Metal	AP[M(acac)$_2$$^+$],^{a} eV	ΔH_{diss}, kcal/mol	E_{M-O}^{tris},^{b} kcal/mol	E_{M-O}^{bis}, kcal/mol
Mn	$\geqslant 8.7 \pm 0.1$	$\geqslant 9 \pm 4$	44.8 ± 0.5	$\leqslant 65 \pm 2$
Fe	$\geqslant 9.4 \pm 0.1$	$\geqslant 30 \pm 4$	55.9 ± 0.6	$\leqslant 76 \pm 2$
Co	10.7 ± 0.1	$\geqslant 51 \pm 4$	50.9 ± 0.7	$\leqslant 63 \pm 2$

^{a} See reference 6. ^{b} J. L. Wood and M. M. Jones, *Inorg. Chem.*, **3**, 1553 (1964).

Most of these complexes have different structures in the gaseous and condensed phases. The available evidence[11] suggests that in the gaseous state the acetylacetonates of Mn(II), Fe(II), Co(II), and Zn(II) are tetrahedral (high spin) while those of Ni(II) and Cu(II) are square planar, and in the solid state they are all polymeric with the exception of Cu(acac)$_2$. Thus, the usual experimental data are not available with which to compare the measured appearance potentials. For example, electronic absorption spectra can, in principle, be used to evaluate ligand field effects, but solution spectra are not likely to be helpful here. Moreover, we are not aware of any theoretical treatment of the gaseous chelate molecules.

In the ionization process two possibilities may be considered, namely, (a) the electron is removed from a molecular orbital localized mainly on the metal and (b) the electron is removed from a molecular orbital localized mainly on the π system of the ligand. It seems that these results do not allow us to distinguish between these possibilities although previous experimental results[6,7,10] on other β-diketonates have suggested the second possibility, and the present results do not seem to be in conflict with this suggestion.

The appearance potentials of the (P − CH$_3$)$^+$ ions fall into two groups. For Mn^{II}, Fe^{II}, Co^{II}, and Ni^{II} the values are 11.6 ± 0.1 V and for Cu(II) and Zn(II) the values are both significantly lower at 10.9 ± 0.1 V. For the ML$^+$ ions the values for Mn^{II}, Fe^{II}, Co^{II}, and Ni^{II} can again be grouped together at 13.7 ± 0.2 V. These observations may be fortuitous, however.

In an earlier paper[6] we have quoted values of the appearance potentials of the M(acac)$_2$$^+$ ions from the tris chelates of Mn(III), Fe(III), and Co(III). For these chelates we can thus calculate the energy of the dissociation: M(acac)$_3$ → M(acac)$_2$ + acac. Making the usual assumptions that the products of the ionization reactions are formed in their ground states and that their total kinetic energy is small, a lower limit for the energy of the homolytic dissociation is given by

$$\Delta H_{diss} = AP[M(acac)_2^+ \text{ from } M(acac)_3] - IP[M(acac)_2]$$

The metal–oxygen coordinate bond energies in the M(acac)$_2$ complexes are given by

$$E_{M-O}^{bis} = \frac{1}{4}(6E_{M-O}^{tris} - \Delta H_{diss})$$

(11) J. P. Fackler, *Progr. Inorg. Chem.*, **7**, 361 (1966), and references therein.

These values and the data necessary to calculate them are given in Table III.

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On the Spontaneous Reduction of Hexachloroiridate(IV) in Aqueous Solution

BY DWIGHT A. FINE

Previous work on the aqueous solution chemistry of iridium(IV) has indicated that hexachloroiridate(IV), IrCl$_6$$^{2-}$, undergoes spontaneous reduction to the +3 state in neutral and weakly acidic solution.[1-4] The rate and extent of the reduction appear to be dependent on acidity.[4] Suggested explanations for the reaction include oxidation of ligand chloride[3] and oxidation of water.[4] Recent irradiation experiments have shown that the redox process is not photochemical in nature.[5] In the course of some investigations of the chemistry of iridium(IV) in basic solution, we have observed that hexachloroiridate(IV) is rapidly and quantitatively reduced in solutions of pH >11. Through mass spectrometry, vapor-phase chromatography, and spectrophotometry we have obtained evidence as to the process of reduction in aqueous solution.

