is mal^{2-} = ox^{2-} > H$_2$O > urea for Cr(III) and H$_2$O > mal^{2-} > ox^{2-} > urea for Fe(III).

Although unequivocal assignments for the ultraviolet transitions observed for the dba and dbm complexes cannot be made, there are two striking features of these spectra which may be noted. First, in each case where a comparison has been made, the lowest energy bands of high intensity for the dba complex of a particular metal are 5000–6000 cm^{-1} higher in energy than the lowest energy, high-intensity bands for the dbm complex. Second, the band profiles for the Be(II), Al(III), and Cr(III) complexes of dba, or dbm for that matter, are quite similar with less than a factor of 10 difference in the extinction of the bands. Thus, a reasonable assumption to make is that the nature of the transitions giving rise to the group of lowest energy ultraviolet bands must be the same in the complexes of these three metal ions and possibly in Cu(II) as well. Inasmuch as charge-transfer bands involving metal orbitals are not expected for the Be(II) complex, the observed spectrum should be composed only of intraligand transitions. If the similarity of the spectrum of the "tetrahedral" Be(II) complex to the spectra of the "octahedral" Al(III) and Cr(III) complexes is real and not just coincidental, then the tentative conclusion may be drawn that the ultraviolet spectra of these complexes all consist of primarily intraligand transitions.

The spectra of Fe(dba)$_3$ and Fe(dbm)$_3$ are in general similar in both profile and extinction to each other. Although each spectrum is more complicated than the spectra of the complexes of the other metals, the Fe(dba)$_3$ spectrum does follow the trend noted with the other dba complexes as the lowest energy, high-intensity bands are shifted some 6000 cm^{-1} or more to higher energy compared to the dbm complexes. Whereas the ground-state configuration of Fe(III) in these two complexes is basically $t_{2g}^3e_g^2$, $e_g \rightarrow \pi^*$ transitions are possible and may account for some of the lower energy bands not observed in the complexes of Be(II), Al(III), or Cr(III). However, a more definitive consideration of the nature of these bands is tentative at best until other complexes in the diamido class which do not contain groups, such as the benzene ring, that contribute to absorption in the ultraviolet region are available for study.

The ultraviolet spectrum of Hg(dba)$_2$ is quite different from that of any of the other dba complexes and offers support to the earlier suggestion that the ligand is not attached to Hg(II) in a normal chelated manner. In addition to the possibility of O–Hg bonds, there may be N–Hg bonds in Hg(dba)$_2$. However, no structural assignment of this compound in the solid state or in solution may be made at this time.

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Mass Spectral Studies of Metal Chelates. III.[1] Mass Spectra and Appearance Potentials of Substituted Acetylacetonates of Trivalent Chromium. Comparison with Other Trivalent Metals of the First Transition Series

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The appearance potentials of some substituted acetylacetonates of chromium are: Cr(acac)$_3$, 8.11 V; Cr(Iacac)$_3$, 8.03 V; Cr(Bracac)$_3$, 8.05 V; Cr(Clacac))$_3$, 8.21 V; Cr(NO$_2$acac)$_3$, 8.63 V; Cr(tfacac)$_3$, 9.09 V; Cr(hfacac)$_3$, 10.13 V; Cr(CH$_3$acac)$_3$, 7.81 V. The values seem to be consistent with the ionization of an electron from the π system of the chelate ring. The mass spectra of these chelates are compared with previously reported mass spectra of Ti(acac)$_3$, V(acac)$_3$, Cr(acac)$_3$, Mn(acac)$_3$, Fe(acac)$_3$, and Co(acac)$_3$, and mechanisms of decomposition are discussed.

In the previous paper[1] in this series, the mass spectra and appearance potentials of the acetylacetonates of trivalent metals of the first transition series were reported (*i.e.*, the acetylacetonates of Ti, V, Cr, Mn, Fe, and Co). The trends in the mass spectra were briefly rationalized using the established chemistry of the metals, while it was shown that the measured appearance potentials did not correlate with the simplified theoretical calculations of Barnum,[2] assuming that the electron was removed from the highest occupied molecular orbital in all cases.

