

utilizing  $^{18}\text{O}$  does give considerable insight into this question, and preliminary results are reported here.

It is known<sup>8</sup> that acidification of solutions of  $\text{Na}_3\text{VO}_4$  (pH 3–6) rapidly and nearly quantitatively gives solutions having the same visible spectral properties as those obtained by dissolving solid  $(\text{NH}_4)_6\text{V}_{10}\text{O}_{28}\cdot 6\text{H}_2\text{O}$  or  $\text{Cs}_6\text{V}_{10}\text{O}_{28}$ . The crystal structure of two closely related compounds  $\text{K}_2\text{Zn}_2\text{V}_{10}\text{O}_{28}\cdot 16\text{H}_2\text{O}$  and  $\text{Ca}_3\text{V}_{10}\text{O}_{28}\cdot 17\text{H}_2\text{O}$ <sup>4,5</sup> shows the solids contain the anion  $\text{V}_{10}\text{O}_{28}^{6-}$ . In basic media (pH 8–10) decomposition of this ion to less polymerized ions, *i.e.*,  $(\text{VO}_3^-)_n$  and  $\text{HVO}_4^{2-}$ , is quite slow ( $k = 5 \times 10^{-5} \text{ sec}^{-1}$ , 25°).<sup>9</sup>  $(\text{NH}_4)_6\text{V}_{10}\text{O}_{28}\cdot 6\text{H}_2\text{O}$  dissolves readily in water and anhydrous  $\text{Cs}_6\text{V}_{10}\text{O}_{28}$  is nearly quantitatively precipitated with excess  $\text{CsCl}$ . Traces of absorbed water are readily removed at 100° under  $10^{-4}$  Torr. Thus this system is amenable to precise  $^{18}\text{O}$  exchange studies.

Our experiments consisted of dissolving  $(\text{NH}_4)_6\text{V}_{10}\text{O}_{28}\cdot 6\text{H}_2\text{O}$  in  $^{18}\text{O}$  enriched water at the desired temperature and adding solid  $\text{CsCl}$  to aliquots at selected time intervals. The  $\text{Cs}_6\text{V}_{10}\text{O}_{28}$  was collected, dried, and the oxygen in it converted to  $\text{CO}_2$  by reaction with  $\text{Hg}(\text{CN})_2$  in a sealed tube.<sup>10</sup> The isotopic composition of the  $\text{CO}_2$  was determined by mass spectrometry (Nuclide RMS-6).

Preliminary experiments showed that at short contact times ( $\sim 2$  min) the oxygen isotopic composition of  $\text{Cs}_6\text{V}_{10}\text{O}_{28}$  was exactly ( $\pm 1\%$ ) that of the  $(\text{NH}_4)_6\text{V}_{10}\text{O}_{28}\cdot 6\text{H}_2\text{O}$  and not that of the enriched solvent. Thus the oxygens are slow to exchange and the procedure does not induce exchange. Two complete kinetic runs have been carried out at this time. Under nearly identical experimental conditions they gave nearly identical ( $\pm 1\%$ ) results. A calcomp graph of  $\ln(1 - F)$  vs. time for the second run is given in Figure 1, the line being the least-squares fit to the data. Less than 1% zero exchange was observed. The last entry (other than the  $\infty$  value) corresponded to 25.4 oxygens exchanged (assuming 28 total). Since the reaction was not followed to completion, a possibility exists that 2 of the 28 oxygens are slow to exchange. Using a calculated  $\infty$  value based on 26 oxygens exchanging gave a highly upward curved graph proving this postulate incorrect. The linearity of the graphed data strongly suggests that by whatever mechanism exchange occurs, all oxygens exchange equivalently. This is surprising since there are several types of oxygen in the ion differing widely in their availability to solvent interaction. Eight are singly vanadium bound, 14 doubly, 4 triply, and 2 have six vanadium nearest neighbors and appear to be completely shielded from association with the solvent.