Mass spectrometry was employed to obtain qualitative identification of gaseous reaction products in basic solution. Hexachloroiridate(IV) salts were dissolved in degassed sodium hydroxide solution, and the gaseous contents of the reaction vessel were analyzed (see Experimental Section for details). When hexachloroiridate(IV) salts are dissolved in alkali hydroxide more concentrated than 10^{-2} *M*, an evolution of gas bubbles takes place and the color of the solution quickly goes from the dark reddish brown characteristic of hexachloroiridate(IV) to the pale yellow-green characteristic of the +3 state. The only gaseous products detected by the mass spectrometer were oxygen and water vapor. In more dilute alkaline solutions, evolution of gas bubbles is not visible, and the color fades more slowly; again, only oxygen and water vapor were detected by the mass spectrometer.

Vapor-phase chromatography was employed to obtain

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quantitative measurements of evolved oxygen. The results are shown in Table I. They indicate the liberation of 0.25 mol of oxygen per mole of hexachloroiridate(IV). This stoichiometry is obeyed by the reaction
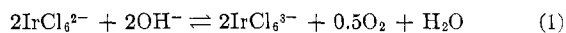
$$2IrCl_6{}^{2-} + 2OH^- \rightleftharpoons 2IrCl_6{}^{3-} + 0.5O_2 + H_2O \qquad (1)$$

TABLE I

VPC MEASUREMENTS OF O_2 LIBERATED FROM
NaOH SOLUTION BY $IrCl_6{}^{2-}$

Wt of K_2IrCl_6, g	mmol of $O_2{}^a$	$\dfrac{\text{mmol of } O_2}{\text{mmol of } IrCl_6{}^{2-}}$
0.1126	22.7×10^{-2}	0.23 ± 0.02^b
0.0710	14.3	0.22
0.0406	8.20	0.24
0.0178	3.59	0.25

^{a} Produced by dissolving the K_2IrCl_6 in 3 ml of 0.200 M NaOH. ^{b} Uncertainty calculated by assuming an uncertainty of ± 0.1 in peak height and of ± 0.02 cm in the pressure of oxygen used to obtain the calibration chromatograms.

Spectrophotometric evidence in support of reaction 1 was obtained. Solutions of hexachloroiridate(IV) in dilute ($<10^{-2}$ M) sodium hydroxide were scanned in the region between 400 and 600 nm immediately after dissolving the salt, and the scan was repeated at *ca.* 3-min intervals. The spectra obtained were all spectra of $IrCl_6{}^{2-}$, decreasing in intensity with time. This indicates reduction of $IrCl_6{}^{2-}$ to the $+3$ state without formation of any aquochloro complexes of the $+4$ state, since the molar extinction coefficients of the aquochloro complexes of the $+4$ state are more than 10 times larger than the extinction coefficients of the corresponding $+3$ species.[6] Solutions concentrated enough in iridium to show appreciable absorbance from species in the $+3$ state were examined in the region between 300 and 450 nm. The spectra showed the formation of peaks at 415 and 355 nm, characteristic of $IrCl_6{}^{3-}$.[2,3,6] The peak at 355 nm was masked within 30 min by absorbance arising from subsequent hydroxylation and oxidation reactions (see below), but the peak at 415 nm persisted for several hours at room temperature.

Previous studies of the behavior of hexachloroiridate(IV) in basic solution include the spectrophotometric work of Desideri and Pantani[7] and the polarographic work of Van Loon and Page.[8] These authors demonstrated the formation with time of a species which they postulated to be $Ir(OH)_6{}^{2-}$; in addition, they found that blue and purple species, most likely polymeric hydroxy complexes of iridium(IV), are formed when the iridium concentration is greater than 10^{-3} M. They noted that these species are formed whether one starts with a hexachloroiridate(IV) or a hexachloroiridate(III) salt and that they are not formed with either salt when oxygen is excluded. Our

results are in line with these observations; they indicate that the first step upon dissolving hexachloroiridate(IV) in basic solution is reduction to hexachloroiridate(III). This reduction occurs much faster than the succeeding hydroxylation and oxidation reactions.

