared to the lone double bond, combined with a stronger σ interaction for the diene. The equilibrium quotient for reaction 4 when combined with the measured values of $E_{1/2}$ for the Os(III)/Os(II) couples for cyclohexadiene and allyl ether complexes makes possible for calculation of the equilibrium quotient for reaction 7.



Since the potentials for the two couples (Table I) are virtually the same (0.67 and 0.65 V), K_7 is almost the same as K_4 . That K_7 is also very large is at first sight surprising; it is less so when the relative tendencies of the two ligands for σ -bond formation

are compared. A measure of the relative tendency is provided by a comparison¹⁵ of ground-state ionization potentials, which show that the work of removing an electron from butadiene is ca. 22 kcal less than it is for ethylene. An additional factor is the residual tendency of [Os(NH₃)₅]³⁺, as a third-row transition metal, to engage in back-bonding interactions. Qualitative rationalizations of this kind however do not account for the fact that the equilibrium quotients in the two cases are so nearly alike.

Changes in driving force are frequently reflected in rates of reaction, and this is the case in the system under discussion. The coordinated allyl ether in the presence of acid is converted to the allyl-cyclohexadiene equilibrium mixture at room temperature within minutes. The conditions reported¹⁶ for the analogous conversion of the free allyl ether are as follows: solvent, triethylene glycol containing 10% by volume of 85% H₃PO₄; temperature, 150–160 °C; reaction time, 1–2 h. The observations made on the partial hydrogenation of 1,4-dimethoxybenzene shows that coordination of the ligand greatly facilitates the reaction



Hydrogenation under the same conditions, absent η^2 coordination to a metal center, can reasonably be expected to yield either dimethoxy- or dihydroxycyclohexane. While little can be said on the basis of our experience on the relative rates of hydrogenation in the two cases, an effect of the metal ion in redirecting the course of the hydrogenation reaction is revealed.

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Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305

Solvent Effects on the Reactivity of Vanadium(II)

John C. Dobson,[†] Mitsuru Sano,[‡] and Henry Taube*

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Absorption spectra of V(II), covering a range wide enough to encompass the expected three absorption bands arising from d–d transitions, were registered in nine solvents. The source of V(II) in most cases was V(DME)₂(O₃SCF₃)₂ (DME is 1,2-dimethoxyethane), but in some cases V(II) was generated by reducing V(O₃SCF₃)₃ with Zn/Hg. Only in the case of the weakly nucleophilic solvent CH₂Cl₂ is there evidence that the DME introduced with the solid affects the spectrum. Striking changes are registered in passing from a solvent such as H₂O to solvents, the molecules of which have π -acid character. In the case of acetone, pyridine, and acetonitrile, strong MLCT absorption sets in, accompanied by hypochromic shifts of those d–d transitions that are not obscured by the charge-transfer bands. Thus the long-wavelength bands ν_1 , which measured 10Dq, for H₂O, acetone, CH₃CN, and pyridine appear at 843, 820, 614, and 490 nm respectively. There are, as well, marked increases in the intensities of the d–d absorptions for the last three solvents, compared to that for H₂O. The reactivity of V(II) to epoxides and to O₂ is a sensitive function of the nature of the solvent. In some solvents, with either kind of oxidant, [VOV]⁴⁺ is the first observable vanadium-containing product. In certain solvents, on continued oxygenation, VO²⁺ is formed, and there is evidence that V(V) can also be produced. In the case of epoxides, the gross features of the differences in rate can be understood in terms of the accessibility of a normal coordination position on V(II) to the epoxides. When O₂ reacts, substitution in a normal coordination site is not necessarily a prerequisite to reaction.

Introduction

Oxygen atom transfer reactions involving transition-metal centers are important in industrial and biological chemistry. Current concern^{1,2} at a basic level with the nature of such processes

is leading to an improved understanding of how the properties of the metal center and of the auxiliary ligand environment affect the reactivity of the metal–oxo bond.

Until recently oxygen atom transfer from metal to substrate has received most of the attention, perhaps in part because of the

* Present address: Monomer Research, Rohm and Hass Co., 727 Norris-road, Spring House, PA 19477.

† Present address: Department of Chemistry, College of General Education, Nagoya University, Chikusa-ku, Nagoya 464, Japan.

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dearth of well-defined metal reducing agents competent for deoxygenation. During the last 2 decades, several metal reducing agents have been studied, prominent among them $\text{TiCl}_3/\text{LiAlH}_4$,³ $\text{WCl}_6/n\text{-C}_4\text{H}_9\text{Li}$,⁴ $\text{CpTiCl}_2/\text{Na}$,⁵ and Cr(II) ⁶ as well as the V(II)-based systems to be mentioned presently, but for the majority of these systems, the nature of the active transition metal reagent is ill-defined.

We have recently begun to investigate⁷ the coordination and redox chemistry of vanadium, covering the range of oxidation states 2+ to 5+, and emphasizing nonaqueous solvents. In this paper, we report the observations we have made in a continuation of these studies, which has been directed to learning the light absorption characteristics of V(II) as the triflate (CF_3SO_3^-) salt in a variety of solvents and its reactivity to epoxides and dioxygen. Hayashi and Schwartz⁸ have shown that the species produced when V(IV) halides are reduced by excess sodium in the presence of β -diketones, are effective in deoxygenating epoxides to olefins, though they are not highly reactive. Olah and co-workers⁹ have reported on the reduction on a variety of organic substrates, including sulfoxides, benzils, aryl azides, and α -halo ketones by V(II) generated in a variety of nonaqueous solvents by the action of LiAlH_4 on VCl_3 .

Experimental Section

Materials. Vanadium(III) chloride, trifluoromethanesulfonic acid, styrene oxide, cyclohexene oxide, *cis*-stilbene oxide, and α -methylstyrene oxide were purchased from Aldrich Chemical Co. *trans*-stilbene oxide, *cis*- and *trans*-2-decene oxide, and authentic samples of the corresponding olefins were a gift from the research group of Professor James P. Collman. Electrochemical grade tetra-*n*-butylammonium hexafluorophosphate (TBAH) was purchased from Fluka Chemical Co. Acetone was dried over B_2O_3 and purified by vacuum distillation.^{10a} Methanol was purified by distillation over $\text{Mg}(\text{OCH}_3)_2$, prepared in situ from Mg(s) (activated by I_2) under argon.^{10b} Diethyl ether, 1,2-dimethoxyethane (DME), and tetrahydrofuran (THF) were distilled under argon over NaK alloy. Dichloromethane (anhydrous, Aldrich Chemical Co.) was distilled under argon over P_2O_5 . Pyridine was distilled from BaO . Burdick and Jackson spectrograde acetonitrile (0.001% H_2O) and THF were used as supplied. All solvents were deoxygenated by purging with argon, and reactions were carried out under argon in a Vacuum Atmospheres Corp. glovebox maintained at 30 °C or by using standard Schlenk techniques.