During the study no spectral change was observed (qualitatively) but the pH changed from 7.2 to 6.7.  $R_N((\text{NH}_4)_6\text{V}_{10}\text{O}_{28}\cdot 6\text{H}_2\text{O}) = 3.927 \times 10^{-3}$ ,  $R_N$  (enriched  $\text{H}_2\text{O}) = 14.87 \times 10^{-3}$ ,  $R_{N\infty} = 9.38 \times 10^{-3}$ ,  $R_{N\infty}$  calcd =  $9.35 \times 10^{-3}$ .<sup>11</sup> The  $[\text{V}_{10}\text{O}_{28}^{6-}] = 0.044 \text{ M}$  and the reaction was shielded from atmospheric  $\text{CO}_2$  and light. The observed exchange rate constant  $k_{\text{obsd}}$  was  $1.32 \pm 0.01 \times 10^{-5} \text{ sec}^{-1}$ <sup>11</sup> at 25°. For comparison the first-order rate constant of dissociation of  $\text{V}_{10}\text{O}_{28}^{6-}$  in buffered (pH 8–10) solutions by Goddard and Gonas<sup>9</sup> was  $4.9\text{--}5.4 \times 10^{-5} \text{ sec}^{-1}$  at 25° with  $\text{NH}_4^+ + \text{NH}_3$  buffer and  $\mu = 2.5(\text{LiCl})$ .

If one accepts the likely postulate that  $\text{V}_{10}\text{O}_{28}^{6-}$  is present in both solid salts,  $(\text{NH}_4)_6\text{V}_{10}\text{O}_{28}\cdot 6\text{H}_2\text{O}$  and  $\text{Cs}_6\text{V}_{10}\text{O}_{28}$ , as strongly suggested by X-ray powder studies, then the lack of zero time exchange proves that *this ion exists essentially unchanged in water solution*. Solvation and protonation probably occur but they must not cause expansion or contraction of the first coordination sphere of any vanadium ion. The equivalence of all oxygens in their isotopic exchange rate over a longer time period strongly

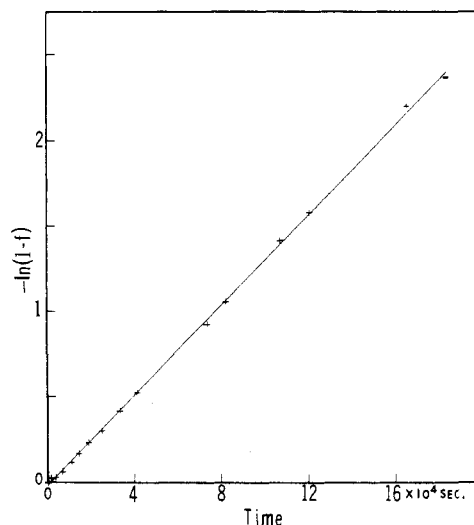
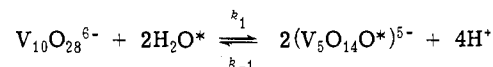


Figure 1.  $^{18}\text{O}$  exchange between  $\text{V}_{10}\text{O}_{28}^{6-}$  and  $\text{H}_2\text{O}$ , 25°.

suggests reversible dissociation to  $(\text{VO}_m^{n-})_p$  units prior to or at the same moment as exchange occurs. When pictured as a symmetrical dissociation the equation is



The degrees of aggregation in the dissociating units and the values of  $K_{\text{diss}}$  are unknown. Finally this rate constant for exchange is of the same order of magnitude as the rate constant of irreversible dissociation at high pH's ( $1.3$  compared to  $5.2) \times 10^{-5} \text{ sec}^{-1}$  under otherwise mildly differing solution conditions. These may or may not be identical, but again suggest that reversible dissociation is the primary pathway for exchange. Because of the potential significance of this comparison, new studies of both rates are being made together with the pH and concentration dependencies and are expected to give a more detailed mechanistic picture of the kinetic behavior of  $\text{V}_{10}\text{O}_{28}^{6-}$  in aqueous media.

