

in the stoichiometry upon slow addition of Fe(II), which can be explained by the occurrence of steps 7 and 8 in the absence of iron(II). Such unexpected situations of stoichiometry are not uncommon in peroxydisulfate oxidations. It is found in the oxidation¹⁷ of Ce(III)- and Cu(II)-catalyzed oxidation¹⁸ of hydrazine. The rate laws under the two conditions are shown in eq 9 and 10.

$$d[\text{Fe(III)}]/dt = 2k_1[\text{Fe(III)}][\text{S}_2\text{O}_8^{2-}] \text{ at } [\text{H}^+] < 0.2 \text{ M} \quad (9)$$

$$d[\text{Fe(III)}]/dt = (k_1 + k_2K[\text{H}^+])[\text{Fe(II)}][\text{S}_2\text{O}_8^{2-}] \text{ at } [\text{H}^+] > 0.4 \text{ M} \quad (10)$$

The effect of ionic strength under the two conditions is found to be quantitatively different. At low $[\text{H}^+] = 0.005 \text{ M}$ and 30°C and with an ionic strength less than 0.02 M , a plot of $\log k_{\text{obsd}}$ vs. $I^{1/2}$ yielded a straight line with a slope of -3.83 . This is quite close to the theoretical value,¹⁹ and hence the reaction appears to be ideally suited for the verification of the Bronsted-Bjerrum²⁰ relationship since the concentrations of

the reactions required for conventional study are small and the ionic strength should be kept less than 0.01 M . When the ionic strength was varied in the range $1-2 \text{ M}$ at constant $[\text{H}^+] = 1.0 \text{ M}$, the slope of the relevant line (plot of $\log k$ vs. $I^{1/2}$) decreased to -1.6 . This is another indication of a different path of reaction in high $[\text{H}^+]$ which would probably be between Fe^{2+} and HS_2O_8^- .

The energy of activation has been variously reported^{3,7} by previous workers from 8.1 to $12.1 \text{ kcal mol}^{-1}$ though $[\text{H}^+]$ was low. Turska and Matuszewska-Czerwik^{4a} have reported a value of $4.34 \text{ kcal mol}^{-1}$, but the hydrogen ion concentration and the ionic strengths are not specified. Our values vary from 12.8 to $14.7 \text{ kcal mol}^{-1}$ with the increase of ionic strength. It appears that the energy of activation is slightly dependent on the ionic strength and that ion pairs^{21,22} like KS_2O_8^- and FeClO_4^+ are likely to participate in the redox process. Our results yield a value of $200 \text{ M}^{-1} \text{ s}^{-1}$ at 30°C and zero ionic strength. Other values at the same ionic strength are 187.8 (30°C),³ 135 (30°C),⁷ and 115 (25°C).⁸ One more value^{4a} at unspecified ionic strength and hydrogen ion concentration is $0.013 \text{ M}^{-1} \text{ s}^{-1}$ which is unusual and unexpected even at high ionic strength and $[\text{H}^+]$.

Registry No. Fe^{2+} , 15438-31-0; $\text{S}_2\text{O}_8^{2-}$, 15092-81-6.

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Aquo Chemistry of Monoarene Complexes of Osmium(II) and Ruthenium(II)

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A number of derivatives of $\eta\text{-C}_6\text{H}_6\text{Os}^{\text{II}}$ (BzOs^{II}) were prepared, exploiting the three positions not preempted by the arene ring and emphasizing ligands which are saturated. The species synthesized include $[\text{BzOs}(\text{NH}_3)_3]^{2+}$, $[\text{BzOs}(\text{NH}_3)_2\text{Cl}]^+$, and $[\text{BzOs}(\text{en})\text{Cl}]^+$. It was shown that a $2+$ ion, presumably $[\text{BzOs}(\text{H}_2\text{O})_3]^{2+}$, is produced in an acidic solution of BzOsCl_2 when Cl^- is removed by Ag^+ . The determination of the acidity of the coordinated water for the aquo species is complicated by the condensation of the hydroxo form. However, $[\text{BzOs}(\text{en})\text{H}_2\text{O}]^{2+}$ prepared from $[\text{BzOs}(\text{en})\text{Cl}]^+$ by adding Ag^+ behaves normally, and the value of $\text{p}K_a$ was found to be 6.3 at 20°C ; for $[\text{BzOs}(\text{NH}_3)_2\text{H}_2\text{O}]^{2+}$ it was found to be 6.4 , and for $[\text{BzRu}(\text{en})\text{H}_2\text{O}]^{2+}$ it is 7.9 . The quotient governing association of Cl^- with $[\text{BzOs}(\text{en})\text{H}_2\text{O}]^{2+}$ was measured as 1.1×10^2 . The acidity of the aquo ion and the stability of the chloride complex testify to the electron-withdrawing ability of the arene ring.

The work being reported was undertaken to develop the aquo chemistry of some monoarene complexes of Os(II) and Ru(II). The $\eta\text{-C}_6\text{H}_6\text{-Os(II)}$ and $\eta\text{-C}_6\text{H}_6\text{-Ru(II)}$ bonds both resist hydrolysis, and there is a good prospect then that species such as $[\eta\text{-C}_6\text{H}_6\text{Os}]^{2+}(\text{aq})$ can be characterized. (It is virtually certain for the work to be reported that the species exists as a trihydrate, and it will hereinafter be represented as such). Taking the work in this direction seems worth while, purely for its descriptive content but also because it helps to bridge the gap between organometallic chemistry and so-called classical coordination chemistry.^{1,2} Of special interest to us were observations which bear on the issue of how the arene ring in replacing a number of saturated ligands, three in our cases, influences the reactivity at the remaining sites (substitution reactions) and of the complex as a whole (redox properties). In studying the substitution properties, we are interested in how the affinities of Os(II) for different ligands are affected by the π -arene unit and, as well, how the rates

of substitution are affected. The equilibrium data in particular are useful in assessing the electron-withdrawing capacity of the arene ligands, and the simplest and most direct data of this kind which bear on this issue involve the replacement of H_2O by OH^- , or, in other words, the acidity of the coordinated water molecules.

In contrast to the situation for the monoarene complexes of Ru(II) which have been the subject of numerous recent studies,³⁻¹⁶ including some^{7,9,11,12} involving H_2O as a solvent

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medium, much less has been reported on those of Os(II), and it is for this reason that the latter mainly have been featured in our work. Many more new compounds were prepared than we were able to investigate in depth. Their preparation and such characterization as we have carried out are nevertheless reported because the information may prove useful to others.

In the following, the unit η -C₆H₆ will be denoted by Bz, dimethyl sulfoxide by Me₂SO, isonicotinamide by isn, imidazole by imid, pyridine by py, and trifluoromethanesulfonic acid by HTFMS. Simplest formulas will be used for the dihalides of BzOs^{II} and BzRu^{II}, even though structural evidence for the latter (vide infra) shows that at least in certain preparations it exists as the dimer.

Experimental Section

A. Materials. 1,3-Cyclohexadiene was distilled before use. Reagent grade chemicals were used as supplied, except for isonicotinamide which was recrystallized from water and acetonitrile, the latter dried by distilling from P₂O₅. Deionized water was redistilled from alkaline potassium permanganate solution. SP-Sephadex C25-120 cation-exchange resin (Sigma Chemical Co.) was used for separations. Trifluoromethanesulfonic acid was distilled before use. Sodium trifluoromethanesulfonate was recrystallized twice from water.

