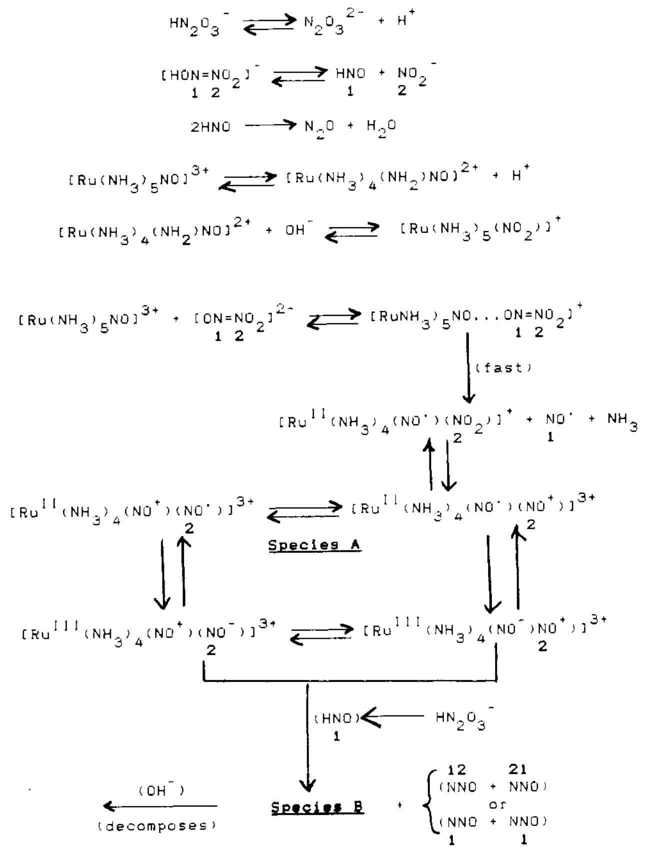
Scheme I



then one in which species A must rearrange to form yellow species B, with simultaneous production of N_2O. While our evidence is not sufficient to determine the detailed nature of this process, we speculate that an intermediate Ru(III) species containing NO^- may form by internal electron transfer and that loss of NO^- then leads to release of N_2O. While we have not succeeded in identifying species B, we note that it should be a Ru(III) complex, that we know it to be unstable in alkali, and that while the composition of its assumed precursor suggests that it may contain an NO^+ group, it does not analyze as a nitro complex.

The pH dependences of product distribution and k_1 may be explained in part by the conversion of pentaamminenitrosylruthenium(II) cation to the nitro species. This species would be unable to oxidize trioxodinitrate, so that as pH is increased, the rate of NO production would be expected to fall and the rate of conversion A → B to decrease as the fraction of complex present in the active form decreases. The apparent p*K* value 12.2 obtained from the pH–k_1 plot is consistent with the known pH dependence of the formation of nitro complex. We have not succeeded in identifying a protonation equilibrium associated with the apparent p*K* value 7.2 obtained at the low-pH end of the k_1–pH plot, which may indicate the presence of a competing reaction.

The interpretations described above are summarized in Scheme I. It accommodates the evidence for production of NO from trioxodinitrate atom N-1 and for formation of some N_2O from N-1 (via NO^- produced in self-decomposition) in combination with a second N atom, whose origin is partly N-2 and partly NO^+. The N-2 and NO^+ nitrogen atoms become equivalent in Scheme I.

Finally, we call attention to the fact that the key step in this mechanism consists of an attack by the ruthenium-bound NO^+ group upon trioxodinitrate that results in rapid cleavage of its N=N bond. This feature is consistent with previously presented evidence that the catalytic cleavage of trioxodinitric acid to yield NO is initiated by HNO_2 nitrosation.[2]

Acknowledgment. We acknowledge the award of SERC studentships (to P.E.W. and H.L.W.) and the financial support of NATO (F.T.B. and M.N.H.) and the People's Republic of China (C.-S.L.).

Contribution from the Department of Chemistry,
University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Assessment of the π-Acceptor Capability of Selected Ligands Based on the Photoelectron Spectra of Ruthenium Ammine Complexes

Rex E. Shepherd,* Andrew Proctor, Wayne W. Henderson, and Terry K. Myser

Received March 24, 1987

ESCA spectra have been recorded for a series of Ru^{II} and Ru^{III} ammine complexes of general formula $[(NH_3)_5RuL]X_n$ (X^- = PF_6^-, Cl^-). Binding energy regions of the C_{1s}, $Ru_{3d_{3/2}}$, $Ru_{3d_{5/2}}$, and $Ru_{3p_{3/2}}$ photopeaks were studied. Binding energies were determined by using nonlinear-least-squares curve fitting. Δ equal to the binding energy difference for ($C_{1s} - Ru_{3d_{5/2}}$) has been used to assign a fractional increase in charge at the Ru^{II} center when L = a series of π-acceptor ligands: *N*-methylpyrazinium (CH_3pz^+), CO, dimethyl acetylenedicarboxylate ester (dmad), CO, pyrazine (pz), pyridine (py), and CH_3CN. Authentic Ru^{II} and Ru^{III} oxidation states were assumed for $[Ru(en)_3]ZnCl_4$, Δ = 5.1 eV, and $[Ru(NH_3)_6]Cl_3$, Δ = 2.5 eV, respectively. The π-acceptor order and effective Ru oxidation state were determined to be as follows: CH_3pz^+, 3.01 > CO, 2.88 > dmad, 2.73 > pz, 2.51 > CH_3CN, 2.31 > py, 2.20. Δ was also found to be linear in the value of $E_{1/2}$ for the $(NH_3)_5RuL^{3+/2+}$ couple. π-Donor ligands exhibit little influence on Δ for Ru^{III} derivatives; Δ = 2.4 ± 0.1 eV for 3,5-dimethylpyrazole, 4-(dimethylamino)pyridine, and 4-aminopyridine.

