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A Raman Study of Complex Formation by Mercury(II), Acetone, and Nitrate Ion in Aqueous Solution[1]

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Received January 27, 1964

Raman spectra of aqueous solutions of acetone and mercuric perchlorate or mercuric nitrate show that reaction occurs between mercuric ion and acetone to produce a complex in which the acetone is bound in the enolate form. Consistent with this formulation are the observations that a proton has been dissociated and that the product reduces MnO_4^- and Br_2. When nitrate ion is also present, Raman spectra show it to also be bound in the resulting complex. Job plots of Raman intensities establish the predominant species to contain equimolar amounts of Hg(II), acetone enolate, and nitrate.

Introduction

In acetone–water mixtures, it has been shown by absorption spectra that cupric ion coordinates acetone molecules[2] and that nickelous and cobaltous ions do likewise.[3] In order to extend such studies to colorless ions and to detect any changes occurring within acetone molecules on coordination, the present Raman spectrophotometric study was undertaken. It was found that for zinc and cadmium ions, the behavior is apparently similar to that found for Cu^{2+}, Ni^{2+}, and Co^{2+} and manifests itself in a *ca.* twofold enhancement of the acetone Raman bands at 490 and 530 cm.$^{-1}$ relative to the carbonyl band at 1710 cm.$^{-1}$. However, for Hg^{2+} much more drastic changes are evident from the Raman spectrum. The present paper presents the results for the mercuric–acetone solutions which were obtained in order to determine the nature of the species formed.

It is perhaps not surprising that significant changes occur when acetone coordinates to mercuric ion in solution, since previous workers have found evidence for such changes under more drastic conditions. Morton and Penner have studied mercuric halides in various ketones under nearly anhydrous conditions where mercury–carbon bonds appear to form which leave the carbonyl function intact.[4] In the presence of base, Fernandez, Snider, and Rietz have found that on coordination to mercuric chloride, acetone molecules quantitatively lose protons.[5] The present paper presents both Raman data and chemical evidence pertinent to the characterization of species formed between Hg(II) and acetone in acidic aqueous solution. For simplicity, mercuric perchlorate and mercuric nitrate were used as Hg(II) sources.

Experimental

The Raman spectra of the reaction mixtures were taken with a Cary Model 81 recording spectrophotometer with the 4358 Å. mercury line used to excite the spectra. The sample holders used contained Liebig-like jackets through which a light-filter solution was circulated to remove interfering mercury lines and to thermostat the samples at 25°. The filter solution consisted of *o*-nitrotoluene and ethyl violet dissolved in isopropyl alcohol. Around the outer jacket was a polaroid screen oriented so that the electric vector of the incident light was perpendicular to the tube axis. In order to correlate the observed Raman intensities from sample to sample, standards were used which corrected for refractive index and lamp intensity changes. Whenever possible, the A_1 line of ClO_4^- was used as an internal standard. In some cases, because of overlap of the emission bands of ClO_4^- and the bands of the species studied, the A_1 line of CCl_4 was used as an external standard. This external standard, while it corrects for changes in lamp intensity, cannot correct for refractive index changes of the solutions. Measurements of refractive index, using the sodium D-line at 25°, of a series of solutions representing the complete scale of mercuric and acetone concentrations studied showed that the outer limit deviation was less than 1%. No refractive index correction was applied.

The integrated band intensities were measured as follows. The spectrum of each solution studied was scanned from the Rayleigh line to beyond the region in question to determine the over-all shape of the background. The standard and sample bands were alternately scanned from at least 100 wave numbers before and beyond the band maximum. The background was drawn in and both bands were then traced with a compensating polar planimeter (Keuffel and Esser Co.). The precision with which this instrument was found to measure was within 1%.

Depolarization ratios, ρ, were determined by measuring the desired integrated band intensities using perpendicular and parallel polarizers alternately. The true experimental values of depolarization ratios were not directly obtainable experimentally since the incident light is not completely parallel as it enters the sample and the polaroids are not 100% efficient. A correction curve was constructed from literature values of the best ρ_{true} values for CCl_4, CCl_3H, and C_6H_6 and compared to the ρ values obtained with our spectrophotometer. The equation which best fit the points was $\rho_{\text{true}} = 0.82(\rho_{\text{obsd}} - 0.18)$.