B. Preparations. 1. Osmium Compounds. The compounds reported are new except for BzOsCl₂ and BzOsI₂ which are precursors for the other preparations and which were reported earlier.^{17,18} We were unable to obtain useful yields following the procedure described in the literature and obtained better yields with the variation on those procedures which we describe.

BzOsCl₂. Ammonium hexachloroosmate(IV) was prepared from OsO₄ following a published procedure.¹⁹ Two grams of the salt was transformed to the hydrated acid by passing the solution down a cation-exchange column in the protic form (Dowex 4G-50W-X2, 200–400 mesh) and taken to dryness by rotary evaporation. The residue, which is hygroscopic, was dissolved in 90% aqueous ethanol, and 2 mL of 1,3-cyclohexadiene was added. The solution was heated to 60 °C under argon for 2 days with stirring. The solid (yellow) was collected by filtration and dissolved in water, and the cation was purified with the Sephadex resin. The portion which was eluted by 0.1 M HCl was collected, taken to dryness, and recrystallized from water. The yield was 42%. The dibromo and diiodo analogues were prepared by metathesis with the appropriate acids.

[BzOs(NH₃)₃](PF₆)₂. Six drops of concentrated aqueous ammonia were added to a solution of BzOsCl₂ (180 mg) dissolved in 30 mL of 90% aqueous methanol. The solution was stirred overnight under argon, filtered, and taken to dryness. The residue was dissolved in methanol, and saturated aqueous NH₄PF₆ was added to precipitate the compound. The yield was 39%.

[BzOs(NH₃)₂Cl](PF₆)₂. The procedure in its early stages follows that just described except that 200 mg of BzOsCl₂ was used and 2 drops of concentrated aqueous NH₃ was added. After the reaction mixture was kept for 17 h, it was acidified with 2 M HCl and filtered. The filtrate was concentrated by rotary evaporation, and saturated NH₄PF₆(aq) was added, producing a light yellow precipitate. This was redissolved in water and purified by using a Sephadex cation-exchange column, with 0.1 M HCl as eluant. The eluate was taken to dryness and redissolved in water, and the compound was precipitated with saturated aqueous NH₄PF₆.

[BzOs(en)Cl]PF₆ and [BzOs(en)Br]PF₆. Three hundred milligrams of BzOsCl₂ or BzOsBr₂ was dissolved in 30 mL of 90:10 CH₃OH/H₂O under Ar. Ethylenediamine in equivalent amount (0.054 g) was added,

and the mixture was heated at 60 °C for 4.5 h and then stirred at room temperature overnight. It was filtered, and the filtrate was taken to dryness. The residue was redissolved in methanol, and a saturated aqueous solution of NH₄PF₆ was added. The precipitate was collected by filtration, redissolved in water, and purified by using a Sephadex cation-exchange resin with 0.1 M HX as eluant. The eluate was dried by rotary evaporation. The residue was dissolved in 0.1 M HCl (1.5 mL) or 0.1 M HBr, and saturated aqueous NH₄PF₆ was added. The yellow crystals were collected by filtration, washed with water, and then dried in a vacuum desiccator. The yield was 51%.

[BzOs(en)NH₃](PF₆)₂. Seventy-five milligrams of [BzOs(en)Cl](PF₆)₂ was dissolved in 20 mL of methanol under argon. Three drops of concentrated aqueous NH₃ were added, and the solution was stirred at room temperature overnight. It was then concentrated by rotary evaporation, and saturated aqueous NH₄PF₆ was added. The product was purified by a Sephadex cation-exchange resin using 0.20 M HCl. The eluate was dried by rotary evaporation and redissolved in 1 mL of water, and saturated NH₄PF₆ solution was added to precipitate the product. The yield was 17%.

[BzOs(en)isn](PF₆)₂. Seventy-two milligrams of [BzOs(en)Cl](PF₆)₂ was dissolved in 90% aqueous methanol under argon. Isonicotinamide (0.14 mmol) and triethylamine (1 drop of neat liquid) were added to the solution. It was heated at 45 °C overnight and then rotary evaporated to dryness. The residue was dissolved in water and put on a Sephadex cation-exchange column. The complex was eluted with 0.2 M HCl. After rotary evaporation to dryness, the solid was dissolved in a few milliliters of water, and NH₄PF₆ was added. The off-white precipitate was collected by filtration. The yield was ~25%.

[BzOs(en)imid](PF₆)₂ and [BzOs(en)py](PF₆)₂. These compounds were prepared in a manner similar to that of the ammonia analogue. The yield was ~16%.

BzOs(glycinato)Cl. This compound was synthesized by a method similar to that described above but using potassium glycinate as the source of the ligand. The product, precipitated directly, was washed with cold water and vacuum-dried. The yield was ~60%.

BzOs(CH₃CN)Cl₂. Eighty milligrams of BzOsCl₂ was dissolved in 10 mL of acetonitrile with refluxing. The solution was cooled and filtered; the filtrate was rotary concentrated to ca. 1 mL. Ethanol and ether were added, and the orange solid was collected by filtration. The yield was 50%.

[BzOs(CH₃CN)₃](PF₆)₂. Excess silver hexafluorophosphate was added to the acetonitrile solution of BzOsCl₂ and the mixture stirred for 3 h. The precipitate was removed, and the filtrate was concentrated by rotary evaporation. Ether was added, and the solid which formed was recrystallized from acetonitrile/ether. The compound obtained was not pure, but the analyses served to show that more than two (but less than three) molecules of CH₃CN had been incorporated per metal.

BzOs(isn)Cl₂ and BzOs(isn)Br₂. A solution of BzOsCl₂ or BzOsBr₂ in 90% aqueous methanol (70 mg in 20 mL) was stirred overnight under argon with an equivalent amount of isonicotinamide. The precipitate was collected, washed with water, and vacuum-dried. The yield was ~60%.

[BzOs(isn)₂Cl]PF₆ and Bromo Analogue. Excess (about fourfold) isn was added to 25 mL of 90% aqueous methanol containing 60 mg of BzOsX₂. The mixture was stirred under argon overnight and then taken to dryness by rotary evaporation. The solid was redissolved in 2 mL of H₂O, and saturated aqueous NH₄PF₆ was added, producing a yellow precipitate. The yield was ~60%.

[BzOs(imid)₂Cl]PF₆. This compound was prepared by using the method described for the isonicotinamide derivative. The proportions were 70 mg of BzOsCl₂ to 60 mg of ligand in 30 mL of 90% CH₃OH. The final product was recrystallized from CH₃OH. the yield was ~5%.

BzOs(py)Cl₂. A solution of 60 mg of BzOsCl₂ in 20 mL of 90% aqueous methanol was degassed, and 5 drops of pyridine were added. The solution was stirred under argon overnight and taken to dryness, and the residue was extracted with methylene chloride. The product obtained after concentrating the solution by rotary evaporation was yellow. The yield was 40%.

BzOs(py)Br₂. This was synthesized by the same method as the dichloro derivative except that 50 mg of BzOsBr₂ was used. The yield was 41%.