Introduction

Electron spectroscopy for chemical analysis (ESCA) is a technique that is used to determine the binding energies of core electrons. The binding energy is dependent not only on the given core level and atom of interest but also on initial- and final-state effects. Changes in the initial-state charge of the atom give rise to a small but measurable chemical shift. In addition, the final-state relaxation energy contributions, caused by screening of the core hole created by photoemission, give rise to considerable absolute binding energy shifts. If one assumes that relaxation energy contributions are constant in a series of similar compounds, then ESCA data can be approximately correlated with effective changes in oxidation state for the atom of interest and with the charge-transfer electron distributions. Previous work includes studies with platinum complexes,[1] ruthenium complexes,[2,3]

---

[1] Cook, C. D.; Wan, K. Y.; Gelius, U.; Hamrin, K.; Johansson, G.; Olsson, E.; Siegbahn, H.; Nordling, C.; Siegbahn, K. *J. Am. Chem. Soc.* **1971**, *93*, 1904.

[2] (a) Citrin, P. H. *J. Am. Chem. Soc.* **1973**, *95*, 6472. (b) Citrin, P. H.; Ginsberg, A. P. *J. Am. Chem. Soc.* **1981**, *103*, 3673.

[3] Matsumura-Inoue, T.; Ikemoto, I.; Umezawa, Y. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *102*, 131.

ethylenediamine and cyano complexes with various metals,[4] and iron cyanide complexes.[5,6]

The study by Cook et al. on $(PPh_3)_2PtL$ complexes establishes the dependence of ESCA photopeaks on the amount of electron density donated from the platinum atom to the ligand.[1] An assumption made was that L = Cl_2 constituted the case where the Pt was in the II oxidation state and L = $(PPh_3)_2$ had Pt in the 0 oxidation state. The expected linear relationship between the Pt $4f_{7/2}$ photopeak energy and the fractional amount of charge transfer occurring gave the following values: L = $PhC{\equiv}CPh$, 0.7 electron; C_2H_4, 0.8; CS_2, 1.3; O_2, 1.8.[1] These values were justified by comparison to other evidence, including crystal structure data, ^{13}C NMR data, and CNDO–MO calculations.

The ESCA results reported for the ruthenium complexes are particularly interesting. Citrin and Ginsberg have studied the Creutz–Taube ions $[(Ru(NH_3)_5)_2pz]^{4+,5+,6+}$ and found that distinct peaks corresponding to the Ru(II) and Ru(III) oxidation states are found in both the Ru 3d and Ru 3p ESCA spectra.[2] The mixed-valence ion $[(NH_3)_5RupzRu(NH_3)_5]^{5+}$ contains both Ru(II) and Ru(III) peaks, which are separated by 2.1 eV in the 3p region and 2.3 eV in the 3d region.[2b] This in itself does not imply that the Creutz–Taube ion is a valence-localized case in its ground state, since the photoionized state will be localized. Nevertheless, observation of separate peaks encourages one to probe the charge transfer of other Ru complexes with ESCA.

When $Ru^{II}(bpy)_2L$ complexes are investigated, a linear correlation between the energy of the Ru 3d photopeaks and the reduction potential as determined by cyclic voltammetry is seen.[3] The oxidation peak potential shifts in the negative direction in the order L = $(py)_2 < (NH_3)_2 <$ en $< (CN)_2$, and as expected, the valence energy becomes higher in the same order.[3] The success of these studies appears to hinge upon the use of a closely related series of complexes, however, so that the ESCA shifts are determined only by the valence-electron distribution in the ground state with relaxation effects of the excited states held nearly constant.

The study presented here contains the data for eight complexes of the type $[Ru(N)_5L]X_n$, where N = saturated nitrogen donor (ammonia or ethylenediamine), L = variable ligand, and X = Cl^-, PF_6^-, or $ZnCl_4^{2-}$. This limited set of data follows the trend established in the previous studies[1–6] but presents an examination of a greater variety of π-acceptor ligands than has been attempted by prior workers. The ligands surveyed here include the key cases of CO, a substituted acetylene, a nitrile, and the pyridine/pyrazine N-heterocycles.