Preparations. Vanadium(III) triflate, $\text{V}(\text{O}_3\text{SCF}_3)_3$, is a convenient entry into the chemistry of vanadium in nonaqueous solvents. It was prepared from VCl_3 and $\text{CF}_3\text{SO}_3\text{H}$ by following a procedure that is described in the literature.¹¹ In many experiments, V(II) was generated in situ by reducing $\text{V}(\text{O}_3\text{SCF}_3)_3$ in the medium of choice, by the action of Zn/Hg. This procedure is ineffective in a weakly polar medium such as CH_2Cl_2 . Solutions in CH_2Cl_2 containing V(II) can be obtained by using $\text{V}(\text{O}_3\text{SCF}_3)_2(\text{THF})_4$ (1), which we prepared following directions supplied by Armstrong et al.¹² To 1 g of $\text{V}(\text{O}_3\text{SCF}_3)_3$ suspended in 10 mL of THF was added Zn/Hg in excess. After 2 h of vigorous stirring, a blue solution resulted, but to ensure complete reduction, the reaction conditions were maintained for an additional 30 min. Thereupon, the solid matter was separated through a fine glass frit. Crystallization was induced by vapor diffusion into the filtrate, diethyl ether being used as a precipitant.

To avoid possible complications that might arise from degradation of THF as solvent, we followed the procedure just described but now with

Table I. Spectrophotometric Data^a for V(II)^b in Various Environments

	ν_1 (ϵ) ${}^4T_{2g} \leftarrow {}^4A_{2g}$	ν_1 (ϵ) ${}^4T_{1g} \leftarrow {}^4A_{2g}$	ν_3 (ϵ) ${}^4T_{1g}(\text{P}) \leftarrow {}^4A_{2g}$
THF	930	600	392
DMSO	920, 830 s	605	
CH_2Cl_2	900, 810 s	610 (7)	350, 390 s, 22
DME	864, 820 s	580 (9.3)	390 (5.9)
$\text{H}_2\text{O}^{c,d}$	843 (4.5)	556 (4.3)	370 (s) ^f
$\text{CH}_3\text{OH}^{c,e}$	843 (4.5)	556 (5.1)	375 (s) ^f
acetone	820	540 (s) ^f	
$\text{CH}_3\text{CN}^{b,c,f}$	614 (38)	446 (40)	290 (s) ^f
pyridine	490 (s) ^f		

^a Units: ν (λ), nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$). ^b Compound 2 as source of V(II); other sources as noted. ^c V(II) also by reduction of $\text{V}(\text{O}_3\text{SCF}_3)_3$ in solvent of choice. ^d Four measurements. ^e Three measurements. ^f Our values differ from those reported for the reaction mixture obtained in the preparation of $\text{V}(\text{CH}_3\text{CN})_6^{2+}$, $\lambda_{\text{max}} = 487$ (600), 680 (70): Chandrasekar, P.; Bird, P. H. *Inorg. Chem. Acta* **1985**, *97*, L31. ^g Shoulders on long λ side of a strong absorption.

1,2-dimethoxyethane (DME) as the reaction medium. Blue, well-formed crystals resulted that were used in a large number of experiments, including those with CH_2Cl_2 as solvent. Analysis however showed that much of the zinc ion formed in the reduction cocrystallizes with the desired vanadium(II) compound and further showed that two molecules of DME (and of the triflate ion) are present for each dicationic ion. A typical analysis shows the ratio of V to Zn to be about 6/4. In quoting extinction coefficients and reporting on stoichiometry, we have taken account of the actual content of V(II). The crystals become amber on exposure to air, and because all individual crystals are affected, we believe we are dealing with a V(II)/Zn(II) solid solution. In the following, where the formula $\text{V}(\text{DME})_2(\text{O}_3\text{SCF}_3)_2$ or its number designation 2 is used, it is understood that the solid is contaminated by Zn.

Deoxygenation Experiments. In a typical experiment, to a 0.50-mL DME- d_{10} solution containing 25 mg of $\text{V}(\text{DME})_2(\text{O}_3\text{SCF}_3)_2$, 2, was added 0.50 mL of a DME- d_{10} solution containing 5 μL of styrene oxide. The ^1H NMR spectrum was recorded, and the reaction mixture was then filtered through silica gel to remove the vanadium-containing species, and the filtrate was analyzed by GC/MS to corroborate the product analyses.

Measurements. UV-vis spectra were recorded in quartz cells at room temperature on a Hewlett-Packard Model 8452A diode array spectrophotometer. The near-infrared region is outside the capability of the H.P. Model 845 2A spectrophotometer, and data in this region were measured on a Beckman Model 5270 instrument. The traces for the two instruments do not mesh. Infrared spectra were recorded on an IBM 98 FTIR spectrometer. GC/MS experiments were performed by using a 25-m (0.2 mm i.d.; 4600 plates/meter) fused silica-AP Ultra 2 HP-5 (crosslinked methylsilicone) column fitted to a HP5890/5970 GC/MS system. ^1H NMR experiments were run on a Varian VXR 400-MHz spectrometer. Cyclic voltammetric experiments were performed under argon by using a PAR Model 173 potentiostat with a PAR Model 175 universal programmer as a sweep generator. Measurements were made in a cell fitted with a Pt^0 working, a Pt^0 auxiliary, and a reference electrode consisting of a Au^0 button immersed in a DME solution containing 0.5 M $\text{NaO}_3\text{-SCF}_3$ separated from the main cell by a Vycor frit. No correction was made for junction potential effects. The reference was calibrated with the ferrocene/ferrocenium couple ($E^0 = 0.55 \text{ V vs NHE}$) kept in situ.