MacDonald and Shannon[3] postulated valency changes in the metal to account for the observed mass spectra

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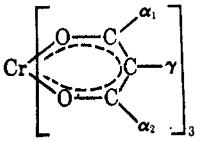
of several acetylacetonates and correlated the occurrence or nonoccurrence of valency changes with the established chemistry of the metal. Although this is undoubtedly an oversimplification, we found, in agreement with this postulate, in the mass spectra of Ti(acac)$_3$ and V(acac)$_3$, which were not reported by these authors, peaks believed to be characteristic of the 4+ valency states of these metals. Furthermore, in the mass spectra of Mn(acac)$_3$, Fe(acac)$_3$, and Co(acac)$_3$ there were peaks believed to be characteristic of the 2+ valency state of these metals. In the mass spectrum of Cr(acac)$_3$, peaks characteristic of the 4+ valency state were absent, and those characteristic of the 2+ valency state were small. This is apparently because Cr^{3+} is so much more stable than Cr^{2+} or Cr^{4+}.

We have therefore undertaken a study of a number of substituted chromium acetylacetonates (Table I). The chromium chelates are convenient to use for two reasons. First, most of them are very stable thermally. Second, as discussed above, Cr exhibits intermediate behavior in the series of metals of immediate interest.

TABLE I

SUBSTITUTED CHROMIUM ACETYLACETONATES



Designation	α_1	α_2	γ
Cr(acac)$_3$	CH_3	CH_3	H
Cr(CH$_3$acac)$_3$	CH_3	CH_3	CH_3
Cr(Clacac)$_3$	CH_3	CH_3	Cl
Cr(Bracac)$_3$	CH_3	CH_3	Br
Cr(Iacac)$_3$	CH_3	CH_3	I
Cr(NO$_2$acac)$_3$	CH_3	CH_3	NO_2
Cr(tfacac)$_3$	CF_3	CH_3	H
Cr(hfacac)$_3$	CF_3	CF_3	H

It would therefore be expected that substitution of electron-withdrawing or -donating substituents into the ligand would markedly change the form of the mass spectra and the values of the appearance potentials. Molecular orbital calculations are not available for these compounds but the electronic spectra of some of these chromium chelates have been published.[4-7] Additionally, we can compare, in a semiquantitative way, the effect of a substituent on the chelate ring with the general chemistry of the substituent.

Experimental Section

The experimental conditions were as described in part II[1] except that the ionization chamber temperature was 250°. All samples were vaporized *via* the direct inlet system with sample temperatures of about 50° but with variations in temperature depending upon the volatility of the chelate.

We are grateful to Dr. W. K. Ong (Chemistry Department, University of Singapore) for samples of the Cl-, Br-, I-, and NO$_2$-substituted chelates. Methods of preparation of these compounds have been reported.[8,9] The other chelates were prepared from the appropriately altered ligand by standard methods[10] and purified by sublimation at reduced pressure. The melting point of the Cr(tfacac)$_3$ sample was 152–153° corresponding to the *trans* isomer (*cis*, mp 112–114°; *trans*, mp 154.5–155°).[11] The sample of Cr(Iacac)$_3$ contained small amounts of impurities of chelates in which Cl was substituted for I, presumably because ICl had been used in the preparation. However, these impurities did not give rise to difficulties in interpreting the mass spectrum.

Appearance potentials of the molecular ions were determined by the semilogarithmic method,[12] since the ionization curves were very closely parallel to those for xenon, which was used as the calibrating gas.

Results and Discussion

Appearance Potentials.—All of the chelates gave abundant molecular ions, and consequently it was possible to measure the appearance potentials of the complete series of compounds with a reproducibility of ±0.05 V and a probable accuracy of ±0.1 V. The appearance potentials of the molecular ions are shown in Table II, as well as those for the ion which has lost a ligand radical.

TABLE II

APPEARANCE POTENTIALS AND SPECTRAL SHIFTS[4] OF SUBSTITUTED CHROMIUM ACETYLACETONATES

Compound	AP(L_3Cr^+) ±0.05, V	AP(L_2Cr^+) ±0.10, V	$\Delta\bar{\nu}$, cm^{-1} (relative to Cr(acac)$_3$) Band B	Band C	$\bar{\nu}_{max}$, cm^{-1} $^2E \longrightarrow {}^4A_2$
Cr(acac)$_3$	8.11	11.3	0	0	12,800
Cr(CH$_3$acac)$_3$	7.81	10.7	−2100	−1300	12,310
Cr(Clacac)$_3$	8.16	11.1	−2300	−1400	12,420
Cr(Bracac)$_3$	8.05	11.0	−2300	−1600	12,390
Cr(Iacac)$_3$	8.03	10.8	−3100	−2200	12,340
Cr(NO$_2$acac)$_3$	8.63	11.6	+1300	+500	12,940
Cr(tfacac)$_3$	9.09	11.9	−300?	−700	12,340
Cr(hfacac)$_3$	10.13	14.3	. . .	−700	. . .

