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Energetics of the Ionization and Fragmentation of Metal Chelates in the Mass Spectrometer

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I. Introduction

One of the most useful aids in the interpretation of the mass spectra of organic compounds, which are dominated by the presence of "even-electron" ions, has been the concept of charge localization. The breakdown patterns of countless organic ions have been depicted in terms of electron shifts to charge and radical sites and have been described in many texts, only the most comprehensive of which is cited here.¹ A more sophisti-

cated interpretation of mass spectra is given by the quasi-equilibrium theory²⁻⁷ in which localization of charge or radical character at the center of fragmentation is not essential. All that is required for decomposition to occur is sufficient vibrational energy concentrated in the appropriate degrees of freedom. In its present stage of development, the quasi-equilibrium theory cannot be easily applied to complex molecules to explain the quantitative features of their mass spectra.

The presence of a transition metal in a compound introduces new aspects to the mass spectra. The important concept of the ability of the metal to change valency and influence fragmentation was introduced by Shannon and co-workers,^{8,9} with the essential features summarized in a later, brief review.¹⁰ These features are often of major importance in the mass spectra of "classical complexes", which may be loosely defined¹¹ as those in which the metal atom has a well-defined oxidation number, usually +2, +3, or +4, and a set of ligands with a discrete electron population. On the other hand, the influence of valency change in the metal is largely suppressed in the case of "non-classical complexes", including organometallic compounds, where the metal oxidation state is indistinct and normally regarded as low (formally +1, 0, or even negative). Support for the charge localization concept as an interpretation of the mass spectra of organic compounds is often obtained from studies of the energetics of ionization and fragmentation of molecules. Correspondingly, studies of similar type made on metal complexes should be useful in interpreting their mass spectra. Much effort has been directed toward determining whether the electron removed upon ionization of the molecule comes from a metal- or a ligand-dominated orbital. Useful information has also been obtained by determining the energies required for simple fragmentations of the molecular ions. Subsequent fragmentations have been less well characterized, and the energetic data more difficult to interpret, when several bonds must be broken in the formation of further fragment ions. In addition to surveying and evaluating the experimental data of this type reported for "classical complexes", a further purpose of this review is to relate these data, where possible, to the valence change concept.

Lack of suitable volatility and/or thermal stability impose limitations on the type and variety of "classical complexes" which can be studied by mass spectrometry. Apart from the halides of transition metals the mass spectra of neutral complexes involving only monodentate ligands have not been fre-

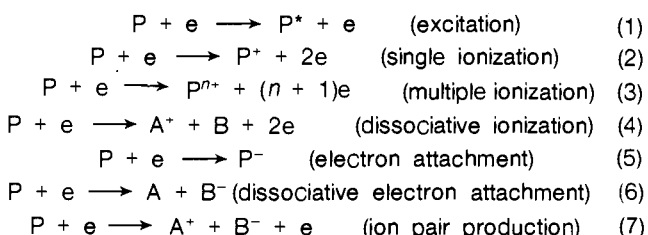
quently reported. The majority of complexes for which spectra have been obtained are neutral chelate complexes. Only in certain cases were energetic studies made. In effect, these considerations restrict the metal chelates described in this review to those involving a central transition metal, bonded to which are ligands having oxygen or nitrogen as the σ -donor atoms. Literature coverage extends to late 1974.

II. Molecular Ionization and Fragmentation

This section briefly outlines features of molecular ionization, and the measurement and significance of ionization and appearance potentials, which will be relevant to interpretation of results contained in the main body of the review.

A. Ionization Processes

The most important processes which occur when an electron of sufficient energy interacts with a neutral molecule P are summarized by eq 1-7. (In this review P and P⁺ are used to



represent the parent molecule and molecular ion respectively, rather than the conventionally used M and M⁺, which here denote metal and metal ion, respectively.) The formation of charged species, positive or negative, in eq 2-7, can be directly studied by means of a mass spectrometer. Determination of the threshold energies for these reactions can be achieved experimentally by interpretation of ionization efficiency curves, via methods to be outlined in section III.

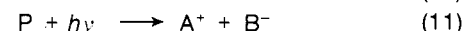
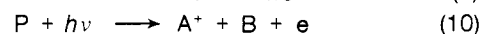
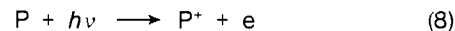
Processes 1-7 are governed by the Franck-Condon principle. When the probability of an ionizing transition, according to eq 2, leading to the ground vibrational state of the molecular ion is high, then the vertical ionization potential (defined as the minimum energy necessary to remove an electron from the neutral molecule without change of molecular configuration) is the same as the adiabatic ionization potential (defined as the energy difference between the ground vibrational level of the lowest energy electronic state of the neutral molecule and the molecular ion). Often the Franck-Condon parameters are such that a high proportion (perhaps virtually all) of the P⁺ ions are produced in vibrationally (or sometimes electronically) excited states, with only a small proportion in the lowest possible energy state. (In extreme cases, the Franck-Condon parameters may be such that ionization is to a point on the potential energy surface above the dissociation asymptote or to a repulsive state, so that molecular ions are not detected.) The experimentally measured value of the threshold potential may depend upon the sensitivity of the mass spectrometer and the ion detecting system used, and also upon the way in which the ionization efficiency curve is interpreted. Thus, the measured threshold value for eq 2 is often larger than the adiabatic ionization potential of P. On the other hand, even though vertical ionization occurs, the measured ionization threshold will be somewhat lower than the vertical ionization potential (particularly if the ion detecting system has high sensitivity) because of the small but finite overlap integral between the ground vibrational state of the neutral molecule and lower vibrational states of the molecular ion. Thus, the measured ionization threshold will lie between the adiabatic and vertical ionization potentials and is usually taken as an upper limit for the former.

The threshold potential for eq 2, as determined by mass

spectrometry, is generally described as an "ionization potential". Strictly speaking, this is incorrect in view of the preceding definition and discussion, since the value may be high, but is consistent with an operational definition given by Field and Franklin,¹² namely ". . . the ionization potential can be defined as the minimum energy of the bombarding electrons at which the formation of molecule-ions (or atomic ions) can be detected in a given apparatus, and similarly, the appearance potential of a fragment ion is the minimum electron energy at which the fragment ion can be detected." These definitions of ionization potential (IP) and appearance potential (AP) will be adopted here. As with the IP, the operational AP is usually larger than the theoretical AP, defined as the energy required to produce the ion and accompanying (neutral) fragment(s) from a given molecule, all entities involved being in their ground states. Contributions to the excess energy potentially arise from a number of sources, e.g., formation of products in excited electronic or vibrational states, kinetic energy release on fragmentation, and/or requirement of sufficient activation energy for fragmentation to occur at a rate compatible with the prevailing conditions in the mass spectrometer (section II.C).

For the process of eq 5 the threshold potential (also known as the resonance potential) yields, in principle, the electron affinity of P. Excess energy is an important consideration in the processes of eq 6 and 7. Further details are postponed until section III.B.

Ionization and fragmentation of molecules, via processes represented by



can also be induced by photons of sufficient energy. Threshold energies for these processes can be determined by a variety of methods. A review of the techniques of photoionization mass spectrometry is available.¹³ Applications have so far been fewer than for electron impact methods, presumably because of the increased complexity and expense of the apparatus. The method requires the availability of photon sources of suitable intensity over a range of energies in the vacuum-ultraviolet extending to about 600 Å, a monochromator, differential pumping, and sensitive detectors for the low ion currents produced. Many important results have been obtained with this technique.

Vacuum-ultraviolet absorption spectroscopy, which requires the analysis of the electronic spectrum of a molecule, is capable of yielding precise and accurate values of the IP, by interpretation of vibrational bands in the electronic transitions.¹⁴⁻¹⁷ It is necessary that the (0,0) transition be positively identified by analysis of the vibrational structure or by comparison with the spectra of isotopic molecules. Because it is difficult to interpret molecular absorption spectra, very few results are available for complex molecules.

Photoelectron spectroscopy has been used to measure adiabatic and vertical IP's of many molecules (from band onsets and band maxima respectively) as well as inner IP's. The subject has been extensively reviewed.¹⁸⁻²⁹ This method can be used to obtain a great deal of information about molecular electronic structures but does suffer from some limitations. As with electron impact methods, the adiabatic transition may have very low probability, and band structure may not be well resolved, making evaluation of the adiabatic IP uncertain. Modern commercially available spectrometers do not include mass analysis so that dissociation processes are not identified. Sample vapor pressures of 0.1-10 N m⁻² ($\sim 10^{-3}$ - 10^{-1} Torr) are required,²⁷ compared with 10^{-6} - 10^{-5} Torr needed for electron-impact mass spectrometry. The requirement of stable, easily volatile complexes may place a serious restriction on the number of

metal complexes that can be studied by photoelectron spectroscopy.

Most of the experimental results to be described in this review have been obtained by electron-impact mass spectrometry. A number of results from photoelectron spectroscopy are also included.

B. Koopmans' Theorem and Ionization Potentials

The ionization potential of a molecule is given by

$$IP = E_{\text{total}}^{\text{ion}} - E_{\text{total}}^{\text{molecule}} \quad (12)$$

To interpret experimental results it is often necessary to attempt to correlate observed IP's with calculated molecular orbital energies. In Koopmans' theorem³⁰ the IP is approximated by

$$IP = -\epsilon_i^{\text{SCF}} \quad (13)$$

in which ϵ_i^{SCF} is the energy eigenvalue of the i th molecular orbital computed in an ab initio self-consistent field (SCF) calculation. Thus, the molecular ionization potential is given by the negative of the energy eigenvalue of the highest occupied molecular orbital. So-called inner ionization potentials are obtained when an electron is removed from an orbital of lower energy. The theorem thus assumes that there is no change in molecular geometry or alteration of wave functions describing the remaining electrons upon ionization. Richards³¹ has discussed some of the approximations inherent in Koopmans' theorem. These are (a) the reorientation approximation, in which it is assumed that in a closed-shell molecule the occupied MO's are unchanged when going from molecule to ion; (b) the relativistic energy approximation, in which relativistic effects are neglected (for outer electrons the correction is small and may be ignored); (c) the correlation energy approximation, in which pair interactions between electrons are assumed to be the same in both the molecule and ion. Generally, the correlation energy will be less in the ion than in its parent molecule. In addition to these approximations there are additional problems in the application of Koopmans' theorem to open-shelled molecules.

Koopmans' theorem must therefore be applied with caution. This is especially true when considering ionization potentials of transition metal complexes, which because of their partially filled d orbitals are not closed-shelled molecules.³²

C. Appearance Potentials of Fragment Ions

By methods which are well known, appearance potentials of fragment ions have often been used to obtain thermochemical information, such as bond dissociation energies, and heats of formation of ions, molecules, and radicals. Such information can also be used to rationalize some of the qualitative features of the mass spectra of the molecules involved. At this stage it is helpful to outline some of the important points which arise from the quasi-equilibrium theory of mass spectra, details of which can be obtained from ref 2-7.

On ionization by electrons, molecular ions are produced having a range of excitational energies distributed among their electronic, vibrational, and rotational degrees of freedom. The quasi-equilibrium theory assumes that the excited molecular ion does not decompose immediately into the various fragment ions and neutral fragments, but that the ion may undergo several vibrations prior to decomposition. During these vibrations there is a high probability of radiationless transitions among the many potential surfaces of the ion (subject to energy and momentum restrictions), which results in a distribution of the energy in a completely random fashion. The molecular ion decomposes only when sufficient energy has concentrated in the necessary degrees of freedom. Assuming the molecule to be a collection of weakly coupled harmonic oscillators and using a statistical approach the following equation

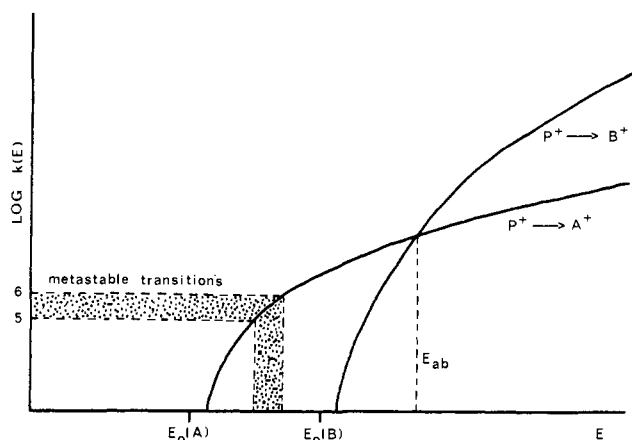


Figure 1. Rate curves as a function of energy, E , of the molecular ion.

$$k(E) = \nu [(E - E_0)/E]^{N-1} \quad (14)$$

was obtained for the unimolecular rate constant, $k(E)$, for the dissociation of the molecular ion. In this equation, E is the total excitational energy of the ion, and $k(E)$ represents the rate constant for decomposition to a given fragment ion in a reaction with activation energy E_0 . The number of oscillators is N , an ν may be regarded as a frequency factor incorporating the ratio of the products of the vibrational frequencies of the reactant to the activated complex multiplied by the number of equivalent ways of choosing the reaction coordinates. The failure of eq 14 to give quantitatively accurate rate constants (in particular, too shallow a rise of $k(E)$ near threshold), at least in many instances, was attributed to the crudeness of the approximations used in its derivation.³³ If the same form of expression is retained, experiment requires a much smaller value for N . Representative plots of k vs. E for a competitive decomposition of the molecular ion $P^+ \rightarrow A^+$ and B^+ are shown in Figure 1. The reaction $P^+ \rightarrow B^+$ has both a higher activation energy and a higher frequency factor than the reaction $P^+ \rightarrow A^+$. When $E < E_0(B)$, decomposition exclusively to A^+ occurs. When $E > E_{ab}$, decomposition to B^+ is preferred.

The residence time of the molecular ion in a conventional electron impact ion source is typically about 10^{-6} s. Therefore, for a fragment ion to be expelled from the ion source and recorded in the mass spectrum it is necessary that $k(E) > 10^6 \text{ s}^{-1}$ approximately. Figure 1 shows that the measured appearance potential will be somewhat greater than the minimum energy required to form the fragment ion in question. The excess energy required to achieve a rate constant necessary for decomposition in the ion source is called the kinetic shift.³³ It has been deduced from quasi-equilibrium theory that the kinetic shift increases with increasing E_0 , increasing molecular size, and decreasing ν . The kinetic shift is often negligible but can sometimes be quite large (see below). Figure 1 also shows that when $k(E)$ for formation of B^+ reaches 10^6 s^{-1} the value of $k(E)$ for formation of A^+ is substantially higher; i.e., formation of B^+ competes unfavorably with formation of A^+ . Thus, the reaction for formation of B^+ has to proceed at a rate considerably faster than 10^6 s^{-1} for B^+ to be observed. The excess energy required in this case is termed the competitive shift.

