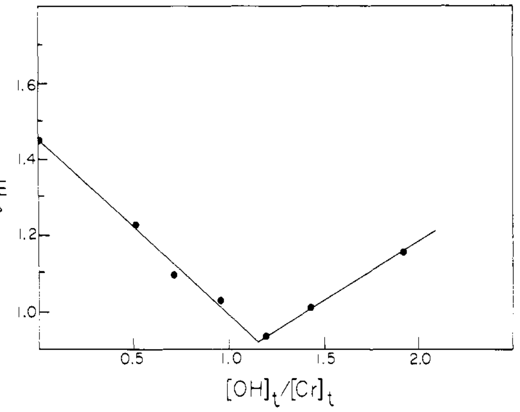

Figure 2. TPVT titration of a solution of $[Cr(bpy)_2(H_2O)_2](NO_3)_3\cdot{}^1/_2H_2O$ in a saturated solution of barium nitrate at 25 °C. Molality of total chromium species in mol Cr per 1 kg water = 0.24*m*.

determined by linear extrapolation to $m = 0$. The validity of (4) was confirmed experimentally in over 40 solute–solvent systems,[6] using solutes with known ν. The precision of ν determinations is ±0.05.

The *solute* used in this work was $[Cr(bpy)_2(H_2O)_2](NO_3)_3\cdot{}^1/_2H_2O$. A saturated solution of barium nitrate was used as solvent. The validity of the linear relationship (4) in this solvent was confirmed with a standard dipositive solute ion ($\nu = 1$), Ca^{2+}. The salt used was $Ca(NO_3)_2\cdot 4H_2O$ (Figure 1). The bis(bipyridine)diaquachromic salt was used for investigating the dimerization of the hydroxoaqua ion. A weighed sample of $[Cr(bpy)_2(H_2O)_2](NO_3)_3\cdot{}^1/_2H_2O$[4] was dissolved in the saturated barium nitrate solution and neutralized *stepwise* by the addition of weighed portions of $Ba(OH)_2\cdot 8H_2O$. ν_m was determined after the addition of each portion of barium hydroxide. Since both the nitrate counterion of the chromic species and the barium ion added in the form of barium hydroxide were common to solute and solvent, they did not affect ν_m, which was exclusively dependent on the chromic species. If dimerization of $[Cr(dpy)_2H_2O(OH)]^{2+}$ occurred, the initial ν_m of the diaqua salt solution should be *reduced* by the addition of barium hydroxide and reach its minimum value after 1 equiv of barium hydroxide was added. The results, presented in Figure 2, confirm this expectation. Addition of more than 1 equiv of OH^- converts the dinuclear hydroxoaqua ion to the mononuclear dihydroxo ion and raises ν_m as expected. However, dimerization is not complete at a molality of 0.24*m* (formula weights of the diaqua salt), since ν_m is not reduced to 50% of its initial value, but only to ~64% (from 1.45 to 0.92). This indicates that an equilibrium is established in solution between the mononuclear and the dinuclear hydroxoaqua ions:

$$2[Cr(bpy)_2H_2O(OH)]^{2+} \rightleftarrows [(bpy)_2Cr(H_3O_2)_2Cr(bpy)_2]^{4+} \quad (5)$$

Dilution of the solution should favor dissociation of the dimer, hence an increase in ν_m. Two ν_m determinations, at $m_2 = 0.202$ and $m_3 = 0.114$, confirm this conclusion. The corresponding values ν_{m_2} and ν_{m_3} are 1.074 and 1.108, respectively.