Results

Spectrophotometry. In Figure 1 are shown selected spectra of 2 in various solvents, the salient features of these spectra as well as those of other solutions being summarized in Table I. We have had difficulty in assigning band maxima, in large part because of the large bandwidth, coupled in some cases with band asymmetry. The limits of error on the band positions are $\pm 3 \text{ nm}$.

For V^{2+} , three bands assignable to spin-allowed d-d transitions are observable¹³ unless they are masked by transitions of a different origin. In both acetone and pyridine, there is interference from absorption in the shorter wavelength region, which because of the high intensity we take to be charge transfer in origin. Such absorption also sets in when CH_3CN is the solvent, though here it appears at sufficiently short wavelength to reveal the highest

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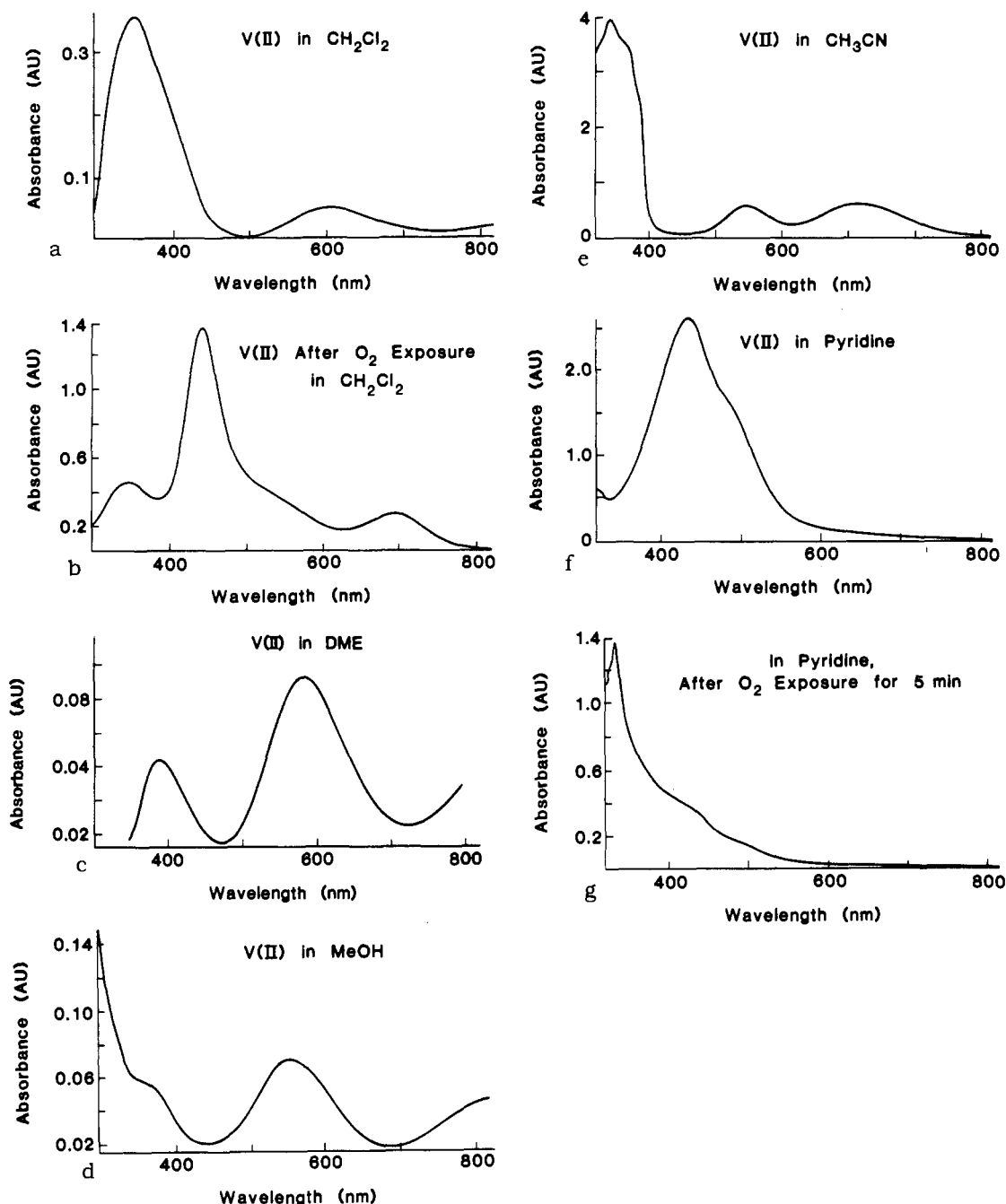


Figure 1. UV-vis absorption spectra for V(II) (compound 2) in various solvents. Parts b and g are spectra for product solutions after exposure to O_2 .

energy transition, ν_3 , as a shoulder on a very strong end absorption.

Cyclic Voltammetry. This technique, so valuable in the chemistry of Ru(III)/Ru(II) and Os(III)/Os(II), is of limited applicability in the vanadium chemistry we have investigated. Only the V(III)/V(II) couple is amenable to this approach, but even here it is useful only in special circumstances. The self-exchange rate for the couple $V(H_2O)_6^{3+}/V(H_2O)_6^{2+}$ ($1.0 \times 10^{-2} M^{-1} s^{-1}$ at $25^\circ C$, $\mu = 2.0 M$)¹⁴ in aqueous solution is lower than that of the corresponding iron couple ($3.3 M^{-1} s^{-1}$ at $22^\circ C$, $\mu = 0.55 M$),¹⁵ which itself responds poorly in the time scale of cyclic voltammetry in ordinary use. Some observations made in applying this technique in the interests of developing an analytical procedure for V(II) concentration are herewith described.

