as "stable thiabenzenes," which have been shown not to be authentic thiabenzenes.[2] Indeed, treatment of 10-selenoxanthylium and 9-phenyl-10-selenoxanthylium perchlorates with excess phenyllithium in ether, as described,[5] afforded powdery tan solids **6** and **7**, respectively.[24] Both of these products are evidentially (molecular weights; mass, nmr, and uv spectra) not 10-selenaanthracenes **2** and **3** but are oligmers of undetermined composition. This conclusion is consistent with the observation[5,6] that deprotonation of 9-phenyl-10-*p*-anisylselenoxanthenium perchlorate (**8**) by sodium hydride in tetrahydrofuran is followed by rearrangement to 9-phenyl-9-*p*-anisylselenoxanthene (**9**). Since this reaction must proceed through a 10-selenaanthracene intermediate, **10**, the latter can only have a transient existence,
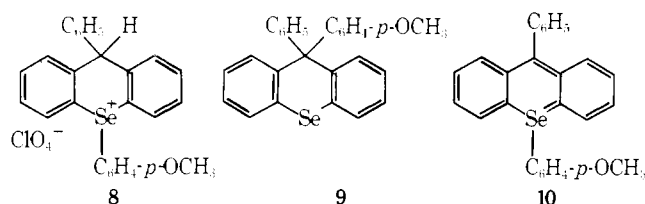
in complete analogy with the corresponding sulfur compounds.[2] Thus, the solid substances isolated[5] from the reaction of phenyllithium with selenoxanthylium salts are assuredly not selenaanthracenes.

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(7) This compound was prepared by a modification of the procedure of Renson and Pirson.[8] α,α'-Diselenodi-*o*-toluic acid[9] was converted to 4-acetoxy-2-seleno-3-chromene, and the product was simultaneously hydrolyzed and reduced to 2-selenochroman-4-ol with sodium borohydride in aqueous ethanolic sodium hydroxide (83%). The alcohol was then converted to 2-selenanaphthalenium perchlorate by the reported procedure.[8]
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(11) This procedure was the same as that used for the preparation of unstable thiabenzenes.[3]
(12) ¹H nmr (toluene-d_8–1,2-dimethoxyethane 0.40 ml/30 μl) δ^{TMS} 1.20 (s, 3 H, ⁷⁷Se side bands at ±6 Hz), 4.89 (d, 1 H, $^3J_{HH}$ = 8 Hz), 6.50–7.25 (m, 6.1 H). Embedded in the multiplet is a signal at δ 6.73 (d, $^3J_{HH}$ = 8 Hz).
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(17) See also A. G. Hortmann and R. L. Harris, *J. Amer. Chem. Soc.*, **92**, 1803 (1970).
(18) Deuterium exchange has been reported in the generation of thiabenzenes by deprotonation in DMSO-d_6.[17]
(19) Mass spectrum (70 eV, material generated *in situ* by heating **4** pulverized with sodium hydroxide on the sample probe at 80°) *m/e* (rel abun-

