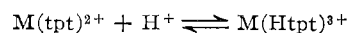


As expected, even though tpt is more basic than tren, it forms less stable complexes with the difference between the formation constants varying between 6.5 log units for cobalt(II) and 4 log units for zinc(II). The reason for this large destabilization must be that the tpt complexes have six-membered chelate rings, and it is well known that these are less stable than analogous five-membered rings. The complexes $M(\text{tpt})^{2+}$ are, with the exception of that of zinc(II), slightly less stable than those of dpt. This is surprising considering that dpt has one less donor amine group.

Thus it may be suspected that only three nitrogen atoms in tpt were involved in coordination (two primary and one tertiary), but in this case the values of the equilibrium constants for



should be very close to the first basicity constant of the free amine. However, the value observed for nickel(II) ($\log K = 7.1$) is too low to justify such a hypothesis, while for copper(II) ($\log K = 8.2$) no conclusions may be drawn.

Acknowledgments.—We are indebted to Dr. M. Secci, University of Cagliari, for supplying samples of tpt, and we wish to thank Professor L. Sacconi for encouragement in this work and the Italian "Consiglio Nazionale delle Ricerche" for financial assistance. We are grateful to the computing Center of the University of Cagliari for the use of computing facilities.

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Mass Spectral Studies of Metal Chelates. II. Mass Spectra and Appearance Potentials of Acetylacetonates of Trivalent Metals of the First Transition Series

By G. M. BANCROFT, C. REICHERT, AND J. B. WESTMORE

Received November 3, 1967

The mass spectra are reported for the tris acetylacetonates of Ti, V, Cr, Mn, Fe, Co, and Al as well as the appearance potentials of $M(\text{acac})_3^+$ and $M(\text{acac})_2^+$ derived from these compounds. The results are not in agreement with theoretical calculations and electronic spectra of these molecules.

Introduction

A number of papers dealing with the mass spectrometric investigation of metal acetylacetonates have recently been published.¹⁻⁴ These studies are potentially useful in elucidating bonding and molecular and electronic structure of these compounds. In this paper we report a systematic study of the mass spectra of the acetylacetonates of trivalent metals of the first transition series and the appearance potentials of ions derived therefrom. Also studied were acetylacetonate and aluminum tris(acetylacetonate). The lack of reproducibility between mass spectra of acetylacetonates of Mn, Cr, Fe, and Co in previous studies^{1,3} is explained with the help of the appearance potential measurements and different conditions of introduction of the compounds into the ionization chamber.

Although appearance potentials have been determined for many organometallic compounds,^{5,6} little effort has been made to interpret the results in terms

of the electronic structures of these compounds. For carbonyl compounds, for example, Winters and Kiser⁶ have simply commented that on ionization the electron is removed from an orbital localized largely on the metal atom.

For metal acetylacetonates, molecular orbital calculations have been published.⁷⁻¹⁰ These calculations have helped toward a better though still controversial interpretation of the electronic spectra. Barnum⁷ has obtained good agreement between calculated and observed energies. Because of difficulties in determining the effect of substituents on the energy of the excited states of a molecule, Price¹¹ has stated that "the simpler changes which occur in ionization potentials are easier to assess and can be regarded as being a first step in elucidating those which occur in absorption bands." Consequently, it is hoped that the results presented in this paper will result in more thorough theoretical calculations and lead to a better interpretation of the electronic spectra of these compounds.

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Experimental Section

All acetylacetonates were prepared by standard methods and sublimed at least once. Reagent grade acetylacetone was distilled before use. Except for $\text{Ti}(\text{acac})_3$ and $\text{V}(\text{acac})_3$, melting points were checked. The compounds melted sharply near the literature values. $\text{Ti}(\text{acac})_3$ and $\text{V}(\text{acac})_3$ were stored under vacuum to prevent oxidation. From the mass spectra, we feel that the $\text{V}(\text{acac})_3$ contained a small amount of $\text{VO}(\text{acac})_2$ (less than 5 mole %) as an impurity which we did not succeed in removing. The mass spectral studies were performed on a Hitachi Perkin-Elmer RMU-6D single-focusing mass spectrometer. The compounds were introduced into the ionization chamber in one of two ways: (a) *via* the heated inlet; (b) by direct insertion. In the first method the compound was vaporized into a reservoir of about 1-l. capacity and from there it effused into the ionization chamber through a pinhole leak. The whole inlet system can be heated at temperatures up to 250°. In the second method the sample was introduced into the ion source on a probe which could be inserted through a vacuum lock. For these compounds the sample temperature did not have to exceed 50° to obtain good spectra.