Metastable decompositions are often useful for estimating energies of ion fragmentations. In conventional magnetic sector instruments without modification the rate constants are typically in the range 10^5 – 10^6 s^{-1} , and the decompositions will be observed for ions having the narrow energy distribution shown in Figure 1. A large difference between the AP's of metastable and daughter ions should be indicative of a large kinetic shift. Thus, for certain fragmentations of the molecular ions of aromatic compounds large kinetic shifts can cause errors in heats of

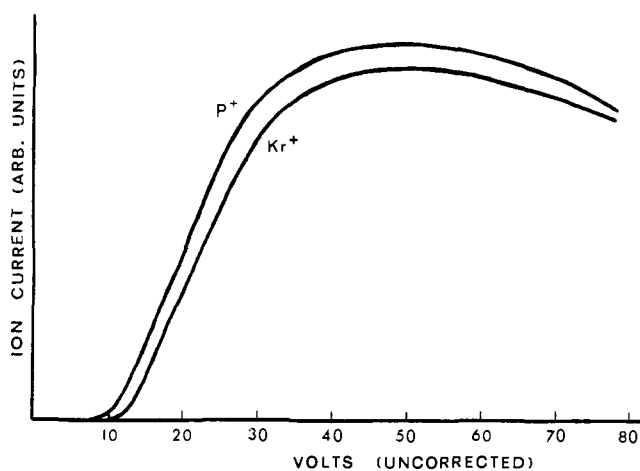


Figure 2. Representative ionization efficiency curves for formation of molecular ion P^+ and calibrating Kr^+ ion.

formation of 1 eV or more.^{4,34-37} The large kinetic shifts have been attributed to low frequency factors for the rearrangement reactions involved.³⁶ Kinetic energy release in metastable ion decompositions can be determined by the technique of ion kinetic energy (IKE) spectroscopy.³⁸

Above certain energies, further decomposition to secondary product ions may occur (e.g., $P^+ \rightarrow A^+ \rightarrow C^+$, etc.). Because excess energy will be distributed between ion and neutral products it can be anticipated that considerable kinetic shifts would contribute to the AP's of such ions.

A further factor which can influence AP determinations is the thermal shift. Since, at the temperature of the ion source, vibrational and rotational energy levels of the parent molecule above the lowest level may be populated, less energy than the true critical energy would be required to produce the ion at threshold. The thermal shift thus acts in opposition to the kinetic shift. For moderately complex molecules the thermal shift may be greater than the experimental uncertainties often quoted for AP's. For *n*-hexane the thermal shift between IP's determined at 28 and 150 °C was found to be 0.16 eV.³⁹ On the other hand, for many molecules AP's seem to vary little with temperature, and the experimental AP's are combined with standard heats of formation of reactants and products at 298 K when derived values are calculated.⁴⁰

For most studies of ionization and ion-dissociation reactions the magnitudes of excess energies, kinetic shifts, and ion kinetic energies have been unknown, and have been assumed to be small. In spite of this, the heats of formation of a given ion by several different routes (excluding rearrangement and/or multicenter decomposition processes) are often consistent, supporting the generalization that a large proportion of fragment ions are formed in reactions involving unexcited products.⁴¹ The possibility that the same excess energy was involved in each case was considered unlikely.

The heats of formation of many ions have been determined. The most comprehensive and up-to-date compilations are found in ref 12 and 42.

III. Experimental Methods for Ionization and Appearance Potential Determination

In principle, threshold potentials for the reactions of eq 2-7 can be obtained from ionization efficiency curves by extrapolation to zero ion current. A typical curve for the formation of the molecular ion is shown in Figure 2. The electron energy can be controlled by a potential difference between the electron-emitting hot filament and the ionization chamber. Unfortunately, because electrons emitted by a hot filament have a nearly Maxwellian energy distribution, the electron beam could have

an energy spread (i.e., the width at half-height of the energy distribution curve) of 0.4 eV or more, depending upon the filament temperature. Further uncertainties in the electron energy arise from field penetration and contact potentials within the ionization chamber. To minimize these difficulties it is usual to calibrate the energy of the electron beam by introduction of a substance of accurately known IP whose ionization efficiency curve can be compared with that of the substance under investigation. The preferred choice of standard would be one having an IP similar to that of the sample under investigation, and giving an ion of *m/e* ratio as close as possible to that of the sample under study (to minimize the effects of mass discrimination in the mass spectrometer). Ideally, the calibrating substance should have similar Franck-Condon parameters to those of the sample under study, but, in practice, this is rarely possible or convenient. The noble gases have frequently been used as standards. Of these, xenon has been most often used because its high mass and lower IP are closer to the respective values for most substances which have been studied. Other calibrating standards which have been used include N_2 , Hg (which is present in the background spectrum when mercury diffusion pumps are used), and benzene.

A. Positive Ions

The most accurate determination of IP's and AP's by electron impact will be achieved using a monoenergetic beam of electrons. Since the instrumentation is complex, and not routinely available with commercial mass spectrometers, most determinations have been made with electron beams having normal energy spreads. The inhomogeneity of the energy of the electron beam is accepted, and the AP's have been extracted from ionization efficiency curves in various ways, none of which is entirely satisfactory.

Many methods of determination have been critically discussed in ref 12. These include the simpler "vanishing current" or "initial break",⁴³ "extrapolated voltage difference",⁴⁴ "linear extrapolation",⁴⁵ "critical slope",⁴⁶ and "semilogarithmic plot" methods.⁴⁷ The "energy compensation" technique⁴⁸ is a rapid method of achieving instrumentally via the use of a dual channel recorder effectively the same result as the "simplified procedure" of the semilogarithmic method.

Alternative approaches to obtaining more information from ionization efficiency curves have been computational in nature, including the "derivative"⁴⁹⁻⁵² and "deconvolution"⁵³ methods of Morrison. Although the results were promising, the methods do not appear to have been widely used for polyatomic molecules, probably because of their relative complexity. A simpler, analytical method of reducing the effective energy spread is the "energy distribution difference" method,⁵⁴ which should find wide applicability. Although not essential, for this latter method a computer program has been designed to remove manual line fitting of the data points obtained.⁵⁵ Curve fitting methods have also been applied to ionization efficiency curves⁵⁶ but it is too early to say whether the method will be widely applied.

The most widely used instrumental method of reducing the effective energy spread of the electron beam is the "retarding potential difference" method.^{57,58} An improved design has been described for the special type of ion source required.⁵⁹

Several efforts have been made to reduce the actual energy spread of the ionizing electron beam.⁶⁰⁻⁶⁵ By means of electron energy selectors a beam with an energy spread of 0.03 eV can be obtained. The maximum ion currents which can be produced are small and the signal-to-noise ratio near threshold is poor. Even though monoenergetic electron beams are being used successfully, there are considerable difficulties involved.⁶⁶ Various types of electron beam sources have been tabulated and assessed.⁶⁷

In summary, of the methods outlined, the most convenient for

the research worker using commercially available general purpose mass spectrometers are the methods based on the use of energetically nonhomogeneous electron beams. The "vanishing current" and "linear extrapolation" methods, although still occasionally used, are not to be recommended. The "extrapolated voltage difference" and "semilogarithmic plot" methods seem to have been preferred in the past, while the more recent "energy distribution difference" method should also become widely used. Reproducible results may usually be readily obtained by these methods, but the absolute accuracy is commonly unknown. Quoted error limits are usually average or standard deviations of several determinations.

B. Negative Ions

Negative ions can be produced by electron impact by the reactions of eq 5–7. The ionization efficiency curves for formation of negative ions by eq 5 or 6 are very different from those for formation of positive ions. In eq 5 the negative ion is formed by electron capture, and there is no product electron to carry away the excess energy as in eq 2–4. Thus, the capture process is a resonance process and will occur only if the energy of the impacting electron lies within a relatively narrow range. This is true in principle, even if the electron capture brings about dissociation of the molecule, as in eq 6, because the range of kinetic energies of the relatively massive particles formed in the dissociation is relatively small. For ion pair production (eq 7) three particles, including an electron, are produced and the reaction is not a resonance process.

The width of the electron capture resonance peak is partly due to inhomogeneities in the energy of the electron beam and partly due to the nature of the transition involved in the formation of the ions. By the retarding potential difference method, it was shown that the resonance capture peak for formation of SF_6^- had a half-width of about 0.1 eV, the same as that of the energy distribution of the electron beam.⁶⁸ Thus, for this reaction the resonance capture occurs over an energy range no greater than 0.1 eV.

Several of the methods applicable to positive ions have been used for the determination of the AP's of negative ions, though the determinations are usually more difficult owing to lack of spectroscopic standards for calibration of the electron energy at low energies, the broadening of the resonance capture peaks due to the thermal energy distribution, and the translational energy of the fragments in a dissociative process. For energy calibration and evaluation of the electron energy distribution the resonance capture peak for the formation of SF_6^- from SF_6 (occurring at 0.08 eV⁶⁹) is often used. A comprehensive review of negative ion mass spectrometry is available.⁷⁰

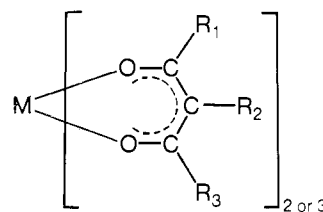
IV. Ionization Potentials of Metal Chelates

In this section the IP's of metal chelates, measured by mass spectrometry, are discussed in the light of present knowledge of structure and bonding in the complexes. Where possible, the values will be compared with results obtained from photoelectron spectroscopy. The linear correlations of IP with a number of other parameters, including Hammett σ constants, stability constants, acid dissociation constants of the ligand, polarographic half-wave potentials, and Mössbauer center shifts will be considered.

Table I summarizes the available IP and AP results. Abbreviations used in this review for ligands are given as a footnote to the table. Most of the results have been obtained for β -diketonate complexes, which are volatile and thermally stable and allow the possibility of studying the effects of substituent changes in the ligand, or of change of metal. Additionally, structural and theoretical studies have been made on complexes of this type.

A. Structure and Bonding in β -Diketonate Complexes

Since a comprehensive review⁷¹ of the chemistry and properties of metal β -diketonate complexes is available, only some relevant features are outlined here. The complexes of concern can be represented by the structural type:



An X-ray structural determination⁷² on $\text{Fe}(\text{acac})_3$ reveals that the chelate rings are planar, the C–C distances (1.39 Å) are equal to each other and to the C–C distance in benzene, and both C–O distances (1.28 Å) are intermediate between single and double bond lengths, indicating delocalization of π electrons over the chelate ring. Similar observations apply to a number of other $\text{M}(\text{acac})_n$ complexes.⁷¹ With a few exceptions, complexes of trivalent metal ions have a nearly octahedral arrangement of the oxygens about the metal. On the other hand, complexes of divalent metals typically have different structures in the gaseous and condensed phases. In the gaseous state the bisacetylacetonates of Mn, Fe, Co, and Zn are tetrahedral while those of Ni and Cu are square planar. In the solid state they are polymeric, with the exception of $\text{Cu}(\text{acac})_2$, while in solution, if the polymeric form does not persist, solvation usually occurs.⁷¹

The chelate rings in β -diketonate complexes have many properties in common with aromatic compounds, in addition to the structural data. For example, they undergo certain reactions characteristic of aromatic compounds, such as halogenation and nitration,^{73–77} and NMR studies indicate some delocalization of electrons between metal and ligand.^{78,79} However, Holm and Cotton⁸⁰ reformulated the "benzenoid" resonance structure of Calvin and Wilson⁸¹ into one in which the principal π delocalization occurs independently of the metal ion and showed that the position of the C–H resonance afforded little evidence for "aromatic character". A truly aromatic ring is not expected since there is an energy barrier at the metal ion to free circulation of π electrons around the ring.⁸² This barrier arises because the t_{2g} orbitals (in a regular octahedral complex) each have a nodal plane perpendicular to the chelate ring with which they interact and are orthogonal to each other. The barrier is not expected to be infinitely high since the orthogonality of the t_{2g} orbitals is partially removed by strain in the chelate ring, and the metal 4p orbitals (for a metal of the first transition series), which offer no such potential barrier, also take part in metal–ligand π -bonding. The chelate ring in β -diketonate complexes is often described as quasi-aromatic.

Hückel semiempirical calculations^{82–85} and self-consistent field calculations^{85,86} were performed in an effort to interpret some of the finer points in the electronic absorption spectra of metal β -diketonate complexes. The important features of the molecular orbital energy level diagram for an acetylacetonate complex of a trivalent metal, showing the upper occupied levels, are illustrated schematically in Figure 3. This diagram is based on octahedral coordination and point group D_3 and includes the effects of π -bonding. The actual positions of the levels depend upon the identity of the transition metal. According to Barnum⁸² the energy of the metal–oxygen π -bond ranges from near zero for $\text{Ti}(\text{acac})_3$ to about 40 kcal/mol per bond for $\text{Co}(\text{acac})_3$ (compared with 63.2 kcal/mol for the π -contribution to the energy of a C=C double bond, and 94 kcal/mol for a C=O double bond). This indicates substantial mixing of the d_{xy} , d_{xz} , and d_{yz} orbitals with ligand π_3 orbitals. Recognizing this mixing, it is often

