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.

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).

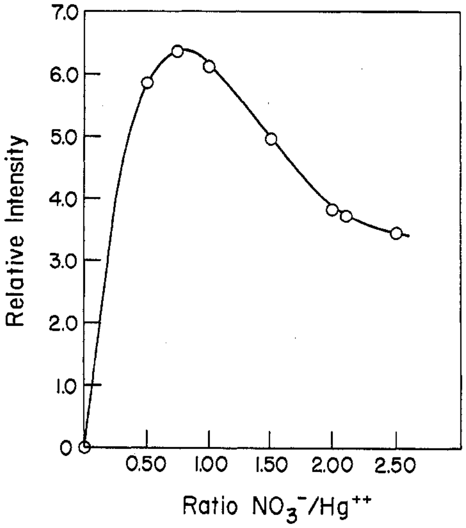

Fig. 2.—Raman intensities (relative to ClO_4^-) of the polarized band at 295 cm.$^{-1}$ for solutions in which the total initial concentration of mercuric plus nitrate ions equals 3.82 *M*.

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

CONTRIBUTION FROM THE CHEMICAL ENGINEERING DIVISION,
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Formation and Spectra of Uranyl(V) Chloride in Molten Chloride Solvents[1]

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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 ± 0.6 × 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.

$$\mathrm{Cl^-} \rightleftharpoons \tfrac{1}{2}\mathrm{Cl_2} + e^- \tag{1}$$

$$\underline{\mathrm{UO_2^{2+}} + e^- \rightleftharpoons \mathrm{UO_2^+}} \tag{2}$$

$$\mathrm{Cl^-} + \mathrm{UO_2^{2+}} \rightleftharpoons \mathrm{UO_2^+} + \tfrac{1}{2}\mathrm{Cl_2} \tag{3}$$

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[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).

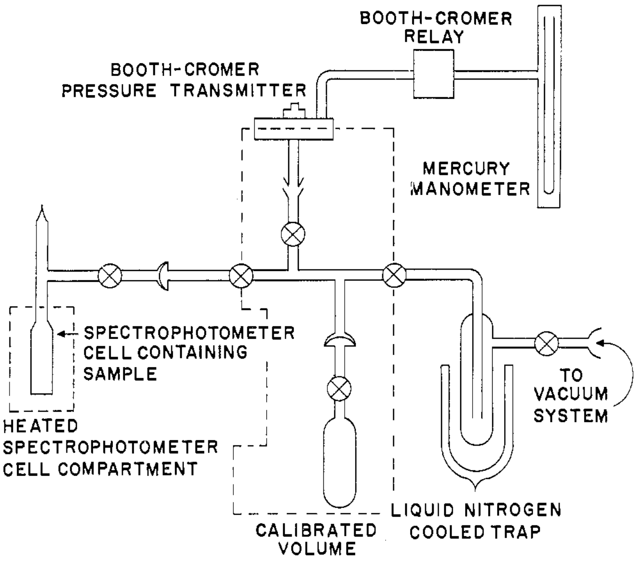

Fig. 1.—Gas measuring apparatus for spectrophotometric studies.

Earlier investigations of the spectra of uranium compounds[3–5] had not shown the presence of UO_2^+, probably because the equilibrium lies far to the left except at high temperatures and low chlorine pressures. In previous studies of the thermal decomposition of UO_2Cl_2 in molten salts, the only products reported were U_3O_8 and chlorine.[6]

Additional measurements have been made in order to provide further evidence for reaction 3, to determine the effects of variations in temperature and solvent on the absorption spectrum of UO_2^+, and to determine an equilibrium constant for reaction 3.

Experimental

The spectrophotometer, cell furnace, absorption cells, salt purification procedures, and techniques for introducing molten salt solutions into the cells were the same as described previously.[2] Uranyl chloride solutions were prepared either by the addition of anhydrous UO_2Cl_2 to the molten salt or by passing chlorine gas through a suspension of U_3O_8 in the salt at about 500°. All purified materials and samples were handled either under vacuum or in a helium-filled drybox.