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#### Designed Synthesis of the $\text{CrMoCl}_9^{3-}$ Anion

Sir:

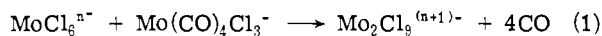
Oxidative displacement of CO from  $\text{Mo}(\text{CO})_4\text{Cl}_3^-$  by  $\text{MoCl}_6^{n-}$  ( $n = 1$  or 2) in  $\text{CH}_2\text{Cl}_2$  has been shown recent-

**Table I.** A Comparison of the Spectra of the  $[(n-C_4H_9)_4N]_3CrMoCl_9$  with Those of an Equimolar Mixture of  $[(n-C_4H_9)_4N]_3Cr_2Cl_9$  and  $[(n-C_4H_9)_4N]_3Mo_2Cl_9$

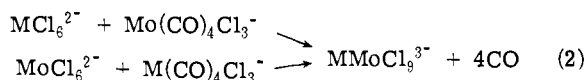
Anion	$10^{-3}\nu, ^a \text{ cm}^{-1}$	$\nu_{M-Cl}, ^{b,c} \text{ cm}^{-1}$
$CrMoCl_9^{3-}$	22.9 (425), 18.6 (260, sh), 18.0 (270), 14.6 (40, sh), 12.5 (41), 9.80 (14), 9.17 (17)	340 (s), 310 (s), 268 (m)
$Cr_2Cl_9^{3-} + Mo_2Cl_9^{3-}$	23.3 (260), 18.8 (390), 17.8 (166), 12.7 (76)	350 (s), 323 (vs), 300 (s), 274 (m)

<sup>a</sup> The electronic spectra were obtained from  $CH_2Cl_2$  solutions. The molar extinction coefficients which are listed for the equimolar mixture are not the true values for each individual anion but are effective values calculated from the total concentration of dinuclear anions. The first and second bands are due to  $Mo_2Cl_9^{3-}$  while the third is due to  $Cr_2Cl_9^{3-}$ . The band at  $12,700 \text{ cm}^{-1}$  is a composite of bands arising from both  $Cr_2Cl_9^{3-}$  and  $Mo_2Cl_9^{3-}$ . <sup>b</sup> The infrared spectra were obtained from Nujol mulls. <sup>c</sup> In the case of the mixture, cocrystallized, equimolar quantities of the dinuclear anions were used.

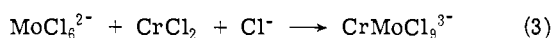
ly<sup>1,2</sup> to lead directly to high yields of  $Mo_2Cl_9^{(n+1)-}$  according to eq 1. It would seem that reactions such as this could



be used to design successful synthesis for confacial, bioctahedral anions containing a single molybdenum atom and another different metal atom (M),  $MMoCl_9^{3-}$ , providing the starting reagents are available. Two possible reactions, which should lead to the same products, are given in eq 2.



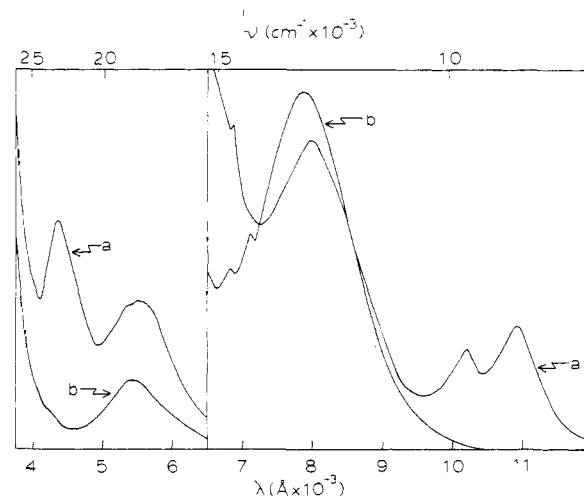
We have chosen to synthesize  $CrMoCl_9^{3-}$  for a variety of reasons but these reactions cannot be used since neither  $CrCl_6^{2-}$  nor  $Cr(CO)_4Cl_3^-$  exist. However, since  $[CrCl_2 + Cl^-]$  is at least formally similar to  $Cr(CO)_4Cl_3^-$ , we examined the reaction shown in eq 3. The principal purpose of



this publication is to demonstrate that this simple reaction yields the desired product whose spectroscopic properties differ vastly from an equimolar mixture of  $Cr_2Cl_9^{3-}$  and  $Mo_2Cl_9^{3-}$ .