Experimental Section

Ruthenium Complexes. $[Ru(NH_3)_6]Cl_3$ was obtained from Johnson Matthey Chemicals Ltd. and recrystallized from HCl by standard laboratory procedures.[7] $[Ru(NH_3)_5Cl]Cl_2$ was prepared from the hexaammine by standard methods.[8] The $[Ru(NH_3)_5L]X_2$ complexes (X = Cl^-, PF_6^-) were prepared by modifications of the Taube syntheses.[9] The details for preparations with L = dmad and the N-heterocyclic members (methylpyrazinium, pyridine, and pyrazine) have been described elsewhere.[10,11] The $[Ru(NH_3)_5CO](PF_6)_2$ complex was prepared fresh for analysis by bubbling purified CO through a solution of $[Ru(NH_3)_5OH_2]Cl_2$ prepared by Zn/Hg reduction of $[Ru(NH_3)_5Cl]Cl_2$ and precipitation of the $[Ru(NH_3)_5CO](PF_6)_2$ salt upon adding saturated NH_4PF_6. The ν_{CO} for the complex (1920 cm^{-1}) agreed with literature values (1918, 1955 cm^{-1}) for the complex prepared by two other methods.[12,13] Products were characterized previously by ^{13}C and ^1H NMR methods, differential-pulse voltammetry, and UV–visible spectroscopy.[10,11,24]

Table I. ESCA Spectral Parameters[a] for Ru(II) and Ru(III) Ammines (eV)

		$E(Ru_{3d_{5/2}})$	$\Delta = E(C_{1s}-Ru_{3d_{5/2}})$
A	$[Ru(en)_3]ZnCl_4$	279.5	5.1
B	$[Ru(NH_3)_5(py)](PF_6)_2$	280.0	4.6
C	$[Ru(NH_3)_5(NCCH_3)](PF_6)_2$	280.3	4.3
D	$[Ru(NH_3)_5(pz)](PF_6)_2$	280.8	3.8
E	$[Ru(NH_3)_5(dmad)](PF_6)_2$	281.3	3.2
F	$[Ru(NH_3)_5CO](PF_6)_2$	281.8	2.8
G	$[Ru(NH_3)_6]Cl_3$	282.1	2.5
H	$[Ru(NH_3)_5(CH_3pz^+)]Cl_3$	282.2	2.4
I	$[Ru(NH_3)_5(3,5\text{-dmpyz})]Cl_3$	282.2	2.4
J	$[Ru(NH_3)_5(dmapy)]Cl_3$	282.2	2.4
K	$[Ru(NH_3)_5(4\text{-ampy})]Cl_3$	282.3	2.3

[a] ±0.2 eV estimated error in Δ (except E, see text), en = ethylenediamine, py = pyridine, pz = pyrazine, dmad = acetylenedicarboxylate dimethyl ester, CH_3pz^+ = N-methylpyrazinium cation, 3,5-dmpyz = 3,5-dimethylpyrazole, dmapy = 4-(dimethylamino)pyridine, 4-ampy = 4-aminopyridine.

ESCA Spectra. ESCA spectra were recorded with an HP 5950 photoelectron spectrometer using monochromatic Al Kα X radiation (600 W, $h\nu$ = 1486.6 eV). Samples were mounted on double-sided tape, and spectra were recorded at ambient temperature with a chamber pressure below 10^{-9} Torr. Data accumulation was comparatively slow due to the use of the monochromator, but no sample degradation as a result of X-ray bombardment was apparent. Data were collected on an IBM PC, which controlled the spectrometer via a custom-made interface. Further data manipulations were carried out on a DEC-10 computer using a TOPS-10 operating system. Excessive positive charging of the insulating samples as a result of X-ray photoionization was limited by use of an electron flood gun. However, it is still necessary to calibrate the energy scale by using some reference peak of known binding energy. (N.B. The linearity of the spectrometer over 0–1000 eV was ±0.1 eV.) When direct measurement of the Fermi level is not possible, it is always better to choose an internal reference rather than an external calibrant such as vacuum-deposited gold or "adventitious carbon" from the vacuum system. The gold deposition method, favored in the early years of ESCA, has certain problems that do not make it a particularly reliable method for calibration. This arises because the Au 4f binding energy varies significantly depending on whether the gold atoms are at the surface, are in the bulk, or constitute small particles. Thus the accuracy of this calibration is very dependent on the uniformity and thickness of the deposited gold layer. In addition, the assumption that the deposited material is in good electrical contact with the sample atoms is also questionable. Therefore in this work we chose to utilize the C_{1s} line as the reference for energy calibration. For the majority of the materials the major C_{1s} signal will be due to carbon associated with the ligand although some fraction of the C_{1s} intensity will be adventitious carbon. The latter is the only source of C in sample G. The reference binding energy peak (i.e. lowest energy C_{1s} peak) was assumed to be 284.6 eV (from adventitious carbon on gold foil, $Au_{4f_{7/2}}$ = 84.0 eV).

As an aid in the determination of peak position in overlapped regions the spectra were curve-fit by using a nonlinear-least-squares program incorporating a mixed Gaussian/Lorentzian line shape.[14]

Results

The ESCA spectra of a series of Ru^{II} and Ru^{III} complexes were obtained. The data are presented in Table I for the positions of the $Ru_{3d_{5/2}}$ photoemission peak and the shift difference, Δ. Of critical importance in this work is the accuracy with which the $Ru_{3d_{5/2}}$ binding energy can be determined. In some cases the $Ru_{3d_{3/2}}/C_{1s}$ overlap can be a significant problem in measurement of the C_{1s} energy for calibration. For the most part, in this work, the $Ru_{3d_{5/2}}$ peaks are generally weaker in intensity than the associated carbon peaks. Since the $Ru_{3d_{3/2}}$ peak is about 69% as intense as the $Ru_{3d_{5/2}}$ peak, the C_{1s} peak will tend to dominate the $Ru_{3d_{3/2}}/C_{1s}$ combined envelope in these cases. Thus measurement of $\Delta = E(C_{1s}-Ru_{3d_{5/2}})$ can be fairly accurately gauged by simply choosing the peak maxima. However, to add a level of consistency

---

(4) Sano, M.; Yamatera, H. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2023.