In the previous paper[1] we suggested that the nature of the ligand had a greater effect than did the metal on the appearance potential of the acetylacetonates and that the electron was removed from a π orbital localized on the ligand rather than from the higher energy, largely metal d orbital. This was postulated to account for the discrepancies between the measured appearance potential data and molecular orbital calculations. Thus in Fe(acac)$_3$ and Mn(acac)$_3$, which have electrons in the higher energy d_γ orbitals, the appearance potentials should have been much lower (>1 V) than in the other acetylacetonates, assuming that the electron is removed from the occupied molecular orbital of highest energy. The results presented here tend to support this suggestion although the evidence is not

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conclusive. In the Cr(III) chelates the d_γ orbitals are not occupied and one complicating factor is thus not present.

There has been much debate about the supposed aromaticity of the chelate ring in the acetylacetonates. While the theoretical grounds for a truly aromatic ring are not convincing, these chelates do undergo certain reactions characteristic of aromatic compounds, such as halogenation and nitration.[7,8] Furthermore, an X-ray structure determination[13] of $Fe(acac)_3$ shows that the ring C–C distances (1.39 Å) are equal to the C–C distance in benzene and both C–O distances (1.28 Å) are intermediate between single and double bond lengths. Recent nmr evidence[14,15] also indicates delocalization of electrons between metal and ligand. It seems worthwhile, therefore, to discuss the variations in appearance potentials of the substituted chromium chelates in terms of the ionization of a π electron from a quasi-aromatic chelate ring using inductive and resonance effects discussed by Bralsford, *et al.*[16]

The α substituents in these chromium complexes are either CH_3 or CF_3. For CF_3, only the inductive effect is likely to be of importance. In the γ-substituted complexes used here, both inductive and resonance effects operate, and, instead of trying to evaluate the magnitude of these two effects on the π system, it is simpler to compare variations in appearance potential with those in suitable model aromatic compounds. In Table III[17] the appearance potentials of some substituted benzenes and toluenes are given, so that they can be directly compared with those of the chromium chelates.

TABLE III

IONIZATION POTENTIALS OF SUBSTITUTED BENZENE AND TOLUENES[a]

Substituent X	Ionization potential, V C_6H_5X	o-$CH_3C_6H_4X$	p-$CH_3C_6H_4X$
H	9.245	8.82	8.82
I	8.73	8.62	8.50
Br	8.98	8.78	8.67
Cl	9.07	8.83	8.69
NO_2	9.92	. . .	9.82
CF_3	9.68	. . .	. . .

[a] All values are from photoionization except those for p-$CH_3C_6N_4NO_2$ (electron impact). All values are from ref 17 except that for $C_6H_5CF_3$ (ref 16).

We may note that substitution of CF_3 for CH_3 in toluene raises the ionization potential by 0.86 V from 8.82 to 9.68 V. Substitution of CF_3 for CH_3 in the α positions of the chelate ring causes successive rises of appearance potential of similar magnitude in the sequence $Cr(acac)_3$, $Cr(tfacac)_3$, $Cr(hfacac)_3$. Although for the γ-substituted chelates the results do not correlate exactly with the substituted aromatic compounds, the order of magnitude of the variations is certainly similar (compare Tables II and III). For example, substitution of CH_3 for H reduces the appearance potential from 8.11 V for $Cr(acac)_3$ to 7.81 V for $Cr(CH_3acac)_3$, and from 9.245 V for benzene to 8.82 V for toluene. An exact correlation would not be expected since the presence of the chromium(III) and oxygen atoms in the chelate ring means that benzenoid aromaticity cannot be assumed. It seems, therefore, that the experimental results are consistent with the ionization of a π electron localized mainly on a ligand.