TABLE I. Ionization and Appearance Potential Data for Metal Chelates

(a) Complexes of Acetylacetonates and Fluorine-Substituted Acetylacetonates: Trivalent Metals, Divalent Metals, and Protonated Ligands						
Complex ^a	IP, V	AP of fragment ions, V			Method ^b	Ref
		[P - L] ⁺	[P - CH ₃] ⁺	[P - CF ₃] ⁺		
Al(acac) ₃	7.95 ± 0.05	9.1 ± 0.2			SLP, EVD(Xe)	87
	8.27 ± 0.13				VC(Hg)	32
Ti(acac) ₃	7.1 ± 0.1	11.8 ± 0.1			SLP, EVD(Xe)	87
	7.9 ± 0.1				SLP, EVD(Xe)	87
V(acac) ₃	7.72 ± 0.10				VC(Hg)	32
	8.10 ± 0.05				SLP, EVD(Xe)	87
Cr(acac) ₃	7.87 ± 0.12	11.3 ± 0.1			VC(Hg)	32
	7.40(estd)				EC(Xe, C ₆ H ₆ , C ₁₄ H ₁₀)	88
Mn(acac) ₃	7.85 ± 0.05	≥8.7 ± 0.1			SLP, EVD(Xe)	87
	7.95 ± 0.10				VC(Hg)	32
Fe(acac) ₃	8.45 ± 0.05	≥9.4 ± 0.1			SLP, EVD(Xe)	87
	8.64 ± 0.11				VC(Hg)	32
Co(acac) ₃	7.80 ± 0.05	10.7 ± 0.3			SLP, EVD(Xe)	87
	7.81 ± 0.10				NS	c
Rh(acac) ₃	7.75 ± 0.1				CS(Xe)	110
	7.34 ± 0.01				EC(Xe, C ₆ H ₆ , C ₁₄ H ₁₀)	89
Al(tfacac) ₃	9.05 ± 0.1	10.2 ± 0.1			SLP(Xe)	118
Cr(tfacac) ₃	9.09 ± 0.05	11.9 ± 0.1			SLP(Xe)	95
Fe(tfacac) ₃	9.10 ± 0.05	9.2 ± 0.1 ^d			SLP(Xe)	118
	9.38 ± 0.11				VC(Hg)	32
Al(hfacac) ₃	9.80 ± 0.1	11.2 ± 0.1		10.7 ± 0.1	SLP(Xe)	118
	10.30 ± 0.11				VC(Hg)	32
Cr(hfacac) ₃	10.13 ± 0.05	14.3 ± 0.1			SLP(Xe)	95
	9.97 ± 0.08				VC(Hg)	32
Fe(hfacac) ₃	9.21 ^e	10.2 ± 0.1 ^d		11.1 ± 0.1	PI	97
	10.2 ± 0.1				SLP(Xe)	118
Co(hfacac) ₃	10.34 ± 0.10				VC(Hg)	32
	10.12 ± 0.15				VC(Hg)	32
Rh(hfacac) ₃	10.15 ± 0.12				VC(Hg)	32
Mn(acac) ₂	8.34 ± 0.05	13.7 ± 0.1	11.7 ± 0.1		SLP, EVD(Xe)	122
Fe(acac) ₂	8.10 ± 0.05	13.9 ± 0.1	11.7 ± 0.1		SLP, EVD(Xe)	122
	7.50 ± 0.04				EC(Xe, C ₆ H ₆ , C ₁₄ H ₁₀)	90
Co(acac) ₂	8.54 ± 0.05	13.9 ± 0.2	11.5 ± 0.1		SLP, EVD(Xe)	122
Ni(acac) ₂	8.23 ± 0.05	13.5 ± 0.2	11.5 ± 0.1		SLP, EVD(Xe)	122
Cu(acac) ₂	8.31 ± 0.05	13.1 ± 0.2	10.9 ± 0.1		SLP, EVD(Xe)	122
	7.75 ± 0.05				EC(Xe, C ₆ H ₆ , C ₁₄ H ₁₀)	90
Zn(acac) ₂	8.62 ± 0.05	14.1 ± 0.2	10.9 ± 0.1		SLP, EVD(Xe)	122
Fe(tfacac) ₂	8.75 ± 0.1	14.5 ± 0.1		12.6 ± 0.1	SLP(Xe)	118
	8.49 ± 0.03				EC(Xe, C ₆ H ₆ , C ₁₄ H ₁₀)	90
Cu(tfacac) ₂	9.05 ± 0.1	13.1 ± 0.1		11.5 ± 0.1	SLP(Xe)	118
Zn(tfacac) ₂	9.40 ± 0.1	14.6 ± 0.1	11.7 ± 0.1		SLP(Xe)	118
Fe(hfacac) ₂	9.7 ± 0.1			13.2 ± 0.2	SLP(Xe)	118
	9.48 ± 0.07				EC(Xe, C ₆ H ₆ , C ₁₄ H ₁₀)	90
Cu(hfacac) ₂	9.86 ± 0.05			11.6 ± 0.1	SLP(Xe)	118
Zn(hfacac) ₂	10.07 ± 0.05	15.3 ± 0.2		11.35 ± 0.1	SLP(Xe)	118
Cu(acac)(hfacac)	8.70 ± 0.04				EC(Xe, C ₆ H ₆ , C ₁₄ H ₁₀)	90
	9.2 ± 0.1				SLP, EVD(Xe)	87
acacH	8.87		10.7 ± 0.1		PI	42
tfacacH	9.8 ± 0.1		11.7 ± 0.1	10.6 ± 0.2	SLP(Xe)	118
	9.96 ± 0.10				VC(Hg)	32
hfacacH	10.55 ± 0.05			11.2 ± 0.1	SLP(Xe)	118
	10.68 ± 0.09				VC(Hg)	32

(b) β-Diketonate Complexes of Chromium(III) and Rhodium(III)				
Complex	IP, V	AP(ML ₂ ⁺), V	Method	Ref
Cr(acac) ₃	See part (a)			
Cr(CH ₃ acac) ₃	7.81 ± 0.5	10.7 ± 0.1	SLP(Xe)	95
Cr(Clacac) ₃	8.16 ± 0.05	11.1 ± 0.1	SLP(Xe)	95
Cr(Bracac) ₃	8.05 ± 0.05	11.0 ± 0.1	SLP(Xe)	95
Cr(lacac) ₃	8.03 ± 0.05	10.8 ± 0.1	SLP(Xe)	95
Cr(NO ₂ acac) ₃	8.63 ± 0.05	11.6 ± 0.1	SLP(Xe)	95
	8.23(estimated)		EC(Xe, C ₆ H ₆ , C ₁₄ H ₁₀)	88
Cr(tfacac) ₃	See part (a)			
Cr(hfacac) ₃	See part (a)			
Cr(acac) ₂ (NO ₂ acac)	7.60(estimated)		EC(Xe, C ₆ H ₆ , C ₁₄ H ₁₀)	88
Cr(acac)(NO ₂ acac) ₂	7.92(estimated)		EC(Xe, C ₆ H ₆ , C ₁₄ H ₁₀)	88
Rh(acac) ₃	See part (a)			
Rh(acac) ₂ (NO ₂ acac)	7.65 ± 0.02		EC(Xe, C ₆ H ₆ , C ₁₄ H ₁₀)	89
Rh(acac)(NO ₂ acac) ₂	7.97 ± 0.03		EC(Xe, C ₆ H ₆ , C ₁₄ H ₁₀)	89
Rh(NO ₂ acac) ₃	8.39 ± 0.04		EC(Xe, C ₆ H ₆ , C ₁₄ H ₁₀)	89

Table I (continued)

(c) β -Diketonate Complexes of Copper(II)						
Complex	IP, V	AP(CuL ⁺), V			Method	Ref
Cu(acac) ₂	See part (a)					
Cu(CH ₃ acac) ₂	7.97 ± 0.05	10.8 ± 0.1			SLP(Xe)	101
Cu(tfacac) ₂	See part (a)					
Cu(hfacac) ₂	See part (a)					
Cu(acac)(hfacac)	9.03 ± 0.05				SLP(Xe)	101
	8.65 ± 0.01				EC(Xe, C ₆ H ₆ , C ₁₄ H ₁₀)	90
Cu(bzac) ₂	8.37 ± 0.05	10.7 ± 0.1			SLP(Xe)	101
Cu(Phacac) ₂	8.05 ± 0.05				SLP(Xe)	101
Cu(bztfac) ₂	9.06 ± 0.05				SLP(Xe)	101
Cu(futfac) ₂	8.89 ± 0.05				SLP(Xe)	101
Cu(thtfac) ₂	8.90 ± 0.05				SLP(Xe)	101
Cu(nptfac) ₂	8.39 ± 0.05				SLP(Xe)	101
Cu(dbm) ₂	8.28 ± 0.05	10.3 ± 0.1			SLP(Xe)	101
Cu(hd) ₂	7.68 ± 0.03				EC(Xe, C ₆ H ₆ , C ₁₄ H ₁₀)	90
Cu(mhd) ₂	7.61 ± 0.06				EC(Xe, C ₆ H ₆ , C ₁₄ H ₁₀)	90
Cu(pvac) ₂	7.59 ± 0.05				EC(Xe, C ₆ H ₆ , C ₁₄ H ₁₀)	90

(d) Carbonyl β -Diketonate Complexes of Rhodium(I) and Iridium(I)							
Complex	IP, V	AP of fragment ion, V			Method	Ref	
		[P - CO] ⁺	[P - 2CO] ⁺	Other ions			
Rh(CO) ₂ (acac)	8.6 ± 0.1	10.1	11.7	[P - 3CO] ⁺ [P - 112] ⁺ RhCO ⁺	12.9 13.6 15.6	CS, EVD(Xe)	107, 108
Rh(CO) ₂ (dbm)	8.4 ± 0.1	9.9	11.5	[P - 112] ⁺	12.7	CS, EVD(Xe)	107, 108
Rh(CO) ₂ (pipo)	7.5 ± 0.1	8.9	10.5			EVD(Xe)	108
Rh(CO) ₂ (tfacac)	8.85 ± 0.1	10.6	12.5	[P - 3CO] ⁺ [P - 112] ⁺ [P - 2CO - CF ₃] ⁺ RhCO ⁺	13.9 14.5 14.1 15.7	CS, EVD(Xe)	107, 108
Rh(CO) ₂ (hfacac)	9.2 ± 0.1	10.9	12.7	[P - 3CO] ⁺ [P - 2CO - CF ₃] ⁺ RhCO ⁺	14.7 15.0 15.5	CS, EVD(Xe)	107, 108
Rh(CO) ₂ (bzac)	8.4 ± 0.1	9.8	11.3	[P - 3CO] ⁺ [P - 112] ⁺	12.7 13.4	CS, EVD(Xe)	107, 108
Ir(CO) ₂ (acac)	8.6 ± 0.1					CS(Xe)	107
Ir(CO) ₂ (hfacac)	8.85 ± 0.1	12.2	12.6			CS, EVD(Xe)	107, 108

(e) Metal Complexes of Dipivaloylmethane							
Complex	ML ₃ ⁺	ML ₂ ⁺	[ML ₃ -t-Bu] ⁺	Other ions	Method	Ref	
							Al(dpm) ₃
Co(dpm) ₃	8.4 ± 0.5	13.2 ± 0.5		[ML ₂ -t-Bu] ⁺ ML ⁺	17.4 ± 0.5 27.0 ± 0.5	VDF(N ₂)	113
La(dpm) ₃	8.0 ± 0.5	14.9 ± 0.5	11.1 ± 0.5			VDF(N ₂)	113
Eu(dpm) ₃	9.8 ± 0.5	16.5 ± 0.5	12.7 ± 0.5	ML ⁺	24.0 ± 0.5	VDF(N ₂)	113
Zr(dpm) ₄	10.5 ± 0.5						

(f) Metal Complexes of Schiff Bases						
Complex	IP, V	Negative ions	Resonance potential, V	Method	Ref	
H ₂ (salen)	8.53 ± 0.07			SLP, EVD(Xe, Kr, SF ₆)	115	
Mn(salen)	7.77 ± 0.08			SLP, EVD(Xe, Kr, SF ₆)	115	
Co(salen)	7.52 ± 0.06	P ⁻	0.08	SLP, EVD(Xe, Kr, SF ₆)	115	
Ni(salen)	7.57 ± 0.09	P ⁻	0.08	SLP, EVD(Xe, Kr, SF ₆)	115	
Cu(salen)	7.69 ± 0.09	P ⁻ [P - 106] ⁻	0.08 3.2	SLP, EVD(Xe, Kr, SF ₆)	115	
H ₂ (oaben)	7.83 ± 0.04			SLP, EVD(Xe, Kr, SF ₆)	115	
Co(oaben)	6.98 ± 0.10	P ⁻	0.08	SLP, EVD(Xe, Kr, SF ₆)	115	
Ni(oaben)	6.84 ± 0.08			SLP, EVD(Xe, Kr, SF ₆)	115	
Cu(oaben)	7.15 ± 0.11	P ⁻ [P - 105] ⁻ [P - 106] ⁻	0.08 3.2 3.8	SLP, EVD(Xe, Kr, SF ₆)	115	
H ₂ (salhlda)	8.26 ± 0.06	P ⁻	Same as SF ₆	SLP(Xe, Kr)	116	
Co(salhlda)	7.78 ± 0.08	P ⁻	Same as SF ₆	SLP(Xe, Kr)	116	
Ni(salhlda)	7.69 ± 0.09	P ⁻	Same as SF ₆	SLP(Xe, Kr)	116	
Cu(salhlda)	7.81 ± 0.07	P ⁻	Same as SF ₆	SLP(Xe, Kr)	116	
H ₂ (saldape)	8.40 ± 0.10	P ⁻	Same as SF ₆	SLP(Xe, Kr)	116	
Co(saldape)	7.53 ± 0.10	P ⁻	Same as SF ₆	SLP(Xe, Kr)	116	
Ni(saldape)	7.61 ± 0.06	P ⁻	Same as SF ₆	SLP(Xe, Kr)	116	

Table I (continued)

Complex	IP, V	(f) Metal Complexes of Schiff Bases		Method	Ref
		Negative ions	Resonance potential, V		
Cu(saldape)	7.75 ± 0.05	P ⁻	Same as SF ₆	SLP(Xe, Kr)	116
H ₂ (saldaps)	8.51 ± 0.10	P ⁻	Same as SF ₆	SLP(Xe, Kr)	116
Co(saldaps)	7.58 ± 0.07	P ⁻	Same as SF ₆	SLP(Xe, Kr)	116
Ni(saldaps)	7.44 ± 0.07	P ⁻	Same as SF ₆	SLP(Xe, Kr)	116
Cu(saldaps)	7.78 ± 0.06	P ⁻	Same as SF ₆	SLP(Xe, Kr)	116
H ₂ (saldpt)	8.31 ± 0.07	P ⁻	Same as SF ₆	SLP(Xe, Kr)	116
Co(saldpt)	7.31 ± 0.07	P ⁻	Same as SF ₆	SLP(Xe, Kr)	116
Ni(saldpt)	7.41 ± 0.08	P ⁻	Same as SF ₆	SLP(Xe, Kr)	116
Cu(saldpt)	7.54 ± 0.08	P ⁻	Same as SF ₆	SLP(Xe, Kr)	116

Complex	(g) Metal Phthalocyanines		Method	Ref
	IP, V			
H ₂ (pc)	7.36 ± 0.10		SLP(Xe)	117
Mn(pc)	7.26 ± 0.10		SLP(Xe)	117
Fe(pc)	7.22 ± 0.10		SLP(Xe)	117
Co(pc)	7.46 ± 0.10		SLP(Xe)	117
Ni(pc)	7.45 ± 0.10		SLP(Xe)	117
Cu(pc)	7.37 ± 0.10		SLP(Xe)	117
Zn(pc)	7.37 ± 0.10		SLP(Xe)	117

^a The following abbreviations are used in the table: acacH, acetylacetonate (pentane-2,4-dione); tfacacH, trifluoroacetylacetonate; hfacacH, hexafluoroacetylacetonate; XacacH, 3-X-pentane-2,4-dione; bzacacH, benzoylacetonate; bztfacacH, benzoyltrifluoroacetonate; futfacacH, 2-furoyltrifluoroacetonate; thtfacacH, 2-thenoyltrifluoroacetonate; nptfacacH, 2-naphthoyltrifluoroacetonate; dbmH, dibenzoylmethane; hdH, hexane-2,4-dione; mhdH, 2-methyl-3,5-hexanedione; pvacH, pivaloylacetonate (2,2-dimethylhexane-3,5-dione); pipOH, 2-N-phenylimino-pentan-4-one (acetylacetonate monophenylimine); dpmH, dipivaloylmethane (2,2,6,6-tetramethylheptane-3,5-dione); salenH₂, bis(salicylidene)ethylenediamine; oabenH₂, bis(o-aminobenzylidene)ethylenediamine; salhtdaH₂, bis(salicylidene)heptanediamine; saldapeH₂, bis(salicylidene)-3,3'-bis(aminopropyl) ether; saldapsH₂, bis(salicylidene)-3,3'-bis(aminopropyl) sulfide; saldptH₂, bis(salicylidene)-3,3'-bis(aminopropyl)amine; pcH₂, phthalocyanine metal-free. ^b Abbreviations used for methods are as follows. The calibrating materials are given in parentheses. SLP, semilogarithmic plot; EVD, extrapolated voltage difference; VC, vanishing current; EC, energy compensation; CS, critical slope; PI, photoionization; VDF, voltage difference at fixed percentage of ion current at standard intensity; NS, unspecified electron impact method. ^c Cited in ref 32 as ref 26: R. W. Kiser, R. M. Teeter, and E. J. Gallegos, private communication. ^d Probably low because of thermal decomposition to bis-chelate in the ion source. ^e Value of 9.60 eV quoted for Cr(hfacac)₃ in ref 32 is the vertical IP (ref 98).