A Hewlett-Packard Model 3459A digital voltmeter was used to monitor both the amplified ion current and the chamber voltage (electron-accelerating voltage) when ionization efficiency curves were being determined. The chamber voltage was usually stable to ± 0.001 V. Ion current readings for a particular ion were taken at 0.100-V intervals upward from the ionization threshold and also at a chamber voltage of 50 V before and after these readings. Appearance potentials were determined, relative to xenon as a standard, by the semilogarithmic method¹² where appropriate (curves parallel to xenon) or by Warren's method.¹³ By similar methods we found the appearance potential of Kr^+ to be in excellent agreement with the spectroscopic ionization potential.

Results

The mass spectra obtained for the chelates (direct insertion method) for 50-V electrons and an ionizing chamber temperature of 150° are summarized in Table I. The effect of the method of sample introduction was investigated. For $\text{Cr}(\text{acac})_3$ the intensities of the main peaks for different conditions of sample introduction are shown in Table II, and are considered acceptably reproducible. However, for $\text{Mn}(\text{acac})_3$, $\text{Fe}(\text{acac})_3$, and $\text{Co}(\text{acac})_3$, vaporization of the compound *via* the heated inlet system led to a much less abundant molecular ion peak and a lower appearance potential for $\text{M}(\text{acac})_2^+$ than those obtained when the compound was vaporized directly into the ionization chamber. If the compound was vaporized directly into the ion source, variation of the ionization chamber temperature from 150 to 250° had very little effect on the form of the spectrum or on the value of the measured appearance potential.

The determined appearance potentials are quoted in Table III for an ionization chamber temperature of 150°. When the mass spectrum is sensitive to the method of sample introduction, the direct insertion method is used. The results are plotted in Figure 1. The errors quoted indicate the reproducibility of the results rather than an assessment of their absolute accuracy, which we feel is probably within ± 0.2 V. The appearance potentials varied by no more than 0.2

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TABLE I

RELATIVE INTENSITIES OF MAJOR IONS IN THE MASS SPECTRA, AT AN ELECTRON ENERGY OF 50 V

Ion	Ti- (acac) ₃	V- (acac) ₃	Cr- (acac) ₃	Mn- (acac) ₃	Fe- (acac) ₃	Co- (acac) ₃
P	100	32	23	16	16	29
P - 15	4
P - 42	2
P - 57	6
P - 82	37	3
P - 83	...	4
P - 99	55	100	100	100	100	100
P - 100	80
P - 114	5	32	47	47
P - 118	12
P - 124	7
P - 141	6
P - 164	7
P - 165	...	7
P - 180	16
P - 181	36	10	12	...	8	...
P - 182	64	26
P - 197	...	3
P - 198	...	5	45	70	74	66
P - 200	18	3
P - 213	4	3	...	7
P - 216	3	3
P - 218	17
P - 281	...	34	...	?
P - 297	2	?	5	2

TABLE II

RELATIVE INTENSITIES OF MAJOR IONS FROM $\text{Cr}(\text{acac})_3$ WITH DIFFERENT CONDITIONS OF SAMPLE INTRODUCTION, AT AN ELECTRON ENERGY OF 50 V

Ion	Chamber temp, °C			
	150°	250°	150°	250°
	Via heated inlet		Direct insertion	
P ⁺	22	22	25	23
[P - ($\cdot\text{acac}$)] ⁺	100	100	100	100
[P - ($\cdot\text{acac}$) - ($\cdot\text{CH}_3$)] ⁺	5	5	6	5
[P - 2($\cdot\text{acac}$)] ⁺	50	50	59	46