BzOs(CO)Cl₂. Fifty milligrams of BzOsCl₂ was dissolved in 10 mL of 95% aqueous methanol under argon with warming. Carbon

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Table I

complex	% calcd				% found			
	C	H	N	X	C	H	N	X
(η -C ₆ H ₆)OsCl ₂	21.24	1.78		20.90 (Cl)	21.05	1.84		21.14 (Cl)
(η -C ₆ H ₆)Os ₂ Br ₂	16.83	1.41		37.33 (Br)	16.56	1.60		37.14 (Br)
(η -C ₆ H ₆)Os ₂	13.80	1.16		48.61 (I)	14.09	1.51		48.1 (I)
[(η -C ₆ H ₆)Os(NH ₃) ₃](PF ₆) ₂	11.83	2.48	6.90		11.72	2.45	6.89	
[(η -C ₆ H ₆)Os(NH ₃) ₂ Cl](PF ₆)	14.93	2.51	5.80	7.34 (Cl)	14.03	2.53	5.99	6.45 (Cl)
[(η -C ₆ H ₆)Os(en)Cl](PF ₆)	18.88	2.77	5.51	6.97 (Cl)	18.52	2.73	5.57	6.82 (Cl)
[(η -C ₆ H ₆)Os(en)Br](PF ₆)	17.37	2.55	5.06	14.44 (Br)	17.34	2.58	5.32	14.67 (Br)
[(η -C ₆ H ₆)Os(en)(NH ₃)](PF ₆) ₂	15.12	2.70	6.61		14.83	2.67	6.58	
[(η -C ₆ H ₆)Os(en)(isn)](PF ₆) ₂	22.71	2.72	7.57		21.21	2.64	7.82	
[(η -C ₆ H ₆)Os(gly)Cl]	25.43	2.67	3.71	9.38 (Cl)	25.40	2.68	3.75	9.37 (Cl)
[(η -C ₆ H ₆)Os(en)(imid)](PF ₆) ₂	19.25	2.64	8.16		19.79	2.85	8.33	
[(η -C ₆ H ₆)Os(en)(py)](PF ₆) ₂	22.39	2.75	6.02		22.31	2.70	5.98	
[(η -C ₆ H ₆)Os(CH ₃ CN)Cl ₂]	25.27	2.39	3.68	18.65 (Cl)	25.51	2.47	3.98	18.25 (Cl)
[(η -C ₆ H ₆)Os(CH ₃ CN) ₂](PF ₆) ₂	21.15	2.22	6.17		15.97	1.84	5.33	
[(η -C ₆ H ₆)Os(isn)Cl ₂]	31.24	2.62	6.07	15.37 (Cl)	31.43	2.61	6.03	15.15 (Cl)
[(η -C ₆ H ₆)Os(isn)Br ₂]	26.19	2.20	5.09	29.04 (Br)	25.52	2.51	4.81	28.81 (Br)
[(η -C ₆ H ₆)Os(isn) ₂ Cl]PF ₆	31.20	2.62	8.08	5.12 (Cl)	30.45	2.56	7.63	4.75 (Cl)
[(η -C ₆ H ₆)Os(isn) ₂ Br]PF ₆	29.31	2.46	7.60	10.85 (Br)	28.91	2.37	7.37	10.62 (Br)
[(η -C ₆ H ₆)Os(imid) ₂ Cl]PF ₆	24.64	2.41	9.58	6.06 (Cl)	24.23	2.58	9.71	5.80 (Cl)
[(η -C ₆ H ₆)Os(C ₅ H ₅ N)Cl ₂]	31.58	2.65	3.35	16.95 (Cl)	31.31	2.66	3.23	17.28 (Cl)
[(η -C ₆ H ₆)Os(C ₅ H ₅ N)Br ₂]	26.05	2.19	2.76	31.51 (Br)	26.58	2.42	2.75	31.76 (Br)
[(η -C ₆ H ₆)Os(CO)Cl ₂]	22.89	1.65		19.31 (Cl)	22.80	1.71		19.04 (Cl)
[(η -C ₆ H ₆)Os(Me ₂ SO)Cl ₂]	23.03	2.90		16.99 (Cl)	22.74	2.85		16.36 (Cl)

monoxide was bubbled for 5 min at room temperature, after which time orange needles had deposited. The crystals were collected by filtration. The yield was 30%.

BzOs(Me₂SO)Cl₂. Fifty milligrams of BzOsCl₂ was dissolved in 5 mL of Me₂SO under argon and then concentrated by rotary evaporation to ca 1 mL. Ten milliliters of absolute ethanol was added, and then ether was added to precipitate the product. The yield was 50%.

Elemental analysis on the osmium compounds are reported in Table I.

2. Ruthenium Compounds. BzRuCl₂.²⁰ Two procedures were followed, that of Zelonka and Baird¹² (Z-B) and that of Bennett and Smith¹¹ (B-S). The product of the Z-B procedure is red. Anal. Calcd: C, 28.8; H, 2.42; Cl, 28.4. Found: C, 28.8; H, 2.50; Cl 28.2. The product of the B-S procedure is brown. Anal. Found: C, 25.7; H, 2.47; Cl, 30.0. The red product is more readily soluble in water than the brown, and because the elemental analyses were closer to the theoretical values, it was used for the experiments to be reported.

BzRu(isn)Cl₂. A reaction mixture containing 150 mg of BzRuCl₂ and 75 mg of isn in 2–3 mL of water was left for 4 h during which time the red solid became yellow-orange. The solid was dissolved in water and the solution passed through a Sephadex cation-exchange column. The fraction eluted by 0.2 M HCl was collected and evaporated to dryness, and the compound was further purified by recrystallizing it from methanol. Anal. Calcd: C, 38.78; H, 3.23; N, 7.53; Cl, 19.06. Found: C, 38.13; H, 3.43; N, 7.29; Cl 18.61.

[BzRu(en)Cl]PF₆. The cation has previously been reported.⁸ We used a preparative method analogous to that described for the osmium compound except heating was continued for only 2 h. The solid residue, after the product mixture was dried, was dissolved in 0.1 M HCl, and NH₄PF₆ was added as precipitant. The solid was collected, dissolved in water, and purified by using a Sephadex cation-exchange column with 0.1 M HCl as eluant. The eluate was dried by rotary evaporation, the residue was dissolved in 0.1 M HCl, and NH₄PF₆ was added. The crystals were collected and dried. The yield was 60%. Anal. Calcd: C, 22.89; H, 3.36; N, 6.67. Found: C, 22.7; H, 3.31; N, 6.67.

C. Physical Measurements. A Perkin-Elmer 621 spectrophotometer was used for the infrared spectra. Samples were prepared as Nujol mulls or in KBr pellets. Ultraviolet and visible spectra were recorded on a Beckman UV 5270 spectrophotometer. Proton nuclear magnetic resonance spectra were taken by using a Varian T-60 instrument. Conductivity measurements were performed with an Industrial Instrument Model 16B2 conductivity bridge on ~10⁻³M solution at room temperature. Elemental analyses were performed by the Stanford Microanalytical Laboratory. Measurements of pH were made with a Metrohm combination glass electrode on a Metrohm pH meter.

In the kinetic experiments, the reactions were studied under pseudo-first-order conditions with ligand in excess, and the rate

constants k_{obsd} were determined by plotting $\ln(A_{\infty} - A_t)$ vs. time or by the Guggenheim method.

For both synthetic and kinetic studies, care was taken to shield the reaction mixtures from room light.