An alternative to the above suggestion is to consider ionization due to removal of an electron from an orbital localized mainly on the chromium atom. It is difficult to estimate the magnitude of the inductive and resonance effects of substituents on the chelate ring on the electron density at the chromium atom. It seems reasonable to assume, however, that it would be a function of the appropriate Hammett σ constants for the various substituents. For the substituents *para* to the chromium atom we have taken the representative values:[18] CH_3, −0.170; Cl, 0.227; Br, 0.232; I, 0.276; NO_2, 0.778. For the substituent *meta* to the chromium atom an appropriate value[18] would be 0.43 for CF_3. Consequently, we would predict the trend in the appearance potentials to be $Cr(CH_3acac)_3 < Cr(acac)_3 < Cr(Cl(acac)_3 \simeq Cr(Bracac)_3 < Cr(Iacac)_3 < Cr(tfacac)_3 < Cr(NO_2acac)_3 < Cr(hfacac)_3$, which differs from the observed order. It seems that the electron is not removed from an orbital localized mainly on the chromium atom, although, in view of the assumptions involved, the evidence must be taken as suggestive rather than as conclusive.

On the basis of substituent effects DeArmond and Forster[4] have made assignments in the uv and visible spectra of these chelates. The spectral shifts, relative to the acetylacetonate, quoted by them for the B and C bands and for the d–d bands, are reproduced in Table II. The B and C bands were assigned to π–π^* transitions. There appears to be no simple correlation of the spectral shifts with the measured appearance potentials. This is not surprising since it has been pointed out[16] that it is a much more difficult task to assess the contribution of the inductive and resonance effects to an excited state of a molecule than to the ground state, although inductive effects are relatively much smaller in the lower than in the more highly excited states. In addition, there is no general agreement as to the assignment of the observed bands.

It is of interest to compare the trend in appearance potentials of the Cr chelates with those of the first-row acetylacetonates.[1] In the acetylacetonates there was a general, but irregular, increase in appearance potential in the sequence $Ti(acac)_3$ to $Co(acac)_3$. In this series there is a general increase in the electronegativity of the

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TABLE IV

RELATIVE INTENSITIES IN THE MASS SPECTRA OF SUBSTITUTED ACETYLACETONATES OF CHROMIUM, AT AN ELECTRON ENERGY OF 50 V[a]

	Ion	$Cr(acac)_3$	$Cr(CH_3acac)_3$	$Cr(Clacac)_3$	$Cr(Bracac)_3$	$Cr(Iacac)_3$	$Cr(NO_2acac)_3$	$Cr(tfacac)_3$	$Cf(hfacac)_3$
a	L_3Cr^+	23	24	18	32	16	23	24	20 (0.16)
	$(L_3Cr - O)^+$						1		
b	$(L_3Cr - F)^+$							2	4 (0.08)
c	$(L_3Cr - \alpha_1)^+$								$6^{a,b}$ (0.8)
	$(L_3Cr - \gamma)^+$				1	22			
	$(L_3Cr - 2\alpha)^+$								(3.3)
	L_2CrO^+						100^a		
d	L_2Cr^+	100^a	100^a	100^a	100^a	54	8	100	100^c (1.1)
	$(L_2Cr - \alpha_1)^+$	5^d	<1					21	3^e
	$(L_2Cr - \gamma)^+$				5	100			
	$(L_2Cr - 2\alpha)^+$								(2.0)
e	$(L_2Cr - CF_2)^+$							8	21^d
	$LCr\gamma^+$			23^d	17				
f	$LCrF^+$							40	
	$(LCrF - CF_2)^+$							25^f	
	$LO_2CrOCCH_3^+$						6		
	$LOCrOCCH_3^+$						2		
	$LOCrOH^+$						24		
	$LCrOH^+$	12	9	3^d	4				
	$LCrO^+$			1	2		27		
g	LCr^+	45	22	11^d	22	17	2	30	64^d
h	$LCr - F)^+$								23
	$(LCr - \alpha_1)^+$	4							38^h
	$(LCr - CF_2)^+$							40	35^g
	$(LCr - H_2O)^+$	3							
	$Cr\gamma^+$			1					
	Cr^+	2							

[a] Detected metastable transitions are indicated by superscripts which identify the parent ion as labeled in column 1. L = ligand; α and γ, as in Table I. The intensities of doubly charged ions are shown in parentheses. In addition, there are several small peaks at masses less than LCr^+ to which no structural significance can be assigned. These peaks may arise from fragmentation of the ligand or from background. Mass 43 is often very abundant and is assigned to CH_3CO^+.

metal atom. In the Cr chelates considered here, the appearance potentials generally increase on addition of electron-withdrawing substituents to the ring. The addition of electron-withdrawing groups should increase the electronegativity of the chromium atom. Barnum's calculations[2] indicate that as the electronegativity of the central atom increases, the highest energy d_ϵ orbitals increase in energy (which would cause a decrease in appearance potential) whereas the π_3 orbitals decrease in energy (which would cause an increase in appearance potential). This trend then provides further evidence for the postulate that the electron is removed from a π ring orbital.