TABLE III

APPEARANCE POTENTIALS AT A CHAMBER TEMPERATURE OF 150°

Compound	$\text{M}(\text{acac})_3^+$	$\text{M}(\text{acac})_2^+$
$\text{Ti}(\text{acac})_3$	7.1 ± 0.1 (2) ^a	11.8 ± 0.1 (2)
$\text{V}(\text{acac})_3$	7.9 ± 0.1 (2)	11.8 ± 0.1 (2)
$\text{Cr}(\text{acac})_3$	8.10 ± 0.05 (6)	11.3 ± 0.1 (6)
$\text{Mn}(\text{acac})_3^b$	7.85 ± 0.05 (2)	$\geq 8.7 \pm 0.1$ (2)
$\text{Fe}(\text{acac})_3$	8.45 ± 0.05 (6)	$\geq 9.4 \pm 0.1$ (5)
$\text{Co}(\text{acac})_3$	7.80 ± 0.05 (5)	10.7 ± 0.3 (3)
$\text{Al}(\text{acac})_3$	7.95 ± 0.05 (2)	9.1 ± 0.2 (2)
$\text{Fe}(\text{acac})_2$...	8.1 ± 0.1
$\text{H}(\text{acac})$	9.2 ± 0.1 for $\text{H}(\text{acac})^+$...

^a Parentheses indicate the number of determinations of the appearance potential. ^b Chamber temperature 100°.

V on varying the chamber temperature from 150 to 250°.

Discussion

The Mass Spectra.—The spectra of $\text{Ti}(\text{acac})_3$, $\text{V}(\text{acac})_3$, and $\text{Mn}(\text{acac})_3$ have not been reported previously. The spectra of $\text{Fe}(\text{acac})_3$, $\text{Co}(\text{acac})_3$, and $\text{Cr}(\text{acac})_3$ were in good agreement with those of MacDonald and Shannon,¹ but these workers were unable to obtain a spectrum for $\text{Mn}(\text{acac})_3$. We were also able to reproduce their mass spectrum of $\text{Al}(\text{acac})_3$.

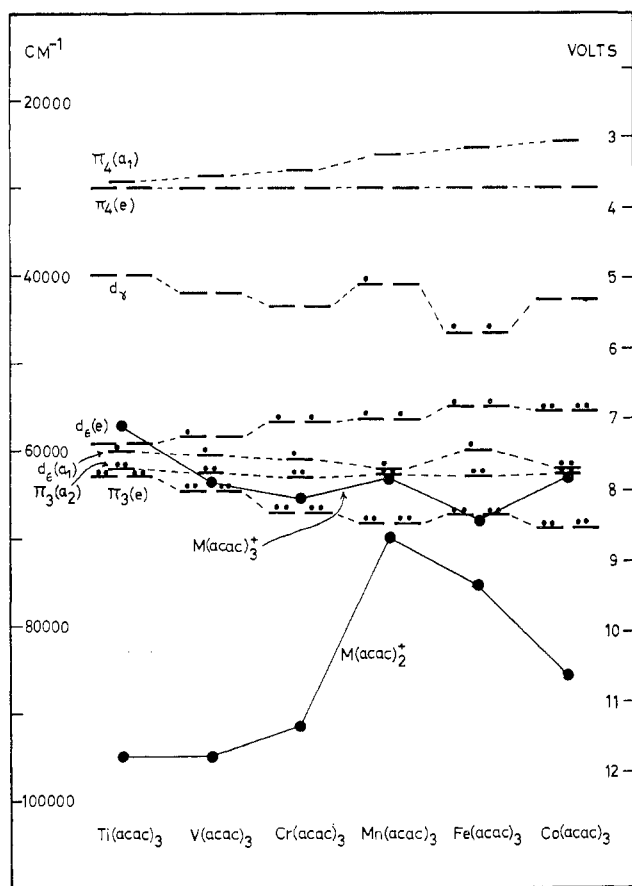


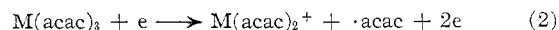
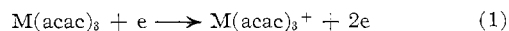
Figure 1.—Appearance potentials of $M(\text{acac})_3^+$ and $M(\text{acac})_2^+$ from $M(\text{acac})_3$. The energy levels have been estimated from data given by Barnum.⁷