Results

Conductance. Conductivity measurements were made on a number of the compounds in a variety of solvents. The concentrations were at the 1×10^{-3} M level, and the measurements were completed approximately 1 h after dissolution. The conductances ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) registered are as follows. BzOsCl₂: H₂O, 792; CH₃OH, 108; CH₃NO₂, 5. BzOs-(CH₃CN)Cl₂: CH₃CN, 19. BzOs(py)Cl₂: Me₂SO, 6. BzOs(gly)Cl: CH₃OH, 12; H₂O, 120. BzOs(Me₂SO)Cl₂: Me₂SO, 12. BzOs(isn)Cl₂: CH₃NO₂, 14. BzOs(isn)Br₂: Me₂SO, 8. [BzOs(isn)₂Cl]PF₆: H₂O, 128. Bromo analogue: CH₃OH, 106. [BzOs(imidazole)₂Cl]PF₆: CH₃OH, 114. [BzOs(NH₃)₃](PF₆)₂: H₂O, 270. [BzOs(NH₃)₂Cl]PF₆: CH₃OH, 150. [BzOs(en)Cl]PF₆: H₂O, 128. [BzOs(en)-Br]PF₆: CH₃OH, 121. [BzOs(en)NH₃](PF₆)₂: H₂O, 258. [BzOs(en)(imidazole)](PF₆)₂: CH₃OH, 201. [BzOs(en)-(py)](PF₆)₂: H₂O, 234. [BzOs(en)(isn)](PF₆)₂: CH₃OH, 202.

IR Spectra. The IR spectra were not fully investigated, and the work of this kind which was done focused on particular ligands. All the compounds showed peaks characteristic of coordinated benzene; thus for BzOsBr₂ peaks appear at 1429 and 840 cm⁻¹. For BzOs(CO)Cl₂ there is a strong peak at 2001 cm⁻¹ which has a shoulder at 1960 cm⁻¹. In BzOs-(Me₂SO)Cl₂ there is a band at 1100 cm⁻¹ attributable to the S-O of Me₂SO. The absorptions corresponding to $\nu_{\text{C=N}}$ in nitriles are surprisingly weak; for BzOs(CH₃CN)Cl₂, bands were observed at 2295 and at 2325 cm⁻¹. The second and weaker band may result from changes in pelletizing. In a Nujol mull, a single peak at 2299 cm⁻¹ was observed. A strong broad band for BzOs(Glycine)Cl at 1630 cm⁻¹ can be attributed to C=O.

NMR Measurements. Proton NMR spectra were taken on solutions in the concentration range 0.03–0.1 M, less than 1 h elapsing before the spectra were recorded. No special measures were taken to control sample temperature, so that during the time of measurement the samples were at approximately 35 °C. Shifts are reported relative to Me₄Si as internal standard.

Under these conditions BzOsCl_2 in D_2O shows a single peak at $\delta = 6.50$ which in $\text{Me}_2\text{SO}-d_6$ appears at $\delta = 6.13$. $[\text{BzOs}(\text{NH}_3)_3](\text{PF}_6)_2$ in acetone- d_6 shows peaks at $\delta = 6.17$ and at $\delta \approx 4.6$, the latter being broad and attributable to coordinated NH_3 . For $[\text{BzOs}(\text{en})\text{Cl}]\text{PF}_6$ in $\text{CH}_3\text{CN}-d_3$ bands are registered at δ 5.90, 2.53, and ~ 4 (br). The intensity ratio for the first two is 3:2, and the second, being a multiplet, is ascribable to the CH_2 of en. The broad band presumably arises from N-bound protons. $[\text{BzOs}(\text{imid})_2\text{Cl}]\text{PF}_6$ shows absorption at δ 6.0, 7.08, 7.18, and 7.87. Counting 7.08 and 7.18 together, the intensity ratios are 3:2:1, and we can conclude that the last three are ascribable to imidazole and that it is N bound. For $\text{BzOs}(\text{CH}_3\text{CN})\text{Cl}_2$ in $\text{Me}_2\text{SO}-d_6$ bands are registered at δ 6.17 and 2.07, the intensity ratio being 2:1. The spectrum of $\text{BzOs}(\text{isn})\text{Cl}_2$ has a puzzling feature. Bands at 7.77 and 8.41 are ascribable to carbon bound protons in isn; the unexplained feature is that two bands $\delta = 6.05$ and 6.17 with an intensity ratio of 2:3 are observed in the benzene region of the spectrum.

UV-Visible Spectra. The main features of the UV-vis spectra are summarized in Table II.

Reactions in Solution—General. Apart from changes ascribable to aquation of Cl^- , BzOsCl_2 shielded from light is indefinitely stable in acidic aqueous solution. Unless otherwise noted, loss of coordinated benzene is not a factor in any of the experiments which are described. The species is also quite stable to oxidation. For an aqueous solution of $[\text{BzOs}(\text{en})\text{Cl}]\text{PF}_6$ in 0.1 M HTFMS, no cyclovoltammetric waves are observed between the limits set, -0.7 – $+1.4$ V vs. NHE, by the solvent background. For BzOsCl_2 in H_2O the upper limit is ~ 1.2 V, the wave here being attributable to oxidation of Cl^- . For $[\text{BzOs}(\text{isn})_2\text{Br}]\text{PF}_6$ in CH_3CN , a reduction wave is observed at ~ -0.9 V, but no oxidation below 1.5 V is observed. An aqueous solution of BzOsCl_2 in 0.8 M trifluoromethanesulfonic acid does not consume a detectable quantity of I_2 even after 4 h.

As already implied, the species is photosensitive. After exposure of a solution of BzOsCl_2 in $\text{DCl}/\text{D}_2\text{O}$ to the arc of a medium-pressure Hg lamp for several hours, the NMR signal characteristic of coordinated benzene was lost, and that of the free ligand appeared. The compound appears to be even more light sensitive in acetonitrile.

The benzene in the Os compound is less susceptible to nucleophilic attack than is the case for the ruthenium analogue. In contrast to the reaction of CN^- with the latter compound, which leads to CN^- addition to the ring,¹² with the former a product is formed showing a single proton signal at $\delta = 7.4$. The reaction was done in $\text{Me}_2\text{SO}-d_6$ with a solution of CN^- in D_2O . The reaction proceeds through several stages until finally a simple NMR spectrum characteristic of free C_6H_6 is observed. With CN^- in excess at 0.1 M, this stage is reached after several hours at room temperature.

Equilibria and Rates. In dilute acidic aqueous solution, the species BzOsCl_2 aquates virtually completely. This is shown by the molar conductance registered for an aqueous solution; in fact, the value is so high ($792 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) that we can conclude that acid is also formed in the process. The process is hastened by Ag^+ and $\text{BzOs}^{2+}(\text{aq})$ is readily formed using Ag^+ to remove Cl^- . The cation when thus prepared in acidic solution is eluted slowly from a cation-exchange column (AG-50W-X12) with 2.0 M HClO_4 . On SP-Sephadex C25, it moves with 0.2 M HClO_4 at the same rate as does $\text{BzOs}(\text{NH}_3)_3^{2+}$, and it seems safe to conclude that an aquo ion of charge 2+ is being dealt with. Two titrations were performed with OH^- on solutions produced as described. In one case, the initial concentration of Os(II) was 1.36×10^{-2} M and in the other 7.5×10^{-4} M. After Ag^+ was added in equivalent amount and the solutions were kept for 3 h, AgCl was re-