The apparatus that was used for these studies is shown schematically in Fig. 1. A quartz spectrophotometer cell with a 1-cm. path length was attached by a side arm to a glass vacuum line equipped with a liquid nitrogen cold trap, a vacuum pump, and a Booth–Cromer pressure transmitter, a nickel diaphragm-type electronic pressure balancing device, leading to a mercury manometer. With this apparatus it was possible to obtain spectrophotometric data simultaneously with measurements of either the amount of chlorine evolved from the molten salt solution or the pressure of chlorine over the solution.

To provide further supporting evidence for reaction 3, several experiments were performed in which the system was evacuated, the spectrophotometer cell containing the UO_2^{2+} solution was brought to the desired temperature, and the chlorine that was released by the reaction was collected in the cold trap. The cell was then isolated from the vacuum line, and the quantity of chlorine was determined by allowing it to expand into a calibrated volume of the apparatus at room temperature and measuring the pressure. The procedure was repeated several times, additional chlorine being removed in each cycle. The absorbance resulting from the UO_2^+ in the solution was found to be directly proportional to the amount of chlorine collected, in accordance with reaction 3. Gas chromatographic analysis showed chlorine to be the only gaseous product of the reaction.

The same general procedure was used for UO_2^+ molar absorptivity determinations. The UO_2^+ concentrations in the solutions were calculated on the basis of reaction 3. Densities (in g. cm.$^{-3}$) of the eutectics, 59 mole % LiCl–41 mole % KCl and 30 mole % NaCl–20 mole % KCl–50 mole % $MgCl_2$, were obtained by extrapolation of the data of Raseman[7]

$$d_{\text{LiCl-KCl}} = 1.8885 - 0.527 \times 10^{-3}t \ (380\text{–}600°)$$

$$d_{\text{NaCl-KCl-MgCl}_2} = 2.226 - 0.778 \times 10^{-3}t \ (420\text{–}610°)$$

Equilibrium constants for reaction 3 were determined by simultaneous measurement of the optical absorbance and the chlorine pressure in equilibrium with the salt solutions. The UO_2^+ concentration in the solution was determined directly from the absorbance, and the UO_2^{2+} concentration was taken as the difference between the total uranium concentration and the concentration of UO_2^+. Chlorine pressures in the range of 2 to 15 mm. were measured directly with the Booth–Cromer pressure transmitter. Because of the low value of the equilibrium constant, however, it was necessary to extend the measurements to chlorine pressures that were below the useful range of the pressure transmitter. These low pressures were fixed by placing a low-temperature slush bath around the cold trap, so that the equilibrium chlorine pressure over the solution would be equal to the vapor pressure of solid chlorine in the cold trap. By using 2-methylbutane and 2,3-dimethylbutane slush baths at measured temperatures of −140 and −133°, respectively, chlorine pressures were obtained in the range of 0.03 to 0.7 mm. as calculated from the vapor pressure equation for chlorine.[8] Equilibrium constants obtained from the two methods of pressure measurement were in agreement. Data from experiments in which the equilibrium had been approached from both higher and lower chlorine pressures were also in reasonable agreement.

Results

The equilibrium reaction represented by eq. 3 has been substantiated by the observation of the UO_2^+ spectrum, identification of the gas evolved, and measurement of its dependence on chlorine pressure. A second reaction was observed when the same solutions were held under vacuum for an extended period of time at temperatures of 750° and above.

$$Cl^- \rightleftharpoons {}^1/_2Cl_2 + e^- \qquad (4)$$

$$\underline{UO_2^+ + e^- \rightleftharpoons UO_2} \qquad (5)$$

$$Cl^- + UO_2^+ \longrightarrow UO_2 + {}^1/_2Cl_2 \qquad (6)$$

This reaction became evident from the precipitation of black UO_2 from the molten salt solution. The precipitate was identified as UO_2 by X-ray diffraction observation of a portion of the solid that had been separated from the salt by filtration. The presence of a small amount of a uranium(IV) species in the solution was evidenced by the appearance of the main absorption peak of uranium(IV) in the region of 1100 to 1150 mμ. By working at lower temperatures and for reasonably brief periods of time, it was possible to avoid this

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(3) D. M. Gruen and R. L. McBeth, *J. Inorg. Nucl. Chem.*, **9**, 290 (1959).

