

able groups. Analysis shows $pK_1 = 2.19 \pm 0.06$, $pK_2 = 3.34 \pm 0.06$, and $k_2 = 4.3 \pm 0.3 \text{ sec}^{-1}$, again agreeing with measurements described above.⁶ Although IIa and IIb are kinetically indistinguishable, IIa contains both the better nucleophile and better leaving group for recyclization, and can close to products I and Im without proton transfer. It seems reasonable, therefore, to postulate that this zwitterionic species is the reactive one.

In summary, our data demonstrate that in the absence of an enzyme a readily reversible nucleophilic reaction of a cyclic sulfonate can be observed. Comparison of the behavior of the five-membered cyclic ester 2-hydroxy-5-nitro- α -toluenesulfonic acid sultone when treated with imidazole² to that of the six-membered sultone I fully supports our premise that intramolecular nucleophilic attack resulting in recyclization should be less favorable and therefore more easily observable in the case of the six-membered system. Exactly the same reactivity pattern has been seen when the corresponding *o*-hydroxy-substituted phenylmethanesulfonyl- and β -phenylethanesulfonylchymotrypsin species are compared.^{1,7} The kinetic and equilibrium behaviors seen in the present study show again that as a model catalyst imidazole is an excellent choice for the simulation of enzymatic reactions.

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(6) This measurement, $k_2/K_2 = (0.94 \pm 0.2) \times 10^4$, agrees reasonably well with $(1.45 \pm 0.05) \times 10^4$ obtained above, especially considering the variations in reaction media (different buffer systems, including strong acids).

(7) Unpublished results of W. Berg.

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Octahedral Vanadium(IV) Complexes. Synthesis and Stereochemistry of Vanadium(IV) β -Diketonates

Sir:

The chemistry of vanadium(IV) is dominated by the VO^{2+} ion and its metal complexes, a great many of which exhibit square-pyramidal coordination,¹ e.g., $VO(acac)_2$ ($acac^- = CH_3COCHCOCH_3^-$). Octahedral complexes of the simple V^{4+} ion, in which the vanadium is not attached to a doubly bonded oxygen atom, e.g., VCl_6^{2-} , are rare,² and, to our knowledge, the recently reported complexes³ with the dinegative anion of 1,2-dihydroxybenzene and its derivatives, $[V(RC_6H_3O_2)_3]^{2-}$, are the only well-characterized octahedral tris chelates of V^{4+} . No cationic complexes are known, with the

possible exception of $[V(en)_3]F_4$.⁴ Apart from $V(acac)_2Cl_2$ and $V(bzac)_2Cl_2$ ($bzac^- = C_6H_5COCHCOCH_3^-$)⁵ the only neutral octahedral complexes of V^{4+} are adducts of VCl_4 .

We now report the synthesis and characterization of the octahedral vanadium(IV) β diketonates $V(acac)_2Cl_2$, $V(dpm)_2X_2$ ($dpm^- = t-C_4H_9COCHCO-t-C_4H_9^-$; $X = Cl, Br, NCO, \text{ or } NCS$), and $[V(dik)_3]^+Y^-$ ($dik = acac$ or dpm ; $Y^- = FeCl_4^-$ or $SbCl_6^-$). The latter compounds represent the first well-characterized cationic complexes of V^{4+} .

The $V(dik)_2Cl_2$ complexes were prepared in good yield by reaction of the diketone with VCl_4 in anhydrous benzene or dichloromethane-hexane. Metathesis reactions of $V(dpm)_2Cl_2$ with $HBr, AgOCN$, and $NaSCN$ in benzene or dichloromethane afforded $V(dpm)_2X_2$ ($X = Br, NCO, \text{ or } NCS$). Similar reactions were attempted with HI and $KSeCN$; however, both resulted in apparent reduction of the vanadium(IV) rather than formation of the $V(dpm)_2X_2$ complex. The cationic complexes, $[V(dik)_3]^+[FeCl_4]^-$ and $[V(dik)_3]^+[SbCl_6]^-$, were prepared by reaction of $V(dik)_2Cl_2$ with anhydrous $FeCl_3$ or $SbCl_5$ in dichloromethane. Satisfactory analytical data have been obtained for all of the complexes. All are readily hydrolyzed on contact with the atmosphere.