The Mass Spectra.—In the previous paper we reported[1] the mass spectra of the tris acetylacetonates of trivalent Ti, V, Cr, Mn, Fe, and Co but did not discuss them in detail since MacDonald and Shannon[3] had earlier discussed the mass spectra of many acetylacetonates. However, their generalizations did not cover all of the features observed in our series of compounds, and the results presented here lead to a clarification of their generalizations. The relative intensities of all except very minor peaks in the mass spectra are given in Table IV.

It is well known that the mass spectra of organic compounds have been rationalized in terms of the formation of even-electron ions and odd-electron neutral species, except when the molecule has special features which may lead to elimination of very stable even-electron neutral molecules such as H_2O, CO, C_2H_4, and a number of others. MacDonald and Shannon[3] postulated from their study that successive losses of odd-electron neutral fragments were associated with metals in which reduction of the metal occurs, *i.e.*, that on losing a neutral radical, transfer of an electron from one of the ligand orbitals to a metal orbital occurs. On a molecular orbital picture, this seems quite reasonable since the energy difference between the π_3 and the lowest energy d orbital is small.[2] It seems reasonable to interpret the differences in mass spectra of metal chelates as being due to changes in electron distribution caused by differences in electron-withdrawing power between the metals and the ligands. In the chromium series we can assess the effect of varying the electron-withdrawing power of the ligand by altering the substituents on the ring. We may then attempt to relate these results with those obtained for the $M(acac)_3$ series. By its very nature the following section has to be highly speculative, and just a few of the possible mechanisms will be considered which correlate our present results and should lead to useful predictions for other compounds of this type.

Mechanisms to account for the important peaks in most of these spectra are summarized in Figure 1. These mechanisms support the proposal of MacDonald and Shannon[3] that the most important factor in the mass spectra is the tendency toward formation of even-electron ions, accompanied when necessary by valency changes in the metal. Thus the first step in the electron-impact process is the removal of an electron from the π system to give I, an odd-electron ion. This process has been discussed earlier in the paper. An even-electron ion and a neutral radical can be formed by homolytic fission of the C–α or C–γ bonds, with transfer of one electron of the bond to the π system, to give species such as II or III. Only in $Cr(Iacac)_3$ does this process give rise to a large peak, although small peaks are present in $Cr(Bracac)_3$ and $Cr(hfacac)_3$ spectra. Such a process would be expected to be significant when