(4) R. Molina, *Bull. soc. chim. France*, 1184 (1961).

(5) N. W. Silcox and H. M. Haendler, *J. Phys. Chem.*, **64**, 303 (1960).

(6) R. S. Wilks, *J. Nucl. Mater.*, **7**, 157 (1962).

(7) C. J. Raseman, *et al.*, United States Atomic Energy Commission Report, BNL-627 (Brookhaven National Laboratory), June, 1960.

(8) Landolt-Bornstein, "Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik, und Technik," Band II, Teil 2, Springer-Verlag, Berlin, 1960.

reaction in the investigations concerning UO_2^+ and its spectrum.

In most of the experimental work on the UO_2^+ spectrum, either the LiCl–KCl eutectic or the NaCl–KCl–$MgCl_2$ eutectic was used as the solvent. The influence of changes of temperature on the UO_2^+ spectra in LiCl–KCl, which is representative of the solvents, is apparent in Fig. 2. Molar absorptivities at 650° in LiCl–KCl of two different compositions and in NaCl–KCl–$MgCl_2$ eutectic are listed in Table I. The uncertainty values, where indicated, represent standard deviations.

TABLE I

WAVE LENGTHS AND MOLAR ABSORPTIVITIES OF ABSORPTION MAXIMA

Solvent	Temp., °C.	λ_{max}, mμ	ϵ_{max}, l. mole^{-1} cm.$^{-1}$
LiCl–KCl eutectic	650	625	8.8 ± 0.4
		800	15.2 ± 0.5
		1535	14.9 ± 0.6
		1610	5.5 ± 0.3
		1665	4.5 ± 0.4
NaCl–KCl–$MgCl_2$ eutectic	650	685	5.6 ± 0.3
		860	8.9 ± 0.4
		1520	15.5 ± 0.6
		1615	5.6 ± 0.2
		1660	5.3 ± 0.2
		1930	0.8 ± 0.1
70 mole % LiCl–30 mole % KCl	650	625	9.9
		800	17.1
		1535	20.2
		1610	7.2
		1665	5.0
LiCl–KCl eutectic	750	625	6
		800	11
		1535	8
		1610	4
		1665	3

The equilibrium constant for reaction 3 can be expressed by the equation

$$K' = \frac{[UO_2^+]^2 P_{Cl_2}}{[UO_2^{2+}]^2[Cl^-]^2} \qquad (7)$$

Since for dilute solutions in a molten chloride solvent $[Cl^-]$ is essentially constant, it can be included in the final equilibrium constant.

$$K_{eq} = K'[Cl^-]^2 = \frac{[UO_2^+]^2}{[UO_2^{2+}]^2} P_{Cl_2} \qquad (8)$$

In the LiCl–KCl eutectic at 650°, K_{eq} has a value of $1.2 \pm 0.6 \times 10^{-6}$ atm. (Table II). Attempts to obtain a reliable value for the equilibrium constant in the NaCl–KCl–$MgCl_2$ eutectic were unsuccessful because of extensive scatter of the data. However, the value appears to be several times larger than in the LiCl–KCl system. It is believed that the low values of K_{eq} account for the fact that UO_2^+ was not found by earlier investigators.

In all of the solvents the spectra were influenced at the shorter wave lengths by absorption due to UO_2^{2+} and by the effect of temperature on charge-transfer absorptions which caused the absorption edge to shift to longer wave lengths with increasing temperature. For this reason spectrophotometric measurements required for the equilibrium constant determinations were made at the 1535 mμ maximum, where these effects were absent.