Table II. UV-vis Spectral Data for Monobenzene Complexes of Osmium(V) and Related Complexes

complex	UV-vis λ , nm ($\epsilon \times 10^{-2}$, $\text{M}^{-1} \text{ cm}^{-1}$)	solvent
$[\text{BzOs}(\text{H}_2\text{O})_3]^{2+ a}$	322 (7.0), 262 (10.5)	1 M HTFMS
$[\text{BzOsCl}_2]^b$	355 sh (10), 293 (21.5)	6 M HCl
	350 sh (9.1), 293 (16.7)	2 M HCl
$[\text{BzOs}(\text{NH}_3)_3](\text{PF}_6)_2$	300 (4.5), 250 sh (10), 255 sh	0.1 N HTFMS
$[\text{BzOs}(\text{en})\text{Cl}](\text{PF}_6)$	325 sh (5.3), 261 (12.5)	H_2O
$[\text{BzOs}(\text{en})(\text{NH}_3)](\text{PF}_6)_2$	305 sh (25.3), 255 sh (11.6), 225 sh (15.4)	H_2O
$[\text{BzOs}(\text{en})(\text{H}_2\text{O})](\text{PF}_6)_2$	300 (4.9), 250 (12.0)	0.1 N HTFMS
$[\text{BzOs}(\text{gly})\text{Cl}]$	335 sh (6.2), 263 (16.9)	CH_3OH
	310 (~ 5), 250 (~ 13)	0.1 N HTFMS
$[\text{BzOs}(\text{py})\text{Cl}_2]$	293 (45)	CH_2Cl_2
$[\text{BzOs}(\text{isn})\text{Cl}_2]$	312 (47), 282 (46)	CH_3OH
$[\text{BzOs}(\text{py})\text{Br}_2]$	298 (79)	CH_2Cl_2
$[\text{Os}(\text{isn})\text{Br}_2]$	313 (77), 280 (78)	CH_3OH
$[\text{Os}(\text{isn})_2\text{Cl}]\text{PF}_6$	310 sh (67), 275 (89)	H_2O
$[\text{Os}(\text{isn})_2\text{Br}](\text{PF}_6)$	313 sh (~ 65), 275 sh (80)	CH_3OH
	237 sh (120)	
$[\text{Os}(\text{en})(\text{isn})](\text{PF}_6)_2$	315 (~ 39), 285 (~ 54), 230 sh	H_2O
$[\text{Os}(\text{en})(\text{py})](\text{PF}_6)_2$	266 (61), 220 (54)	H_2O
$[\text{Os}(\text{Me}_2\text{SO})\text{Cl}_2]$	470 sh (~ 2.8), 394 (3.8), 315 (4.7)	Me_2SO
$[\text{Os}(\text{en})(\text{imid})](\text{PF}_6)_2$	316 sh (~ 4.2), 250 sh (~ 14)	CH_3OH
$[\text{Os}(\text{imid})_2\text{Cl}](\text{PF}_6)_2$	334 sh (6), 266 (15.9)	CH_3OH
$[\text{Os}(\text{CH}_3\text{CN})\text{Cl}_2]$	360 sh (6), 280 sh (180)	CH_3CN
$[(\text{NH}_3)_5\text{Os}(\text{isn})]^{2+}$	508 (170), 768 (30)	0.1 M HCl
$[(\text{NH}_3)_5\text{Os}(\text{py})]^{2+}$	553 (35), 430 (110)	pH 8

^a Vide infra for preparation. ^b Formula of compound used. Does not necessarily represent formula in solution.

moved. It was shown that the coordinated chloride ion is removed completely by this procedure. For the more concentrated solution, the apparent pK_a was determined as ~ 2.3 while for the more dilute, as ~ 3.4 . In each case 1.5 mol of OH^- per Os(II) was consumed at the equivalence point. The variation of pK_a with concentration shows that the product of proton loss condenses; the change of pK_a with concentration is so marked that the extent of polymerization is greater than 4 (the results of a structure determination for a tetrameric hydroxy-bridged species derived from BzRu^{2+} has been reported).¹⁰

So that condensation of the hydroxo product was avoided, determinations of pK_a were made with solutions of $[\text{BzOs}(\text{en})\text{Cl}]\text{PF}_6$ and $[\text{BzOs}(\text{NH}_3)_2\text{Cl}]\text{PF}_6$, which had been treated with sufficient AgNO_3 to remove Cl^- . In each case, 1.00 ± 0.05 mol of OH^- was consumed at the equivalence point per mole of compound. For $[\text{BzOs}(\text{en})]^{2+}$, the value of pK_a (6.3 at 20°C and $\mu = 0.10$) was shown to be independent of the concentration of the salt (solutions 9.7×10^{-3} and $1.39 \times$

Table III. Anation Reaction of $[\eta\text{-C}_6\text{H}_5\text{Os(en)H}_2\text{O}]^{2+}$ with NaCl at 25 °C, pH 1, and $\mu = 1^a$

$[\text{Cl}^-]$, M	k_{obsd} , s^{-1}
0.1	1.58×10^{-4} , 1.55×10^{-4}
0.2	2.86×10^{-4}
0.3	4.22×10^{-4}
0.4	5.33×10^{-4} , 5.35×10^{-4}
0.5	6.75×10^{-4} , 5.36×10^{-4}
0.7	8.98×10^{-4} , 8.69×10^{-4}
0.8	9.50×10^{-4} , 9.28×10^{-4}
0.9	1.09×10^{-3} , 1.07×10^{-3} , 9.87×10^{-4}
1.0 ^b	1.16×10^{-3}

^a Adjusted with NaTFMS. ^b $\mu = 1.1$.

10^{-3}M were titrated). For $[\text{BzOs}(\text{NH}_3)_2]^{2+}$, only a single concentration ($8.1 \times 10^{-3}\text{M}$) was used, and $\text{p}K_a$ was found to be 6.4.

Chloride Ion as Ligand. So that complications arising from condensation could be minimized, the experiments on replacement of H_2O from BzOs^{II} by Cl^- were made with the monoquo species, rather than $\text{BzOs}(\text{aq})^{2+}$ which presumably is a triquo species. As indicated by the structural results for the condensed BzRu^{II} species, condensation involves the formation of multiple hydroxo-bridged species.

Aquation of chloride from $[\text{BzOs}(\text{en})\text{Cl}]^+$ was followed spectrophotometrically in a medium containing 0.10 M trifluoromethanesulfonic acid made up to $\mu = 0.50$ with the sodium salt. The specific rate of aquation at 25 °C was measured as $(1.2 \pm 0.08) \times 10^{-5} \text{ s}^{-1}$ (mean of three runs). No significant amount of en is lost from the complex even after 10 half-lives for the aquation of Cl^- .

For a study of the anation reaction, a solution containing $[\text{BzOs}(\text{en})\text{H}_2\text{O}]^{2+}$ was prepared by adding AgNO_3 to $[\text{BzOs}(\text{en})\text{Cl}]\text{PF}_6$ in $10^{-3} \text{ M HCF}_3\text{SO}_3$, leaving the mixture at 40 °C for ca. 12 h, filtering, and passing the liquid through a Sephadex column. The portion that was eluted with 0.20 M HCF_3SO_3 was used for the kinetic runs. The reaction was followed at 280 nm at varying concentrations of chloride ion. Good pseudo-first-order behavior was observed in each experiment. The results are summarized in Table III.

Preliminary studies on the rate of aquation of $[\text{BzOs}(\text{gly})\text{Cl}]^+$ shows that the chloride is much more labile in this species than in $[\text{BzOs}(\text{en})\text{Cl}]^+$. The specific rate at 25 °C in an $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ mixture (83:17) and at 0.083 M HCF_3SO_3 was measured as $1.9 \times 10^{-2} \text{ s}^{-1}$.