It was suggested[2] that a hydrogen oxide bridged dimer of an aqua ion may be the reactive intermediate in olation reactions such as

$$2L_4M(H_2O)(OH)^{(n-1)+} \rightarrow L_4M(OH)_2ML_4^{2(n-1)+} + 2H_2O \quad (6)$$

which is believed to proceed by

$$2L_4M(H_2O)(OH)^{(n-1)+} \overset{K}{\rightleftarrows} L_4M(H_3O_2)_2ML_4^{2(n-1)+} \quad (7)$$

$$L_4M(H_3O_2)ML_4^{2(n-1)+} \rightarrow L_4M(OH)_2ML_4^{2(n-1)+} + 2H_2O \quad (8)$$

This mechanism is supported by the evidence, reported here, for a monomer–dimer equilibrium in aqueous solution. The olation of *cis*-$[Cr(C_2O_4)_2(H_2O)(OH)]^{2-}$, which was investigated by Grant and Hamm,[9] is a first-order reaction at chromium concentration >0.01 M. Its order increases at lower concentrations. A monomer–dimer equilibrium explains the kinetics of this reaction. The equlibrium constant K should be higher for the negative oxalato complex ion than for the positively charged bipyridine complex.

The existence of hydrogen oxide bridges between metal ions in concentrated aqueous solutions is not unexpected, if one considers the bond energy of the hydrogen bond that links the hydroxide and water ligands of that bridge. The energy of this short symmetrical bond, with an internuclear O–O distance of 2.44 Å, was estimated to be over 100 kJ/mol.[10,11] The alternative weak and unsymmetrical H bond that may be formed between an OH ligand and an H_2O solvent molecule has an O–O distance of 2.75 Å.[12] This distance equals the O–O separation in the solvent itself (2.76 Å in ice[13]), and the hydrogen bond energies of these bonds are probably similar (21 kJ/mol[13]).

Over 30 years ago, an H atom transfer mechanism was proposed by Silverman and Dodson,[14] as an alternative to an outer-sphere mechanism in reactions such as

$$(H_2O)_5Fe^*(OH)^{2+} + (H_2O)Fe(H_2O)_5^{2+} \rightleftarrows Fe^*(H_2O)_6^{2+} + (HO)Fe(H_2O)_5^{2+}$$

In view of the results reported here, this mechanism seems to merit serious reconsideration. Although the equilibrium concentration of the $[Fe(H_3O_2)Fe]^{4+}$ dimer is probably low in *dilute* aqueous solutions, it could, nevertheless, constitute a plausible intermediate in the exchange reaction.

Work is in progress on a precise determination of the equilibrium constant of reaction 5 and on reactions of similar hydroxoaqua ions such as $Cr(H_2O)_5OH^{2+}$.

Registry No. $[Cr(bpy)_2(H_2O)_2](NO_3)_3$, 59186-33-3; $[Cr(bpy)_2H_2O(OH)]^{2+}$, 57651-38-4; $[Cr(bpy)_2(OH)_2]^+$, 47514-01-2.

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Stepwise Metal-Assisted Oxidative Decarboxylation of Vanadium(V) Ethylenebis((*o*-hydroxyphenyl)glycine). Isolation of a Possible Intermediate

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We have previously examined the chelate chemistry of ethylenebis((*o*-hydroxyphenyl)glycine) (EHPG) with a variety of metals.[3] Vanadium complexes of this ligand have proved to be especially interesting, and we report here a novel metal-assisted, stepwise, oxidative decarboxylation of the ligand to yield ultimately vanadyl *N,N'*-disalicylideneethylenediamine (SALEN).

A dark blue complex, **1**, can be isolated from a solution of EHPG and vanadyl ion in aqueous ethanol solution. This complex has been characterized by the appropriate techniques[4] as V^VO-

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(3) (a) Patch, M. G.; Simolo, K. P.; Carrano, C. J. *Inorg. Chem.* **1982**, *21*, 2972. (b) Patch, M. G.; Simolo, K. P.; Carrano, C. J. *Ibid.* **1983**, *22*, 2630.

(4) All compounds were characterized by elemental analysis, ^1H and ^{13}C NMR, infrared, and UV-visible spectrophotometry, and where appropriate mass spectrometry.