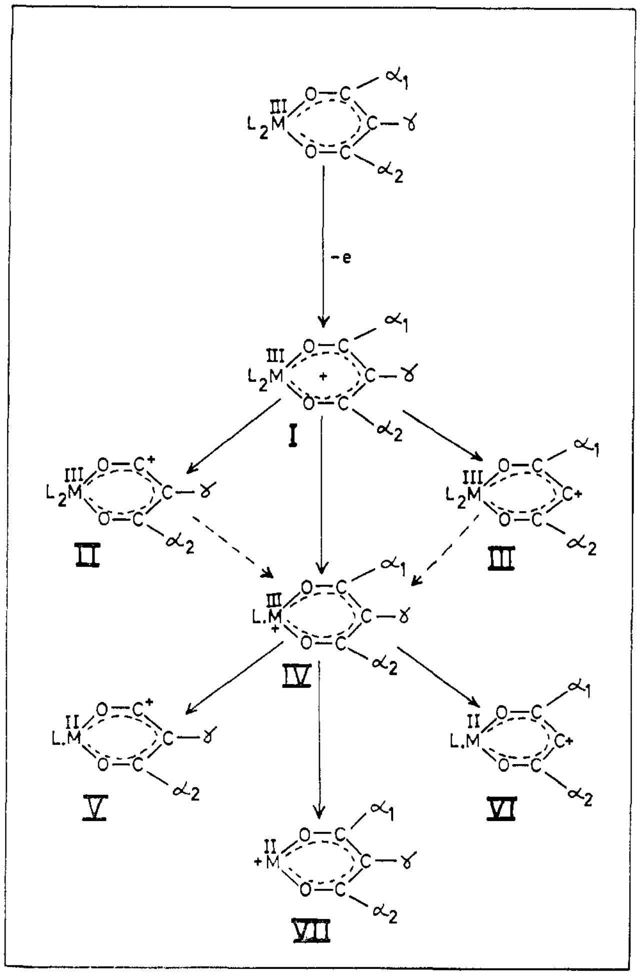

Figure 1.—Partial scheme showing some suggested fragmentations. Other pathways are possible. The ions II, III, V, and VI could also be written with open chain structures.[8]

the C–α or C–γ bonds are weak or when there are other electronegative groups on the ring to increase the positive charge on the ring. The former appears to be important for the present series of γ-substituted acetylacetonates where the intensity of the peak due to III is consistent with the relative bond strengths C–I < C–Br < C–Cl ≤ C–NO_2 in aromatic compounds but not consistent with the order C–NO_2 < C–I < C–Br < C–Cl in aliphatic compounds. The second factor is probably of importance in explaining the nonexistence of II in the spectrum of $Cr(tfacac)_3$, whereas there is a small peak in the spectrum of $Cr(hfacac)_3$. The CF_3 group will increase the positive charge on the ring more than will a CH_3 group.

An alternative process to the above is the loss of a ligand to give ions such as IV. This process is preferred in nearly all of these compounds. An exception is the nitro-substituted chelate which exhibits different behavior from the others and will be discussed separately later. The precursor of IV could be II or III, but metastable peaks (Table IV) indicate that IV will usually be formed on decomposition of I. There appears to be no significant trend in the intensities of this peak, either in this series of chromium chelates or in the acetylacetonates of part II,[1] and this peak will not be discussed further. It should be noted, however, that we postulate the valency of the metal to remain at 3, for reasons which will become evident presently.

We may now consider fragmentation of the even-electron ion IV to either V or VI. In agreement with MacDonald and Shannon's proposal, this process requires both (a) the breaking of the C–α or C–γ bond and (b) the transfer of an electron from ligand to metal. The electron transfer seems reasonable in this reaction since in the acetylacetonates of part II the intensity of the peak due to V increased in the same order as the normal ease of reduction of the central metal atom. Part a of the process would be favored by weak C–α or C–γ bonds, whereas part b would be hindered by electron-withdrawing substituents on the same ring because the ligand electrons would be more tightly held, even though the chromium atom becomes more electronegative itself owing to electron-withdrawing substituents on the other ring. Thus, V is abundant in the spectrum of $Cr(tfacac)_3$ in which the C–α_1 bond is relatively weak and the rest of the ligand is not sufficiently electronegative to prevent relatively facile electron transfer to the metal. The ion V is much less abundant in the case of $Cr(hfacac)_3$ because the second CF_3 group increases the electronegativity of the rest of the ligand and reduces the ease of electron transfer to the metal as the first CF_3 group is eliminated. The ion VI is abundant only in the spectrum of $Cr(Iacac)_3$ and the only other compound in which it is present is $Cr(Bracac)_3$, an observation which is consistent with the strengths of the C–γ bonds as discussed earlier.

The even-electron ion IV can also fragment to the ion VII. MacDonald and Shannon postulated a valency change for this reaction because the intensity of this peak in the metal acetylacetonates increases with ease of reduction of the metal atom. In this reaction the strength of the metal–oxygen bonds and the ease of transfer of an electron from ring to metal again appear to be important, and there appears to be no clearly defined trend in the relative intensities of VII in the mass spectra of these chromium chelates, since these effects are in opposition. Thus, there is considerable evidence from stability constant data,[19,20] polarographic half-wave potentials,[21–24] and infrared spectra[25,26] that electron-withdrawing substituents decrease the metal–oxygen bond strength. On this

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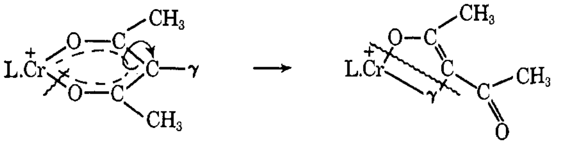
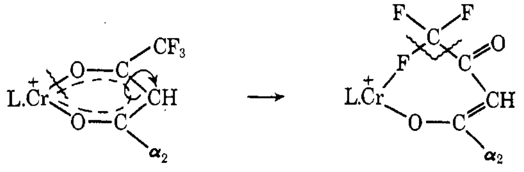
basis, we would expect $Cr(acac)_3$ to have a smaller VII peak than the other chromium chelates (except for $Cr(CH_3acac)_3$) whereas it is one of the largest. Again, we postulate that electron-withdrawing substituents on the ring hinder electron transfer to the metal, making the reaction IV → VII more difficult.