A solution of 2 in CH_3CN ($1.9 \times 10^{-2} M$, 0.10 M tetrabutylammonium hexafluorophosphate as electrolyte) shows no electrochemical activity in the oxidation sweep (100 mV/s) until

a potential of 1.25 V vs NHE is reached. No reduction wave is observed on the reverse sweep except for one attributable to Zn^{2+} at $-0.80 V$, this assignment being corroborated by the appearance of the wave for the oxidation of the Zn metal deposited. The absence of a reduction wave cannot be ascribed to the formation of $[VOV]^{4+}$ (which does not respond well in cyclovoltammetry) because this highly colored species does not appear as an intermediate. The nature of the species formed by the irreversible oxidation of 1.25 V is not known, but the electrochemical behavior suggests that the structure is sufficiently different from that of $V(CH_3CN)_6^{2+}$ that the self-exchange rate for the couple in question is slow. When a 10-fold excess of 2,2':6',2''-terpyridine is added, couples characteristic⁷ of $V(trpy)_2^{2+}$ appear, but reaction is complete only after 3 h. Similar observations are made on adding 2,2'-bipyridine; in this case, quantitative conversion to $V(bpy)_3^{2+}$ was confirmed by spectrophotometry, the extinction coefficient of this species at 660 nm being known.¹⁶ The rate

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Table II. Reduction of Epoxides with Vanadium(II) Triflate^a (Mole Ratio 1/1) in CD₂Cl₂

epoxide	react time, Min	% convn	% product yield	
			olefin	carbonyl
styrene oxide	15	100	45	55
styrene oxide ^b	15	100	95	<5
<i>trans</i> -stilbene oxide	30	100	~0	>95
<i>trans</i> -stilbene oxide ^b	30	100	>95 (trans)	~0
<i>cis</i> -stilbene oxide	30	100	...	>95
<i>cis</i> -stilbene oxide ^b	30	100	95 (trans)	~9
<i>trans</i> -2-decene oxide	120	75	20 (trans), 30 (cis)	25
<i>trans</i> -2-decene oxide ^b	90	40	16 (trans), 24 (cis)	0
cyclohexene oxide	30	60	47	~13

^aCompound 2. ^bIn the presence of 1 equiv of triethylamine.

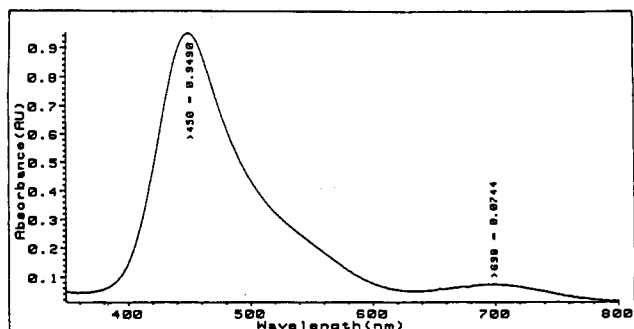


Figure 2. Absorption spectrum of the product of the reaction of compound 2 with styrene oxide in DME. Concentrations of reaction solution: [oxide] = 4.2×10^{-2} M; [V(II)], 1.4×10^{-2} M.

of substitution is, as expected, dependent on solvent. In acetone or CH₂Cl₂ the reaction is complete in ca. 30 min under identical conditions.

Reactivity with Epoxides. Both 1 and 2 in appropriate environments are effective reagents for the deoxygenation of epoxides to olefins. The addition of styrene oxide (epoxide/V(II) = 1/1) to CD₂Cl₂, DME-*d*₁₀ or THF-*d*₈ solutions containing 1.0×10^{-2} M V(II) results in a rapid color change from violet to an intense amber upon mixing. The ¹H NMR spectrum recorded after 15 min shows that no styrene oxide remains and that the product solutions contain a mixture of the deoxygenated product (styrene) and the rearrangement product (phenylacetaldehyde). When styrene oxide is in excess, all excess epoxide is converted to the rearranged product. If the reactions are carried out in the presence of an equivalent of a weakly coordinating base (triethylamine or 1,8-bis(dimethylamino)naphthalene), the product ratios can be altered dramatically. Under these conditions, the rearrangement products are minimized or even eliminated and yields of deoxygenated products maximized. The rates of the reactions show a marked solvent dependence. For our experiments, the rates of reaction are CH₂Cl₂ > DME >>> CH₃CN ≈ CH₃OH. Compound 2 in CH₂Cl₂ showed no measureable reduction of DMSO, OPPh₃, acetone, or benzaldehyde, even after 24 h. Table II summarizes the results of deoxygenation experiments carried out in CD₂Cl₂.

The nature of the oxidized vanadium species was also investigated. The UV-vis spectrum of the resulting intense amber solution from a deoxygenation experiment carried out in DME is shown in Figure 2. Both the band shape and intensity are similar to those observed for [VOV]⁴⁺.^{17,18} In a separate experiment, the vanadium species was isolated by removing the solvent under reduced pressure. An infrared spectrum of this sample displayed no absorption bands in the (V^{IV}=O) region, 800–1000 cm⁻¹, again pointing the formation of [VOV]⁴⁺.

Reactivity with O₂. The reaction of V(II) with O₂ was also investigated. As expected, both 1 and 2 are O₂-sensitive. The

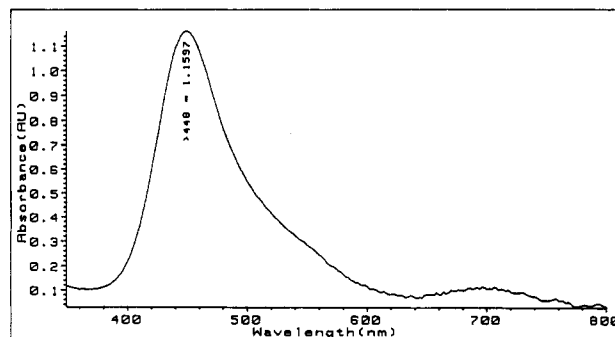


Figure 3. UV-vis absorption spectra for V(II) (compound 2, 2.8×10^{-2} M) in DME after O₂ (saturated with DME) was bubbled through the solution for 45 min.