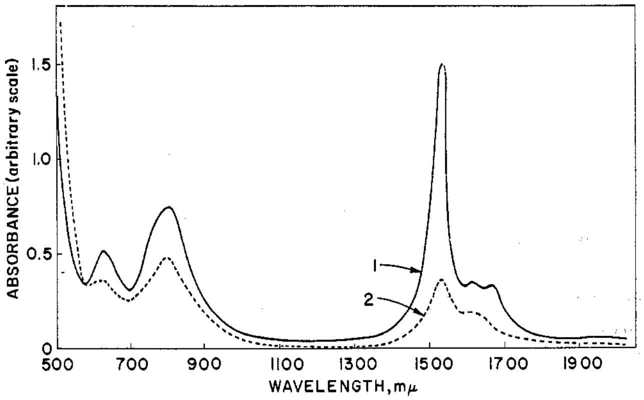

Fig. 2.—UO_2^+ spectrum in LiCl–KCl eutectic: 1, 450°; 2, 750°.

TABLE II

EQUILIBRIUM CONSTANT FOR REACTION 3 IN LiCl–KCl EUTECTIC AT 650°

$[UO_2^{2+}]$, M	$[UO_2^+]$, M	Cl_2 pressure, atm.	K_{eq}, atm.
0.143	0.0041	2.6×10^{-3}	2.1×10^{-6}
0.158	0.0023	2.6×10^{-3}	5.6×10^{-7}
0.158	0.0017	1.7×10^{-2}	1.9×10^{-6}
0.179	0.0183	1.6×10^{-4}	1.7×10^{-6}
0.172	0.0247	4.0×10^{-5}	8.2×10^{-7}
0.195	0.0023	9.9×10^{-3}	1.4×10^{-6}
0.138	0.0108	1.2×10^{-4}	7.3×10^{-7}
0.133	0.0161	4.0×10^{-5}	5.9×10^{-7}
		Av.	1.2×10^{-6}
		Std. dev.	0.6×10^{-6}

To determine the effect of solvent composition on the UO_2^+ spectrum, data were also obtained in several salts other than the two mentioned previously. These were: pure $MgCl_2$ at 750°, equimolar LiCl–$MgCl_2$ at 650°, and LiCl–KCl–$MgCl_2$ in the mole ratio 50:35:15 at 450°. The UO_2^+ absorption maxima in these and the previously mentioned salt mixtures are presented in Table III.

Discussion

All of the evidence collected in this study indicates that reaction 3 represents the initial step of the thermal decomposition of UO_2^{2+} in molten chloride solvents. The reaction appears to be easily reversible and to reach a measurable equilibrium at temperatures of 600–650°. On increasing the temperature to about 750°, further decomposition to UO_2 and chlorine occurs, as indicated by reaction 6. The fact that UO_2 suspended in a molten chloride solvent can be converted to UO_2^{2+} by passing chlorine through the mixture indicates that reaction 6 is also reversible.[9]

The peaks observed in the UO_2^+ spectrum at 625–685, 800–860, 1515–1535, and 1925–1930 mμ show the same

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(9) S. Lawroski, *et al.*, *Reactor Fuel Process.*, **6** (3), 32 (1963).

TABLE III

ABSORPTION MAXIMA OF UO_2^+ IN DIFFERENT SALTS AT 650°

Solvent compn., mole %	Wave lengths of maxima, mμ					
(1) 59 LiCl–41 KCl	625	800	1535	1610	1665	(1925)[a]
(2) 50 LiCl–35 KCl–15 $MgCl_2$	660	825	1525	1610	1660	
(3) 50 LiCl–50 $MgCl_2$	670	855	1520	1610	1660	1930
(4) 100 $MgCl_2$[b]	670	855	1515	1615	1660	1930
(5) 30 NaCl–20 KCl–50 $MgCl_2$	685	860	1520	1615	1660	1930

[a] Uncertain. [b] 750°.