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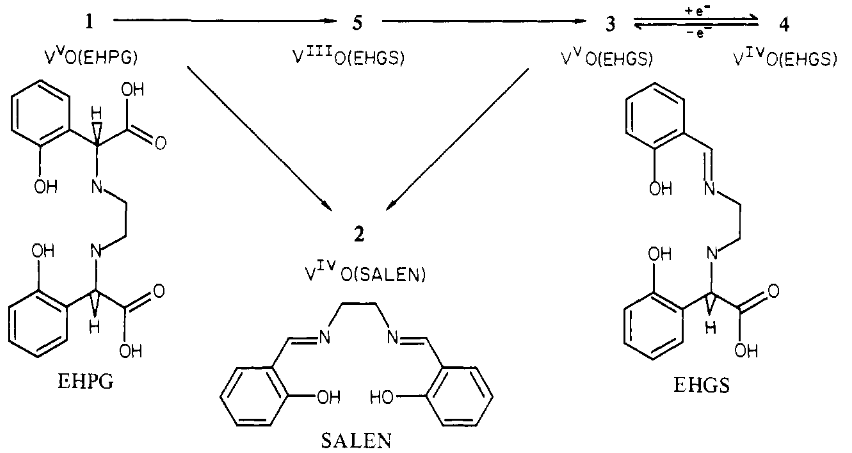
Scheme I



(EHPG), a neutral species in which we believe a VO^{3+} moiety is bound to the potentially hexadentate EHPG through the two ethylenediamine nitrogens, two phenolates, and a carboxylate group. The remaining carboxylate group is protonated and uncoordinated.[5] This complex is intensely blue colored (λ_{max} 590 nm, (ϵ 2800 L mol^{-1} cm^{-1})) due to a phenolate-to-metal charge-transfer transition.

In air the solid is stable indefinitely, but solutions were found to decompose more or less rapidly depending upon solvent. Allowing a solution of **1** to stand in warm acetone for several days yields large green crystals of the decomposition product. These crystals have been identified by X-ray crystallography[6] to be the previously reported vanadyl(SALEN), **2**. This remarkable transformation of the EHPG complex to the SALEN complex requires the loss of two CO_2 molecules, three protons, and three electrons per EHPG ligand with the concomitant oxidation of the two amino nitrogens to imino nitrogens. Although there are a number of reported metal-assisted ligand oxidation reactions which convert coordinated amines to imines,[7-9] most notably involving Fe^{3+} or Ru^{2+}, to our knowledge this is the first example of this type reaction involving an oxidative decarboxylation and the first with V^{5+}. The reaction can be conveniently followed by optical spectroscopy upon heating **1** to 50 °C in DMF. The reaction occurs rapidly in this solvent and proceeds cleanly. The same reaction occurs only slowly in alcoholic solvents; however, the formation of a new dark blue species, **3**, is observed by thin-layer chromatography. Isolation of **3** and its characterization demonstrate it to be the monodecarboxylated, monoimine, monooxovanadium(V) product *N,N'*-ethylene((*o*-hydroxyphenyl)glycine) salicylidenimine (EHGS).[10] Thus the expected intermediate in the transformation of **1** to **2** can be isolated in hydroxylic solvents. Electrochemistry of **3** shows a single chemically reversible one-electron reduction to the vanadyl complex. This is confirmed by exhaustive electrolysis of **3** in methanol which consumes 1.0 electron/mol and produces the orange vanadyl(EHGS), **4**, with a typical eight-line EPR spectrum. This vanadium(IV) complex, **4**, can also be prepared by reaction of EHPG with vanadium(V) in aqueous solution. Oxidation of **4** yields a dark blue material identical with **3**. Thus **3** and **4** represent two ends of a reversible redox couple.

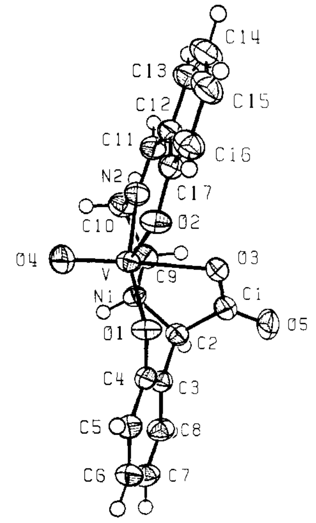


Figure 1. View of the structure of **4** indicating the atom numbering scheme. Non-hydrogen atoms are drawn as ellipsoids of 30% probability; hydrogen atoms are shown ass spheres of radius 0.1 Å. Selected bond lengths: V–O(1) = 1.949 (1) Å, V–O(2) = 1.943 (1) Å, V–O(3) = 2.285 Å, V–O(4) = 1.606 (1) Å, V–N(1) = 2.126 (2) = 2.055 (2) Å.