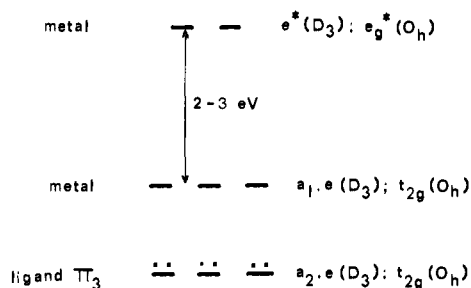


Figure 3. Portion of energy level diagram of acetylacetonate complex of a trivalent transition metal, showing ordering of upper occupied energy levels.

convenient to speak of metal d or ligand π orbitals when the major contribution is from the metal or ligand, respectively. Not shown in Figure 3 are small splittings of the π_3 and d_{xy} , d_{xz} , d_{yz} levels into their a_2 and e , and a_1 and e components, respectively. The source of these splittings differs in the Hückel⁸² and SCF⁸⁶ approaches. Figure 3 thus differs little from the energy level diagram for a regular octahedral complex. It is seen that the π_3 orbitals lie below the metal d_{xy} , d_{xz} , and d_{yz} orbitals, as required by chemical observations.⁸² If partly filled d orbitals were to lie below the filled π_3 orbitals, electrons would spontaneously fall to fill the vacancies. Thus, for example, Mn^{3+} would be reduced by acetylacetonate. This does not occur, so the d_{xy} , d_{xz} , d_{yz} orbitals must lie above the π_3 orbitals. Similar arguments were used to confirm the relative positions of the $d_{x^2-y^2}$, d_{z^2} , and π_4 orbitals. Another important feature of Figure 3 is the separation between the d_{xy} , d_{xz} , d_{yz} , and $d_{x^2-y^2}$, d_{z^2} orbitals (the well-known ligand field splitting energy) amounting to 2–3 eV.

B. Acetylacetonates and Fluorine-Substituted Acetylacetonates

The IP's of acetylacetonate and fluorine-substituted acetylacetonate complexes of trivalent metals, divalent metals, and protonated ligands are listed in Table Ia. In general, where determinations have been made by different groups of workers, agreement is fairly good. Thus, in two closely related, independent studies^{32,87} agreement is usually within 0.3 eV with no systematic difference between the two sets of data being apparent. However, in one set of studies⁸⁸⁻⁹⁰ the reported IP's are consistently lower. Most, if not all, of the lowering can be attributed to the use of benzene and anthracene, in addition to xenon, as calibrants for the electron energy. A justification of this approach is the closer resemblance of the metal complexes to the aromatic compounds than to a noble gas (e.g., Franck-Condon parameters may be similar) but a serious limitation concerns assumptions regarding the relationship of electron impact IP's to true IP's of the calibrants. Whatever the validity of the method, the IP's tend to be lower than those obtained by conventional calibrations, by an amount which increases as the IP decreases. Except for the numerical values involved, the conclusions drawn from these results will not be altered.

The effect of the metal on the IP's can be demonstrated by considering the data for the acetylacetonate complexes, for which the most complete results are available. For the trivalent complexes of the first transition series the IP's are compared with molecular orbital energy level diagrams in Figure 4, using data from a single source⁸⁷ for internal consistency, and reported d electron configurations for acetylacetonate complexes.⁹¹⁻⁹⁴ No obvious correlation between the IP of the complexes and those of the neutral metal atoms (or even their second or third

IP's) has been found or, for that matter, any other simple parameter of the complexed metal ion. Figure 4 implies that the IP's of $\text{Mn}(\text{acac})_3$ and $\text{Fe}(\text{acac})_3$ should be 2–3 eV lower than those of the other $\text{M}(\text{acac})_3$ complexes in the series, assuming that Koopmans' theorem applies, i.e., that the electron removed comes from the highest occupied molecular orbital in each case, namely, a metal-dominated orbital. In fact, $\text{Fe}(\text{acac})_3$ has the highest IP in the series. The IP's of the transition metal acetylacetonates are lower than those of $\text{H}(\text{acac})$ but are generally similar to the IP of $\text{Al}(\text{acac})_3$. Since, in the latter complex, the metal has no d electrons it was proposed^{87,95} that upon ionization of the complexes the electron was removed from a π orbital of the chelate ring π system. The energies of the ligand π orbitals would, of course, depend upon the metal, probably not in a simple way. It can be noted, for example, that with the first transition series there is a general but not regular increase in IP as the nuclear charge of the metal (and electronegativity of the neutral element) increases.

These observations also apply to the IP's of the fluorine-substituted acetylacetonate complexes. The IP's increase by almost 1 eV on replacement of acac by tfacac , and a further increase of almost 1 eV occurs on replacement of tfacac by hfacac . The IP's of $\text{Al}(\text{tfacac})_3$, $\text{Cr}(\text{tfacac})_3$, and $\text{Fe}(\text{tfacac})_3$ are very similar (within 0.1 eV for a given set of authors) as are those of $\text{Al}(\text{hfacac})_3$, $\text{Cr}(\text{hfacac})_3$, $\text{Fe}(\text{hfacac})_3$, $\text{Co}(\text{hfacac})_3$ and $\text{Rh}(\text{hfacac})_3$. Like the acetylacetonate complexes it is to be anticipated that $\text{Fe}(\text{tfacac})_3$ and $\text{Fe}(\text{hfacac})_3$ should have IP's 2–3 eV lower than those of the corresponding complexes of the other metals. This is not observed.

By extending Barnum's methods⁸² to hexafluoroacetylacetonate complexes it has been predicted³² that if an electron is removed from a metal-dominated orbital on ionization of the complex, the increase in IP on going from $\text{M}(\text{acac})_3$ to $\text{M}(\text{hfacac})_3$ should be only a fraction of a volt, rather than almost 2 eV as observed. It was therefore suggested that the electron was removed from an orbital concentrated on the ligand. Since the qualitative correctness of the molecular orbital description of these complexes is strongly supported by a large body of spectroscopic, magnetic, and chemical evidence, the applicability of Koopmans' theorem to these systems was questioned, and it was pointed out³² that the theorem should only apply well to SCF calculations on closed-shell systems, which these are not. The same authors noted, but did not actually propose, that what is required to make Figure 3 consistent with the IP data is an inversion of the e^* and π_3 orbitals upon ionization. Since the e^* orbital is largely metal 3d in character, this was said to be analogous to the well-known 3d–4s inversion observed on ionization of the neutral metal atoms.

In view of the foregoing difficulties, it has been suggested⁹⁶ that the simple Hückel theory is much too approximate to be useful in interpreting detailed electronic spectra, and some aspects of the original treatment were criticized. Since the original Hückel molecular orbital treatment failed to reproduce even qualitatively the trends in IP measured by electron impact, the calculations were repeated to see if it was possible to correlate a simple one-electron scheme with the IP's. The IP's of the complexes were fitted to the energy of the highest occupied molecular orbital, but no consistent trend in the values of any of the variable parameters could be found.

The IP's of acetylacetonate and fluorine-substituted acetylacetonate bis complexes show, for a given ligand, some dependence on the metal, but are more susceptible to the identity of the ligand. For each ligand the ranges of IP are similar to, but not identical with, those observed for the corresponding complexes with trivalent transition metal ions. As described in section IV.A, the bis complexes have different structures in the gaseous and condensed phases. Because of this, physical data, such as electronic absorption spectra and magnetic properties, with which to correlate the variations in IP with ligand field effects

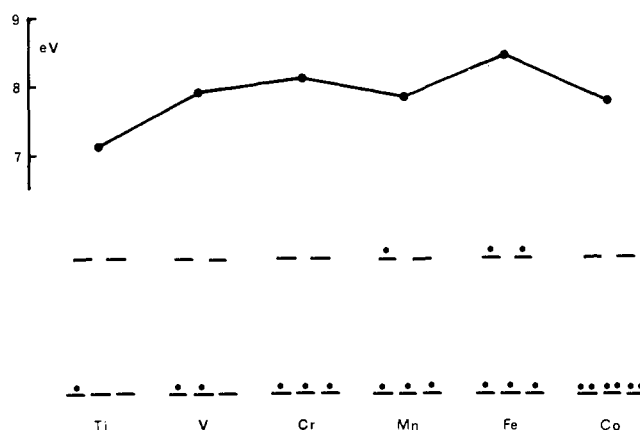


Figure 4. Comparison of IP's with molecular orbital energy level diagram for acetylacetonate complexes of trivalent metals of the first transition series.

TABLE II. Ionization Data for β -Diketones, from Photoelectron Spectroscopy⁹⁷

β -Diketone	Band maxima (vertical IP), eV	IP(electron impact), eV ^a
H(acac)	9.18, 9.74, 12.68	8.87, 9.2
H(tfacac)	9.92, 10.53, 13.27	9.8, 9.96
H(hfacac)	10.74, 11.25, 14.03	10.55, 10.68
H(dpm)	8.86, 9.23, 11.37	

^a From Table I.

are lacking. In the absence of comparative experimental data, we resort to the intuitive notion that the metal d orbitals will lie above the ligand π orbitals in energy (in T_d symmetry the occupied t_2 orbitals should lie 1–1.5 eV above the highest energy occupied ligand orbitals assuming typical ligand field splittings for tetrahedral complexes). The similarity of the IP's to those of the corresponding tris complexes invites a similar interpretation of the ionization process, namely electron loss from a ligand-dominated π orbital.

To this point there is a lack of overall correlation between the experimental results from electron ionization and those anticipated from the molecular orbital description of the complexes. A possibility which is now considered is that the IP's obtained by electron impact, in spite of the agreement between the results obtained by different workers, contain unsuspected errors, in particular an undetected, low probability ionization occurring at energies 2–3 eV below the apparent IP's of the Mn^{III} and Fe^{III} complexes (the measured IP's are substantially higher than anticipated from the molecular orbital calculations). That this is not so is confirmed by ionization energies obtained via photoelectron spectroscopy.^{97–100} Available results are collected in Tables II and III. The low-energy bands only are given, and these are compared with IP's obtained by electron impact methods. For the protonated ligands (Table II) the two low-energy bands have been assigned⁹⁷ to removal of a $b_2(\pi_3)$ electron and to removal of an oxygen lone-pair electron (from the antisymmetric combination $n_-(b_1)$ of the two oxygen in-plane p orbitals). The relative ordering could not be obtained from the spectra of the free β -diketones, but from the spectra of the metal chelates it was deduced that the ordering was $b_2(\pi_3) > b_1(n_-)$. Consequently, the lowest energy band corresponds to removal of a π electron. The electron impact IP's (which lie within the adiabatic and vertical limits) correlate very well with this band.

The low-energy bands in the photoelectron spectra of the metal chelates, summarized in Table III, have been interpreted.⁹⁷ The assignments are very useful in clarifying the electron impact results. Bands A and B are observed for complexes of both nontransition and transition metals. Band A was assigned to unresolved $e(\pi_3)$ and $a_2(\pi_3)$ ionizations (see Figure 3) and band

TABLE III. Ionization Data for Metal β -Diketonate Complexes, from Photoelectron Spectroscopy^a

Complex	Band								IP(electron impact), eV ^b
	Y	Z	K	L	M	A	B'	B''	
Be(acac) ₂						8.41	9.67		
Cr(acac) ₃	7.46					8.06	8.96	9.48	7.40, 7.87, 8.10
Mn(acac) ₃		(7.32)				8.14 ^c			7.85, 7.95
Fe(acac) ₃						8.10 ^c	8.93 ^c	9.22 ^c	8.45, 8.64
Co(acac) ₃			7.52	8.03	8.49		8.99	9.54	7.80, 7.81
Al(tfacac) ₃						9.22	10.35		9.05
Cr(tfacac) ₃	8.58					9.12	10.01	10.51	9.09
Fe(tfacac) ₃						9.18 ^c	10.40 ^c		9.10, 9.38
Be(hfacac) ₂						10.39	11.66		
Al(hfacac) ₃						10.33	11.47		9.80, 10.30
						~10.25 ^d			
						~9.5 ^d			
						(adiabatic)			
Sc(hfacac) ₃						10.13	10.82	11.12	
Ga(hfacac) ₃						10.19	11.13	11.47	
Ti(hfacac) ₃	7.94					10.24	10.87	11.28	
V(hfacac) ₃	8.68					10.10	10.96	11.39	
Cr(hfacac) ₃	9.57					10.18	11.10	11.61	9.97, 10.13
	9.54 ^e					10.12 ^e			
	9.67 ^d								
	9.19 ^d								
	(adiabatic)								
Mn(hfacac) ₃		(9.2)				10.03	10.94	11.41	
Fe(hfacac) ₃						10.13 ^c	11.30 ^c		10.2, 10.34
						10.14 ^{e,f}			
						10.13 ^g			
Co(hfacac) ₃			9.73	10.13	10.73		11.15	11.75	10.12
			9.56 ^e	9.95 ^e	10.62 ^e				
Ru(hfacac) ₃	8.85, 9.07					10.30	11.06	11.65	
(CO) ₄ Mn(hfacac)	8.11					9.31	10.31		
Fe(dpm) ₃						7.92 ^c	8.76 ^c		

^a From ref 97, except as noted. Band maxima in eV (vertical ionization energy), except as noted. Shoulders are indicated by parentheses. ^b From Table I. ^c Assigned by correspondence with other spectra. Not specifically assigned in ref 97. ^d From ref 98. Approximate values are estimated from diagrams. ^e From ref 99. ^f Note probable error in ref 99. See ref 100. ^g From ref 100.

B to electron removal from the oxygen lone-pair orbitals (the in-plane $e(n_-)$ and $a_2(n_-)$ components). These components are not resolved for the Be^{II} and Al^{III} complexes, but two bands, B' and B'', are apparent for most of the other complexes. For Ga^{III} the splitting was attributed to increased interaction between oxygen in-plane lone-pair p orbitals and the metal 4p orbitals, while for Sc^{III} and the other transition metal complexes, it was assigned to interaction with metal d orbitals.

Band Y was assigned to ionization from d orbitals which correlate with the t_{2g} orbitals of octahedral symmetry. (This ionization can lead in some cases to more than one ion state, but they were believed to be unresolved.) This band shifts progressively to higher energy in the sequence Ti^{III} \rightarrow Cr^{III}, and in the spectra of the Cr^{III} complexes merges partially with band A which remains essentially unshifted as the metal varies. At the same time the splitting between B' and B'' increases as the extent of the $e(n_-) - e(d)$ interactions increases in parallel with stabilization of the 3d orbitals.