Isonicotinamide as Ligand. The species $[\text{BzOs}(\text{en})\text{H}_2\text{O}]^{2+}$ for these experiments was prepared as described for the reaction with Cl^- . The experiments were done by making up a stock solution of $[\text{BzOs}(\text{en})\text{H}_2\text{O}]^{2+}$ in 0.20 M trifluoromethanesulfonic acid. Measured quantities of a solution of isonicotinamide at known concentration were added until the pH reached the desired value. The reactions were followed at 330 nm. Although the total change in optical density ascribable to association of isonicotinamide was in every case close to the expected value, each run itself was anomalous in that curvature appeared in the first-order plots after a single half-life. The specific rates recorded in Table IV were obtained from initial slopes.

Observations with BzRu^{II} . The red product obtained from the Z-B preparation is assumed, because of its solubility, to be dimeric. By using the appropriate cyclohexadiene, Bennett and Smith¹¹ obtained the *p*-cymene complex, and this proved to be sufficiently soluble in CHCl_3 to make feasible the determination of molecular weight by osmometry; the compound was found to be dimeric. The IR spectrum of BzRuCl_2 as obtained in a KBr pellet shows two $\nu_{\text{C}=\text{C}}$ bands at 1438 and 839 cm^{-1} , features characteristic of π -bonded benzene. At low frequencies, bands were observed at 295 and 260 cm^{-1} , which are assigned to terminal and bridging Cl modes.

Table IV. Reaction between $[(\eta\text{-C}_6\text{H}_5)\text{Os}(\text{en})\text{H}_2\text{O}]^{2+}$ and Isonicotinamide^a

$[\text{isn}]$, M	pH	k_{obsd} , s^{-1}
0.44	4.85	8.9×10^{-6}
0.44 ^b	4.80	8.9×10^{-6}
0.25	4.97	4.6×10^{-6}
0.17	4.62	2.13×10^{-6}
0.077	4.40	7.1×10^{-7}

^a $[\text{Os}(\text{II})] = \sim 3 \times 10^{-4} \text{ M}$; at 25 °C; monitored at $\lambda = 380 \text{ nm}$. Protonated isn is present at a concentration consistent with $[\text{isn}]$ and pH. ^b By Guggenheim's method.

The compound BzRuCl_2 is soluble in strongly coordinating solvents, and presumably in such solvents the dimeric structure is broken up. This was in fact shown¹² to be the case in CH_3CN by a molecular weight determination: 232 observed vs. 250 calculated for monomer. Conductimetric measurements show¹² the chloride to be a nonelectrolyte in CH_3CN (and in Me_2SO), thus completing the proof as to its molecular nature.

The NMR observations by Zelonka and Baird¹² on solutions of BzRuCl_2 in D_2O , which show that in solutions at the centimolar level two species are present, one being formed by the addition of HgCl_2 and the other by the addition of NaCl, were fully reproduced and were elaborated only on the point that the concentration ratio of the chloride-rich to the chloride-depleted form when BzRuCl_2 is $1 \times 10^{-2} \text{ M}$ proved to be 7:3.

A dilute ($1.22 \times 10^{-3} \text{ M}$) solution of BzRuCl_2 showed absorption at 400 ($\epsilon 5.1 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$), 311 ($\epsilon 8.4 \times 10^2$) and 250 nm ($\epsilon 1.4 \times 10^3$). In a more dilute solution in 0.1 M trifluoromethanesulfonic acid two bands were observed: 380 ($\epsilon 6.0 \times 10^2$) and 265 nm ($\epsilon 6 \times 10^3$). Hydrolysis is suppressed in this solution, and very little Cl^- complex can be present. Cation exchange showed the Ru-containing cation to carry a charge of 2+, and we conclude that spectrum reported is that of $\text{C}_6\text{H}_6\text{Ru}(\text{H}_2\text{O})_3^{2+}$.

As is the case for $[\text{BzOs}(\text{isn})]^{2+}$, the ruthenium complex also shows two benzene peaks ($\delta = 5.95$ and 5.75) in the NMR spectrum, the ratio being 4.5:1. The spectrum was taken in Me_2SO .

The value of $\text{p}K_a$ for $[\text{BzRu}(\text{en})\text{H}_2\text{O}]^{2+}$ was determined by titrating a solution prepared by adding an equivalent amount of AgNO_3 to $7.6 \times 10^{-3} \text{ M}$ $[\text{BzRu}(\text{en})\text{Cl}]\text{PF}_6$ in water. The titration curve was of normal shape for a monobasic acid. The value of $\text{p}K_a$ (20 °C, $\mu = 0.1$ with NaClO_4) was measured as 7.9.

A rough estimate of the rate of substitution of isn in $\text{BzRu}^{2+}(\text{aq})$ was made by preparing a solution $2 \times 10^{-3} \text{ M}$ in the aquo cation, 0.10 M in NaCF_3SO_3 , and $2 \times 10^{-2} \text{ M}$ in isn. The aquo ion was prepared by adding an equivalent amount of AgNO_3 to BzRuCl_2 in water. The specific rate was measured as $0.5 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C.

Discussion

A point of interest in connection with the preparative procedures for the osmium compounds is that, in methanol as solvent, replacement of halide from Os(II) by a large variety of ligands is efficient. This is in marked contrast to the reaction of BzOsCl_2 in neat Me_2SO or in neat CH_3CN where in spite of the fact that the entering ligand is concentrated, only one molecule of it enters the coordination sphere. This behavior is in line with ideas now commonly accepted, that Me_2SO and CH_3CN do not solvate anions strongly, whereas CH_3OH , because it is a protic solvent, does. In converting BzOsCl_2 to the triacetonitrile complex, it was found necessary to remove Cl^- with Ag^+ . (We did not obtain a pure preparation of $[\text{BzOs}(\text{CH}_3\text{CN})_3](\text{PF}_6)_2$, but the analogous operation was carried out successfully by Bennett and Smith²² on BzRuCl_2 .)

The observations on the molar conductances of the various compounds prepared are generally in harmony with the foregoing remarks. In CH_3NO_2 , CH_3CN , or Me_2SO as solvents, halide remains bound to Os(II). Dissociation tends to be most complete in H_2O —but note that $[\text{BzOs}(\text{isn})_2\text{Cl}]\text{PF}_6$, for example, behaves as a 1:1 electrolyte—while CH_3OH is intermediate in dissociating power between H_2O and the nonprotic solvents. A factor affecting the extent of dissociation which was not thoroughly investigated is the time. As has been mentioned, about 1 h elapsed after dissolution before the conductance measurements were made, and there is uncertainty as to whether dissociation equilibrium was established in the allotted time. This uncertainty is not great for the nonprotic solvents because the preparative results indicate that in these solvents, the affinity of halide ion for the Os(II) center is very great and that halide ion is not replaced even after protracted heating at temperatures of 40 °C and above. For $[\text{BzOs}(\text{isn})_2\text{Cl}]\text{PF}_6$ in water, however, it is likely that equilibrium had not been reached in the hour or so which elapsed before measuring conduction.