However, Sasaki, *et al.*,³ did not observe a molecular ion peak for $\text{Fe}(\text{acac})_3$, $\text{Co}(\text{acac})_3$, and $\text{Cr}(\text{acac})_3$. The absence of these peaks appears to be a result of either thermal decomposition of the compounds before they entered the ionization chamber or the presence of volatile impurities (such as acetylacetone) in the compounds. In our work, the small molecular ion peak for $\text{Mn}(\text{acac})_3$, $\text{Fe}(\text{acac})_3$, and $\text{Co}(\text{acac})_3$ when the compound was introduced *via* the heated inlet system appears to be a result of thermal decomposition to the bis chelate before the compound enters the ionization chamber. Additional confirmation for this proposal is obtained from appearance potential measurements. When $\text{Fe}(\text{acac})_3$ is introduced into the ionization chamber *via* the heated inlet system the appearance potential of $\text{Fe}(\text{acac})_2^+$ is 8.2 V, *i.e.*, lower than that of $\text{Fe}(\text{acac})_3^+$. This does not appear to be energetically feasible. However, when the compound is introduced *via* the direct inlet system, the appearance potential of $\text{Fe}(\text{acac})_2^+$ rises to 9.4 V and becomes reproducible over a range of chamber temperature from 150 to 250°. When $\text{Fe}(\text{acac})_2$ was introduced into the ionization chamber, the appearance potential of $\text{Fe}(\text{acac})_2^+$ was 8.1 V. We may conclude that, from $\text{Fe}(\text{acac})_3$, $\text{Fe}(\text{acac})_2^+$ may be formed in two ways, namely, by fragmentation of $\text{Fe}(\text{acac})_3^+$ or by ionization of $\text{Fe}(\text{acac})_2$ formed by thermal

dissociation of $\text{Fe}(\text{acac})_3$. This study thus indicates that, for thermally unstable compounds, the conditions of sample introduction can be of great importance both to the nature of the mass spectra and to the accuracy of the appearance potential measurements.

Although it does not seem appropriate to discuss the spectra in detail here, a number of trends in the spectra are immediately obvious. An outline of the possible processes and an assignment of the masses is shown schematically in Figure 2. We intend to discuss spectra of these and similar compounds in a later publication. MacDonald and Shannon¹ have postulated valency changes in the metal to rationalize the formation of various fragment ions. Although this is undoubtedly an oversimplification, we may note that for $\text{Ti}(\text{acac})_3$ and $\text{V}(\text{acac})_3$, fragmentation proceeds with formation of oxy or hydroxy species, which are absent in the spectra of the other chelates. This trend is in complete accordance with the established chemistry of the metals, the tendency for Ti and V to form MO^{2+} compounds. Another marked trend is the variation in intensity of the $[\text{P} - (\cdot\text{acac}) - (\cdot\text{CH}_3)]^+$ peak (P = parent or molecular ion). This peak is absent for $\text{Ti}(\text{acac})_3$ and $\text{V}(\text{acac})_3$ and generally increases in intensity from $\text{Cr}(\text{acac})_3$ to $\text{Co}(\text{acac})_3$. The intensity of this peak appears to parallel the ease with which the +3 state of the metals is reduced. A similar trend is also observed for the $[\text{P} - 2(\cdot\text{acac})]^+$ peak. The variation in intensity of the molecular ion peak can also be correlated with the increasing stability of the +2 state relative to the +3 state of the metals with increasing atomic number. It is hoped that the appearance potential determinations will aid in the eventual theoretical understanding of the mass spectra.