Bands K-M for the Co^{III} complexes were assigned to ionization from the π_3 and d orbitals (which correlate with t_{2g} in octahedral symmetry). Since these orbitals are rather close in energy, the ordering was regarded as speculative but the preferred assignments were given as: K, $e(\pi_3)$; L, $a_2(\pi_3) + a_1(d)$; M, $e_a(d)$.

Band Z was observed as a faint, barely discernible shoulder on the leading edge of band A in the spectra of the Mn^{III} complexes and was assigned to ionization from the $e_b(d)$ orbital (correlating with e_g in octahedral symmetry). The ionization cross section for this orbital is apparently much less than that observed for the $a_1(d)$ and $e_a(d)$ orbitals previously encountered above. Other bands expected by ionization from d orbitals were believed to lie in the region spanned by bands B', B'', and C (data on band C are not included in Table III). Like the Mn^{III} complexes, the spectra for the Fe^{III} complexes were disappointingly amorphous.

Significantly, there was no evidence at all of any bands at lower energies than band A, which could be assigned to ionization from metal 3d orbitals. It was presumed that the $e_b(d)$ orbital, correlating with e_g in octahedral symmetry, was sufficiently stabilized relative to Mn^{III} that the band due to ionization from this orbital was lost under the intense band A. Other bands expected by ionization from d orbitals were thought to lie in the region of bands B and C. It was considered unlikely that the enhanced intensity of band A in the spectra of the Fe(acac)₃ and Fe(hfacac)₃ complexes was due to a near coincidence of the ligand π_3 and metal 3d bands.

The spectrum of the low-spin d⁵ complex, Ru(hfacac)₃, is in contrast to that of Fe(hfacac)₃. Here, ionization from metal 4d orbitals is clearly evident as band Y, which is partially resolved into two components. The pronounced separation of bands B' and B'' indicates a high degree of covalency in this compound. The spectrum of the low-spin d⁶ complex, (CO)₄Mn(hfacac), also shows a clearly separated band Y due to ionization from the 3d orbitals.

For a given metal, bands A and B show a nearly linear progression to higher ionization energies in the sequence $M(acac)_n \rightarrow M(tfacac)_n \rightarrow M(hfacac)_n$, the increases (approximately 1.0 eV per CF₃ for CH₃ substitution) being rather greater than for the β -diketonates themselves. The Cr^{III} and Co^{III} complexes show that those metal 3d bands correlating with t_{2g} in octahedral symmetry are every bit as sensitive to variations in β -diketonate species as are the ligand bands A and B.

Comparisons between the photoelectron bands and the electron impact IP's of the complexes included in Table III reveal that, in most cases, the electron impact values (expected to be slightly lower than vertical IP's) correlate best with band A, or for the Co^{III} complexes, with band L (on this basis, the electron impact IP for Fe(acac)₃ is higher than anticipated). This is to be

expected for those complexes for which band A is the lowest energy band, but requires further discussion for the Cr^{III}, Mn^{III}, and Co^{III} complexes. Most easily reconciled is the Mn(acac)₃ complex, for which band Z was a weak shoulder on the leading edge of band A. If the ionization cross section is also very low for electron impact ionization, this process would remain undetected.

The electron impact method apparently fails to detect band Y of the Cr^{III} complexes. (Even the lowest value, 7.40 eV, for the adiabatic IP of Cr(acac)₃ is significantly higher than the adiabatic value from band Y, estimated to be ~7.0 eV.) A possible explanation is suggested by the fact that the intensity of band Y is much lower than that of band A and is not completely resolved from it. If the relative ionization cross-sections for photon and electron impact are similar, the ionization efficiency curves near threshold would, for the Cr^{III} complexes, be heavily weighted in favor of ionization from π_3 with no obvious evidence, via structure in the curve, for ionization from the d orbitals. Interestingly, inspection of the ionization efficiency curves⁸⁷ for formation of Ti(acac)₃⁺ and V(acac)₃⁺ from the neutral complexes does suggest a lower probability ionization process near threshold which could be assigned to ionization from metal d orbitals (the difference in ionization energy from d and π_3 orbitals for these complexes will be greater than for the Cr^{III} complexes if the trends for the M(hfacac)₃ complexes apply).

The electron impact methods also seem to miss the lowest energy ionization (band K) of the Co^{III} complexes. Since the bands K, L, and M are of comparable intensity, though not completely resolved, a simple explanation is currently lacking, unless relative ionization cross sections for the possible processes differ significantly for photon and electron impact for the Co^{III} complexes. Here again, the ionization efficiency curve⁸⁷ for formation of Co(acac)₃⁺ is not exactly comparable to the curves for the corresponding ion from complexes of Cr^{III}, Mn^{III}, and Fe^{III}.

C. β -Diketonates of Chromium, Rhodium, and Copper

It has been seen that the IP's of the metal β -diketonate complexes are influenced by both the metal and the ligand. When determined by the electron impact method the values are generally more susceptible to variations in the ligand than to variations in the metal. It has been suggested that this is because of a larger ionization cross section for ligand orbitals than metal orbitals near threshold. The influence of the ligand can be investigated in greater detail by comparisons of the IP's of several β -diketonate complexes in which substituents on the chelate ring are varied as the identity of the metal remains the same. Results are available for complexes stable to oxidation and reduction, and stable thermally so that errors due to impurities or decomposition products should be minimal.

The most extensive series of determinations of IP have been made on complexes of Cr^{III} and Cu^{II}. Because of the dominant effect of the ligand on the IP of the complex and the previously discussed quasi-aromatic nature of the chelate ring, the variations in IP's of the complexes were compared with those for similarly substituted aromatic compounds. For both the Cr^{III} and Cu^{II} complexes the changes were similar to those for the aromatic compounds.^{95,101} The relationship between the IP's of monosubstituted benzenes and Hammett σ constants has long been known.¹⁰² From the analysis of much experimental data, it has been demonstrated^{103,104} that the IP's of both meta- and para-disubstituted benzenes correlate with the sum of the σ_p^+ constants of the substituents by the equation

$$IP = k[\sigma_p^+(1) + \sigma_p^+(2)] + 9.25 \quad (15)$$

in which the numbers in parentheses identify the σ_p^+ values for each of the two substituents. The value of k is often fairly con-

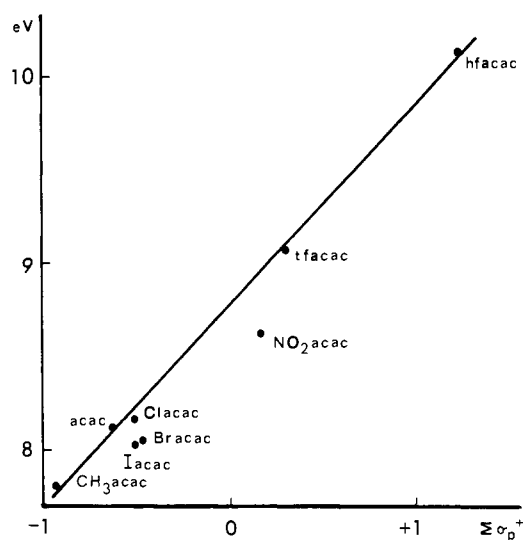


Figure 5. Correlation of IP's of β -diketonate complexes of Cr^{III} with $\Sigma\sigma_p^+$ for substituents in the ligand.

stant when compounds of a given type (e.g., nitrobenzenes, chlorobenzenes, etc) are considered, and normally falls within the range 0.76 ± 0.20 , frequently close to the center of the range. Figure 5 shows the relationship between the IP's of the Cr^{III} complexes from Table I and σ_p^+ values tabulated by Brown and Okamoto.¹⁰⁵ The IP's of the halogen and nitro-substituted β -diketonates fall below the straight-line correlation shown. The behavior of halogen substituents is similarly anomalous for benzenoid systems.^{102,103} In the case of the nitro-substituted complex the two methyl groups on the two adjacent positions of the chelate ring prevent the nitro group from becoming coplanar with the ring, and the full effect of the mesomeric withdrawal of negative charge from the ring by the nitro group is prevented. The slope of the correlation line, assuming that an equation of similar form to eq 15 holds for these complexes, gives a value for k equal to 1.11, rather higher than observed for disubstituted benzenes. Because the IP's of mono- and disubstituted arenes correlate with the sum of the σ_p^+ constants irrespective of the orientation of the substituents with respect to one another, it has been suggested¹⁰³ that the positive charge in the molecular ion is located predominantly on the aromatic ring rather than on either of the substituents. By analogy, a similar interpretation for the chromium complexes would, at the ionization threshold, place the charge predominantly on the chelate ring rather than on the chromium atom. Even though the analogy is of doubtful validity because the photoelectron spectra show that the bands assignable to ionization from metal d and ligand π_3 orbitals show almost exactly the same shift in energy with variation of ligand, this conclusion provides the most suitable interpretation of the observations since the electron-impact IP's correlated with band A of the photoelectron spectra.

A linear correlation of the IP's of several β -diketonates of Cu^{II} with the sum of the σ^+ values of the substituents has been demonstrated.¹⁰¹ An overall better correlation was obtained when σ_p^+ constants were used for all substituents without regard to their position than when a combination of σ_p^+ and σ_m^+ values was used to reflect the position of the substituent with respect to the metal atom. Linear correlations of the IP's of these complexes with pK_a values of the parent β -diketone and formation constants and polarographic half-wave potentials of the complexes were also observed.¹⁰¹ A further linear relationship was observed¹⁰⁶ between the IP's of the copper β -diketonates and the isomer shifts, determined by Mössbauer spectroscopy, of Fe^{III} in its complexes with the same ligands. This indirect correlation between properties of Fe^{III} and Cu^{II} complexes was necessary because sufficient IP data for the Fe^{III} complexes were

not available, but nevertheless demonstrates the importance of the electronic effects of the ligand. Mössbauer spectroscopy has often been used to study the σ -donor and π -acceptor properties of ligands. The s electron density at the iron nucleus is altered by ligands by both σ and π effects, σ effects directly by changing the electron density in the $4s$ orbital, π effects indirectly by changing the shielding of the iron nucleus.

All of the foregoing correlations are remarkably good when the uncertainties involved in the accurate determination of IP's by the electron impact method are considered. The observations reinforce the view that similar Franck-Condon parameters apply to the ionization of the complexes and that relative IP's are sensibly reliable.

An alternative viewpoint on the ionization of d^3 and low-spin d^6 complexes has been advanced.^{88,89} A linear progression of IP's was observed on successive introduction of nitro substituents onto the central carbon atoms of the three acetylacetonate rings of Cr^{III} , Co^{II} , and Rh^{III} complexes. It was argued that if ionization occurs from the highest energy filled orbital on any of the ligands, the simple picture assuming independence of the orbitals of each ligand would require that as long as any ring in the complexes remains un-nitrated, the electron should be lost from the highest energy filled orbital of that ring. Hence, for ionization from the ligand, the partially nitrated compounds should have nearly the same IP as the $\text{M}(\text{acac})_3$ compound while that of $\text{M}(\text{NO}_2\text{acac})_3$ should be considerably higher. Ionization from a metal-dominated orbital or any orbital in which each ligand influences the orbital energy equally, should give a steady progression of IP's, as observed.

Two other models, based on ionization from ligand orbitals, were discussed. The first of these required that energy be transmitted very inefficiently through the central metal atom and that ionization occur from the ring first interacting with the ionizing electron. The ion current would then be a composite of the appropriate ion currents from ionized molecules in which electron loss had occurred from unsubstituted or nitro-substituted rings, which should be additive under the conditions of low transmittal of energy. The ionization efficiency curve for a partially nitrated compound would then be expected to fall between the curves for the completely substituted and completely unsubstituted compounds, the spacing being determined by weighting of the contributions from each type of ring. If this were the case, it was expected that there would be breaks in the ionization efficiency curves for the partially nitrated compounds. Such breaks could not be detected, but it was noted that the breaks could be masked by the convolution of the ionization efficiency with the thermal energy spread. This is, in fact, very probable. The problem is analogous to detecting excitation to higher energy states of the molecular ions, lying slightly above the ionization threshold. This has been achieved with an energetically nonhomogeneous electron beam, using analytical methods (section III.A) to reduce the effective energy spread, for simple molecules and atoms only when the excited state does not lie too close to the ground state; i.e., the separation between the states should be at least 0.5 eV and preferably more. The metal chelates are much more complex than the molecules for which excited states of the molecular ion have been detected from ionization efficiency curves, and therefore have a higher density of vibrationally excited states. This would contribute to making breaks in the curve more difficult to detect. The difference in IP between $\text{M}(\text{acac})_3$ and $\text{M}(\text{NO}_2\text{acac})_3$ is approximately 0.75⁸⁸ or 0.53 eV⁹⁵ when $\text{M} = \text{Cr}$, and 1.05 eV⁸⁹ when $\text{M} = \text{Rh}$. (For $\text{M} = \text{Cr}$ the variance between the two values is probably due mainly to different methods of electron energy calibration.) These energy differences represent the maximum energy differences between the highest filled orbitals in the substituted and unsubstituted ligands. As will be discussed below, electronic effects in the complexes will reduce these values to some extent. Consequently, it is probable that any breaks in the ionization

efficiency curve of a partially nitrated complex would not be detected.

The second model required that substitution in one ring influences the IP of the whole system so greatly that it is improper to speak of localization on an individual ring. It was noted that in organic molecules, π systems of the same molecule, perpendicular to each other but in close proximity, influence each other's energy manifolds dramatically. Thus for a partially nitrated complex the ionization energy from a nonsubstituted ring would be increased by the presence of a nitro-substituted ring, and the IP's of the complexes would increase as the number of nitro groups increases.

It was stated that differences in the variations of IP upon nitration of the acetylacetonates of Cr^{III} and Rh^{III} were difficult to reconcile with the picture in which ionization occurred directly from the ligand in both systems.^{88,89} However, since substantial mixing of metal and ligand orbitals does occur the metal should influence the magnitude of these variations. Corresponding effects have been observed for disubstituted arenes where the first substituent can modify the effect of the second.¹⁰³

An interpretation of the results in this section is suggested by the photoelectron spectra (Table III). For the Cr^{III} complexes the energy of band Y is just as sensitive as that of band A to variations in the ligand, indicating substantial mixing of the metal and ligand orbitals. In a partially substituted complex, bands Y and A would consist of three components. Each component of band Y interacts with all three ligands. Thus, there would be reasonably efficient transmittal of electronic effects from one ligand to another, via the metal atom. A broadening, or even partial resolution, of each of the photoelectron bands Y and A is to be expected, with a net decrease in the energy separation of the bands. For the $\text{Cr}(\text{acac})_3$ complex, bands Y and A are incompletely resolved from each other, so that a partially substituted complex would likely show a single broad band comprising the original A and Y bands. An IP determined for such a situation, from an ionization efficiency curve, would not correspond exclusively to ionization from a particular orbital, though it would probably be weighted in favor of ionization from a ligand π_3 orbital because of the relatively greater ionization cross section generally observed (see section IV.B).

The IP of the mixed ligand chelate $\text{Cu}(\text{acac})(\text{hfacac})$ is close to that of $\text{Cu}(\text{tfacac})_2$ and also to the mean of the IP's of $\text{Cu}(\text{acac})_2$ and $\text{Cu}(\text{hfacac})_2$. Presumably the foregoing discussions can also be applied to the mixed complex.