(5) Fluck, E.; Inoue, H.; Nagao, M.; Yanagisawa, S. *J. Inorg. Nucl. Chem.* **1979**, *41*, 287.

(6) Yatsimirskii, K. B.; Nemoshkalenko, V. V.; Nazarenko, Yu. P.; Aleshin, V. G.; Zhilinskaya, V. V.; Tomashevsky, N. A. *J. Electron Spectrosc. Relat. Phenom.* **1977**, *10*, 239.

(7) Shepherd, R. E. Ph.D. Thesis, Stanford University, 1971.

(8) Vogt, L. H.; Katz, J. L.; Wiberley, S. E. *Inorg. Chem.* **1965**, *4*, 1157.

(9) Ford, P.; Rudd, DeF. P.; Gaunder, R. G.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1187.

(10) Henderson, W. W.; Bancroft, B. T.; Shepherd, R. E.; Fackler, J. P. *Organometallics* **1986**, *5*, 506.

(11) Johnson, C. R.; Shepherd, R. E. *Synth. React. Inorg. Met.-Org. Chem.* **1984**, *14*, 339.

(12) Stanko, J. A.; Starinshak, T. W. *Inorg. Chem.* **1969**, *8*, 2156.

(13) Campbell, C. H.; Dias, A. R.; Green, M. L. H.; Saito, T.; Stanwick, M. G. *J. Organomet. Chem.* **1968**, *14*, 349.

(14) Proctor, A.; Hercules, D. M. *App. Spectrosc.* **1984**, 505.

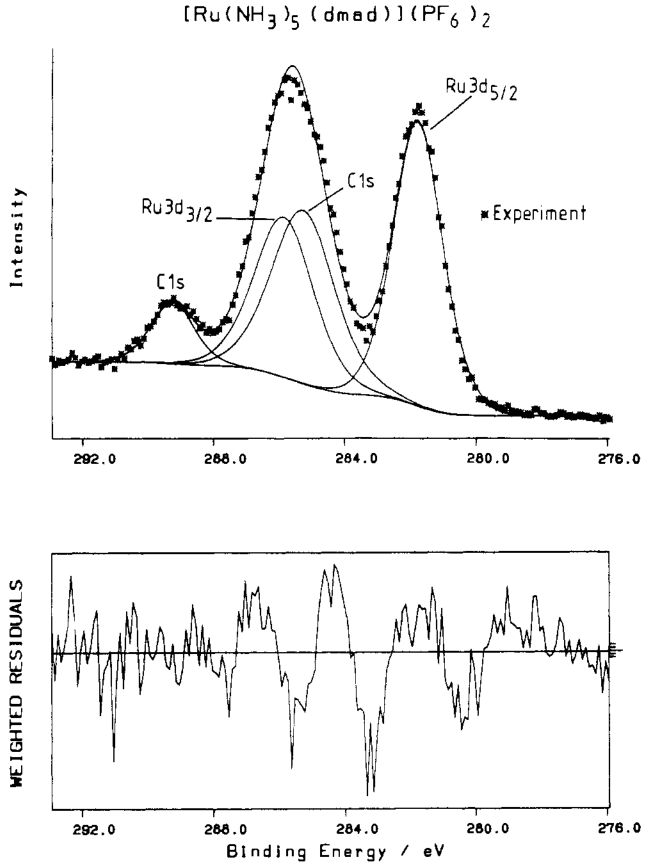


Figure 1. C_{1s}/Ru_{3d} spectrum of $[Ru(NH_3)_5(dmad)](PF_6)_2$ curve-fit by using two C_{1s} peaks.