Molecular weight and conductance data indicate that the $V(dik)_2X_2$ complexes are monomeric and essentially nonelectrolytes in nitrobenzene; $[V(dik)_3]^+Y^-$ are 1:1 electrolytes. Effective magnetic moments (1.66–1.80 BM), measured by nmr in dichloromethane, are approximately equal to the spin-only value (1.73 BM) expected for vanadium(IV). $[V(dpm)_3]^+[SbCl_6]^-$ (in dichloromethane at room temperature) gives a very broad esr signal having a line width of ~ 600 G and a g value of 1.93. Superimposed on this broad, single line is a sharp, eight-line spectrum which is believed to arise from a trace of a hydrolysis product containing the VO^{2+} moiety.

All of the complexes are intensely colored red or violet owing to charge-transfer bands at 15,000–18,000 and $\sim 28,000 \text{ cm}^{-1}$ (ϵ 2000–8000) which are assigned to diketonate(π) \rightarrow metal(d) and metal(d) \rightarrow diketonate(π^*) transitions, respectively. Additional bands in the visible spectra of the $V(dik)_2X_2$ complexes appear to involve halogen(π) \rightarrow metal(d) charge transfer. Unfortunately, the d-d transitions are obscured by the charge-transfer bands.

The far-infrared spectrum of $V(dpm)_2Cl_2$ (Figure 1) depends on phase, and the changes in the spectrum on changing the solvent suggest that there is an equilibrium in solution between the cis and trans isomers, with the isomer present in the solid state decreasing in concentration with increasing dielectric constant of the solvent. Most important are changes in the V-Cl stretching region. A band at $\sim 385 \text{ cm}^{-1}$ in the solution spectra increases in intensity with increasing solvent dielectric constant at the expense of the strong band at $\sim 362 \text{ cm}^{-1}$; only the latter band is present in the spectrum of the solid. Measurement of the orientation molar polarization in carbon tetrachloride (335 cm^2) and in benzene (498 cm^2) permits the 385-cm^{-1}

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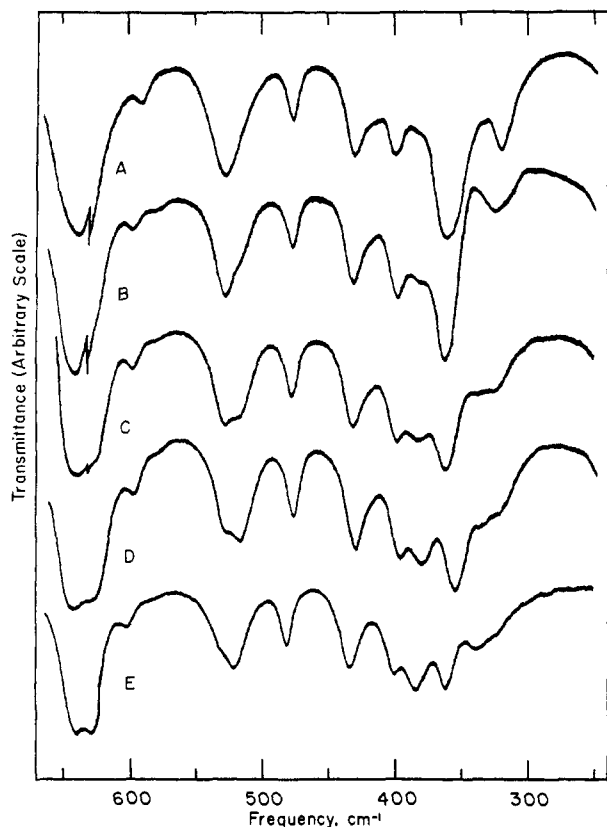


Figure 1. Far-infrared spectra of $V(dpm)_2Cl_2$ in (A) Nujol mull, (B) carbon tetrachloride, (C) benzene, (D) chloroform, and (E) dichloromethane. Solution spectra are arranged in order of increasing solvent dielectric constant. The discontinuities at $\sim 630\text{ cm}^{-1}$ are due to a grating change.

band to be assigned to the cis isomer and the 362-cm^{-1} band to the trans isomer. Thus, $V(dpm)_2Cl_2$ has the trans configuration in the solid state, and it is the cis isomer which increases in concentration with increasing solvent dielectric constant. If one assumes that *cis*- $V(dpm)_2Cl_2$ and *cis*- $Ti(dpm)_2Cl_2$ have the same orientation molar polarization (1336 cm^2), the equilibrium constant for isomerization of $V(dpm)_2Cl_2$, $K = [\text{cis}]/[\text{trans}]$, can be estimated to be 0.33 in carbon tetrachloride and 0.59 in benzene.