The reaction was conducted at the millimolar level in  $CH_2Cl_2$  using procedures which were previously described.<sup>3</sup> The addition of solid  $CrCl_2$  caused the yellow solution of  $[(n-C_4H_9)_4N]_2MoCl_6$  and  $[(n-C_4H_9)_4N]Cl$  to turn deep red-brown. The mixture was stirred continuously for 15 hr although the complete disappearance of  $CrCl_2$  occurred after about 40 min. The slow distillation of ether into the solution caused the crystallization of the red-brown product, which was then recrystallized from another  $CH_2Cl_2$  solution by the same procedure (ca. 70% yield). Analyses established that the empirical composition of the product was indeed  $[(n-C_4H_9)_4N]_3CrMoCl_9$  with 3.04 reducing equivalents per mole.

Although the product clearly has the correct stoichiometry, two possible compositions for this product exist: (a) equimolar mixtures of  $Cr_2Cl_9^{3-}$  and  $Mo_2Cl_9^{3-}$  or (b)  $(1-x)CrMoCl_9^{3-} + (x/2)Cr_2Cl_9^{3-} + (x/2)Mo_2Cl_9^{3-}$ . We compare in Table I the spectroscopic properties of the product to an equimolar mixture of  $[(n-C_4H_9)_4N]_3Cr_2Cl_9$  and  $[(n-C_4H_9)_4N]_3Mo_2Cl_9$  under identical conditions. Conditions were chosen for the electronic spectra such that the mole fractions of Cr or Mo in the solution of the product were identical with those in the solution of the equimolar



**Figure 1.** A comparison of the electronic spectrum of  $[(n-C_4H_9)_4N]_3CrMoCl_9$  (a) obtained in  $CH_2Cl_2$  with that of the product which results from the oxidation by dry air (b). The results at the left were obtained with a concentration of  $1.48 \times 10^{-3} M$  while those on the right were obtained at  $2.00 \times 10^{-2} M$ .

mixture. The molar extinction coefficients for the latter are only apparent values since they were calculated from the total concentration of dinuclear anions. The differences in these spectra, particularly between 9000 and 10,000  $\text{cm}^{-1}$  are readily apparent. Similarly, the infrared spectrum of the product is compared in Table I to that of a cocrystallized equimolar mixture  $[(n-C_4H_9)_4N]_3Cr_2Cl_9$  and  $[(n-C_4H_9)_4N]_3Mo_2Cl_9$ . Again, large differences can be seen. All of these differences rule out composition a.

Since we observed that  $CH_2Cl_2$  solutions of the product are particularly sensitive to oxidation by dry air, we compared the reactivity of the product toward dry air with that of an equimolar mixture of  $Cr_2Cl_9^{3-}$  and  $Mo_2Cl_9^{3-}$ . Surprisingly, the spectrum of the equimolar mixture remained virtually unchanged after a 24-hr exposure, but the red-brown solutions of the product quickly became violet after only a brief exposure to dry air. As shown in Figure 1, the entire band system between 9000 and 10,000  $\text{cm}^{-1}$  disappears as does the band at 22,900  $\text{cm}^{-1}$ . A small band at 23,300  $\text{cm}^{-1}$ , the exact frequency of a band in the spectrum of  $Mo_2Cl_9^{3-}$ , can then be seen. Other bands in the spectrum, which are readily assigned as chiefly due to a  $Cr^{11}Cl_6$  chromophore, would mask the remaining bands of  $Mo_2Cl_9^{3-}$  if that anion is indeed present. Using the known extinction coefficient for the 23,300- $\text{cm}^{-1}$  band in  $Mo_2Cl_9^{3-}$ , we estimate that  $(1-x)$  in composition b is  $\geq 0.96$ . It is apparent that the product is formed with a high degree of stereospecificity.