Table III. Reported Band Maxima Values (nm) for Selected V(II) Species

Species	medium	ν_1	ν_2	ν_3	ref
aqueous 0.7 M ClO ₄ ⁻ , H ⁺ ^a			560 (5.2) ^b		19
aqueous, 0.1 M ClO ₄ ⁻ , H ⁺ ^a			560 (4.4) ^b		20
aqueous 2M H ₂ SO ₄			563	368	21
aqueous SO ₄ ²⁻ , HSO ₄ ⁻ , H ⁺		850	566	360	22
in (NH ₄) ₂ Zn(H ₂ O) ₆ (SO ₄) ₂ (s) ^c		810 ^d	540	335	21
VSO ₄ ·7H ₂ O(s) ^c		842 (4.1) ^b	540 (6.0) ^b	359 (3.1) ^b	23
VBr ₂ ·6H ₂ O(s) ^c		855	568	333	24
V(CH ₃ OH) ₆ Cl ₂ in CH ₃ OH ^e		857 (810 s)	565	375	25
VCl ₂ in CH ₃ OH ^f		854	573	377	26
VI ₂ ·6CH ₃ OH(s) ^c		833	565	356	24
VCl ₂ in THF		994	643	407	26
[V ₂ Cl ₃ (THF) ₆]Cl in THF		1000	641	408	27
VCl ₂ in CH ₃ CN		685	495		26
VCl ₂ in pyridine ^g		>700	526		26

^aThe concentrations of ClO₄⁻ exceed those of H⁺. ^b ϵ , M⁻¹ cm⁻¹. ^cOn solid samples by reflectance spectroscopy; cations are the hexasolvates. ^dValue uncertain; instrument limit. ^e[Cl⁻] = 0.14 M. ^f[Cl⁻] unspecified. ^gWork done in these laboratories by Phalguni Ghosh shows that there is no absorption at wavelengths > 700 nm extending to 1000 nm. The band at 526 nm appears as a shoulder on a very strong band, maximum at 482 nm, which is in all likelihood charge transfer in origin. On tetragonal distortion, ν_1 is split. The band at 526 nm can be assigned to the higher energy component, which measures 10Dq. While no band is discernible at lower energy, it is clearly resolved for the corresponding bromide and iodide salts and appears at 840 nm and 960 nm, respectively. For the chloride complex, it is apparently masked by the low-energy wing of the charge-transfer band.

exposure to dry O₂ of a solution of 2 in DME results in the rapid formation of an amber solution characterized by a broad, intense absorption band at $\lambda_{\max} = 448$ nm; this spectrum is indistinguishable from the spectrum obtained in the deoxygenation of epoxides by 2 in DME (compare Figures 2 and 3). Formation of this highly colored solution is accompanied by the disappearance of ν_1 , the ⁴T_{2g}(F) ← ⁴A_{2g} transition at 864 nm in the near-infrared region. With time, the band at $\lambda_{\max} = 448$ nm disappears. In dilute solutions (<10⁻⁴ M), the disappearance of amber is followed by the appearance of pink, characterized by a broad absorption ($\epsilon > 500$ M⁻¹ cm⁻¹ per V) at $\lambda_{\max} = 490$ nm. In more concentrated solutions (>10⁻³ M), the production solution is blue with a broad absorption band at $\lambda_{\max} = 732$ nm ($\epsilon = 24$). If an equivalent of H₂O is added to this blue oxidized solution, the solution becomes cloudy with formation of an orange suspension. Addition of excess H₂O results in the formation of a flocculent green precipitate, which is insoluble in CH₃OH, CH₃CN, acetone, or CH₂Cl₂. If the blue oxidized solution is degassed and titrated with V(II), the average oxidation state of the vanadium is found to be greater than 4+ (at the end point, V(II) is in excess and all states above 3+ are absent). Titration of I₂ formed on the addition of I⁻ also indicates the presence of V(V).

The rate of reaction of 2 with O₂ is solvent-sensitive. For solutions of 2 in CH₂Cl₂, acetone, or THF the initial product solution on exposure to O₂, as in the case of DME, is amber and is characterized by an intense absorption band at $\lambda_{\max} = 442$, 466, and 450 nm, respectively. In CH₃OH or CH₃CN, 2 is very much less reactive to O₂, and upon exposure, the intense amber color

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does not develop. In fact, no charge-transfer transitions appear in the visible region even though V(II) is eventually consumed.

Discussion

Spectrophotometric Results. In Table III are summarized literature data that are relevant to the spectrophotometric measurements we have made. In the case of V(II) in an aqueous environment, we have omitted some of the earliest measurements, when internal evidence suggests that the vanadium was not fully reduced.

In most of our measurements, the solutions in the different environments were prepared from compound **2**, and thus they contain DME at approximately 3 times the concentration of V(II) or about 0.12 M. For the measurements in water, CH₃OH, and CH₃CN, V(II) was also prepared by reducing V(O₃SCF₃)₃ in the same medium, with results indistinguishable from those obtained by dissolving **2**. Because of the low concentration of DME and because an ether function does not have a high affinity for metal ions, it is unlikely that DME affects the spectrophotometric results we obtained except in the case of CH₂Cl₂ as solvent.

When the results for V(II) in various aqueous media as solvent including our own (Table III) are compared, at most only minor effects are observed. Notably, even SO₄²⁻ does not perturb the spectra markedly. For [Co(NH₃)₅H₂O]³⁺, it has been shown²⁸ that SO₄²⁻ in replacing H₂O produces a bathochromic shift, while outer-sphere SO₄²⁻, as it is presented in an ion pair, does not affect the d-d transitions noticeably. In this particular case, the equilibrium between the inner- and outer-sphere forms was determined. This has not been done for a dipositive ion, but the results shown in Table III suggest that there is little inner-sphere complex formation of V²⁺(aq) with SO₄²⁻. When all the aqueous data are considered, including those for the solids that contain V(H₂O)₆²⁺, ν_3 appears to be the most sensitive to the environment (λ ranging from 333 to 370 nm), a result which is not surprising considering that it involves the excitation of two electrons from the nonbonding t_{2g} to the antibonding e_g levels.

Effects of change of anion on the spectra are discernible when our data with CF₃SO₃⁻ as the counterion are compared to literature data for the same solvent, but where the counterion now is Cl⁻. The differences observed between our results and those reported in the literature for CH₃OH as solvent suggest that there is some complexation in CH₃OH by the weak-field ligand Cl⁻. The anion CF₃SO₃⁻, it should be noted, produces a bathochromic shift²⁹ when it replaces H₂O in the coordination sphere of Cr(III), and in view of the fact that ν_1 for V²⁺ in H₂O and CH₃OH are much the same, the difference between the spectra in the presence of Cl⁻ and CF₃SO₃⁻ cannot be ascribed to complexation by CF₃SO₃⁻. Published data make possible also comparisons for THF, CH₃CN, and pyridine as solvents, where pyridine in particular shows a marked change in comparison to THF—in pyridine very strong absorption is observed, which we take to be charge transfer in origin, extending to low energies covering most of the visible region of the spectrum, with λ_{\max} at 430 nm, $\epsilon > 1.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. The only structure discernible is a shoulder at 490 nm, and there being no other absorption at lower energy, we ascribe it to ν_1 .