Appearance Potentials.—The two processes which are considered to be of importance to this study are



For the first process we make the assumption that, at the ionization threshold, the excess energy (in the form of kinetic or excitation energy) associated with the process is small, or at least approximately constant, for the series of compounds. Since the ionization efficiency curves, shown in Figure 3, had a similar form, except for $\text{Ti}(\text{acac})_3$ and $\text{V}(\text{acac})_3$, we feel this assumption to be justified. Thus the measured appearance potentials should give at least accurate relative ionization potentials and probably accurate absolute appearance potentials.

Similarly, for the second process, we assume that the excess energy is small, so that

$$\text{AP}[\text{M}(\text{acac})_2^+] = \text{IP}[\text{M}(\text{acac})_2^+] + 2E(\text{M}-\text{O})$$

where $E(\text{M}-\text{O})$ is the energy of the metal-oxygen bond. Unfortunately, we were unable to determine the ionization potentials of the bis chelates of all of the metals, so that a correlation of bond energies with electronic structure was not possible. Though not necessarily related to the above reaction, the energy of the process

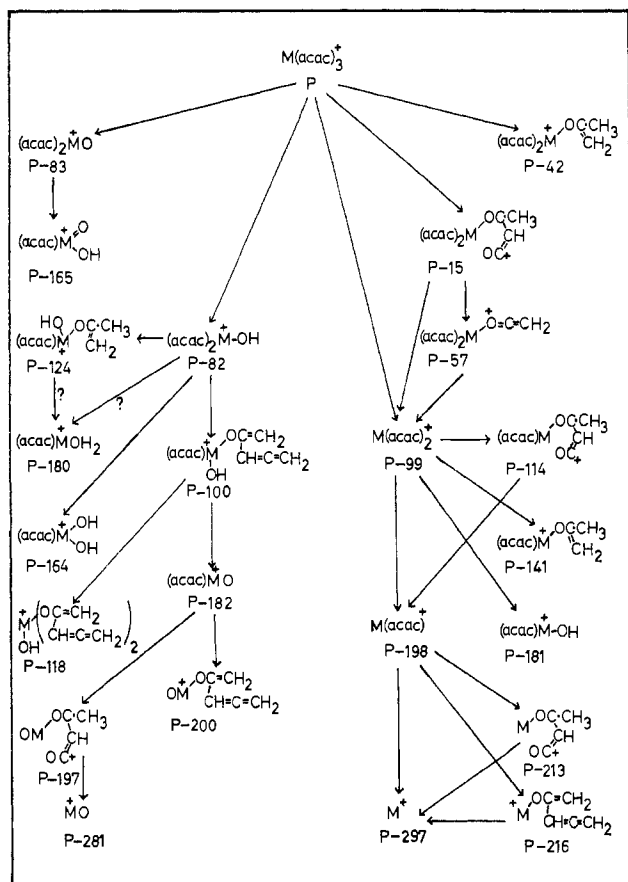


Figure 2.—Some suggested decomposition pathways for the formation of ions in the mass spectra. Other pathways are possible, and only one canonical form of each ion is shown. In many cases, confirmation of the suggested pathway was given by the presence of a metastable peak.

$M(acac)_3^+ \rightarrow M(acac)_2^+ + \cdot acac$ was assumed to be given by $AP[M(acac)_2^+] - AP[M(acac)_3^+]$ and the variation in energy of this process with the transition metal, we believe, is significant.

Studies of proton resonance and ultraviolet spectra of metal acetylacetonates led Holm and Cotton¹⁴ to state that the experimental data could not be correlated with any simple parameter of the complexed metal ion, although they believed that the ability of the metal ion to participate in π interaction with the chelate ring was important. Similarly, in this study, we have been unable to find any simple correlation between the measured appearance potentials and a parameter relating to the complexed metal ions.