For the measurement of moderate H^+ concentrations (0.09–0.17 *M*) a Leeds and Northrup pH meter was used. For higher H^+ concentrations, methyl violet was used as a color indicator. Solutions of known H^+ concentration were prepared to which aliquots of a methyl violet solution were added. The samples were run immediately on a Cary Model 14 recording spectrophotometer at 430 mμ. Since the indicator was destroyed with time, the absorbancy values were extrapolated to zero time. A calibration curve of initial absorbancy *vs.* H^+ concentration was obtained and applied to solutions of unknown H^+ concentration.

Standard permanganate and bromine tests were made of reaction mixtures to detect the presence of olefinic groups. Blanks containing H^+ concentrations and acetone similar to the reaction mixtures were also tested and compared to the reaction mixtures.

Analytical reagent grade mercuric nitrate was used throughout

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[1] Abstracted from the thesis of Ralph R. Miano submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] N. J. Friedman and R. A. Plane, *Inorg. Chem.*, **2**, 11 (1963).

[3] R. F. Pasternack, Thesis, Cornell University, 1962.

[4] A. A. Morton and H. P. Penner, *J. Am. Chem. Soc.*, **73**, 3300 (1951).

[5] J. B. Fernandez, L. T. Snider, and E. G. Rietz, *Anal. Chem.*, **23**, 899 (1951).

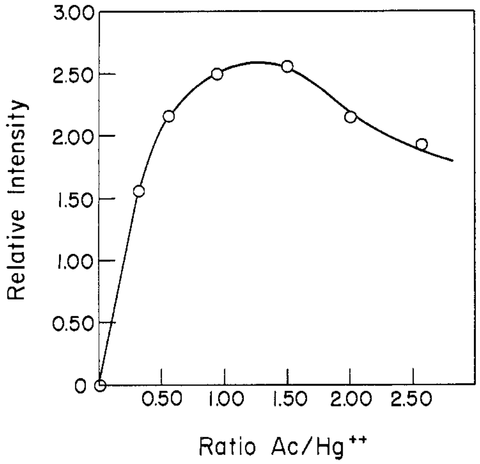

Fig. 1.—Raman intensities (relative to CCl_4) of the polarized band at 640 cm.$^{-1}$ for solutions in which the total initial concentration of mercuric ions plus acetone equals 4.50 *M*.

without further purification. Mercuric perchlorate solutions were prepared by dissolving mercuric oxide in perchloric acid. Analytical reagent grade acetone was used without further purification. Mercuric nitrate and perchlorate solutions were standardized by the thiocyanate method. The solutions in which Raman spectra were taken were prepared by transferring aliquots of standardized mercury(II) solutions and acetone to volumetric flasks and diluting to the mark with water or acid when necessary.

It was found from intensity measurements that at least 3 hr. was required for the aqueous solutions of Hg(II) and acetone to equilibrate. Before Raman spectra were taken, the samples were allowed to stand with intermittent shaking 4–5 hr. after the initial mixing.

Results

Raman spectra of 2.5 *M* $Hg(NO_3)_2$ plus 3 *M* acetone and of 2.5 *M* $Hg(ClO_4)_2$ plus 3 *M* acetone are given in Table I. All observed lines are listed except those due to H_2O or to free anions (NO_3^- or ClO_4^-). For comparison, the table also includes the spectrum of acidified aqueous acetone. Raman spectra of aqueous solutions of $Hg(NO_3)_2$ and $Hg(ClO_4)_2$ do not show the rich spectra observed for the Hg(II)–acetone solutions.[6] Thus, it seems clear that new species result from reaction of mercury salts with acetone. The additional lines observed when $Hg(NO_3)_2$ is used in place of $Hg(ClO_4)_2$ indicate that a species is formed which contains not only mercury and acetone, but also bound nitrate.