The comparison of the electronic spectrum of  $CrMoCl_9^{3-}$  with that of an equimolar mixture of  $Cr_2Cl_9^{3-}$  and  $Mo_2Cl_9^{3-}$  makes it clear that many bands in the latter are retained in the former. Furthermore, the band system between 9000 and 10,000  $\text{cm}^{-1}$  in the spectrum of  $CrMoCl_9^{3-}$ , although not present in the spectrum of the equimolar mixture, compares favorably to a spin-forbidden band at 9650  $\text{cm}^{-1}$  in the spectrum of  $MoCl_6^{3-}$ .<sup>4</sup> We have previously established<sup>2,5</sup> that the ligand-field spectra of  $MCl_6^{3-}$  ( $M = Ti, V, Cr, \text{ and } Mo$ ) bear a close resemblance to the spectra of the corresponding  $M_2Cl_9^{3-}$  anions for all transitions involving no change in spin multiplicity. This evidence provides a good deal of proof that at least these  $M^{11}Cl_6$  chromophores provide a characteristic spectrum which, to a good approximation, is independent of the remainder of the environment. The close similarity in the positions of the principal bands in the spectrum of  $CrMoCl_9^{3-}$

with those in the spectrum of the equimolar mixture (see footnote a to Table I for assignments) then points clearly to the contributions from  $\text{Cr}^{III}\text{Cl}_6$  and  $\text{Mo}^{III}\text{Cl}_6$  chromophores in the spectrum of  $\text{CrMoCl}_9^{3-}$ . This information makes it equally clear that reaction 3 involves electron transfer. Furthermore, the electronic spectrum of  $\text{CrMoCl}_9^{3-}$  is in full accord with a confacial, biocuboidal structure since this structure is the only one which will simultaneously accommodate both  $\text{Cr}^{III}\text{Cl}_6$  and  $\text{Mo}^{III}\text{Cl}_6$  chromophores. Finally, the magnetic moment per formula unit of  $[(n\text{-C}_4\text{H}_9)_4\text{N}]_3\text{CrMoCl}_9$  is 4.38 BM at 295°K and 3.10 BM at 77°K. These results are in accord with antiferromagnetic coupling between the two  $S = 3/2$  spin systems.

The only other dinuclear or polynuclear species containing both chromium and molybdenum is the Cr(II)-Mo(II)-acetate compound,  $\text{CrMo}(\text{OAc})_4$ , which was recently prepared.<sup>6</sup>

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Contribution No. 2550

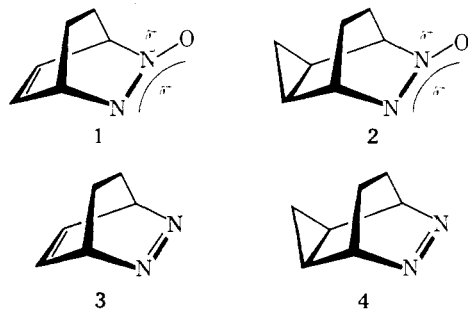
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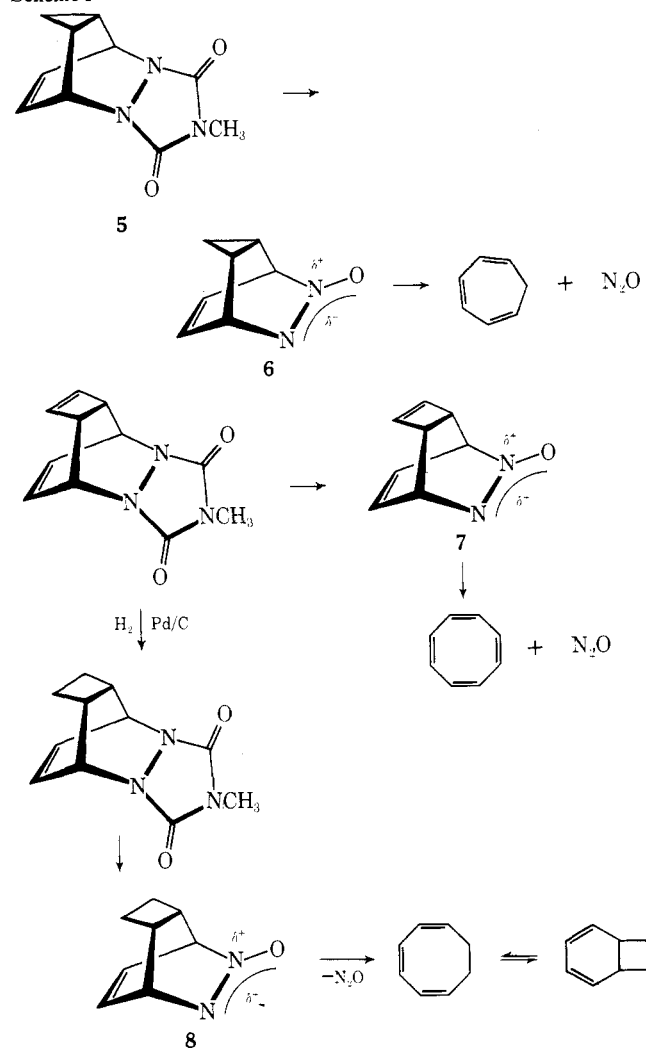
### *cis*-Azoxyalkanes. V. Concerted Retrocycloaddition of $\text{N}_2\text{O}^1$