Barnum⁷ has calculated energy levels, taking account of π interaction for these compounds, the results being shown in Figure 1. If we define the ionization potential as being the minimum energy required to remove the electron from the highest occupied molecular orbital, then these results do not correlate with Barnum's simplified calculations. For example, $Mn(acac)_3^+$ should have a much lower ionization potential than $Cr(acac)_3^+$ (at least 1.5 V lower). Similarly, low-spin $Co(acac)_3^+$ should have a much higher ionization potential than $Fe(acac)_3^+$. These conclusions

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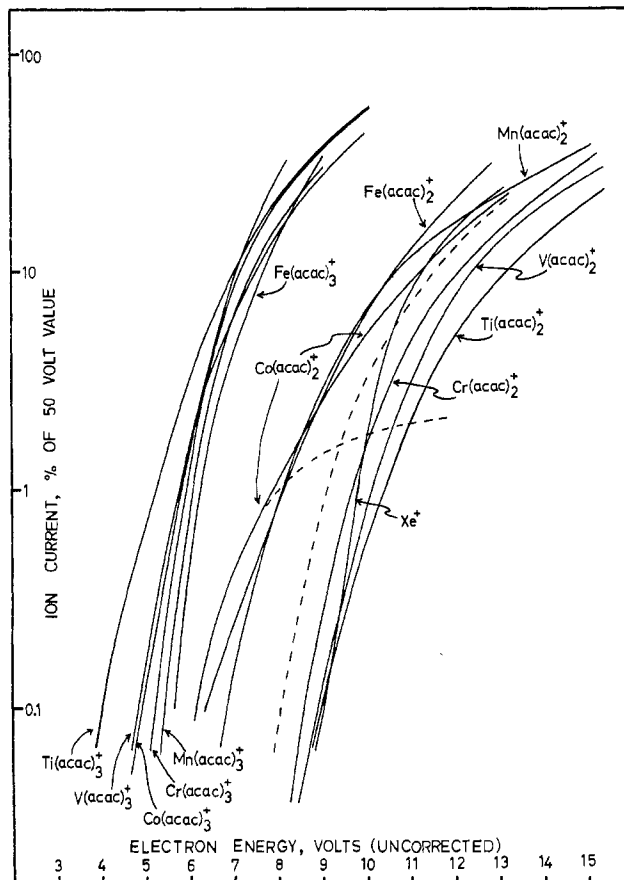


Figure 3.—Ionization efficiency curves for $M(acac)_3^+$ and $M(acac)_2^+$. The curves for $Mn(acac)_2^+$, $Fe(acac)_2^+$, and $Co(acac)_2^+$ probably reflect the thermal instability of the corresponding tris chelate. The effect is most marked in the curve for $Co(acac)_2^+$, where it has been assumed that the experimental curve is the sum of the contributions indicated by the broken lines. The lower curve is taken as $Co(acac)_2^+$ arising from thermal decomposition; the appearance potential was estimated from the upper broken curve and contains considerable uncertainty. For $Mn(acac)_2^+$ the quoted value of the appearance potential is probably a lower limit. This may be true also for $Fe(acac)_2^+$, but we believe the quoted value to be a good one.

are not in agreement with the measured appearance potentials.

Since our assumptions about the energetics of processes 1 and 2 should be essentially correct, we are forced to conclude that Barnum's calculations are not even qualitatively correct or that the electron is not removed from the highest occupied molecular orbital in all cases. Even if Barnum's calculations were seriously in error, there is still the trend in the appearance potentials of $M(acac)_2^+$ to be explained. The d_γ orbitals are antibonding. It would be expected, therefore, that, for the manganese chelate if the d_γ electron is removed, the difference between the appearance potentials of $Mn(acac)_2^+$ and $Mn(acac)_3^+$ would be of similar magnitude to that for the chelates of Ti, V, and Cr, instead of the large decrease which is actually observed. If the electron is assumed to be removed from either the d_σ or π_3 orbitals, then better correlation with Barnum's calculations is obtained, and, furthermore, the variation in appearance potential of $M(acac)_2^+$

formed from $M(\text{acac})_3$ can be rationalized, although the results could be complicated by structural rearrangement (e.g., to square-planar or tetrahedral ions). It is perhaps worth noting for $\text{Al}(\text{acac})_3$ in which little or no π interaction between metal and ligand is expected that the appearance potential of $\text{Al}(\text{acac})_2^+$ is only 1.1 V higher than that of $\text{Al}(\text{acac})_3^+$.