Some comments on the absorption spectra for the osmium compounds seem called for. Complexes with simple σ donors as auxiliary ligands, i.e., NH_3 , H_2O , gly, etc., show a band at 300 nm or somewhat above with an extinction coefficient of several hundred. In view of its intensity and energy, this band can be reasonably assigned to a metal d-d transition. The trend in energy as a function of ligand is seen to follow the spectrochemical series. The second band around 250 nm is assigned $d(M) \rightarrow \pi^*(L)$. The highest energy band, a shoulder at 225 nm, is assigned to the benzene $\pi \rightarrow \pi^*$ transition. For complexes with π acids as auxiliary ligands, i.e., py, isn, CO, Me_2SO , etc., the d-d transition is obscured by MLCT which has an extinction coefficient around several thousand. Compared with the reported data on pentaammineosmium(II) N-heterocyclic complexes²¹ where MLCT occurs at much lower energy, the presence of benzene has greatly disturbed the back-bonding system; i.e., benzene is effectively competing for the d electron density. In harmony with these assignments, the lowest energy band for dilute BzRuCl_2 in water (380 nm) appears at longer wavelength than for the osmium compound, and the extinction coefficient is again below $10^3 \text{ M}^{-1} \text{ cm}^{-1}$. The band at 311 nm observed for the Ru species is also likely a ligand field band while that at 250 nm is probably the metal to ligand charge-transfer absorption. It should be noted that $[\text{Ru}(\text{NH}_3)_6]^{2+}$ has d-d bands at 390–400 and 320 nm,^{22,23} which are d-d in origin, and a strong band at 268 nm, which corresponds to a charge-transfer process.

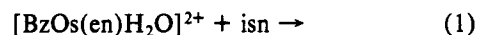
The structural pattern that Os(II) bears three monodentate ligands in addition to the aromatic one is consistently followed in all of the species, and this makes it reasonably certain that the aquo ion has the formula $[\text{BzOs}(\text{H}_2\text{O})_3]^{2+}$. The determination of the acidity of the coordinated water in this species was vitiated by the condensation of the hydroxo forms. For the mono aquo species this complication was not significant, and good values of pK_a were obtained (6.3 for $[\text{BzOs}(\text{NH}_3)_2(\text{H}_2\text{O})]^{2+}$). The dissociation constant of $[\text{Os}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ is not known, but it is reasonable to suppose that it will not be greater than it is for $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ for which a value of ca. 10^{-13} has been reported.²⁴ As expected C_6H_6 in replacing three ammonia molecules is powerfully electron withdrawing. Comparisons with a π acid such as CO are not possible for Os(II) as the metal center, the necessary experiments with $[\text{Os}(\text{NH}_3)_4(\text{CO})\text{H}_2\text{O}]^{2+}$ not having been

done. However, for Ru(II), a comparison can be made: 7.9 for $[\text{BzRu}(\text{en})\text{H}_2\text{O}]^{2+}$ as measured in this work, 6.3 for *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{CO})\text{H}_2\text{O}]^{2+}$ and ~ 8 for *cis*- $[\text{Ru}(\text{NH}_3)_4(\text{CO})\text{H}_2\text{O}]^{2+}$, the latter two as measured by Baar.²⁵ Surprisingly, C_6H_6 in replacing three NH_3 molecules is not clearly more effective in promoting the acidity of coordinated water than is a single molecule of CO.

When the values of k_{obsd} for the anation of $[\text{BzOs}(\text{en})(\text{H}_2\text{O})]^{2+}$ are plotted against $[\text{Cl}^-]$, they are found to increase linearly with this variable up to above 0.5 M, in which region there is evidence of rate saturation. From the linear portion of the plot, the second-order specific rate for anation is found to be $1.34 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. On combination of this value with the specific rate for aquation, the quotient governing the association of Cl^- with $[\text{BzOs}(\text{en})\text{H}_2\text{O}]^{2+}$ is calculated as 1.1×10^2 at 25 °C and $\mu = 1.0$. Comparison with a value for Os(II) in an environment of neutral saturated ligands cannot be done owing to a lack of the necessary data. However, a rough value for the equilibrium quotient governing anation of $[\text{BzRu}(\text{H}_2\text{O})_3]^{2+}$ by Cl^- can be calculated from the NMR data for solutions containing Cl^- . The value so obtained is 1.2×10^2 . This can be compared with 1.6 ,²⁶ the quotient governing association of Cl^- with $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{2+}$. Even when the statistical factor of 3 is allowed for, the affinity of Cl^- for Ru(II) is seen to be considerably enhanced when NH_3 is replaced by C_6H_6 . This of course is again a reflection of the electron-withdrawing power of $\eta\text{-C}_6\text{H}_6$ compared to the saturated ligand NH_3 , its effect being more strongly felt in Cl^- than in H_2O , because the former ligand is more polarizable.

In considering the important issue of labilities, perhaps the point should be reiterated that the arene–Os(II) and arene–Ru(II) bonds, at least in the dark, are indefinitely stable at ordinary acidities even in water. The BzOs–ammine bonds also resist aquation sufficiently well so that this side reaction did not vitiate the determinations of pK_a . An idea of the lability of H_2O in $[\text{BzOs}(\text{H}_2\text{O})_3]^{2+}$ can be gotten from the anation rate with Cl^- as entering ligand, $1.34 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, which is really quite low for an aquo or aquoammine cation of oxidation state 2+, but is not unprecedented when species are considered in which the effective charge of the metal ion is increased by a π -acid ligand.²⁷

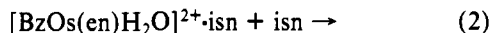
The data obtained for isn as ligand also bear on the issue of lability (this ligand has been used for a similar purpose in earlier studies).²⁷ In plotting k_{obsd} for the formation of the isn complex of $[\text{BzOs}(\text{en})\text{H}_2\text{O}]^{2+}$ against $[\text{isn}]$ the data shown a trend which, in the light of past experience, is anomalous. Whereas in other cases in which k_{obsd} for substitution is nonlinear in the concentration of π -acid ligand, the plots show rate saturation, in ours, the plots are concave upward. In the other cases showing nonlinear plots, it has been necessary^{28–30} to invoke a preequilibrium involving labile association of the ligand with the metal ion. The effects arising from this are particularly clearcut for the tetraammine(phosphito)ruthenium(II) species reacting with pyrazinium ion. In all the cases previously encountered, k_{obsd} as a function of ligand concentration shows a saturation effect. To explain the concave upward shape in our system, we would need to assume that the process



is slower than

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In other words we would need to invoke an activated complex with two entering ligands, one of them acting to labilize the Os(II) center but not disposed to enter the coordination sphere. It seems prudent to defer further speculation until the system and related ones have been more thoroughly explored. The datum at the lowest isonicotinamide concentration can be taken as being the most directly related to the specific rate for reaction 1. The value of specific rate calculated from it is $0.9 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$, to be compared to $1.3 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for Cl^- as entering group. A factor of 100 is not unreasonable as resulting from the difference in charge between the two entering groups, and in this respect at least, our observations are not out of line.

In the matter of substitution lability, a remarkable qualitative result is the rapidity with which the CO complex is formed. Referring back to the procedure which was followed, when CO is present at atmospheric pressure—corresponding perhaps to 10^{-3} M in methanol solution—reaction is largely complete in 5 min. Even on the assumption that the half-life is 5 min, the second-order specific rate is calculated as ca. 3, to be compared to 0.9×10^{-5} for isn. A large factor directly

involved in the rate difference is that, in the CO case, the reactant species is $\text{BzOsCl}_2\text{CH}_3\text{OH}$, and the labilizing effect of the two chloride ions is being exploited in the facile substitution. The labilizing effect of $\text{NH}_2\text{CH}_2\text{CO}_2^-$ as compared to en has already been noted.