Calculations from published oxidation potentials[9] yield an equilibrium constant of 10^{21} atm$^{1/2}$ mol^{-2} l.^{2} at 25° for reaction 1. One can write the corresponding reaction for acid solution

$$2IrCl_6{}^{2-} + H_2O \rightleftharpoons 2IrCl_6{}^{3-} + 0.5O_2 + 2H^+ \qquad (2)$$
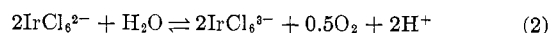
This reaction was postulated by Peixoto Cabral to explain the "mobile redox equilibrium" observed in neutral and weakly acidic solutions of hexachloroiridate(IV) salts.[4] Our results for basic solutions and the pH dependence observed lend support to this hypothesis. Calculations for reaction 2 yield an equilibrium constant of approximately 7×10^{-8} atm$^{1/2}$ mol^2 l.$^{-2}$ at 25°. This indicates that the reverse of the reaction as written ought to be favored in strongly acid solution. We have found this to be true. When sodium hexachloroiridate(III) is dissolved in concentrated perchloric or hydrochloric acids (12 M), partial oxidation to $IrCl_6{}^{2-}$ occurs immediately at room temperature. Aging or heating leads to complete oxidation.

Equations 1 and 2 represent, of course, net processes. The formation of hydroxyl radicals has been suggested as a possible mechanism for reaction 2.[4] Our results do not permit any conclusions as to mechanism.

Experimental Section

The iridium salts used were Platinum Chemicals Co. sodium hexachloroiridate(IV), potassium hexachloroiridate(IV), and sodium hexachloroiridate(III). For quantitative work, the potassium salt was used exclusively. The iridium(IV) content of the salt was checked by addition of potassium iodide to solutions of weighed portions of the salt and titration of the liberated iodine with thiosulfate. The average value obtained was 2.02×10^{-3} mequiv of Ir(IV)/mg, which corresponds to 97% of the theoretical value. Chlorination of solutions of the salt produced no increase in iridium(IV) content, indicating the absence of iridium(III).

Sodium hydroxide solutions were prepared from Harleco standard "CO_2-free" concentrate.

For the work with the mass spectrometer, a vessel consisting of a tube-shaped flask with a side arm and standard-taper neck was employed. The iridium salt was placed in the side arm and the solvent (3 ml of NaOH of known concentration) was pipetted into the flask. Solutions 0.200, 0.100, 0.010, and 0.005 M in NaOH were investigated. The vessel was placed on a vacuum line and the solvent was degassed. The vessel was then removed from the vacuum line and the solvent was mixed with the salt in the side arm. When mixing was complete, the vessel was connected to a Perkin-Elmer Hitachi mass spectrometer, RMU-6E, and the gaseous contents analyzed.

Quantitative measurements of evolved oxygen were made with a Carle Detector vapor-phase chromatograph, using a 5A sieve column, starting at $-196°$ and programmed to 100°. The same reaction vessel employed for the mass spectrometric work was used. After degassing of solvent and mixing of solvent and iridium salt, the gaseous contents of the vessel were evacuated into a stainless steel flow-through sample flask immersed in

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(9) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1952, pp 340–348.

liquid nitrogen. The flask was then connected to the chromatograph. The peaks obtained were compared with those on calibration chromatograms. The calibration chromatograms were run from a known pressure of oxygen (0.50 ± 0.02 cm) in a flow-through sample flask of known volume (85.9 cm³).

Absorption spectra were taken on a Cary 14 spectrophotometer, Serial 244. Quartz absorption cells of 1- and 0.1-cm lengths were employed.

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The Rate and Stereochemistry of the Aquation of *trans*-Dichlorotetraamminecobalt(III)