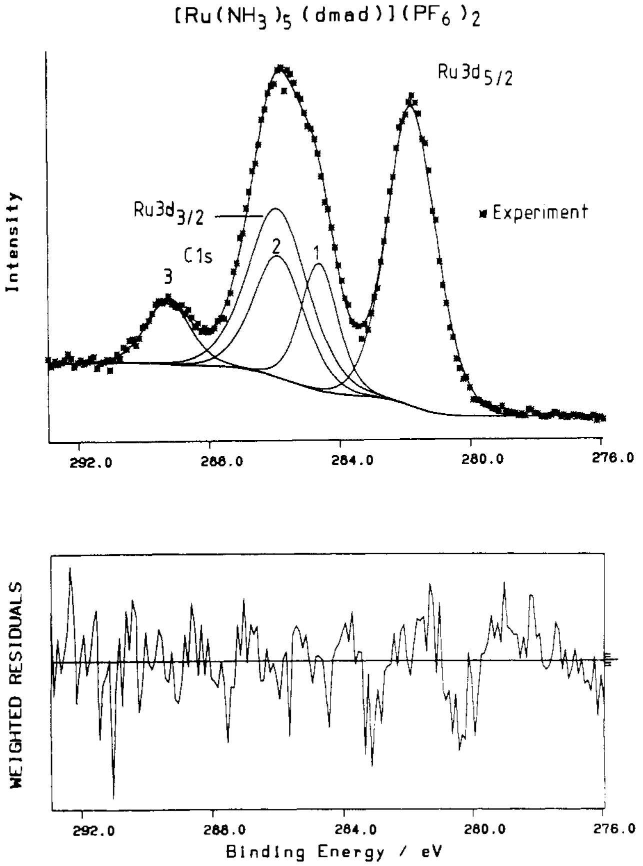


Figure 2. C_{1s}/Ru_{3d} spectrum of $[Ru(NH_3)_5(dmad)](PF_6)_2$ curve-fit by using three C_{1s} peaks.

to the analysis, all spectra were curve-fit to aid in determining the correct peak positions. Most results were very similar to the simple "by hand" estimates; however, sample E ($[Ru(NH_3)_5(dmad)](PF_6)_2$) did prove more difficult to analyze. Since this is a pivotal sample, it is worth examining in more detail.

Fitting parameters for the Ru_{3d} doublet were as follows: spin–orbit separation = 4.1 eV;[15] $Ru_{3d_{3/2}3d_{5/2}}$ area ratio = 0.69.[16] In addition, the $Ru_{3d_{3/2}}$ peak width was constrained to be 20% greater than that of the $3d_{5/2}$ peak.[15] This latter restriction comes about because of core hole lifetime considerations, whereby the $Ru_{3d_{3/2}}$ core hole can relax via a Coster–Kronig Auger transition, which decreases its lifetime. The $Ru_{3d_{5/2}}$ core hole has no such relaxation pathway. The nonlinear integral type background accounts for inelastic electron energy loss features.[14]

Figures 1 and 2 show the C_{1s}/Ru_{3d} spectrum of sample E curve-fit by using two and three carbon peaks, respectively. Visual comparison, particularly emphasized by the weighted residuals, clearly indicate that three carbon peaks produce a better fit. Statistically this is manifested in the weighted variances of the fits, which are 4.904 for two peaks and 2.690 for three peaks. Three C_{1s} peaks can be explained in terms of the constituents of the organic part of the ligand. Beginning at low binding energy, the peaks correspond to (1) aliphatic CC, CH, and C≡C, (2) –CO (ester), and (3) $-CO_2^-$ (carboxyl). While the improvement in variance after using two and then three peaks is significant, further analysis is suggested because the width of the first C_{1s} peak is narrower (1.3 eV) than might be expected for this type of sample.

Figure 3 shows the same spectrum, fit by using only the Ru_{3d} doublet. The base line displacement serves to display the two-component peaks better. In this case the residual plot is of particular interest since it is simply the difference spectrum, which should be the C_{1s} spectrum alone. Slight asymmetry of the main peak of the difference spectrum suggests the presence of at least two C_{1s} components but this is not overwhelming evidence. Clearly the results of the fits and the difference spectrum are very de-

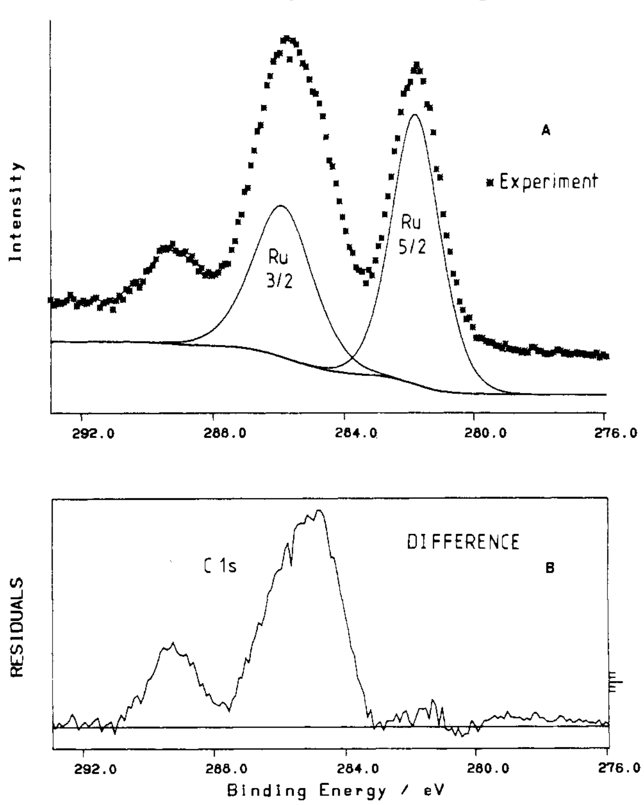


Figure 3. Ru_{3d} spectrum of $[Ru(NH_3)_5(dmad)](PF_6)_2$ curve-fit by using no C_{1s} peaks.

---

(15) *Handbook of X-ray Photoelectron Spectroscopy*; Merilerberg, G. E., Ed.; Perkin-Elmer Corp.: Eden Prairie, MN, 1979.

(16) Scofield, J. H. *J. Electron Spectrosc. Relat. Phenom.* **1976**, *8*, 129.

(17) Maartenson, N.; Nyholm, R. *Phys. Rev. B.* **1981**, *24*, 7121.