We turn now to intercomparisons among our own data. For a d³ ion in an octahedral field, the long-wavelength transition measures 10Dq.³⁰ In this connection, it is of some interest that

Table IV. Comparisons of Spectrochemical Data (10Dq $\times 10^{-3}$, cm⁻¹)

ML ₆	V ²⁺		Ni ²⁺ ^a		Cr ³⁺ ^a	
	10Dq	β_{35}	10Dq	β_{35}	10Dq	β_{35}
H ₂ O	11.7	0.94	8.5	0.89	17.4	0.79
CH ₃ CN	16.3	0.80	10.7	0.83		
CH ₃ OH	11.7	0.95	8.4	0.88		
acetone	12.2	0.96			16 ^b	
pyridine	20.4		10.0			
¹ / ₂ en ^c	15.6	0.80	11.5	0.81	21.9	0.67
CN ^{-d}	22.3	0.64			26.7	0.58
Cl ⁻	7.20	0.98			13.2	0.61

^a Unless otherwise noted, data were from ref 30. See ref 30 also for calculation of β_{35} . ^b Cr(ClO₄)₃·6H₂O (0.087 g) was dissolved in 8.2 mL of dry acetone and activated molecular sieves 3A (4 g) were added. The mixture was stored for 12 h whereupon the spectrum was measured. It should be noted that conversion of Cr(H₂O)₆³⁺ to the acetone complex can occur by substitution on carbon. The conversion may not be complete, and thus the bathochromic shift compared to H₂O is to be regarded as a lower limit. ^c Reference 33. ^d Reference 34.

ν_1 for DME is at shorter wavelength than it is for THF as a solvent. We ascribe this to the fact that DME is able to act as a chelating ligand, and the observed shift to higher energy is consistent with ligand field differences observed for other monodentate compared to bidentate environments, such as NH₃ compared to ethylenediamine. DME is undoubtedly a much stronger field ligand than is CH₂Cl₂, and thus the fact that ν_1 in CH₂Cl₂ and in DME is much the same, 900 vs 864 nm, indicates that in CH₂Cl₂, DME remains coordinated to V(II). This is supported by the fact that although V(O₃SCF₃)₃ is not reduced cleanly in CH₂Cl₂, reduction does take place readily when some DME is added to the reaction mixture. That the coordination environment of V(II) in the solutions in CH₂Cl₂ is unsymmetrical is suggested also by the fact that ν_2 shows structure (λ_{\max} at 350 nm with a shoulder at 380 nm) and that it is unusually intense compared to ν_2 ($\nu_3/\nu_2 = 20/3$ as compared to 4/6 in an aquo environment). Striking changes in ν_3 are observed when DMSO or CH₃OH even in small amount (<6 mol/mol of V(II)) is added. On such addition, ν_3 at 350 nm disappears and the ν_3 band characteristic of the DMSO (or CH₃OH) complex appears.

Quite unexpected is the close agreement of the observations made with CH₃OH compared to those in an aquo environment. The methanol was dried, and the water content could not have been high enough to have led to the formation of the hexaqua complex in methanol. Some precedent for the behavior reported is found in Table III. It is to be noted that all the absorption bands for V₁₂·6CH₃OH lie at higher energy than those for VBr₇·6H₂O, despite the fact that the interionic forces, because of smaller ionic radii, are likely greater for the hexahydrate species.

The most striking results we have obtained are with V(II) in the solvents acetone, CH₃CN, and pyridine. The molecules of these three solvents have in common the property that they are π -acids, thus making possible back-bonding interactions. It should be recalled that the electrochemical data show that the oxidation of V(II) in CH₃CN calls for a potential (irreversible) of 1.25 V vs NHE. The charge-transfer absorption observed for pyridine as solvent has already been noted. Absorption of like origin is intense also for V(II) in acetone, though solutions in acetone are orange-brown, and visually resemble those of [VOV]⁴⁺, enough so that when we first introduced V(II) into acetone, we assumed that it had been oxidized. With CH₃CN as ligand, as is commonly observed, charge-transfer absorption appears at much shorter wavelengths than for pyridine. For the latter solvent, it extends far enough into the low-energy region so that ν_1 appears on the low-energy shoulder of the charge-transfer band. Furthermore, there is considerable enhancement of the intensity for these solvents compared to water, THF and the like, the values of ϵ for ν_1 being 27, 38, and $\sim 50 \text{ M}^{-1} \text{ cm}^{-1}$ for acetone, CH₃CN, and pyridine respectively, compared to $4.5 \text{ M}^{-1} \text{ cm}^{-1}$ for H₂O.

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Table V. Comparisons of Systems Used for the Reduction of Epoxides to Olefins by Transition-Metal Reducing Agents

reducing agent	olefins	ratio ^a	solvent	reacn time, temp	convn %	ref.
2/(NEt ₃)	<i>b</i>	1/1/1	CD ₂ Cl ₂	30 min, 30 °C	47	this work
"V(acac) ₂ "	<i>b</i>	4/1	DME	19 h, 76 °C	61	8
TiCl ₃ /LiAlH ₄	<i>b</i>	4/1/2	CH ₂ Cl ₂	15 h, room temp	69	3
WCl ₆ /RLi	<i>c</i>	1/1.7/1	THF	3 h, -5 °C	89	4
Cr(II)/cn	<i>b</i>	7/17/1	DMF	48 h, room temp	73	6

^a Where only two ingredients, the ratio is reducing agent/epoxide. ^b Cyclohexene oxide. ^c Cyclooctene oxide.