There are several additional pieces of evidence which suggest that the nature of the ligand has a far greater effect than the metal on the appearance potentials of the metal chelates. First, the metal trifluoroacetylacetonates¹⁵ have appearance potentials about 1 V higher and the hexafluoroacetylacetonates about 2 V higher than

(15) G. M. Bancroft, C. Reichert, and J. B. Westmore, submitted for publication.

the corresponding acetylacetonates.¹⁵ Second, in a series of 3-substituted acetylacetonates of chromium¹⁵ the difference in appearance potential between the NO_2^- and the Br-substituted chelate is about 0.5 V.

Our experimental results, therefore, do not agree with Barnum's simple theoretical calculations. Owing to lack of a large body of experimental data, knowledge of the ionization process in inorganic complexes is very limited and we are pursuing further research on these and related compounds. It is hoped that these results will stimulate more theoretical work on these compounds.

Acknowledgments.—We thank the National Research Council of Canada and the Faculty of Graduate Studies, University of Manitoba, for financial assistance.

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Sulfamate Complexes of Plutonium(IV)¹

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Received November 15, 1967

Spectrophotometric studies indicate that plutonium(IV) is complexed by sulfamate ion but give no evidence of sulfamate complexes of plutonium(III) and plutonyl(VI). From the influence of sulfamate concentration on the plutonium(IV) spectrum, the stability constant of the monosulfamate complex of plutonium(IV) was calculated to be 1.3 ± 0.4 at 23°. Spectra of solutions containing predominantly the monosulfamate complex were changed significantly by the addition of sulfamic acid, indicating the formation of a mixed sulfamate-sulfamic acid complex of plutonium(IV), or the interaction of sulfamic acid with sulfamate ion thereby decreasing the concentration of the monosulfamate complex. The latter reaction was verified by determining the solubility of sulfamic acid in ammonium sulfamate and ammonium nitrate solutions, but the extent of interaction ($K = 0.3$) was insufficient to account fully for the spectral changes observed. Hence it is concluded that mixed sulfamate-sulfamic acid complexes of plutonium(IV) are formed in solutions containing appreciable concentrations of sulfamate ion and sulfamic acid.

Sulfamic acid is an acid of moderate strength, with an ionization constant of 0.10 at 25°. An early suggestion² that sulfamic acid exists in the solid form as the zwitterion is supported by X-ray crystallographic data and by the relatively high melting point of the solid.⁴ Despite a previous statement to the contrary,³ there is evidence from the entropy of ionization⁵ and non-aqueous solvent studies⁶ that the acid also exists in solution as the zwitterion.

Sulfamic acid solution has found practical application as a solvent for plutonium metal,⁷ but there has been very little investigation of the chemistry of plutonium in sulfamate solution. This paper describes spectrophotometric studies of plutonium complexes in

aqueous sulfamate media. These data suggest an interaction between sulfamic acid and sulfamate ion, and this interaction was investigated by determining the solubility of sulfamic acid in ammonium sulfamate and ammonium nitrate solutions of various concentrations.

Experimental Section

The plutonium(III) solutions used in this study were prepared by dissolution of plutonium metal in 5–6 *M* perchloric acid. Plutonium(IV) was prepared by oxidation of plutonium(III) with ozone, and plutonyl(VI) was made by fuming a perchloric acid solution of plutonium(III). In each case the presence of only the desired oxidation state of plutonium in appreciable concentration was verified spectrophotometrically.

Reagent grade sulfamic acid was used without further purification. The limited solubility and dissociation of sulfamic acid required the use of ammonium sulfamate to obtain the sulfamate concentrations necessary for this study. Since commercially available ammonium sulfamate was found to contain sulfate, this salt was prepared by the room-temperature evaporation of a sulfamic acid solution neutralized with ammonium hydroxide.

When necessary, lithium perchlorate was used to maintain constant ionic strength. This salt, obtained from G. Frederick Smith Chemical Co., was recrystallized four times before use.

Solubility measurements were made by sealing an excess of

(1) Work performed for the U. S. Atomic Energy Commission under Contract AT(29-1)-1106.

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