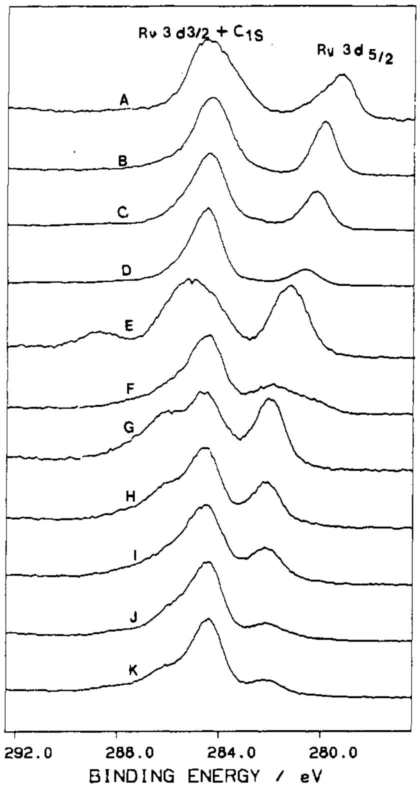


Figure 4. Ru_{3d} and C_{1s} intensity binding energy profiles for compounds listed in Table I.

pendent upon the chosen Ru_{3d} line shape.

Variation of the spin-orbit splitting, area ratio, or peak widths can cause significant differences. In order to try to gauge the best value for Δ, we can consider all three possibilities. It should be remembered that the best fit in a statistical sense does not mean it is the true explanation in a chemical or spectroscopic sense.

Using the results of Figures 1 and 2 gives values for Δ of 3.5 and 2.8 eV, respectively. Use of the peak maximum of the difference spectrum in Figure 3B vs. the $Ru_{3d_{5/2}}$ line of Figure 3A gives approximately Δ = 3.2 eV. This latter value roughly splits the first two values, as may be expected. Since use of the difference spectrum maximum is very similar to the approach used in the measurements of the other Δ values, it seems to produce the most appropriate value of Δ for sample E. It should be noted that the associated error for the dmad complex is larger than in the other cases (±0.4 vs. ±0.2 eV). The appearances of the ESCA spectra for compounds A–K are shown for the $Ru_{3d_{3/2}}$, C_{1s}, and $Ru_{3d_{5/2}}$ photopeaks in Figure 4 and for $Ru_{3p_{3/2}}$ in Figure 5. The shift difference relative to C_{1s} (Δ) has been plotted against the standard reduction potential $(E_{1/2})^{10,12,25}$ for the $(NH_3)_5RuL^{3+/2+}$ couple in Figure 6.

All the $[Ru^{II}(NH_3)_5L](PF_6)_2$ complexes exhibit Δ values between those for $[Ru(en)_3]ZnCl_4$ and $[Ru(NH_3)_6]Cl_3$. If the Δ value for $[Ru(en)_3]ZnCl_4$ is taken as the authentic Δ value for a Ru(II) complex having no back-donation to the ligands and the Δ value for $[Ru(NH_3)_6]Cl_3$ is assigned the value for a Ru(III) complex, the Δ values of the other complexes may be taken to represent a linear increase in fractional charge for each $[Ru^{II}(NH_3)_5L](PF_6)_2$ complex. The implied effective oxidation state of the Ru center is then observed to be as follows for the $[Ru(NH_3)_5L]X_2$ ($X = PF_6^-, Cl^-$) complexes (L, oxidation state): py, 2.20; CH_3CN, 2.31; pz, 2.51; dmad, 2.73; CO, 2.88; CH_3pz^+, 3.01.

Discussion

It is apparent from the data in Table I that for the Ru(II) complexes (A–F) an increase in Δ occurs upon changing the π-acceptor ability of the sixth ligand in $[Ru(NH_3)_5L]X_2$ complexes. The largest Δ occurs for A, $[Ru(en)_3]ZnCl_4$, in which a Ru(II) center is coordinated by saturated ethylenediamine ligands with no π-acceptor character. The value of Δ decreases to ca. 2.4 ± 0.1 eV for all of the Ru(III) complexes (G–K) including the ammine salt, $[Ru(NH_3)_6]Cl_3$. $[Ru(NH_3)_6]Cl_3$ has a Δ value of 2.5; the NH_3 ligand also has no π-donor ability and therefore is a useful reference for other π-donors. Other π-donor ligands including 3,5-dmpyz, dmapy, and 4-ampy, which are known to introduce LMCT bands into the spectra of the Ru(III) ammines, giving rise to the dark red to blue colors of these compounds, do not show any significant differences in Δ from one π-donor to another. Yet the influence of the π-acceptor ligand is significant. The same sensitivity toward π-acceptor ligands and insensitivity toward π-donors have been observed in the electrochemistry of these compounds.[11] The ESCA data imply a π-acceptor order that is the same as indicated by prior work based on $E_{1/2}$ values[11] spectral data,[18] or equilibrium[19,20] data from which estimates of π-acceptor strength have been made: CH_3pz^+ > CO > dmad > pz Δ CH_3CN > py ≫ NH_3. This π-acceptor order is supported by the reasonably linear correlation of Δ vs. $E_{1/2}$