The observations of ν_1 are particularly significant because the corresponding energies measure $10Dq$ directly. Interesting differences in the spectrochemical series for V^{2+} as compared to the normal order are to be noted. For V^{2+} we have, in order of increasing $10Dq$: Cl^- (H_2O , CH_3OH), acetone, en, CH_3CN , py. The "normal order" as compiled from data for Ni^{2+} , Cr^{3+} , and $Co(NH_3)_5^{3+}$ is Cl^- , acetone, H_2O (CH_3OH , H_2O), py, CH_3CN , en. Acetone being left of H_2O in the "normal" series is shown by observations made with the acetone complex of pentaamminecobalt(III)³¹ and with results we have obtained on Cr(III) (see footnote, Table IV). The position of acetonitrile is based on observations made with the acetonitrile complex of pentaamminecobalt(III).³² The "normal" order has been developed from observations made with metal ions which do not participate significantly in back-bonding. This tendency is important for V(II), in part, because there are no electrons in the antibonding level and because the πd electrons are readily excited, as is evidenced by the fact that the $V(H_2O)_6^{3+/2+}$ couple is strongly reducing.

In Table IV are shown the spectrochemical data for V(II) compared to data for two ions of the first-row transition elements of related electronic structure. Noteworthy are the large changes in $10Dq$ observed for V(II), when H_2O is replaced by CH_3CN or pyridine (4.6×10^3 and 8.7×10^3 cm^{-1} respectively) compared to corresponding shifts for $Ni(II)$ (2.2×10^3 and 1.5×10^3 cm^{-1}). Back-bonding is not recognized as a significant factor in the chemistry of high-spin $Ni(II)$.

The calculations of β_{35} ³⁰ are not particularly revealing, in part perhaps because the data are incomplete. Our efforts to prepare solutions of Ni^{2+} in acetone failed, and we are left with a single comparison between V^{2+} and Ni^{2+} in an environment where back-bonding can be significant perturbation. Only a slight decrease in β_{35} for V^{2+} in CH_3CN as compared to that for Ni^{2+} in the same solvent is registered, despite the evidence that the interactions in the two cases are different in important respects.

Reduction of Epoxides and of O_2 . It is not surprising that the reduction of epoxides by V(II) occurs, but the results obtained here are surprising when the relative rates of these reactions are compared to the "V(acac)₂" deoxygenating reagent reported previously⁸ as well as other well-known reducing reagents. To put this in perspective: typical reaction conditions for the "V(acac)₂" systems are at elevated temperatures (60–80 °C) and extended reaction times (18–24 h). Our reactions occur at room temperature and, in some cases, are complete within seconds. In Table V is presented a comparison of reaction conditions and times for several of the established reagents used to deoxygenate epoxides. On the basis of the relative rates only Sharpless' tungsten reagent is comparable to V(II) to CH_2Cl_2 in showing reactivity under such mild conditions.

Differences in driving force in the various media are undoubtedly factors in determining the rates at which epoxides are reduced by V(II), but since the values for the relevant couples are not known, discussion is unwarranted. It is nevertheless appropriate to point out that the operative couples are likely not V^{3+}/V^{2+} but rather $[VOV]^{4+}/V^{2+}$ or, if VO^{2+} rather than $[VOV]^{2+}$ is the

primary product of the reaction, VO^{2+}/V^{2+} . It is highly unlikely that reaction takes place by outer-sphere electron transfer from V(II) to the epoxide and much more likely that it involves direct binding of the oxygen of the epoxide to a normal coordination position of V(II). Thus, accessibility of the epoxide to the metal ion is also an important factor in determining rates, and it goes a long way to explain the main features of the observations.

In the case of CH_3CN as a solvent, both driving force and accessibility are factors in reducing the rate of reaction. Back-bonding stabilizes V(II) with respect to any form of higher oxidation state; at the same time it increases the affinity of the ligand for V(II) and decreases the lability. For CH_3OH , the major factor in leading to a slow rate of reaction may well be the greater potency of CH_3OH compared to epoxide as a ligand, so that the concentration of the V(II)-epoxide precursor complex is kept low. Accessibility is also a major factor in accounting for the low reactivity¹⁸ of V(acac)₂. The bis(acetylacetonate) complexes of dipositive ions are known to adopt structures in solution in which the metal ions achieve coordination number 6 by intramolecular association, the oxygens of the ligands assuming bridging roles.³⁵

Environments that are favorable to reaction are provided by **2** dissolved in CH_2Cl_2 , where the complex has at least two accessible coordination positions, be they occupied by CH_2Cl_2 or by $CF_3SO_3^-$, or in DME as solvent, where binding is relatively weak because of the steric bulk of the groups attached to oxygen.

That the addition of a base dramatically alters product ratios for styrene and stilbene in our reactions is not unexpected. Trace amounts of acid, which catalyze the rearrangement of epoxide, can be generated by trace water and the highly acidic V(III) and V(IV) reaction products (the pK_a of $V^{III}-OH_2$ in aqueous solution is between 3 and 4).³⁶

In contrast to the reaction of epoxides with V(II), that of O_2 with the same reagent almost certainly does not involve direct substitution on the metal. The specific rate of the reaction between $V(H_2O)_6^{2+}$ and O_2 has been measured³⁷ as 2×10^3 $M^{-1} s^{-1}$. The rate of exchange of water between $V(H_2O)_6^{2+}$ at the same temperature is³⁸ 90 ± 20 s^{-1} . Even if H_2O and O_2 could compete at the same specific rate for an intermediate of reduced coordination number, the maximum value of the rate of forming a precursor complex of the formula $V(H_2O)_5O_2^{2+}$ would be only about 90/55.5 or ca. 2 $M^{-1} s^{-1}$. To bolster the argument: a large category of redox reactions is known^{39,40} in which substitution on $V(H_2O)_6^{2+}$ is rate determining, for entering groups that are more polar than O_2 and that have specific rates on the order of 10 $M^{-1} s^{-1}$. Loss of an electron from $V(H_2O)_6^{2+}$ to O_2 leaves vacant a t_{2g} orbital, and a reasonable mode of attack by O_2 would be on the face of the octahedron, where a bond to O_2^- can be formed in the act of electron transfer. The immediate fate of the intermediate of coordination number 7 that results cannot be predicted with certainty, but a reasonable reaction course would be collapse to $[V(H_2O)_5O_2]^{2+}$, which can be regarded as comprising of O_2^- bound to V(III). The suggested initial mode of attack of course blurs the distinction between inner- and outer-sphere modes of attack

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and is a reaction possibility long recognized.