To obtain the relative numbers of acetone molecules, mercury(II), and nitrate ions which form the new species, a series of experiments was performed employing the Job method of continuous variation.[7] In order to obtain the relative numbers of mercury(II) ions and acetone molecules forming the new species, a series of solutions in which the total stoichiometric concentration of mercuric ions and acetone equalled 4.50 *M* was used. The intensities of the band at 640 cm.$^{-1}$ were measured for these solutions and are plotted *vs.* the ratio acetone/Hg^{2+} in Fig. 1. To obtain the relative numbers of nitrate ions and mercuric ions forming the species, a series of solutions at constant initial acetone concentration (2.71 *M*) was used with the total stoichiometric concentration of NO_3^- + Hg(II) equal to 3.82 *M*. Known amounts of sodium nitrate were added to mercuric perchlorate solutions to give the desired initial nitrate and mercuric ion concentrations. The intensities of the band at 295 cm.$^{-1}$ were measured for these solutions and are plotted *vs.* the ratio NO_3^-/Hg(II) in Fig. 2. From the data of Fig. 1 and 2, the predominant new species is seen to be formed from equimolar amounts of Hg(II), acetone, and NO_3^-.

Table I

Raman Spectra of Acidified Aqueous Solutions of Acetone, $Hg(ClO_4)_2$–Acetone, and $Hg(NO_3)_2$–Acetone[a]

Acetone	$Hg(ClO_4)_2$–acetone	$Hg(NO_3)_2$–acetone
		295 m, $\rho = 0.32$
395 w	410 w, sh	410 w, sh
	460 s	454 s, $\rho = 0.39$
490 w	490 w, sh	490 w, sh
530 m	544 m	544 m
	635 m	640 m, $\rho = 0.28$
		755 w
788 vs	800 w	800 w
903 w		1010 s
1070 w	1100 s	1098 s
1223 m	1240 w	1240 w
		1275 w
1350 m	1368 m	1368 m
1430 s	1427 s	1427 s
		1510 w
	1625 w, sh	1625 w, sh
	1670 s	1670 s, $\rho = 0.42$
1710 vs	1710 w, sh	1710 w, sh
2710 w	2710 w	2710 w
	2790 w	2790 w
2850 w	2850 w	2850 w
2930 vs	2930 vs	2930 vs
	2937 w, sh	2937 w, sh
2970 s	2970 s	2970 s
3020 s	3020 s	3020 s
	3055 w	3055 w

[a] Bands of free nitrate and perchlorate not included. Abbreviations: w, weak; m, medium; s, strong; vs, very strong; sh, shoulder; ρ, depolarization ratio.

Table II

H^+ Concentrations for Aqueous $Hg(NO_3)_2$–Acetone Solutions[a]

Hg(II), *M*	pH	H^+, *M*
0.062	1.02	0.09
0.087	0.89	0.13
0.122	0.77	0.17
0.148	0.72	0.19
0.183	0.65	0.22
0.209	0.60	0.25

[a] Stoichiometric concentration of acetone 0.541 *M* in all solutions.

It was observed that the hydrogen ion concentration increased when acetone was added to aqueous mercuric nitrate and perchlorate solutions, and a series of experiments was performed to correlate the equilibrium hydrogen ion concentration with the initial mercury and acetone concentrations. A solution of mercuric nitrate was prepared in which the initial hydrogen ion

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[6] R. E. Hester and R. A. Plane, *Inorg. Chem.*, **3**, 769 (1964).

[7] P. Job, *Ann. Chim.*, (10) **9**, 113 (1928).

concentration corresponded to that due to hydrolysis of mercury(II) alone. Aliquots of this solution were mixed with a known amount of acetone. The solutions were allowed to equilibrate (to constant pH), and the pH of the solutions was measured. The results, given in Table II, show that in every case more than one H^+ is produced per Hg(II). It was also found that reaction mixtures of aqueous Hg(II) and acetone decolorized permanganate and bromine immediately, whereas identical solutions lacking Hg(II) decolorized bromine very slowly, and permanganate not at all.