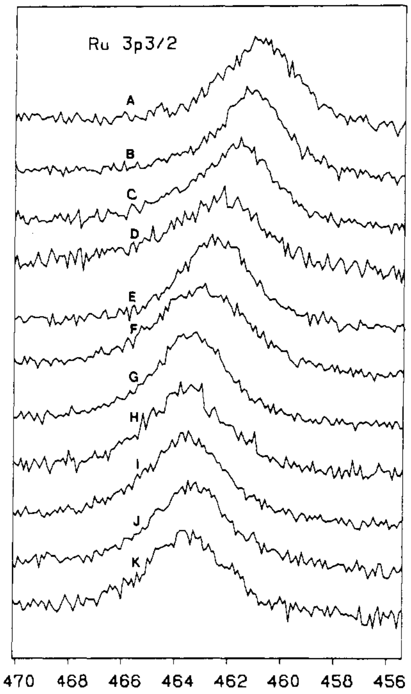


Figure 5. Ru_{3p} intensity/binding energy profiles for compounds listed in Table I.

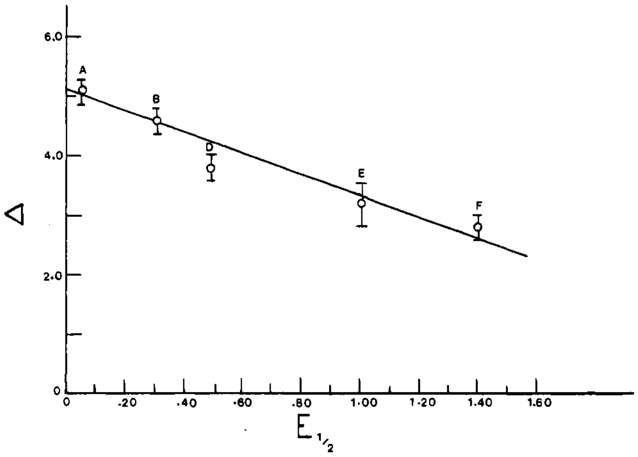


Figure 6. Linear correlation of Δ and $E_{1/2}$ values of $(NH_3)_5RuL^{3+/2+}$ couples: (A) $(en)_3$; (B) py; (D) pz; (E) dmad; (F) CO. Reduction potentials are taken from ref 10, 11, and 25.

---

[18] Zwickel, A. M.; Creutz, C. *Inorg. Chem.* **1971**, *10*, 2395.

[19] Wishart, J. F.; Taube, H.; Breslauer, K. J.; Isied, S. S. *Inorg. Chem.* **1984**, *23*, 2997.

[20] Siddiqui, S.; Henderson, W. W.; Shepherd, R. E. *Inorg. Chem.*, in press.

shown in Figure 6. Similar behavior was noted for $Ru(bpy)_2L_2^{3+/2+}$ data.[3] The interesting additional information to be obtained from our studies is an estimate of the extent of fractional charge transfer from the Ru(II) center into the ligand π-acceptor orbitals, i.e.

$$\underset{1.0}{CH_3pz^+} > \underset{0.88}{CO} > \underset{0.73}{dmad} > \underset{0.51}{pz} > \underset{0.31}{CH_3CN} > \underset{0.20}{py}$$

The estimate for the $Ru(NH_3)_5pz^{2+}$ ion is modestly higher than the 0.20 electron (22% ligand character to the ground-state MO),[21,22] which has been estimated from the ground- and excited-state pK_a's. Protonation is sure to alter the solvation in the resultant $Ru(NH_3)_5(pzH)^{3+}$ complex, and this could lead to a small error in the estimate of the extent of back-donation from Ru(II) by the pK_a method.[19] The results here are in good agreement with the estimates of Zwickel and Creutz based on $Ru(NH_3)_4L_2^{2+}$ spectra.[18] The result that CO and the coordinated acetylenic unit occurs with more significant charge transfer than the N-heterocycles is in keeping with prior studies.[10,23,24] This effect has been attributed to the synergistic stabilization of π-accepting/σ-donating with small molecules with triple bonds (e.g. CO, CN^-, R_2C_2, N_2, NO^+).[23] Cook et al. estimated 0.8 ± 0.2 electron transferred from $Pt(PPh_3)_2Pt(C_2H_4)$ and 1.8 ± 0.2 for O_2 as the acceptor.[1] Assuming less good π-donation from a d^6 Ru(II) center compared with a d^{10} Pt(0) center, one might anticipate that C_2H_4 or dmad would receive a somewhat smaller charge from Ru(II). This is observed with ~0.7 electron received with dmad.

Citrin has studied the Creutz–Taube ion in some detail.[2] Values for Δ in these complexes were taken from their published spectra. The (II,II) complex, $[(NH_3)_5Ru]_2pz^{4+}$, shows a Δ value of 4.2 eV compared to the 3.8-eV difference for $[Ru^{II}(NH_3)_5pz](PF_6)_2$ in our work. Similarly Citrin's data[2a] give a Δ value of 1.8 eV for the (III,III) complex compared to 2.4 ± 0.1 eV for Ru(III) complexes in this work. The mixed-oxidation-state (II,III) complex has Δ values of 4.1 eV for the "Ru^{II} site" and 1.8 eV for the "Ru^{III} site".[2a] This is in reasonable agreement with the data presented in Table I for 11 compounds in which Δ values for Ru(II) complexes are larger than those for Ru(III) complexes unless the strongest π-acceptor, CH_3pz^+, is present.