The slow rate of reaction of O₂ with V(II) in CH₃CN is not unexpected in view of the high oxidation potential (1.25 V). That the reaction takes place at a noticeable rate suggests strongly that oxidation by O₂ is assisted by bond formation as suggested above. Quite unexpected is the slow rate of reaction of V(II) in CH₃OH as compared to that in H₂O. A contributing factor may well be steric demands of the methyl groups, which would interfere with bond formation through the faces of the octahedron. Equally unexpected is the observation that in neither CH₃CN or CH₃OH does [VOV]⁴⁺ appear as an intermediate product in a recognizable amount.

The dominant product of the reaction of epoxides and of O₂ with V(II) in CH₂Cl₂ or DME as solvent is [VOV]⁴⁺. To learn whether this species is the immediate product of the reaction of O₂ with V(II) or whether V(IV) is the immediate product, which then reacts with V(II) to form [VOV]⁴⁺, two kinds of experiments were performed. In one approach, the order of mixing for the most reactive epoxide, namely that derived from styrene, was reversed. The usual procedure was to add the epoxide to a solution of V(II), an arrangement that favors the reaction of V(IV) as a primary product with V(II). Reversing the order of mixing did not lead to a substantial reduction in the yield of the binuclear ion. The experiment however must be regarded as inconclusive because we cannot be sure that the reaction of V(II) with epoxide is rapid enough to make this simple strategy effective. In the second approach, efforts were made to measure the rate of reaction of V(II) with V(IV), the latter prepared by the reaction of V(II) with O₂. Reaction was continued, passing O₂ until the color of [VOV]⁴⁺, which is the product first formed, was depleted—this leaves a solution that is a clear blue, characteristic of VO²⁺—or in some cases, some residual [VOV]⁴⁺ was left. The interaction of V(II) with VO²⁺ thus prepared is slow enough so that we could be certain that in the case of the more reactive epoxides, [VOV]⁴⁺ is indeed a direct product of the reaction, were it not for the fact that unexpected complications were encountered in the studies.

One of these complications was namely that when clear blue solutions of VO²⁺ were used, in some cases a considerable amount of V(II) was consumed before the color characteristic of [VOV]⁴⁺ appeared. This effect can be attributed to the presence of some

V(V) in such solutions, as is indicated also by experiments in which I⁻ is used as reducing agent. More difficult to understand is the observation that as the V(II) is increased in proportion to VO²⁺ kept in excess, the concentration of [VOV]⁴⁺, making due allowance for the effect of dilution, does not increase linearly. Rather a saturation effect is observed, as would be expected for a system in which there is a measurable equilibrium between reactants and products, so that the end points is obscured. Reasonable conjectures are that V(II) and VO²⁺, or mononuclear V(III), are in equilibrium with [VOV]⁴⁺, but as described elsewhere,¹⁶ the effects expected on dilution, if a simple equilibrium such as



were involved, are not observed. Finally, measurements of the rate of reaction show complex kinetics. In experiments with V(II) in excess, the rate is almost independent of the concentration of V(II) (over the range 10⁻⁵–10⁻² M) while when V(IV) is in excess, the reaction shows an induction period.

We conclude that we cannot be certain of the physical state of either [VOV]⁴⁺ or VO²⁺ in these solutions, and one or both may be polynuclear. As a result, we can reach no conclusion on the issue that motivated us to undertake these experiments, because there is a real possibility that V(IV), as first produced, is different from V(IV) as it is present in the aged solutions we have dealt with in the experiments just mentioned, which we have not reported in detail.

It needs to be acknowledged that the composition of the first sphere of coordination of V(II) in the solvents acetonitrile, pyridine, and acetone with triflate as the counter ion is not known. These solvents, being non-protic, do not greatly stabilize the free anion, and thus, while we have tacitly assumed that in acetonitrile, for example, the cation exists as V(CH₃CN)₆²⁺, the anions may in fact be ligated to the metal ion. This issue is now under investigation.

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Contribution from the Department of Physical and Inorganic Chemistry, University of Adelaide, South Australia 5001, Australia

Complexation of Lithium(I) and Silver(I) by 4,7,13,16-Tetraoxa-1,10-diazabicyclo[8.8.2]eicosane in a Range of Solvents. A ⁷Li Nuclear Magnetic Resonance and Potentiometric Titration Study

Amira Abou-Hamdan and Stephen F. Lincoln*

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Complexation of Li⁺ and Ag⁺ by the clamlike cryptand 4,7,13,16-tetraoxa-1,10-diazabicyclo[8.8.2]eicosane (C22C₂) to form the cryptate [Li.C22C₂]⁺ has been studied in seven solvents by ⁷Li NMR spectroscopy and potentiometric titration. A considerable variation in the [Li.C22C₂]⁺ and [Ag.C22C₂]⁺ stability constants (shown as the respective log (K/dm³ mol⁻¹) values at 298.2 K after each solvent) occurs with solvent variation: acetonitrile (7.8, 9.4), acetone (8.9, 13.1), water (<2, 6.0), methanol (4.0, 10.2), dimethylformamide (3.5, 9.4), diethylformamide (3.1, 8.2), and pyridine (4.0, 5.0). The exchange of Li⁺ on [Li.C22C₂]⁺ falls within the ⁷Li NMR time scale in methanol, dimethylformamide, and diethylformamide, in which the monomolecular decomplexation process is characterized by *k*_d(298.2 K) = 971 ± 42, 240 ± 7, and 916 ± 28 s⁻¹, respectively, Δ*H*_d[‡] = 31.0 ± 0.4, 22.5 ± 1.3, and 26.7 ± 0.6 kJ mol⁻¹, respectively, and Δ*S*_d[‡] = -83.9 ± 1.8, -124 ± 5, and -99 ± 2 J K⁻¹ mol⁻¹, respectively. In acetonitrile, acetone, and pyridine the exchange rate is in the very slow regime of the ⁷Li NMR time scale close to the solvent boiling point and in the very fast regime in water close to the freezing point. These data are discussed in the context of the effects of cryptand structure and solvent characteristics on cryptate lability and stability.

Introduction

Complexation of alkali-metal ions by (polyoxa)diazabicycloalkanes, or cryptands, to form cryptates has generated substantial interest since Lehn first reported the cryptands.¹⁻¹⁹ We

have been particularly interested in the relationship between cryptate structure, stability, and lability and herein report a kinetic

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