D. Relative Influence of Metal and Ligand upon Ionization Potentials of β -Diketonate Complexes

It has been seen that for β -diketonate complexes of Cr^{III} and Cu^{II} there is a linear correlation between their IP's and the sum of the σ_p^+ constants of the substituents attached to the chelate rings. In Figure 6 it has been assumed that a similar correlation applies to the available, but limited data, for complexes of a number of other metals. The differing slopes of the correlation lines illustrate the varying susceptibilities to changes in IP with substituent as the metal is changed. Overall, the slopes are larger than the value of 0.76 ± 0.2 typically observed for substituted arenes,¹⁰³ being larger for complexes of trivalent than of divalent metals, which in turn give larger slopes than that for the parent β -diketones. Insufficient results are available to predict whether these observations are generally true for this class of metal complex.

E. Carbonyl Metal β -Diketonate Complexes

The IP's of a number of $(\text{CO}_2)\text{M}(\beta\text{-dik})$ complexes, where $\text{M} = \text{Rh}$ or Ir , and $\beta\text{-dik}$ represents the β -diketonate ligand (Table Id), have been interpreted^{107,108} in terms of ionization by electron

removal from a molecular orbital delocalized on the whole molecule and having significant participation of metal atomic orbitals. This interpretation was based on the observations that (i) the IP's of $\text{Co}(\beta\text{-dik})_3$ and $\text{Rh}(\beta\text{-dik})_3$, and of $(\text{CO})_2\text{Rh}(\text{acac})$ and $(\text{CO})_2\text{Ir}(\text{acac})$ are similar, but a difference of 0.35 eV is observed between the IP's of $(\text{CO})_2\text{Rh}(\text{hfacac})$ and $(\text{CO})_2\text{Ir}(\text{hfacac})$, and (ii) the IP of $\text{Rh}(\text{acac})_3$ is lower than that of $(\text{CO})_2\text{Rh}(\text{acac})$ by about 0.84 eV, while that of $\text{Rh}(\text{hfacac})_3$ is higher than that of $(\text{CO})_2\text{Rh}(\text{hfacac})$ by about 0.95 eV. These differences seemed to be too large to be explained by an indirect effect of the different electronic situation of the central metal atom on the chelated rings. It was suggested that, on ionization, electron removal occurred from an orbital with significant metallic character. There was the possibility that for the $\text{M}(\beta\text{-dik})_n$ complexes, where $n = 2$ or 3 , the influence of substitution in the ligands might overwhelm that of the metal. The changes in IP per substituent were evaluated by dividing the change in IP by the total number of substituent changes on all rings. This gave the magnitude of the substituent effect for the whole molecule. The values obtained were metal dependent, as would be expected from Figure 6. The substituent effects were also obtained for $(\text{CO})_2\text{M}(\beta\text{-dik})$, when lower values resulted.

It now appears that certain reservations apply to comparisons between IP's of $(\text{CO})_2\text{M}(\beta\text{-dik})$ and $\text{M}(\beta\text{-dik})_n$ complexes. In particular, the IP's of metal carbonyls typically fall in the range 8.3 ± 0.3 eV (see ref 42 for specific values and references). For the group VI metal hexacarbonyls it has been proposed that ionization occurs via electron removal from a metal-dominated orbital.¹⁰⁹⁻¹¹¹ This is easily reconciled with the high IP of CO (14.0 eV⁴²) and the well-known molecular orbital description¹¹² of the metal hexacarbonyls in which the metal \rightarrow ligand $t_{2g}(\pi)$ orbitals are the filled orbitals of highest energy. Consequently, the difference in IP between $(\text{CO})_2\text{M}(\text{acac})$ and $(\text{CO})_2\text{M}(\text{hfacac})$ would reflect mainly the change in energy of the M-CO π orbitals. Whatever the origin of the electron lost upon ionization of $(\text{CO})_2\text{M}(\text{acac})$ (the energies of the M-CO π orbitals and ligand π_3 orbitals are anticipated to be very similar), the electron lost upon ionization of $(\text{CO})_2\text{M}(\text{hfacac})$ likely comes from the M-CO π orbitals, of energy influenced by the electronic effects of the chelate ring. This view is supported by the photoelectron results for $(\text{CO})_4\text{Mn}(\text{hfacac})$ (Table III) where band Y (assignable to ionization from the Mn-CO π orbitals) occurs at 8.11 eV (vertical IP), well separated from band A, and in the range of IP's of metal carbonyls.

F. Metal Complexes Derived from Dipivaloylmethane

The mass spectra of complexes formed from dipivaloylmethane and lanthanide elements were initially studied¹¹³ because they were the first lanthanide complexes to be successfully analyzed by gas chromatography.¹¹⁴ The AP's of the complexes of La^{III} and Eu^{III} , together with those of Al^{III} , Co^{III} and Zr^{IV} , are given in Table Ie, while values for other lanthanide complexes were illustrated graphically.¹¹³ The precision of the results is low (± 0.5 eV quoted by the authors). Furthermore, N_2 was used for electron energy calibration. The calibration would be unreliable if significant intensities of CO^+ (from the complexes) arose during the determinations. Consequently, it is difficult to assess whether the IP variations in Table Ie are real. Comparisons with IP's of other complexes in Table I, together with the anticipated electronic effects of the $t\text{-C}_4\text{H}_9$ groups, would indicate strongly that the values for the dpm complexes of Al^{III} , Eu^{III} and Zr^{IV} are unexpectedly high.

G. Metal Complexes Derived from Schiff Bases

The only metal complexes of this class for which IP's have been reported are represented by the structural types:

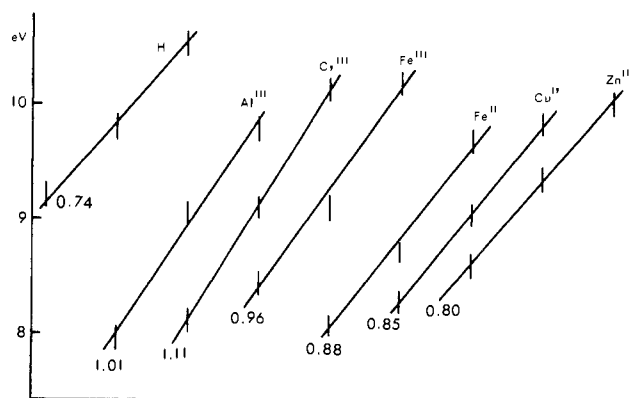
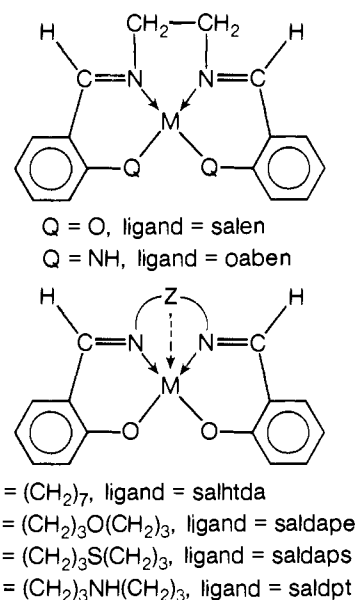


Figure 6. Correlation of IP's of acac, tfacac, and hfacac complexes of various metals with $\Sigma\sigma_p^+$ values. The lines, which are displaced horizontally for clarity, have gradients indicated by the numerical values.



The IP's of the complexes of each ligand with Co^{II} , Ni^{II} , and Cu^{II} , together with a value for $\text{Mn}(\text{salen})$, are collected in Table If. For a given ligand, the IP's of the complexes show only small variations, the values for the Cu^{II} complexes appearing to be slightly higher than those of Co^{II} and Ni^{II} , for which the differences are comparable to the experimental standard deviations. For every complex the IP's are significantly lower than the IP of the parent Schiff base. The IP's of the tetracoordinate, square-planar complexes derived from salen and oaben were directly influenced by the strength of the metal-ligand bonding,¹¹⁵ being lower for the more stable oaben complexes. When the IP's of the other complexes are compared with these, it has been pointed out¹¹⁶ that structural variations, changes in denticity of the ligand, and changes in spin state, may influence the relative values. Thus, like the salen complexes, the four-coordinate Ni(salhdta) and Cu(salhdta) complexes are square planar while Co(salhdta) is tetrahedral. It can be anticipated that for the former complexes the C_7H_{14} chain would cause some distortion from the basic square-planar structure. The higher IP's of the salhdta complexes compared to the salen complexes are consistent with the expected weaker bonding in the former compounds.

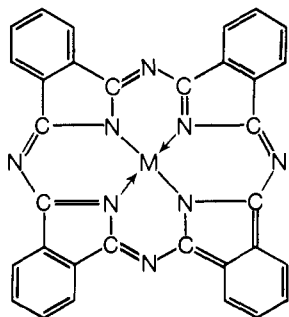
The ligands saldape, saldaps, and saldpt are potentially pentadentate. The coordinating abilities of the ether oxygen of saldape and the thioether sulfur of saldaps are relatively poor. The Co^{II} complexes formed from these ligands are four-coordinate and tetrahedral, while those of Cu^{II} were believed¹¹⁶ to have four-coordinate, distorted square-planar structures. The Ni^{II} complexes were believed to be weakly five-coordinate

low-spin compounds. The $M(\text{saldpt})$ complexes are all high-spin five-coordinate compounds, reflecting the greater coordinating ability of the secondary NH group, compared to oxygen and sulfur. It was argued¹¹⁶ that the additional electron density on the metal brought about by a fifth coordinating group would tend to lower the IP of the complex, a point which will be discussed in more detail below. Consequently, the IP's of the Co^{II} and Cu^{II} complexes of *saldape* and *saldaps* should be approximately equal to those of the *salhda* complexes, while the IP's of the *saldpt* complexes should be lower. For Cu^{II} these qualitative predictions agree with the experimental results. For Co^{II} the IP's of the *saldape* and *saldaps* complexes are too low when compared to the values for the *salen* and *salhda* complexes. The reason for this is not clear but may indicate five-coordination in the gas phase, in contrast to the structural data.¹¹⁶ The IP's of the Ni^{II} complexes agree reasonably well with the relative coordinating abilities of the ligands.

It has been suggested¹¹⁵ that the IP's of the *salen* and *oaben* complexes could be interpreted by electron removal from an orbital where the metal makes a significant contribution, though it was conceded that variation in the donor atom would be expected to cause approximately parallel variations in the energies of metal- and ligand-dominated orbitals, and that molecular orbital calculations on the complexes suggested that ionization would occur via electron loss from a ligand orbital since an orbital of this type was the filled orbital of highest energy in the complexes. The fifth coordinating group of the five-coordinate complexes would not only increase the electron density on the metal, as previously stated,¹¹⁶ but the effect would also be transmitted through the metal to increase the electron density in the other predominantly ligand orbitals involved in the bonding of the original four groups; i.e., the IP would be expected to decrease in any case if electron removal is from either metal- or ligand-dominated orbitals. (An alternative viewpoint would attribute the IP lowering to the increased stability of the resulting molecular ion due to greater opportunities for delocalization of positive charge when five-coordinating groups are present. These increased opportunities exist whether the electron is removed from either a predominantly metal or ligand orbital.) Consequently, it would appear that these results do not allow a conclusion to be made concerning the origin of the electron lost at the ionization threshold for these complexes. (Thus, for example, there is no obvious effect attributable to electron removal from metal orbitals for high- and low-spin Ni^{II} complexes.) Quite possibly the IP's obtained from ionization efficiency curves can be interpreted in much the same way as for the β -diketonate complexes. That is, if the ionization energies from the highest energy, filled metal- and ligand-dominated orbitals are quite similar, and show parallel energy variations with changes in the ligand, the experimentally determined IP will be an intermediate value weighted in favor of ionization from ligand orbitals, reflecting their expected greater ionization cross sections.

H. Metal Phthalocyanines

The IP's of a number of metal phthalocyanines¹¹⁷ together with that of metal-free phthalocyanine, given in Table Ig, are



nearly the same, the variations being comparable to the experimental standard deviations. The low values suggest a molecular ion stabilized by extensive delocalization of the positive charge over the macrocyclic ligand, and the effect of the metal on the IP is correspondingly small.

I. Negative Ions

Reports on studies of negative ions in the mass spectra of metal complexes are relatively few.^{9,70,115,116,118-121} These have been mainly concerned with relative abundances, and only in the case of the metal-Schiff base complexes listed in Table If have energetic studies been made.^{115,116} For every complex, except $\text{Ni}(\text{oaben})$, the resonance capture curve was identical with that for SF_6^- (the calibrant). It was reasoned¹¹⁶ that increasing electron density on the metal, resulting from increasing donor ability of the ligand, would prohibit electron capture, but even with the fifth coordinating group the potentially five-coordinate Schiff base ligands were not as effective in this way as the tetradentate ligand *oaben*. However, only for $\text{Ni}(\text{oaben})$ was the resonance capture of thermal electrons not observed, possibly because of the relative instability of the Ni^{I} state.¹¹⁵ Otherwise, from the negative ion energetic studies, there appeared to be no correlation with the ability of the metal to be reduced.¹¹⁶

The 70-eV negative ion spectra of metal complexes of fluorinated β -diketonates contain abundant molecular ions.^{120,121} It was suggested that these were formed as a result of secondary electron capture.

J. Summary and Conclusions

The IP's, determined by electron impact, of a large number of metal complexes have led to conflicting views concerning the nature of the orbital from which the electron is removed upon ionization. A large body of experimental evidence obtained for β -diketonate complexes has been interpreted in terms of ionization by electron removal from an orbital having mainly ligand character, but alternative explanations have been suggested. A major problem concerns the difficulty of reconciling the experimental results with theoretical models of the electronic structure of the metal complexes, which place the energies of the metal orbitals above those of the ligand orbitals. Qualitative and quantitative variations of the IP's determined by electron impact are inconsistent with these models.

Three alternative interpretations of the observations on β -diketonates may be advanced as follows:

(i) Koopmans' theorem fails. Transition metal complexes are less than ideal compounds to which to apply this theorem. Many features of the experimental results could be explained if inversion of the energies of the metal d orbitals and ligand π_3 orbitals occurred upon ionization, effectively resulting in electron removal from a ligand π_3 orbital. A serious difficulty arises with this interpretation since occupied ligand π orbitals now lie above the vacant metal d orbitals and spontaneous reduction of the metal should occur; i.e., the molecular ion is formed in an excited electronic state rather than its ground state.

(ii) Electron removal by electron impact is from the highest energy occupied molecular orbital, assumed to be an orbital of mainly metal character but of energy strongly influenced by the ligands. This interpretation has certain advantages, e.g., in the explanation of IP variations of mixed ligand chelates, but, as will be seen in section V, there are difficulties in explaining the variations in energy required to bring about fragmentation of the molecular ion.