essential features as the spectrum of the isoelectronic NpO_2^{2+} in $DClO_4$–D_2O solution[10] and are shifted to higher wave lengths, as would be expected because of the lower atomic number of uranium. The two small maxima at 1610–1615 and 1660–1665 mμ, which merge into one at higher temperatures (Fig. 2), may arise from a splitting of an energy level by ligand field effects in the molten chloride solvent. Qualitatively, the NpO_2^{2+} and UO_2^+ spectra seem to be in reasonable agreement with a theoretical electronic energy level scheme formulated by McGlynn and Smith which is based on molecular orbital consideration of a linear O–M–O molecular species having 13 valence electrons and predicts four observable transitions.[11]

It is apparent from Fig. 2 and Tables I and III that the UO_2^+ spectrum is strongly influenced by solvent and temperature variations, especially in the lower wave length regions. Jørgensen has indicated that perturbations from the ligands for a partly filled shell seem to be larger for 3d than for 5f shells. Direct splittings of the energy levels caused by the ligand field increase in the same manner.[12] It could be expected, then, that energy level splittings in a UO_2^+ complex species would increase as the ligand field around the uranium increased, shifting the absorption maxima in the 625–685 and 800–865 mμ regions toward shorter wave lengths.

The U–O bond length and infrared vibration frequencies are known to vary in uranyl(VI) compounds. Several explanations have been given for this variation. Hoekstra has suggested that the difference in the UO_2 asymmetric vibrational frequencies in the salts UO_2F_2 and $K_3UO_2F_5$ may be attributed to a decrease in the U–O dative bonding (resulting in increased bond length) caused by the attraction between K^+ and the uranyl oxygens in the latter compound.[13] McGlynn has asserted that in a series of uranyl(VI) complexes with various ligands there is a decrease in the U–O vibrational frequencies as the ligands become better donors because this piles up electronic charge on the uranium atom, and, due to increased electrostatic repulsion with the negative axial oxygen atoms, causes a loosening of the U–O bond.[14]

Although the mechanisms are different, either explanation would appear to produce the same result in explaining the shifts in the absorption maxima wave lengths for UO_2^+ species dissolved in molten chloride solvents. The decreases in absorption energies (increase in wave length) of the lower wave length maxima (625–860 mμ) would correspond to decreases in energy level splitting resulting from smaller ligand fields in the vicinity of the uranium atom. Therefore, in accordance with the wave length changes seen in Table II, one could postulate an increase in the attraction between the cations in the molten salt and the oxygen or chlorine atoms in a negatively charged $UO_2Cl_x^{1-x}$ complex in proceeding from solvent 1 to solvent 5, since in either case there would be a corresponding decrease in the ligand field around the central uranium. Variations of the intensities of the absorptions with solvent and temperature (Table I) may also be a result of the above type of interactions.

In molten chloride solutions, the probable $UO_2Cl_4^{3-}$ complex would have cations as the nearest neighbors. On the basis of size and charge, it is reasonable that in solvents 1 through 4 the cations would have an increasing attraction for the oxygen or chlorine atoms in the complex, since there is an increase in the concentration of the small Li^+ and Mg^{2+} ions. Solvent 5 appears to be the exception because of the presence of the larger Na^+ and K^+ ions. However, this simple picture could be complicated by factors such as nonstatistical distribution of ions in molten salts containing several components. The tendency toward the formation of complex ions such as $MgCl_4^{2-}$, which is probably the greatest in solvent 5, might alter the predicted variations in oxygen or chlorine–cation interactions based only on cation size and charge considerations.

Acknowledgment.—The authors wish to thank Dr. D. M. Gruen of the Chemistry Division for helpful discussions of this work. The analytical assistance of Drs. R. P. Larsen, R. J. Meyer, and M. H. Barsky of the Chemical Engineering Division is also gratefully acknowledged.

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[10] D. Cohen and B. Traylor, *J. Inorg. Nucl. Chem.*, **9**, 290 (1959).

[11] S. P. McGlynn and J. K. Smith, *J. Mol. Spectry.*, **6**, 188 (1961).

[12] C. K. Jørgensen, *Mol. Phys.*, **2**, 96 (1959).

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[14] S. P. McGlynn, J. K. Smith, and W. C. Neely, *J. Chem. Phys.*, **35**, 105 (1961).