The orange complex, **4**, can be isolated in crystalline form from MeOH and has been characterized by the appropriate techniques. Crystals of the sodium salt of **4** suitable for X-ray diffraction were grown by slow evaporation from MeOH, and features of this structure are summarized in Figure 1.[11,12]

In light of the completely reversible electrochemistry of **4** to **3** no gross structural changes are to be expected and the structure of **3** can safely be assigned as simply the vanadium(V) analogue of **4**. Thus both **1** and **3** are well-characterized chelate complexes of the VO^{3+} moiety, which to our knowledge are unknown or quite rare.[13]

That **3** is an intermediate in the conversion of **1** to **2** is further supported by its extremely rapid breakdown into **2** in DMF even at room temperatures (<1 min, 50 °C). Thus no buildup of **3** would be expected in the conversion of **1** to **2** under these conditions since **3** decomposes as quickly as it forms.

While the mechanism of this reaction has not been elucidated, certain features are clear. No production of **2** from either **1** or **3** is observed in the absence of oxygen. When **1** is heated in DMF

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[5] The presence of an uncoordinated protonated carboxylate group is indicated by a broad NMR peak integrating to one proton at 13.6 ppm and a characteristic infrared band at 1704 cm^{-1}.

[6] While this work was in progress a report of the crystal structure of **2** appeared in Pasquali, M; Marchetti, F.; Floriani, C.; Cesari, M. *Inorg. Chem.* **1980**, *19*, 1198. Our results are in agreement with this published work.

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[10] This species is best prepared by oxidation of **4** by a variety of mild oxidants. The NMR spectrum reveals the characteristic imine C–H resonance at 8.9 ppm integrating to a single proton.

[11] The stoichiometry of these crystals is $NaV(C_{17}H_{15}N_2O_5)\cdot CH_3OH\cdot 1.5H_2O$. Anal. Calcd: C, 46.9; N, 6.1; H, 4.8. Found: C, 46.8; N, 6.6; H, 5.0.

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in the absence of oxygen a pale yellow species, **5**, is formed. If air is allowed into a hot solution of this complex, **2** is rapidly generated. If, however, the solution is cooled and O_2 admitted, the major product is **3** as indicated by a return of a deep blue coloration. These observations suggest that upon heating **1** in DMF in the absence of O_2 the ligand is oxidatively decarboxylated and the V(V) reduced to V(III).[14] The V^{III} (EHGS) complex thus formed can then be oxidized by molecular oxygen to **3**. These transformations are outlined in Scheme I. The proof of such speculation awaits further characterization of **5** and the completion of our kinetic studies with these complexes.

Acknowledgment. This research is supported in part by a grant from the Research Corp. We thank Prof. K. N. Raymond and Dr. P. E. Riley for permission to use the structure of **4** prior to publication.

Registry No. 1, 89890-27-7; **2**, 36913-44-7; **3**, 89890-28-8; $Na4 \cdot CH_3OH \cdot 1.5H_2O$, 89890-30-2; **5**, 89890-31-3; EHPG, 1170-02-1; EHGS, 89890-32-4.

Supplementary Material Available: Table of atomic positional parameters with estimated standard deviations (1 page). Ordering information is given on any current masthead page.

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[14] Physical evidence for the vanadium(III) formulation of **5** comes from Evans solution magnetic moments and the similarity in chemistry of **5** with synthesized V^{III}(EHPG) complexes.