A mechanism for the formation of the $LCrOH^+$ ion has been given by MacDonald and Shannon.[3] It is also formed in small amounts in the $Cr(Clacac)_3$ and $Cr(Bracac)_3$ spectra.

There are a number of noteworthy rearrangement peaks, involving migration of halogen atoms, in the spectra. The site to which the halogen migrates is not known but is presumably the metal atom. Probably the driving force for the reaction is the strength of the metal–halogen bond. A suggested mechanism for the process involves fission of one Cr–O bond, followed by a suitable rotation of part of the ligand about the 2,3 C–C bond, which brings the halogen atom close to the metal atoms as in VIII and IX or in X and XI. In a presumed concerted process the metal–halogen bond is formed and a neutral species is eliminated. The neutral species is the rest of the ligand moiety, or in the CF_3 substituted chelates it is CF_2. The peaks which may arise in this way are $(L_2Cr - CF_2)^+$, $LCr\gamma^+$, $LCrF^+$, $(LCr - CF_2)^+$, and possibly $Cr\gamma^+$. The process does not seem to occur readily until one ligand has already been lost. This may be due to steric hindrance in the parent molecule ion. The rearrangement processes, which have been observed in many of these volatile chelates,[27,28] are often accompanied by prominent metastable peaks (see Table IV).



VIII IX



X XI

Further fragmentation of the chelate to lighter species than VII was not extensive in any of the chelates examined here. A peak at *m/e* 43, assigned to CH_3CO^+, was often the only peak which was obviously distinguishable from background peaks.

The NO_2-substituted chelate deserves some separate discussion. A distinctive feature of the spectrum is the relatively great abundance of oxyions (the base peak is assigned to $CrO(NO_2acac)_2{}^+$). The origin of the oxygen atom bonded to the chromium atom has not been confirmed, but it seems reasonable to assume that it is not from the nitro group. Migration of an oxygen atom from the NO_2 group to the metal would require a rearrangement process similar to the one described above for the halogenated chelates, and in the tris-NO_2 acac chelate would probably be sterically hindered.

The NO_2 group is a powerful electron-withdrawing group, the resonance effect directing the positive charge to the chromium atom. The positive charge on the metal could be reduced by the resonance effect by the formation of chromium–oxygen double bonds, in for example $L_2Cr{=}O^+$ and $LCr{=}O^+$. Another prominent oxy species is $LOCrOH^+$. The only other ions worthy of comment in this spectrum are $LO_2CrOCCH_3{}^+$ and $LOCrOCCH_3{}^+$, which are of low abundance and are possibly formed by elimination of $CH_3C{\equiv}C\text{-}NO_2$ from L_2CrO^+ and L_2Cr^+, respectively.

Very small $LCrO^+$ peaks are also observed in the $Cr(Bracac)_3$ and $Cf(Clacac)_3$ spectra. For these compounds the resonance effect is smaller.

Doubly charged ions were observed in the mass spectrum of $Cr(hfacac)_3$. A possible mechanism for their formation, consistent with the foregoing discussion, speculates that the two electrons are lost from different chelate rings and is as follows. The ions $(L_3Cr^{III} - F)^{2+}$ and $(L_3Cr^{III} - \alpha)^{2+}$ achieve even-electron character in one of the rings from which an electron was lost by eliminating F and $\cdot CF_3$, respectively, although the ion as a whole remains an odd-electron ion. The ion $(L_3Cr^{III} - \alpha)^{2+}$ can give rise to an even-electron ion by eliminating $\cdot CF_3$ from the second ring to give $(L_3Cr^{III} - 2\alpha)^{2+}$, the most abundant of the doubly charged ions. This ion can now eliminate the remaining intact ligand radical with consequent electron transfer to the metal to give the even-electron ion $(L_2Cr^{II} - 2\alpha)^{2+}$.