By R. G. Linck

Studies of the rate and stereochemistry of the spontaneous aquation of Co(III) complexes continue to be an area of active research. Recently it was argued that all aquations in complexes of the type $Co(en)_2ACl^{n+}$ proceed by an activation process that is principally bond breaking in nature.[1] A recent analysis by Tobe[2] has supported this point of view and has correlated the value of the entropy of activation with stereochemical change. This correlation was primarily for complexes of the type $Co(en)_2ACl^{n+}$, although complexes in which the two ethylenediamine groups were replaced by 1,4,8,11-tetraazacyclotetradecane, 1,4,7,10-tetraazadecane, or 1,4,8,11-tetraazaundecane also fit the correlation. There exist in the literature sufficient data[3-8] to apply the correlation to one complex in which four ammonias replace the two ethylenediamines—$Co(NH_3)_5Cl^{2+}$. Although this complex satisfactorily fits Tobe's correlation,[9] a second example would be more conclusive. In addition, an early paper[10] on the rate of the aquation of $trans$-$Co(NH_3)_4Cl_2^+$ reported the absence of steric change in the first aquation step. Because this result would imply a significant difference

between the behavior of the tetraammine and the corresponding bis-ethylenediamine complex,[11] a reinvestigation of the rate and stereochemistry of the aquation of $trans$-$Co(NH_3)_4Cl_2^+$ was undertaken. In that investigation, reported herein, advantage is taken of the systematic variation of rate of reduction of Co(III) complexes by Fe(II) as the nonbridging ligands are varied[12] to analyze the composition of the solutions.

Experimental Section

The solutions of Co(III) complexes and the Fe(II) solutions used were the same as those previously described.[12] In experiments designed to determine the composition of a partially aquated solution of $trans$-$Co(NH_3)_4Cl_2^+$ it was important to remove as much Fe(III) from the ferrous ion solution as possible, for Fe(III) absorbs relatively strongly at the wavelength used. In order to remove the Fe(III), a degassed solution of ferrous perchlorate in perchloric acid was treated with amalgamated Zn until an aliquot showed very little absorption in the region of interest. The solution was then transferred to a vessel free of Zn under an atmosphere of N_2. The concentration of Zn^{2+} introduced into the solution by this process was negligible, because only a small fraction of the total Fe in the solution was initially Fe(III) and little H_2 evolution took place in the reduction step.

All kinetic runs were followed spectrophotometrically on a Cary Model 14 spectrophotometer equipped with a thermostated cell block.

Results and Discussion

Spectral Characteristics.—The aquation of $trans$-$Co(NH_3)_4Cl_2^+$ in 1.0 N $HClO_4$ is accompanied by a decrease in absorbance at 2530 Å, a wavelength where the molar extinction coefficient of $trans$-$Co(NH_3)_4Cl_2^+$ is 2.4×10^4 l. mol^{-1} cm^{-1}. However, at shorter wavelengths, the absorbance of the aquation products, cis- and $trans$-$Co(NH_3)_4H_2OCl^{2+}$ both absorb more strongly than does $trans$-$Co(NH_3)_4Cl_2^+$—the maximum for an equilibrium mixture of cis- and $trans$-$Co(NH_3)_4$-H_2OCl^{2+} is found at 2330 Å with ϵ 1.57×10^4 l. mol^{-1} cm^{-1}. The feature of these spectral characteristics that is of the most pertinence here is the observation that the absorbance near 2400 Å (depending on temperature) remains constant within ±1.0% during the time necessary to allow the aquation of $trans$-$Co(NH_3)_4Cl_2^+$ to proceed for 10 half-lives. As will be shown below, this is a time during which there is a substantial change in the concentrations of both the cis- and $trans$-chloroaquo species. Therefore, within experimental error, the extinction coefficients of the three species are equal at 2400 Å (ϵ 1.40×10^4 l. mol^{-1} cm^{-1}).

The Aquation of $trans$-$Co(NH_3)_4Cl_2^+$.—This process can be studied easily at a number of wavelengths because of the spectral similarity of the cis- and $trans$-chloroaquo species. The change in absorbance is largest at 2530 Å, and hence this wavelength was chosen for most extensive study. That both the products absorb approximately equally at this wavelength is established from the quality of the first-order plots—these plots

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(9) From the various sources,[3-7] a value of $\Delta H^{\ddagger}$ = 23.5 ± 1.0 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −6 ± 3 cal mol^{-1} deg^{-1} can be calculated. The fit of this negative $\Delta S^{\ddagger}$ to Tobe's correlation depends upon the assumption that the stereochemical consequences of the aquation of $Co(NH_3)_5Cl^{2+}$ are the same as those of $Co(NH_3)_5Br^{2+}$—see ref 8 for the experiments on the latter complex.

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