dance, %) 376 (18), 374 (9), 363 (11), 362 (43), 361 (28), 360 (23), 359 (21), 358 (13), 341 (10), 296 (11), 295 (48), 294 (10), 282 (26), 281 (100), 275 (12), 274 (15), 261 (23), 255 (10), 195 (13), 193 (13), 121 (23), 115 (26) (peaks reported ≥10% relative abundance). Exact mass: calcd, 375.9789; found, 375.980 ± 0.004. A similar spectrum was obtained from material from an nmr sample of **1**.
(20) 1-Pentafluorophenyl-2-seleno-3-chromene was isolated (ca. 30%) from the decomposition mixture by chromatography on florisil with hexane eluent.
(21) The procedure was the same as the one used to monitor the thermal decomposition of thiabenzenes by their visible spectrum.[3]
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(24) For **6**: mp 135–155°. *Anal.* Calcd for C₁₉H₁₄Se: C, 71.03; H, 4.39. Found: C, 67.88; H, 4.43. Molecular weight: calcd, 321; found, 973 (osmometry in benzene). The ¹H nmr spectrum of this material featured a broad envelope absorption centered at δ^{TMS}(CDCl₃) 7.2 ($W_{1/2}$ = 0.5 ppm) and additional minor signals at 5.28 and 1.5–0.5 (aliphatic region). The uv spectrum (ethanol) of this material showed a broad absorption, tailing into the visible (220–450 nm) with shoulders (λ_{max} (log ε)) at 275 (3.83) and 255 (3.94) nm. The reported maximum[5] at 211 nm is due to uv cutoff of the solvent. The mass spectrum (70 eV) of this material showed peaks at *m/e* (rel abundance, %) 338 (10), 336 (6), 324 (5), 323 (8), 322 (26), 321 (15), 320 (15), 319 (13), 318 (8), 317 (5), 261 (22), 246 (85), 244 (46), 242 (20), 165 (52), 164 (69), 154 (100), 153 (26), 152 (40), 149 (29), 94 (25), 77 (28), 76 (23), 71 (74), 70 (33), 69 (21), in addition to minor peaks from *m/e* 400–700. Only peaks with a relative abundance greater than 20% are reported below *m/e* 300. For **7**, two fractions, **7a** and **7b**, were obtained by repeated work-up of the crude reaction mixture. **7a** (less soluble fraction) mp 140–160°. *Anal.* Calcd for C₂₅H₁₈Se: C, 75.56; H, 4.57. Found: C, 74.83; H, 4.98. Molecular weight: calcd, 397; found, 986 (osmometry in benzene). The ¹H nmr spectrum of this material featured a broad absorption envelope centered at δ^{TMS}(CDCl₃) 7.2 ($W_{1/2}$ = 0.5 ppm) and additional minor absorptions in the aliphatic region (1.5–0.5). The uv spectrum (ethanol) of this material showed a broad absorption, tailing into the visible (220–550 nm) with shoulders (λ_{max} (log ε)) at 280 (4.23) and 260 (4.31) nm. The reported maximum[5] at 211 nm is due to uv cutoff of the solvent. The mass spectrum (70 eV) of this material showed peaks at *m/e* (rel abundance, %) 476 (1), 475 (2), 474 (5), 473 (2), 472 (3), 471 (2), 470 (2), 455 (2), 409 (2), 400 (6), 399 (15), 398 (31), 397 (47), 396 (18), 395 (33), 394 (15), 393 (13), 392 (2), 391 (2), 323 (38), 322 (55), 321 (100), 320 (36), 319 (99), 318 (41), 317 (46), 245 (63), 243 (31), 241 (38), 240 (20), 239 (57), 165 (28), in addition to minor peaks beyond *m/e* 500. Only peaks with a relative abundance greater than 20% are reported below *m/e* 390. **7b** (more soluble fraction) mp 95–120°. *Anal.* Calcd for C₂₅H₁₈Se: C, 75.56; H, 4.57. Found, C, 75.25; H, 4.99. Molecular weight Calcd, 397; Found, 737 (osmometry in benzene). The ¹H nmr spectrum (CDCl₃) and uv spectrum (ethanol) were closely similar to those of **7a**. The mass spectrum (70 eV) showed peaks at *m/e* (rel abundance, %) 476 (1), 475 (1), 474 (3), 473 (1), 472 (2), 471 (1), 455 (2), 453 (1), 401 (2), 400 (8), 399 (17), 398 (40), 397 (49), 396 (23), 395 (33), 394 (16), 393 (12), 392 (2), 391 (2), 323 (35), 322 (46), 321 (100), 320 (28), 319 (99), 318 (37), 317 (43), 245 (27), 241 (26), 239 (42), in addition to minor peaks beyond *m/e* 500. Only peaks with a relative abundance greater than 20% are reported below *m/e* 390.

Joseph Stackhouse, G. H. Senkler, Jr.
Bruce E. Maryanoff, Kurt Mislow*

Department of Chemistry, Princeton University
Princeton, New Jersey 08540
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¹⁸O Exchange Studies on $V_{10}O_{28}{}^{6-}$ in Aqueous Media

Sir:

Over recent years a continuing interest has been shown in the aqueous polymerization of ions of the type $MO_4{}^{n-}$, including $VO_4{}^{3-}$.[1,2] While the understanding of the vanadium system has improved, little structural information nor modes of reaction are available even in aqueous media. The decavanadate ion $V_{10}O_{28}{}^{6-}$ appears to be a well-defined, easily prepared ion[3] and may be the best starting point for future studies in the vanadium(V) system. Thus it is vital that the aqueous nature of this ion be well understood. While solid structures containing the ion have been reported[4,5] they can only suggest the structure of the ion in solution. Likewise the precise potentiometric and spectral studies[6,7] do not give much information about the exact species present in solution. A kinetic study of oxygen exchange between solutions of $(NH_4)_6V_{10}O_{28}\cdot 6H_2O$ and H_2O