Conclusions

The ESCA spectra of the Ru(II) pentaammines have given a reasonable order to the π-acceptor series of $CH_3pz^+ > CO >$ dmad > pz > CH_3CN > py. The calculated values of fractional electron transfer from the Ru(II) site to the π-acceptor ligands are in concert with estimates in the literature that were derived on the basis of titration data[19] and UV–visible spectra of complexes.[18] The values reported here on the basis of ESCA would seem to be a more reliable quantitative estimate of the extent of back-donation in these complexes because the influence of solvation on the values of the other methods has been minimized by use of a similar series of salts.

Acknowledgment. We gratefully acknowledge support for this work through grants from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and from the National Science Foundation (CHE 8417751). We also express appreciation to D. M. Hercules for use of the HP 5950 ESCA spectrometer in the Surface Science Center of the University of Pittsburgh. Preliminary assistance by J. Ledford with the ESCA spectra of a few trial compounds is gratefully acknowledged.

---

(21) Taube, H. *Survey of Progress in Chemistry*; Scott, A. F., Ed.; Academic: New York, 1973; Vol. 6, Chapter 1.

(22) Johnson, C. R.; Shepherd, R. E. *Inorg. Chem.* **1983**, *22*, 1117.

(23) Kuehn, C.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689.

(24) Johnson, C. R.; Shepherd, R. E. *Inorg. Chem.* **1983**, *22*, 3056.

(25) (a) Johnson, C. R.; Henderson, W. W.; Shepherd, R. E. *Inorg. Chem.* **1984**, *23*, 2754. (b) Johnson, C. R. Ph.D. Thesis, University of Pittsburgh, 1983. (c) Henderson, W. W. Ph.D. Thesis, University of Pittsburgh, 1986.

(26) Isied, S. S.; Taube, H. *Inorg. Chem.*, **1976**, *15*, 3070.

Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

Kinetics of Base Hydrolysis of Cyanogen and 1-Cyanoformamide

Yi Lai Wang, Hsiupu D. Lee, Mark W. Beach, and Dale W. Margerum*

Received February 11, 1987

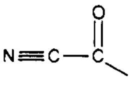
The rate of cyanogen hydrolysis in base is first order in OH^- and first order in $(CN)_2$, but the reaction proceeds by two paths. Only 25% at 5 °C to 33% at 40 °C of the cyanogen reacts directly by C–C bond cleavage to give CN^- and OCN^- ($k_1 = 8.9 \times 10^2$ M^{-1} s^{-1} at 25.0 °C, $E_a = 15.8$ kcal mol^{-1}). The rest of the cyanogen forms 1-cyanoformamide via a second path ($k_2 = 2.17 \times 10^3$ M^{-1} s^{-1} at 25.0 °C, $E_a = 13.8$ kcal mol^{-1}). A common reactive intermediate, $N{\equiv}CC(OH){=}N^-$, is postulated for the k_1 and k_2 paths. The 1-cyanoformamide that forms also decomposes by C–C bond cleavage, but at a much slower rate than cyanogen. The reaction proceeds by deprotonation of 1-cyanoformamide (pK_a = 10.8) to give $N{\equiv}CC({=}O)NH^-$, which reacts to give CN^- and OCN^- ($k_3 = 0.556$ s^{-1} at 25.0 °C, $E_a = 22.5$ kcal mol^{-1}).

Introduction

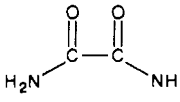
Cyanogen is often considered to be a pseudohalogen, and its hydrolysis reaction in base (eq 1) is written to parallel the hydrolytic disproportionation of halogens.[1,2] Evidence for this reaction and preliminary information about its rate were obtained from conductivity studies of Naumann[3] in 1910. No kinetics studies of base hydrolysis of cyanogen have been reported since this early work, with the exception of an unsuccessful attempt to reanalyze Naumann's limited data.[4] In fact, very little information[5] is available about the UV spectrum and molar absorptivity of cyanogen in aqueous solution or about the rate and products of its hydrolysis in acidic, neutral, or basic solutions.

$$(CN)_2 + 2OH^- \rightarrow CN^- + OCN^- + H_2O \qquad (1)$$

It is known that in weakly acidic solution cyanogen hydrolyzes to give 1-cyanoformamide (**1**) and that in very strong acid oxamide (**2**) is formed.[6] Hydrolysis of cyanogen in the presence of



1



2

---

(1) Durrant, P. J.; Durrant, B. *Introduction to Advanced Inorganic Chemistry*; Longmans: London, 1962; p 581.

(2) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 368.

(3) Naumann, R. *Z. Elektrochem.* **1910**, *18*, 772–778.

(4) Kuhn, A. T.; Rice, C. L. *Oberflaeche-Surf.* **1977**, *18*, 119–123.

(5) Brotherton, T. K.; Lynn, J. W. *Chem. Rev.* **1959**, *59*, 841–883.

(6) Welcher, R. P.; Castellion, M. E.; Wystrach, V. P. *J. Am. Chem. Soc.* **1959**, *81*, 2541–2547.