(iii) The electron impact method is relatively insensitive to detecting adiabatic ionization from metal orbitals; i.e., the measured IP's are higher than these values and correspond more closely to ionization energies from ligand π orbitals. Support for

this view is obtained by comparison with results from photoelectron spectroscopy where the electron impact results correlate best with the photoelectron band corresponding to ionization from a ligand π orbital, rather than with the lowest energy band in every case. Thus the electron impact method apparently fails to detect ionization from the metal t_{2g} orbitals (assuming octahedral symmetry) of Cr^{III} and Co^{III} complexes listed in Table III. Even in the photoelectron spectra, Fe^{III} complexes show no evidence of ionization from t_{2g} or e_g^* orbitals, while Mn^{III} complexes show a weak shoulder assignable to ionization from a metal e_g^* orbital.

To this reviewer, the third interpretation is to be preferred. In the case of the Cr^{III} complexes (and by analogy for the Co^{III} complexes), it was proposed here that an IP determined from an ionization efficiency curve would probably be weighted in favor of ionization from a ligand π_3 orbital because of the greater ionization cross section for this process. Because Table III shows that the energy difference between the t_{2g} and π_3 ionizations is only about 0.6 eV for the Cr^{III} complexes (less for the Co^{III} complexes), the lower probability ionization from the t_{2g} orbitals would likely not be detectable in ionization efficiency curves. Since, for the Mn^{III} and Fe^{III} complexes the energy difference between e_g^* and π_3 is expected to be 2–3 eV, a low probability ionization from the e_g^* orbitals would be more readily detected. An explanation of the results for these complexes is now offered. Assuming the molecular orbital description of these complexes to be substantially correct, ionization from a metal e_g^* orbital must have low probability for both electron and photon impact. Removal of an antibonding electron from an e_g^* orbital would lead to a decrease of the metal–oxygen bond lengths. A two-dimensional representation of the potential energy surface for a vibrational mode is schematically presented in Figure 7. The curve, P_2^+ , for the ground electronic state of the molecular ion is steeper and displaced to shorter bond lengths than that for the ground state of the neutral molecule. Direct ionization to this state in a vertical transition has very low probability, and it is further necessary to assume that production of this ionic state from excited states of the molecule, such as P^* , lying at higher energy, is unfavorable with respect to other processes for dispersal of the energy of the excited molecule. In other words, vertical ionization by removal of a metal e_g^* electron produces a molecular ion in which the bond lengths (in any vibrational mode) are far from their equilibrium values, leading to a highly vibrationally excited molecular ion. The energy for this process is, at least, comparable to the energy for vertical ionization by removal of a bonding ligand π electron to give P_1^+ . Thus, in the photoelectron spectrum, ionization to P_2^+ appears either as a weak shoulder or is lost under bands corresponding to ionization from ligand π orbitals. Ionization to P_2^+ would be undetectable in an ionization efficiency curve.

V. Appearance Potentials of Fragment Ions from β -Diketonate Complexes

The factors which can influence the accuracy of an AP determination have been given in section II.C. The contribution of excess energy to the AP data of Table I is unknown, and in the following discussion the assumptions made will be clearly stated. In the present section, AP's for ions formed from molecular ions by loss of ligand radicals, and other simple radicals, for transition metal β -diketonates are assessed. Interpretation of more complex processes than these is of doubtful validity.

A. Coordinate Bond Energies

For acetylacetonate complexes of Mn, Fe, and Co the data in Table I can, in principle, be used to obtain the energy of the dissociation:

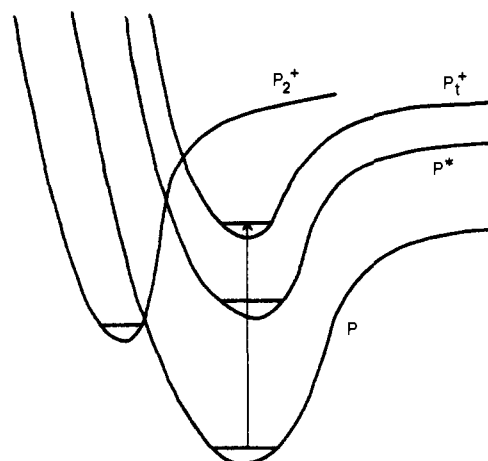
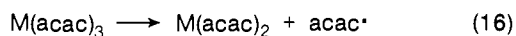


Figure 7. Two-dimensional representation of vertical ionization of an $\text{M}(\text{acac})_3$ complex in which removal of a bonding electron produces ion P_1^+ and removal of an antibonding e^* (or e_g^*) electron produces ion P_2^+ . Probability of direct ionization to P_2^+ is very small. P^* is an excited state of the neutral molecule.

which is given by eq 17

$$\Delta H_{\text{diss}} = \text{AP}[\text{M}(\text{acac})_2^+ \text{ from } \text{M}(\text{acac})_3] - \text{IP}[\text{M}(\text{acac})_2] \quad (17)$$

if it is assumed that activation energies and other excess energies associated with the ionization processes are small enough to be neglected. From this, and known bond energies in $\text{M}(\text{acac})_3$ complexes, the metal–oxygen bond energies in $\text{M}(\text{acac})_2$ complexes can be calculated. Values obtained¹²² were: $\text{Mn}(\text{acac})_2 \leq 65 \pm 2$; $\text{Fe}(\text{acac})_2 \leq 76 \pm 2$; $\text{Co}(\text{acac})_2 \leq 63 \pm 2$ kcal/mol. These values are not directly accessible by calorimetric determinations because of the associated or polymeric nature of the complexes in the solution or solid phases (see section IV.A). Unfortunately, because of difficulties described below, only upper limits to the values of the metal–oxygen bond energies are obtained.

It has been observed that $\text{Mn}(\text{acac})_3$, $\text{Fe}(\text{acac})_3$, and $\text{Co}(\text{acac})_3$ are somewhat sensitive to thermal decomposition⁸⁷ with the result that small amounts of the $\text{M}(\text{acac})_2$ species exist in the ion source. Structure in the ionization efficiency curve for $\text{Co}(\text{acac})_2^+$ obtained from $\text{Co}(\text{acac})_3$ was attributed to this cause and a correction applied, but this could not be done for the Mn^{III} and Fe^{III} complexes for which the $\text{M}(\text{acac})_2^+$ curves showed no obvious structure.

It can also be deduced from thermodynamic considerations that the metal–oxygen bond energies in these $\text{M}(\text{acac})_2$ complexes are upper limits. From Table I, values of ΔH_{diss} for $\text{Mn}(\text{acac})_3$ and $\text{Fe}(\text{acac})_3$ are $\geq 9 \pm 4$ and $\geq 30 \pm 4$ kcal/mol, respectively. Making reasonable assumptions for the entropy change for eq 16 it can be estimated that at typical ion source temperatures and pressures (~ 500 K and $\sim 10^{-8}$ atm, respectively) the $\text{Mn}(\text{acac})_3$ complex would be almost completely dissociated and $\text{Fe}(\text{acac})_3$ would be dissociated to the extent of a percent or so. Thermodynamic equilibrium in the ion source is unlikely, in part because of the very long mean free path of the molecules under the prevailing conditions, but it appears very probable that enough $\text{Mn}(\text{acac})_2$ and $\text{Fe}(\text{acac})_2$ would be present in the ion source to lower considerably the apparent AP of $\text{M}(\text{acac})_2^+$ from $\text{M}(\text{acac})_3$. Their presence could easily remain undetected in the $\text{M}(\text{acac})_2^+$ ionization efficiency curves. Similar estimates applied to $\text{Co}(\text{acac})_3$ predict negligible dissociation under prevailing ion source conditions. The small amount of $\text{Co}(\text{acac})_2$ assumed to be present from the structure in the ionization efficiency curve of $\text{Co}(\text{acac})_2^+$ may have arisen from local hot spots (e.g., filament assembly) or as an impurity.

It cannot be emphasized too strongly from these observations that caution is required when using AP's to calculate bond

TABLE IV. Values of AE(L)^a for Acetylacetonates and Fluorine-Substituted Acetylacetonates

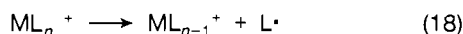
Trivalent complexes		Divalent complexes	
Complex	AE(L), eV	Complex	AE(L), eV
Al(acac) ₃	1.05	Mn(acac) ₂	5.4
Ti(acac) ₃	4.7	Fe(acac) ₂	5.8
V(acac) ₃	3.9	Co(acac) ₂	5.4
Cr(acac) ₃	3.2	Ni(acac) ₂	5.3
Mn(acac) ₃	≥0.85	Cu(acac) ₂	4.8
Fe(acac) ₃	≥0.95	Zn(acac) ₂	5.5
Co(acac) ₃	2.9	Fe(tfacac) ₂	5.75
Al(tfacac) ₃	1.15	Cu(tfacac) ₂	4.05
Al(hfacac) ₃	1.4	Zn(tfacac) ₂	5.2
Cr(tfacac) ₃	2.8	Zn(hfacac) ₂	5.2
Cr(hfacac) ₃	4.15		
Fe(tfacac) ₃	0.1 ^b		
Fe(hfacac) ₃	0 ^b		

^a Reproducible to ±0.2 eV. ^b Probably too low owing to thermal decomposition.

energies in complexes where thermal decomposition, even to a minor extent, may occur.

B. Fragmentation of Molecular Ion by Loss of a Ligand Radical

The following equation represents the loss of a ligand radical from the molecular ion. If it is assumed that excess energies



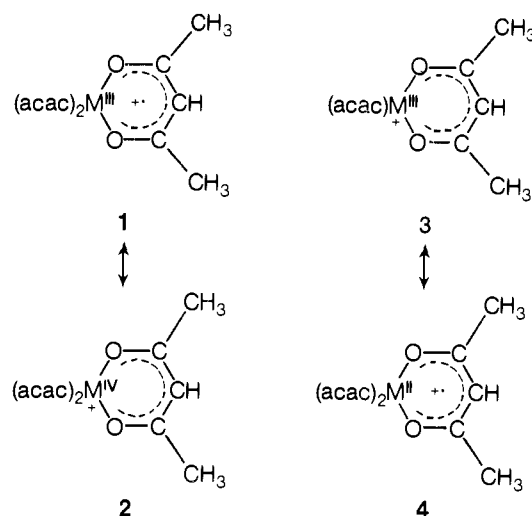
involved in the formation of the ML_{n-1}^+ ions are either small, or at least sensibly constant for a series of complexes of a given ligand with different metals, then the activation energies for the loss of the ligand radical, obtained from the equation

$$AE(L) = AP(ML_{n-1}^+) - IP(ML_n) \quad (19)$$

can be compared to determine the influence of the metal. Values calculated from Table I data are given in Table IV for acetylacetonates and fluorine-substituted acetylacetonates.

The nature of any geometrical changes in the metal-containing ion, which may occur on loss of the neutral ligand species, is unknown since ion structures cannot be directly determined. For the tris chelates a change from octahedral to tetrahedral or square-planar coordination of the metal is to be expected, with changes in the electronic structure depending upon the d electron configuration. Geometrical changes would make the interpretation of the AE(L) values more complicated. In addition, it has been suggested that the loss of the ligand from the molecular ions of complexes of this type generally occurs in two steps rather than one.¹²³ This was demonstrated only in the case of Al(hfacac)₃ for which loss of CF₃ preceded the loss of the remainder of the ligand.

Acknowledging the preceding complications, the variations in AE(L) for the trivalent complexes are now considered. Ignoring the probably low values for the Mn^{III} and Fe^{III} complexes it is interesting to note that for a given ligand the AE(L) values are significantly lower for the Al^{III} chelates than for those of Ti^{III}, V^{III}, Cr^{III}, and Co^{III}. It is thus apparent that the d orbitals of a transition metal play a role in the stabilization of the molecular ion relative to the fragment ML_2^+ ion. The stabilization decreases in the sequence Ti^{III} > V^{III} > Cr^{III} > Co^{III} >> Al^{III}. The actual structures of the molecular ions have not been directly determined, of course, but the following structures, which are presented as an aid in the interpretation of the mass spectra in chemical terms, are consistent with the energetic data. Accordingly, the molecular ion, $M(acac)_3^+$, may be represented by the canonical forms **1** and **2**, and the $M(acac)_2^+$ ion by the forms **3** and **4**. In the limiting representations **2** and **4** a formal change in the oxidation



state of the metal occurs, while **2** and **3** have even-electron structures (which, in the mass spectra of organic compounds, are preferred over odd-electron structures). Representation **3**, which combines the favorable even-electron structure with the stable +3 oxidation state of the metal (the only stable oxidation state for Al) is likely to make the major contribution to the actual structure of $M(acac)_2^+$ with only small differences from metal to metal. Thus, variations in AE(L) must be due mainly to differences in the stability of $M(acac)_3^+$ for different identities of M. (The relationship of this proposal to the valence change concept⁸⁻¹⁰ for rationalizing relative intensities of ion types in the mass spectra of metal complexes will be considered in section VI.)

The canonical forms **1** and **2** correspond to electron removal from ligand or metal orbital, respectively, of the neutral complex. In the case of the aluminum chelate only **1** can make a significant contribution to the molecular ion, and little stabilization due to a contribution from **2** can result. The electron impact IP's of transition metal chelates are also interpreted by electron removal from a ligand orbital, but for these complexes contributions from **2** can be important. In molecular orbital terms this is equivalent to increased metal t_{2g} orbital participation (assuming O_h symmetry), in the molecular ion, in what was formerly a mainly ligand, mixed metal-ligand orbital in the neutral complex. Or, in physical terms, this could be regarded as an expansion of the metal t_{2g} orbitals into the ligand π system to spread out the positive charge. For each of these interpretations the value of AE(L) should generally increase with increasing relative stability of the +4 to that of the +3 oxidation state. Although it has been pointed out¹²⁴ that many factors influence the relative stabilities of oxidation states, it appears generally accepted that, for ligands which bond through oxygen, the relative stability of the +4 oxidation state decreases with increasing atomic number in the first transition series. The trend, noted above, in the AE(L) values is consistent with this and not with the increasing strength of π -bonding from Ti^{III} to Co^{III} in the neutral complexes (section IV.A).

There appears to be no obvious trend in the AE(L) values of the chelates of the divalent metals given in Table IV. The values are significantly greater than for most complexes of the trivalent metals. Suggested explanations for this are (a) steric repulsions between ligands in the molecular ion, if significant, are likely to be smaller for bis than for tris chelates; (b) only two ligands compete for metal d_{π} electrons in the bis chelates, compared with three ligands in the tris chelates.

Values of AE(L) for Cr^{III} and Cu^{II} chelates can also be obtained from Table I. Relative values for different ligands are not directly or easily comparable, and it is found that, for a given metal, AE(L) values vary widely. For example, for Cu^{II}, extreme values of 2.0 and 4.8 eV may be found in Table Ic.