Similar results were obtained for $V(dpm)_2Br_2$, $K = 0.18$ in benzene, and, again, the trans isomer is present in the solid state. These results are of considerable interest in view of the fact that only the cis isomer has been found for dichloro- and dibromobis(β -diketonato)-titanium(IV) complexes.⁷ Steric effects may be an important determinant of the trans configuration in the case of the vanadium complexes since the crystal radius of V^{4+} (0.60 \AA) is appreciably smaller than that of Ti^{4+} (0.68 \AA).⁸ It is pertinent to note that both cis and trans isomers have been found for $Ge(dpm)_2Cl_2$ and $Ge(dpm)_2Br_2$ ⁹ ($r_{Ge^{4+}} = 0.53\text{ \AA}$), whereas only the cis

(6) Low-temperature nmr spectra indicate that $Ti(dpm)_2Cl_2$ is 100% cis in dichloromethane. It is probably cis in the solid state as well, since its far-infrared spectrum is unchanged on going from the solid to dichloromethane solution.

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isomer is known in the case of dihalobis(β -diketonato)-tin(IV) complexes^{7c,10} ($r_{Sn^{4+}} = 0.71\text{ \AA}$). The existence of both cis and trans isomers for $Ti(acac)_2I_2$ ¹¹ but only the cis isomer for $Ti(acac)_2X_2$ ($X = F, Cl, \text{ or } Br$) also suggests the importance of a steric effect.

The cis configuration is indicated for the pseudohalide complexes $V(dpm)_2(NCX)_2$ by the presence of two CN stretching bands in the infrared spectra [2166 and 2206 cm^{-1} for $V(dpm)_2(NCO)_2$, 2010 and 2060 cm^{-1} for $V(dpm)_2(NCS)_2-CH_2Cl_2$ solution] and by the dipole moment of $V(dpm)_2(NCO)_2$ ($8.38 \pm 0.22\text{ D}$, C_6H_6 solution). The frequencies of the NCX vibrations and the integrated intensities of the CN stretching bands are consistent with an N-bonded attachment of the pseudohalide ligands.

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Acidity of Hydrocarbons. XLIX. Equilibrium Ion Pair Acidities of Fluorinated Benzenes for Cesium Salts in Cyclohexylamine. Extrapolation to pK of Benzene¹

Sir:

The hydrogen isotope exchange rates of the ortho, meta, and para hydrogens in fluorobenzene with lithium cyclohexylamide in cyclohexylamine relative to benzene have been shown to be almost identical with the partial rate factors for exchange of ortho, meta, and para fluorine substituents in hydrogen isotope exchange of polyfluorobenzenes with methanolic sodium methoxide (Table I).^{2,3} Arguments have been presented that these substituent rate effects also represent substituent

Table I. Partial Rate and Equilibrium Factors

| Fluorine position | R_f^a NaOMe, MeOH | $\log k_{rel}^b$ LiCHA | ΔpK^c |
|-------------------|---------------------------|---------------------------|---------------|
| Ortho | 5.25 | 5.43 | 5.7 |
| Meta | 2.07 | 1.95 | 2.3 |
| Para | 1.13 | 1.03 | 1.1 |

^a Partial rate factors at 40° (ref 3). ^b Relative rates for tritium exchange of fluorobenzene with lithium cyclohexylamide in cyclohexylamine at 25° (ref 2). ^c Calculated from the following equations: $pK(\text{benzene}) - pK(C_6F_5H) = 2o-F + 2m-F + p-F$; $pK(\text{benzene}) - pK(1,2,3,4-C_6F_4H_2) = o-F + 2m-F + p-F$; $pK(\text{benzene}) - pK(o-C_6H_4F_2) = o-F + m-F$.

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