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

It is known[8] that acidification of solutions of Na_3VO_4 (pH 3-6) rapidly and nearly quantitatively gives solutions having the same visible spectral properties as those obtained by dissolving solid $(NH_4)_6V_{10}O_{28} \cdot 6H_2O$ or $Cs_6V_{10}O_{28}$. The crystal structure of two closely related compounds $K_2Zn_2V_{10}O_{28} \cdot 16H_2O$ and $Ca_3V_{10}O_{28} \cdot 17H_2O^{4,5}$ shows the solids contain the anion $V_{10}O_{28}^{6-}$. In basic media (pH 8-10) decomposition of this ion to less polymerized ions, i.e., $(VO_3^-)_n$ and HVO_4^{2-}, is quite slow ($k = 5 \times 10^{-5}$ sec^{-1}, 25°).[9] $(NH_4)_6V_{10}O_{28} \cdot 6H_2O$ dissolves readily in water and anhydrous $Cs_6V_{10}O_{28}$ is nearly quantitatively precipitated with excess CsCl. Traces of absorbed water are readily removed at 100° under 10^{-4} Torr. Thus this system is amenable to precise ^{18}O exchange studies.

Our experiments consisted of dissolving $(NH_4)_6V_{10}O_{28} \cdot 6H_2O$ in ^{18}O enriched water at the desired temperature and adding solid CsCl to aliquots at selected time intervals. The $Cs_6V_{10}O_{28}$ was collected, dried, and the oxygen in it converted to CO_2 by reaction with $Hg(CN)_2$ in a sealed tube.[10] The isotopic composition of the CO_2 was determined by mass spectrometry (Nuclide RMS-6).

Preliminary experiments showed that at short contact times (~ 2 min) the oxygen isotopic composition of $Cs_6V_{10}O_{28}$ was exactly ($\pm 1\%$) that of the $(NH_4)_6V_{10}O_{28} \cdot 6H_2O$ 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 ∞ 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 ∞ 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. $R_N((NH_4)_6V_{10}O_{28} \cdot 6H_2O) = 3.927 \times 10^{-3}$, R_N (enriched H_2O) = 14.87×10^{-3}, $R_N\infty = 9.38 \times 10^{-3}$, $R_N\infty$ calcd = 9.35×10^{-3}.[11] The $[V_{10}O_{28}^{6-}] = 0.044 M$ and the reaction was shielded from atmospheric CO_2 and light. The observed exchange rate constant k_{obsd} was $1.32 \pm 0.01 \times 10^{-5}$ sec^{-1}[11] at 25°. For comparison the first-order rate constant of dissociation of $V_{10}O_{28}^{6-}$ in buffered (pH 8-10) solutions by Goddard and Gonas[9] was $4.9-5.4 \times 10^{-5}$ sec^{-1} at 25° with $NH_4^+ + NH_3$ buffer and $\mu = 2.5$(LiCl).

If one accepts the likely postulate that $V_{10}O_{28}^{6-}$ is present in both solid salts, $(NH_4)_6V_{10}O_{28} \cdot 6H_2O$ and $Cs_6V_{10}O_{28}$, 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
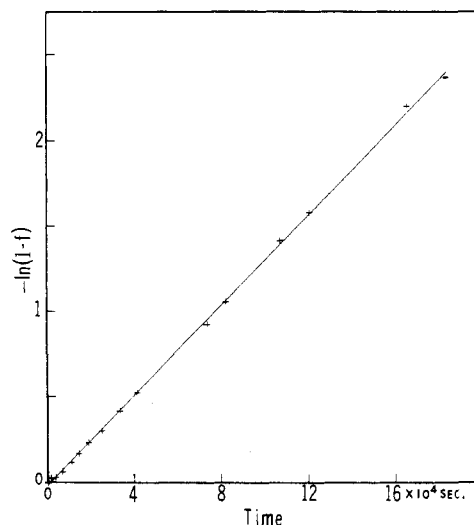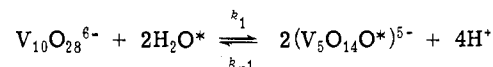

Figure 1. ^{18}O exchange between $V_{10}O_{28}^{6-}$ and H_2O, 25°.

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

$$V_{10}O_{28}^{6-} + 2H_2O^* \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2(V_5O_{14}O^*)^{5-} + 4H^+$$

The degrees of aggregation in the dissociating units and the values of K_{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) $\times 10^{-5}$ 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 $V_{10}O_{28}^{6-}$ in aqueous media.

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R. Kent Murmann

*Department of Chemistry, University of Missouri
Columbia, Missouri 65201*

Designed Synthesis of the $CrMoCl_9^{3-}$ Anion

Sir:

Oxidative displacement of CO from $Mo(CO)_4Cl_3^-$ by $MoCl_6^{n-}$ ($n = 1$ or 2) in CH_2Cl_2 has been shown recent-