We are now in a position to compare these spectra with those of the tris acetylacetonates previously reported.[1] The main decomposition pathways are illustrated in Figure 1. For the acetylacetonates, a similar mechanism has been described by MacDonald and Shannon.[3] We have shown in the previous paper[1] that species V and VII increase in intensity from $Ti(acac)_3$ to $Co(acac)_3$. In the present paper, we have suggested that the reaction IV → V should be enhanced by a weak C–α bond and rapid electron transfer from ligand to metal. For the acetylacetonates, as the electronegativity of the central metal atom increases from Ti to Co, we would expect the C–α bond to weaken slightly and the electron transfer to be facilitated, leading to an increase of the peak due to V, from Ti to Co. Similarly, for the reaction IV → VII, the metal–oxygen bond energies decrease from Ti to Co,[29] and the electron transfer should be facilitated in the same order owing to the increase in electronegativity of the central metal atom. The intensity of the (P −

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[27] C. Reichert, G. M. Bancroft, J. B. Westmore, and H. D. Gesser, unpublished results.

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2(acac))$^+$ peak (VII) increases, as would be expected from this approach.

In discussing these results we have not considered the geometry of the species, *e.g.*, whether the L$_2$Cr$^+$ ions are tetrahedral or square planar. We have assumed that any geometrical rerrangement does not have a great effect on the mass spectra. The results suggest that this is a valid assumption, since, apart from the electronic effects of one ring at the central metal atom, the rings fragment independently of each other, and in most cases one ring fragments completely before fragmentation of the next begins.[3]

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A Proton Magnetic Resonance Ligand Preference Study of Complexes of Acetone, Diethyl Ether, N,N-Dimethylformamide, Dimethyl Sulfoxide, Tetrahydrofuran, Tetramethylene Sulfone, Tetramethylene Sulfoxide, and Tetramethylurea with Boron Trifluoride

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A proton magnetic resonance ligand preference study of complexes of acetone (A), diethyl ether (EE), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), tetramethylene sulfone (TMSO$_2$), tetramethylene sulfoxide (TMSO), and tetramethylurea (TMU) with boron trifluoride has been completed. By adding boron trifluoride to pure, excess ligand and cooling to temperatures suitable to slow solvent exchange, proton magnetic resonance signals were observed for bulk and complexed ligand molecules. By studying samples containing two organic bases and integrating all signal areas, a direct, quantitative measure was made of the amount of boron trifluoride complexed by each component. In this way complexing ability was estimated to decrease in the order TMSO > DMF, DMSO > TMU $\gg$ THF $\gg$ EE > A > TMSO$_2$. This order reflects the relative basic strengths of these molecules toward BF$_3$.

Introduction

Many calorimetric[1-5] and spectroscopic[6-12] studies of metal ion or boron trihalide complexes have been carried out with the purpose of assessing the relative acceptor strengths of these Lewis acids or the donor strengths of the variety of organic bases investigated. Some of these representative calorimetric studies include complexes of the boron trihalides with pyridine and nitrobenzene,[1] alkyl ethers, sulfides, and amines,[2] and dimethyl sulfoxide and ethyl acetate.[3] By similar methods, the relative acceptor strengths of the gallium halides toward pyridine and triethylamine[4] and ethyl ether and methyl and ethyl sulfides[5] have been estimated. Nuclear magnetic resonance (nmr) chemical shift investigations of boron trihalide complexes include ligands such as trimethylamine,[6] ethers,[7,8] benzophenone, pyridine, and triethylamine (^{11}B resonance),[9] N,N-dimethylformamide,[10] ureas and thioureas,[11] and water (^{19}F and proton resonance).[12] The proton magnetic resonance (pmr) studies are based on the observation of chemical shift differences between pure ligand and the presumed 1:1 complex, each investigated in an inert solvent. It has been demonstrated recently[13-15] that a more quantitative approach involves the study of the complex in the presence of excess ligand, at temperatures low enough to slow solvent exchange and permit the direct observation of pmr signals of bulk and complexed molecules of the base. This method allows a more accurate measure of the chemical shift separation between pure and complexed ligand proton signals and a quantitative measure of the composition of the complex. Systems already reported include ethers,[13,14] pyridines,[15] and several biochemicals.[15]

Another problem which has been approached by a variety of experimental methods is the evaluation of

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