Conclusions

From the Raman results, it is evident that mercuric ion and acetone react in equimolar amounts to form a new species, which in the presence of nitrate ion also contains a bound nitrate ion. The loss of a proton from the species and the reaction with MnO_4^- and Br_2 indicate that the acetone is probably bound to the mercury as the enolate anion. The Raman spectrum of the species also supports this formulation. Thus, the appearance of the strong, polarized band at 1670 cm.$^{-1}$ indicates an olefinic group is present and the loss of the 788 cm.$^{-1}$ band indicates loss of the C–C–C structure. The strong band at 1100 cm.$^{-1}$ can be accounted for by vibrations, principally of the C–O–Hg grouping, and the bands at 2937 and 3055 cm.$^{-1}$ can be accounted for by ethylenic hydrogens.

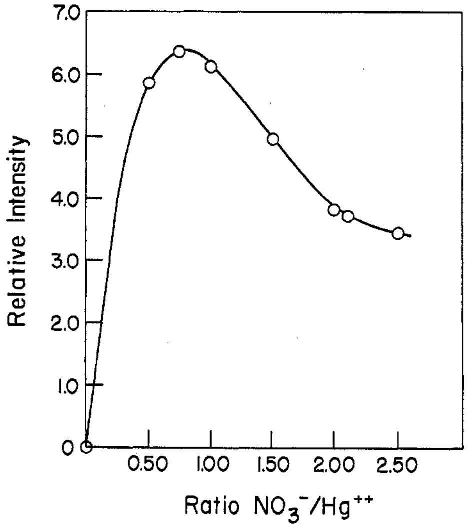

Fig. 2.—Raman intensities (relative to ClO_4^-) of the polarized band at 295 cm.$^{-1}$ for solutions in which the total initial concentration of mercuric plus nitrate ions equals 3.82 *M*.

For Hg(II)–acetone solutions which also contained NO_3^-, the additional Raman lines (not present for perchlorate solutions) observed at 295, 755, 1010, 1275, and 1510 cm.$^{-1}$ closely resemble the Raman spectrum of CH_3HgNO_3 observed by Goggin and Woodward.[8] For this compound in water they report lines at 292, 566, 762, 1001, 1204, 1289, 1420, 1505, 2941, and 3025 cm.$^{-1}$, of which those at 292, 762, 1001, 1289, and 1505 cm.$^{-1}$ are assigned to modes involving the bound nitrate group. It is interesting that the nitrate bound in both the acetone–Hg and the methyl–Hg species gives a considerably more prominent spectrum than does nitrate bound to the hydrated mercuric ion.[6] Apparently, the bonding of Hg to O in nitrate is significantly affected by the nature of other groups bound to Hg(II).

[8] P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, **58**, 1495 (1962).

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Formation and Spectra of Uranyl(V) Chloride in Molten Chloride Solvents[1]

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Received January 9, 1964

Additional studies have been made of the thermal decomposition of UO_2^{2+} in molten chloride solutions to form UO_2^+ and chlorine. An equilibrium constant of $1.2 \pm 0.6 \times 10^{-6}$ atm. at 650° was obtained in molten LiCl–KCl eutectic. Further decomposition of UO_2^+ to UO_2 and chlorine was observed under vacuum at 750°. Molar absorptivities are given for UO_2^+ spectra in a number of molten chloride solvents at various temperatures. Variations of the spectrum with changes in the solvent and temperature are attributed to differences in their influence on the U–O bonds.

Introduction

Spectrophotometric and chemical evidence for the existence of a soluble pentavalent uranium species, UO_2^+, in molten chloride solvents was reported previously.[2] This species can be formed in molten chlorides by several methods, including the reaction of UO_2 with UO_2Cl_2, the addition of U_3O_8 or UO_3 to the salt under vacuum, or the thermal decomposition of UO_2Cl_2. An equilibrium was found to exist between UO_2^{2+} and UO_2^+ in these solvents as represented by the following reactions.

$$Cl^- \rightleftharpoons {}^1/_2Cl_2 + e^- \qquad (1)$$

$$\underline{UO_2^{2+} + e^- \rightleftharpoons UO_2^+} \qquad (2)$$

$$Cl^- + UO_2^{2+} \rightleftharpoons UO_2^+ + {}^1/_2Cl_2 \qquad (3)$$

[1] This work performed under the auspices of the United States Atomic Energy Commission.

[2] M. D. Adams, D. A. Wenz, and R. K. Steunenberg, *J. Phys. Chem.*, **67**, 1939 (1963).