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Registry No. $[\text{BzOs}(\text{NH}_3)_3](\text{PF}_6)_2$, 75700-71-9; $[\text{BzOs}(\text{NH}_3)_2\text{Cl}](\text{PF}_6)$, 75700-73-1; $[\text{BzOs}(\text{en})\text{Cl}](\text{PF}_6)$, 75700-75-3; $[\text{BzOs}(\text{en})\text{Br}](\text{PF}_6)$, 75700-77-5; $[\text{BzOs}(\text{en})\text{NH}_3](\text{PF}_6)_2$, 75700-79-7; $[\text{BzOs}(\text{en})(\text{isn})](\text{PF}_6)_2$, 75700-81-1; $[\text{BzOs}(\text{en})(\text{imid})](\text{PF}_6)_2$, 75700-83-3; $[\text{BzOs}(\text{en})(\text{py})](\text{PF}_6)_2$, 75700-85-5; $\text{BzOs}(\text{gly})\text{Cl}$, 75700-86-6; $\text{BzOs}(\text{CH}_3\text{CN})\text{Cl}_2$, 72765-28-7; $[\text{BzOs}(\text{CH}_3\text{CN})_3](\text{PF}_6)_2$, 75700-88-8; $\text{BzOs}(\text{isn})\text{Cl}_2$, 75700-89-9; $\text{BzOs}(\text{isn})\text{Br}_2$, 75700-90-2; $[\text{BzOs}(\text{isn})_2\text{Cl}](\text{PF}_6)$, 75716-24-4; $[\text{BzOs}(\text{isn})_2\text{Br}](\text{PF}_6)$, 75700-92-4; $[\text{BzOs}(\text{imid})_2\text{Cl}](\text{PF}_6)$, 75700-94-6; $\text{BzOs}(\text{py})\text{Cl}_2$, 75700-95-7; $\text{BzOs}(\text{py})\text{Br}_2$, 75700-96-8; $\text{BzOs}(\text{CO})\text{Cl}_2$, 75700-97-9; $\text{BzOs}(\text{Me}_2\text{SO})\text{Cl}_2$, 75700-98-0; $\text{BzRu}(\text{isn})\text{Cl}_2$, 75700-99-1; $[\text{BzRu}(\text{en})\text{Cl}](\text{PF}_6)$, 75701-00-7; $[\text{BzOs}(\text{en})(\text{H}_2\text{O})](\text{PF}_6)_2$, 75701-02-9; BzOsCl_2 , 53886-43-4; BzOsBr_2 , 75701-03-0; BzOsI_2 , 75701-04-1; $[\text{BzOs}(\text{H}_2\text{O})_3]^{2+}$, 75701-05-2; $[\text{BzRu}(\text{H}_2\text{O})_3]^{2+}$, 75701-06-3; $[\text{BzOs}(\text{NH}_3)_2\text{H}_2\text{O}]^{2+}$, 75701-07-4; $[\text{BzRu}(\text{en})\text{H}_2\text{O}]^{2+}$, 75701-08-5; $[(\text{NH}_3)_5\text{Os}(\text{isn})]^{2+}$, 70252-43-6; $[(\text{NH}_3)_5\text{Os}(\text{py})]^{2+}$, 70252-47-0; $[\text{BzRuCl}_2]_2$, 37366-09-9; ammonium hexachloroosmate(IV), 12125-08-5.

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The First Acidification Step of the Tris(carbonato)dioxouranate(VI) Ion, $\text{UO}_2(\text{CO}_3)_3^{4-}$

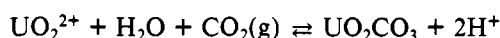
LIBERATO CIAVATTA, DIEGO FERRI, INGMAR GRENTHE,* and FRANCESCO SALVATORE

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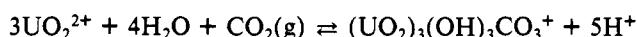
Potentiometric measurements with a glass electrode combined with solubility determinations of $\text{CO}_2(\text{g})$ have indicated that, at 25 °C in 3 M NaClO_4 medium with $[\text{U(VI)}] < 0.05 \text{ M}$ and $\log [\text{HCO}_3^-] \geq -1.2$, the prevailing form of uranium(VI) is the species $\text{UO}_2(\text{CO}_3)_3^{4-}$ ($=\text{UO}_2(\text{OH})_6(\text{CO}_2)_2^{4-}$). On acidification of $\text{UO}_2(\text{CO}_3)_3^{4-}$, and before solid uranyl carbonates start to precipitate, a polynuclear complex $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ ($=(\text{UO}_2)_3(\text{OH})_{12}(\text{CO}_2)_6^{6-}$) was found to form according to $3\text{UO}_2(\text{CO}_3)_3^{4-} + 3\text{CO}_2(\text{g}) + 3\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_3(\text{CO}_3)_6^{6-} + 6\text{HCO}_3^-$ with the equilibrium constant, $\log \beta_{3,12,6} = -6.43 \pm 0.08$. No evidence for the species $\text{UO}_2(\text{CO}_3)_2^{2-}$ or mixed species $(\text{UO}_2)_p(\text{OH})_q(\text{CO}_3)_r$ was obtained in the experimental range investigated: $10^{-3} \leq [\text{U(VI)}] \leq 0.03 \text{ M}$, $0.1 \leq P_{\text{CO}_2} \leq 1 \text{ atm}$, and $-3.0 \leq \log [\text{HCO}_3^-] \leq -0.7$. The ^{13}C NMR spectra of the two complexes indicate the presence of three equivalent carbonate groups in the mononuclear complex and two different carbonate sites with the ratio 1:2 between the integrated intensities in the trinuclear complex. The NMR data are compatible with a structure containing both bridging and terminal carbonate groups.

Introduction

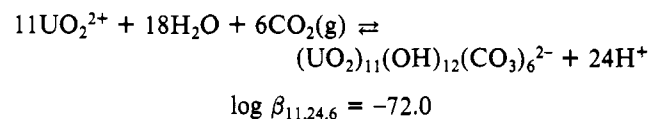
The equilibria between UO_2^{2+} , H_2O , and $\text{CO}_2(\text{g})$ at 25 °C have been previously¹ studied in a 3 M NaClO_4 medium at acidities ranging from $[\text{H}^+] = 10^{-3} \text{ M}$, where complexing is negligible, to $[\text{H}^+] = 10^{-4.8} \text{ M}$, when a precipitate of U(VI) carbonates starts to form. The extensive data collected were interpreted by assuming the formation of the carbonate complexes: UO_2CO_3 , $(\text{UO}_2)_3(\text{OH})_3\text{CO}_3^+$, and a large species, probably $(\text{UO}_2)_{11}(\text{OH})_{12}(\text{CO}_3)_6^{2-}$. The following equilibrium constants were determined:



$$\log \beta_{1,2,1} = -9.02$$



$$\log \beta_{3,5,1} = -16.34$$



Exploratory experiments indicated that the precipitate of uranium(VI) carbonates redissolves at lower acidities and that clear solutions result at $[\text{H}^+] < -5.7 \text{ M}$, provided the equilibrium pressure of $\text{CO}_2(\text{g})$ is $> 10^{-2} \text{ atm}$. These figures are somewhat dependent on $[\text{U(VI)}]$ but are not likely to change dramatically in the U(VI) concentrations between 10^{-3} and 0.1 M .

Previous workers, whose results are reviewed in ref 1, generally agree in assuming $\text{UO}_2(\text{CO}_3)_3^{4-}$ as the final result of the reaction.

The aim of the work is the study of the equilibria occurring in the acidity range from the dominance of $\text{UO}_2(\text{CO}_3)_3^{4-}$ to

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