Sir:

Pericyclic processes characterized by high symmetry proceed in a relatively well-defined manner.<sup>2</sup> Removal of symmetry by the introduction of strong perturbations, however, may possibly affect both the stereochemistry<sup>3</sup> and the energetics<sup>4</sup> of a concerted reaction. Few asymmetric but formally pericyclic transformations have been unambiguously demonstrated to take place without the intervention of intermediates.<sup>5</sup> Consider the retrocycloaddition of heterocycles 1-4. The thermal stability of *N*-oxides 1 and 2 stands in stark contrast to that of the corresponding azo analogs 3 and 4. A lower limit of  $10^6$  has been placed on the relative rate of nitrogen extrusion *vs.* the corresponding loss of nitrous oxide.<sup>6</sup> The azo compounds are believed to eject molecular nitrogen by way of a single concerted step.<sup>7</sup> *A priori*



Scheme I



several pathways exist for the analogous *cis*-azo-*N*-oxide system. We now wish to present evidence that the thermolysis of highly condensed azoxy alkanes is likewise concerted. The analogy between the azo and the azoxy series extends to the participation of cyclopropane and cyclobutane rings in the transition state for fragmentation.

As previous we have taken advantage of the great stability of azo-*N*-oxides to prepare several new systems with hydrocarbon backbones inaccessible in the azo series.<sup>8</sup> Hydrolytic oxidation of cycloadduct 5 with strongly basic hydrogen peroxide<sup>1,6</sup> generates compound 6 (mp 48-50°, 50% yield) in a single step.<sup>9</sup> *N*-Oxides 7 (mp 101-102°, 65%) and 8 (mp 119-120°, 80%) arise similarly as outlined in Scheme I.

Bicycle 6 decomposes quantitatively and exclusively to cycloheptatriene at temperatures slightly above ambient. First-order rates of decomposition were determined by measuring the change in absorption at 275 nm in the temperature range 30-60° ( $k_{\text{CCl}_4} = 1.66 \times 10^{-4} \text{ sec}^{-1}$  (39.4°)). The *N*-oxides 1, 7, and 8 are completely stable at 30° and require temperatures more than 100° higher for conveniently monitored rates of decomposition. In nitrobenzene (131.6°) compounds 7 and 8 deliver cyclooctatetraene and 1,3,5-cyclooctatriene,<sup>10</sup> respectively, in quantitative yield. Azoxy 1 gives rise to both cyclohexadiene and benzene. Control experiments demonstrate the latter to be a secondary product derived from oxidation of the primary diene product.<sup>11</sup> First-order rate constants were determined in nitrobenzene by periodic integration of appropriate disappearing azoxy protons against the methyl protons of anisole