Ab Initio Calculation of the Transition State for the Cope Rearrangement

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The mechanism of the Cope rearrangement has been the subject of numerous experimental studies.[2] In addition to a concerted pericyclic process, two distinct, nonconcerted pathways are possible a priori. One involves σ-bond cleavage to afford two allyl radicals; the other involves σ-bond formation to give cyclohexane-1,4-diyl.

σ-Bond cleavage is ruled out by labeling studies[3] and by the fact that the activation energy of 56 kcal/mol for dissociation of 1,5-hexadiene to two allyl radicals[4] is substantially higher than that of 34 kcal/mol for its Cope rearrangement.[5] Formation of cyclohexane-1,4-diyl as an intermediate has received much more serious consideration.[2] Although revised estimates of the heat of formation of this diradical now place it about 7 kcal/mol above the transition state for the Cope rearrangement,[6] MINDO calculations have found that cyclohexane-1,4-diyl is a metastable intermediate on the potential surface for this reaction.[7] Dewar has used these MINDO results to support his general contention that multibond reactions cannot normally be synchronous.[8]

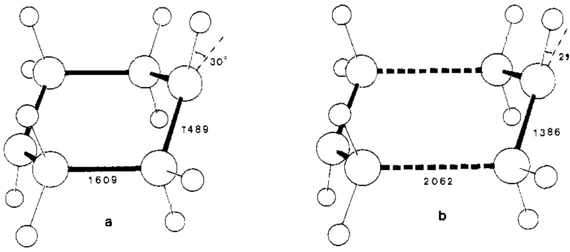

Figure 1. Optimized C_{2h} geometry found using the 3-21G basis set and (a) the TCSCF wave function and (b) the MCSCF wave function, described in the text.

In this communication we report the findings of our ab initio studies of the Cope rearrangement. In contrast to the MINDO results, we find that the lowest energy chair (C_{2h} symmetry) species is the transition state for a concerted pericyclic process. However, this ab initio result is obtained only when a flexible basis set is used and when electron correlation is properly treated.

Calculations were carried out using both STO-3G[9] and 3-21G[10] basis sets. A two-configuration (TC) SCF wave function appropriate for cyclohexane-1,4-diyl was employed, as well as a multiconfiguration (MC) SCF wave function. The latter involved all 52 ^1A_g spin adapted configurations that are possible when the three orbitals occupied by the six "active" electrons are correlated with three virtual orbitals. For the TCSCF wave functions geometries were optimized with the aid of analytically evaluated gradients, using a program written by Kato and Morokuma.[11] For the MCSCF calculations with the STO-3G basis set, GAMESS[12] was employed.

Unfortunately, MCSCF calculations with the 3-21G basis required more computer memory than was available at either IMS or at the University of Washington. Consequently, with this basis set six-electron, six-orbital MCSCF calculations were simulated by using ALIS[13] to find the optimal orbitals for an MCSCF wave function consisting of the 12 most important configurations. These optimized orbitals were then used to perform a full six-electron, six-orbital CI. A test of this procedure was provided by the calculation of the energy of two allyl radicals at a large internuclear separation (14 Å). The energy of −231.6788 hartrees that was computed was only 0.0016 hartrees above twice the three-electron, three-orbital π MCSCF energy for allyl.

With the STO-3G basis set both the TCSCF and MCSCF calculations found cyclohexane-1,4-diyl to be the lowest energy structure of C_{2h} symmetry. The optimized structures with this basis set resembled closely the optimal C_{2h} structure that was found using the 3-21G basis set and a TCSCF wave function. The diradical nature of the latter structure was indicated not only by the bond lengths, shown in Figure 1a, but also by the large size (0.52) of the second coefficient in the wave function. Evaluation of the Hessian matrix showed that the structure was a minimum on the TCSCF potential surface. The energy of −231.6597 hartrees for the diradical was computed to be 6.4 kcal/mol below that of the transition state that was found to connect it with 1,5-hexadiene.

That these predictions of a diradical intermediate in the Cope rearrangement were spurious was suggested by comparison of the MCSCF energy of the structure shown in Figure 1a with that of a TCSCF optimized structure in which the two equivalent bond lengths, *r*, in the six-membered ring were each constrained to be

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