C. Fragmentation of Molecular Ion by Loss of Small Radicals

The uncertainties of the last section, involved in the interpretation of AE(L) values, are reduced when energies required to remove simple substituents such as CH₃ or CF₃ from the molecular ion are considered. A single-step process is definitely involved and the precursor ion is unambiguously known. Values of AE(CH₃) and AE(CF₃), given by

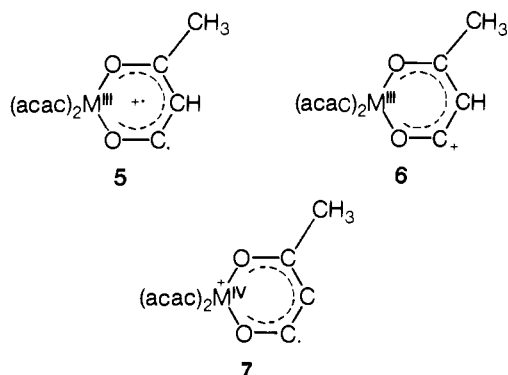
$$\text{AE}(\text{CH}_3) = \text{AP}[(\text{P} - \text{CH}_3)^+] - \text{IP}[\text{P}] \quad (20)$$

$$\text{AE}(\text{CF}_3) = \text{AP}[(\text{P} - \text{CF}_3)^+] - \text{IP}[\text{P}] \quad (21)$$

and calculated from Table Ia, are summarized in Table V. (The formation of (P - CF₃)⁺ in an ion-pair process is considered unlikely, since CF₃⁻ has not been detected in negative ion spectra.^{118,120,121}) If it is assumed that excess energies associated with these dissociations are small, or sensibly constant from compound to compound, then comparisons based on Table V can be made. The intensities of the (P - CF₃)⁺ and (P - CH₃)⁺ peaks in the mass spectra of many compounds were too small for accurate AP determinations to be made, but sufficient information is available in Table V to show that real variations do occur.

Contributions to a bond dissociation energy, in addition to a σ term, may also contain a π term, and a reorganization term. This latter arises from adjustments of other bonds (lengths and angles) when the bond of concern is breaking. The π term can be positive or negative depending upon whether the greater π energy is associated with the original molecule or product radicals. By use of certain assumptions the σ contribution (uncorrected for reorganization) to the dissociation of a CH₃ or CF₃ radical from a chelate ring should be about 90–95 kcal/mol (3.9–4.1 eV/molecule).¹¹⁸ The values of AE(CH₃) and AE(CF₃) shown in Table V are all lower than this, usually much lower. It thus becomes necessary to assess the probable magnitude of π energy differences between P⁺ and (P - CH₃)⁺ or (P - CF₃)⁺ ions for likely cyclic or acyclic structures of the ligand moiety before and after decomposition of the molecular ion. Three possibilities are now considered.

In the first possibility it is assumed that the chelate ring remains intact upon decomposition of the molecular ion. As before, the P⁺ ion of an M(acac)₃ complex, for example, would be represented by the canonical forms **1** and **2**, while the (P - CH₃)⁺ ion has the forms **5–7**. The effect of the metal on the stability



of P⁺ has already been discussed. It is doubtful that any but a small π stabilization, relative to P⁺, results if any of the forms **5–7** contribute significantly to (P - CH₃)⁺. Even though **6** has an even-electron structure, achieved by electron transfer from the radical site of **5** to the π system, it would have a highly strained ring due to a preferred 180° bond angle at the C⁺ site. If the metal has a relatively stable +4 oxidation state, then contributions from **7** to (P - CH₃)⁺ could become important, though probably not significantly different from the contribution of **2** to P⁺. As for the IP variations of the complexes, an analogy

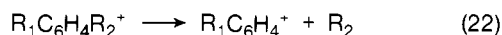
TABLE V. Values of AE(CH₃) and AE(CF₃) for Acetylacetonates and Fluorine-Substituted Acetylacetonates^a

M	M(acac) _n		M(tfacac) _n		M(hfacac) _n	
	AE(CH ₃), eV	AE(CH ₃), eV	AE(CF ₃), eV	AE(CF ₃), eV	AE(CF ₃), eV	AE(CF ₃), eV
H	1.5	1.9	0.8		0.6	
Al ^{III}					0.9	
Fe ^{III}					0.9	
Mn ^{II}	3.35					
Fe ^I	3.6		3.85		3.5	
Co ^{II}	2.95					
Ni ^{II}	3.4					
Cu ^{II}	2.6		2.45		1.7	
Zn ^{II}	2.3	2.3	1.9		1.3	

^a Reproducible to ±0.2 eV.

with the behavior of aromatic systems may be drawn to help clarify the decomposition pathway. In a review¹²⁵ of energetic data for benzene derivatives it was suggested that the C₆H₅⁺ ion formed from a number of monosubstituted benzenes (e.g., phenyl halides) and acyclic compounds is the cyclic phenyl ion ($\Delta H_f = 282$ – 285 kcal/mol) while from others (e.g., benzene, toluene) it was an acyclic ion ($\Delta H_f = 299$ – 306 kcal/mol). In particular, for toluene (IP = 8.9 eV; AP of C₆H₅⁺ = 13.7 eV) we have AE(CH₃) = 4.8 eV, whereas the calculated value would be 3.9 eV, based on a cyclic phenyl ion, a value very close to that given above for the estimated σ contribution to the energy of dissociation of CH₃ or CF₃ from a chelate ring. This suggests that there would be little difference in π energies between **1** and **5** or **6**, or between **2** and **7**.

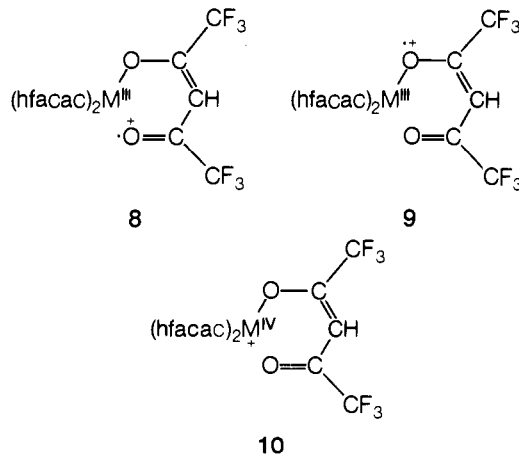
The effect of substitution in the benzene ring upon AE values has also been studied. For the reaction of eq 22 for meta- and para-disubstituted benzenes, eq 23 was obtained.¹²⁶



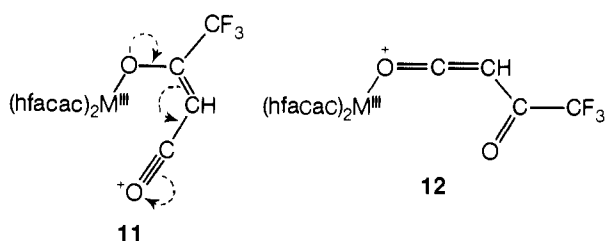
$$\text{AE}_{1,2} = (k_2 - 0.77)\sigma_1^+ + \text{AE}_2 \quad (23)$$

AE₂ is the energy of the reaction for R₁ = H and k₂ is a constant which depends upon R₂. For chlorobenzenes (R₂ = Cl) and nitrobenzenes (R₂ = NO₂), for which direct cleavage of the C–R₂ bond occurs, the experimental results give k₂ = 0.71 ± 0.12 and 0.44 ± 0.14, respectively. These electron-withdrawing substituents thus reduce AE_{1,2}. If a similar relationship applies to the acetylacetonate complexes, with AE₂ = 3.9 eV, then the metal should influence the value of AE(CH₃). However, the observed variations in AE(CH₃) are much too large, assuming reasonable values for k₂ and σ^+ . Similar arguments apply to the M(tfacac)_n and M(hfacac)_n complexes.

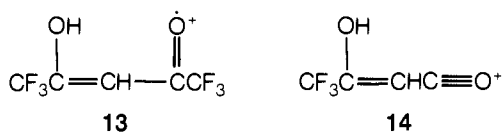
In the second possibility it is assumed that the P⁺, (P - CH₃)⁺, and (P - CF₃)⁺ ions have acyclic structures. For an M(hfacac)₃ complex, P⁺ is represented by the canonical forms **8–10** while



(P - CF₃)⁺ has the isomeric forms **11** and **12**. In the case of a complex such as Al(hfacac)₃ where increase of the metal oxi-



dation state is very difficult, only **8** and **9** would make a significant contribution to P^+ . The preferred decomposition would be to **11** (for which other canonical forms are possible) which has a longer conjugated system than **12**. The value of $AE(CF_3)$ should be closely similar to those obtained for $tfacacH$ and $hfacacH$ when comparisons with the structures presumed for these latter compounds (shown as **13** and **14** for $hfacacH$) are made. Much greater charge delocalization is possible in **14** than in **13** ac-



counting for an $AE(CF_3)$ value much lower than the σ contribution of ~ 4 eV. In cases where an increase of metal oxidation state is easier, the contribution of **10** to P^+ will be enhanced, while no further stabilization of $(P - CF_3)^+$, **11**, is anticipated. Values of $AE(CF_3)$ greater than for $hfacacH$ are to be expected. Table V shows that $AE(CH_3)$ and $AE(CF_3)$ are always greater for the metal complexes than for the β -diketones, sometimes only slightly greater, i.e., for Al^{III} , Fe^{III} , and Zn^{II} for which metal oxidation does not occur readily. For easily oxidized species such as Mn^{II} and Fe^{II} much larger values are observed. A weakness of this second possibility is that the measured IP's are consistent with intact chelate rings in the molecular ion, at the ionization threshold. If this were not so, the energy of dissociation of the metal-oxygen bond would contribute to the measured IP. Complexes of metals expected to form strong bonds to the ligands, e.g., Cr^{III} and the divalent metals, do not have IP's significantly different from complexes of those metals expected to have small binding power to their third ligand, e.g., Mn^{III} and Fe^{III} .

In the third possibility it is assumed that, at the ionization threshold, the molecular ion retains intact chelate rings to give canonical forms analogous to **1** and **2**, but undergoes ring opening on loss of CH_3 or CF_3 to give structures analogous to **11**. The energies $AE(CH_3)$ or $AE(CF_3)$ of the process should exceed the values for the β -diketones (as in fact observed) by the energy required to break the metal-oxygen bond. These metal-oxygen dissociation energies are not known but may qualitatively follow the $AE(L)$ values of Table IV. It is reasonable to assume that if the $AE(L)$ value is small then the first metal-oxygen bond dissociation energy will also be small. The relative magnitudes of the $AE(CH_3)$ and $AE(CF_3)$ values should parallel the previously discussed trends in the $AE(L)$ values. Tables IV and V do show a qualitative parallel between these sets of values with the $AE(L)$ values always being somewhat larger. The small value of $AE(CF_3)$ for $Fe(hfacac)_3$ probably means that $AE(L)$ is also small for this complex, but greater than 0.9 eV.

It must be conceded that conclusions based on probable (but unestablished) ion structures and comparisons of coordination compounds with organic systems is necessarily speculative. To this reviewer it appears that the third possibility is most consistent with the energetic data (a revision of an earlier proposal¹¹⁸). Weaknesses of the first two possibilities have already been pointed out. The third possibility is consistent with the energetic information and, for $Al(hfacac)_3$ at least, is also consistent with some requirements of the quasi-equilibrium theory. The observation of the fast, consecutive dissociations $[Al(hfa-$

$cac)_3]^+ \rightarrow [Al(hfacac)_3 - CF_3]^+ \rightarrow [Al(hfacac)_2]^+$ by studies of metastable peaks, led to the suggestion¹²³ that the activation energies for the two reactions should not differ by more than 1 eV. This agrees with values obtained from Tables IV and V which are 0.9 and 0.5 eV (i.e., 1.4–0.9 eV) for the first and second dissociations, respectively. It was further suggested that this consecutive dissociation decomposition scheme was a general one for acetylacetonates. It was reasoned that a preceding loss of CF_3 may facilitate the breaking of two metal-chelate bonds, since a stable neutral species, $CF_3COCHCO$, can subsequently be eliminated.

The third interpretation is also consistent with the view that on ionization of a β -diketonate complex an electron is removed from a ligand π orbital. Values of $AE(CF_3)$ were the same for $Al(hfacac)_3$ and $Fe(hfacac)_3$, i.e., 0.9 eV, and substantially less than ~ 4 eV expected for the σ contribution to C–C bond fission. For the Al^{III} complex a ligand π electron is almost certainly removed, and this is presumably also true for the Fe^{III} complex, for, if instead an antibonding e_g^* electron (assuming O_h symmetry) were removed, a substantially higher value of $AE(CF_3)$ would be expected. (This constitutes additional evidence that molecular ions of Fe^{III} high-spin complexes are formed in vibrationally excited states, even at threshold, and indicates that the adiabatic value for the IP corresponding to removal of an e_g^* electron should be substantially lower.)

D. Summary and Conclusions

From the limited data currently available, it appears that the energies required for dissociation of the molecular ion of a metal β -diketonate by loss of ligand, CH_3 , or CF_3 radicals are smaller for complexes of trivalent than of divalent metals. The energy for removal of CH_3 or CF_3 is less than that required for removal of the whole ligand. Although other factors no doubt contribute, the stability of the molecular ion is enhanced if the metal has a tendency to undergo oxidation. Dissociation of CH_3 or CF_3 from the molecular ion appears best described in terms of simultaneous or prior chelate ring opening though just above the ionization threshold the chelate rings remain intact.

VI. Energetics of Fragmentation and the Concept of Metal Valency Change

To rationalize some striking differences between the mass spectra of metal complexes, Shannon and coworkers^{8–10} proposed that the modes of ion decomposition were markedly dependent on the oxidation states normally assumed by the metal concerned. It was postulated that the odd- or even-electron character of a metal-containing ion is determined by the capacity of the complexed metal species to accept one or more electrons from the ligands (valence decrease in metal) or to donate one or more electrons to the ligands (valence increase in metal). While recognizing that in any given complex specific effects can modify the mass spectrum considerably, in the light of the energetics of fragmentation presented here, Shannon's proposals can be extended as follows:

1. The molecular ion will be stabilized if metal \rightarrow ligand π donation occurs readily, i.e., if facile increase of oxidation state can occur. The molecular ion will be relatively abundant and the loss of even-electron neutral species from the molecular ion will be enhanced.

2. If the metal ion does not undergo facile increase or decrease of oxidation state, the molecular ion is not appreciably stabilized and may, though not necessarily, be of low abundance. Fragmentation typically proceeds through loss of a neutral radical, followed by loss of even-electron neutral species.

3. If the metal ion can undergo facile decrease of oxidation state, the molecular ion may be of low abundance. Fragmentation typically occurs through two successive losses of neutral

TABLE VI. Partial Mass Spectra of $M(\text{acac})_3$ Complexes⁸⁷

Ion	Ti	V	Cr	M Mn	Fe	Co	Al ^a
L_3M^+	100	32	23	16	16	29	9
$(L_3M - 82)^+$	37	3					
L_2M^+	55	100	100	100	100	100	100
$(L_3M - 100)^+$	80						
$(L_2M - 82)^+$	36	10	12		8		4
$(L_2M - \text{CH}_3)^+$			5	32	47	47	
LM^+		5	45	70	74	66	1

^a Ref. 9.

radicals. Succeeding losses will normally occur through loss of odd- or even-electron neutral species depending upon whether, or not, further reduction in oxidation state can readily occur.

It was pointed out in section V.B that many factors influence the relative stabilities of oxidation states¹²⁴ so that demarcation between generalizations 1, 2, and 3 will often be diffuse. To illustrate the applicability of the generalizations, a partial tabulation of the mass spectra of acetylacetonate complexes of trivalent metals of the first-row transition elements, together with aluminum, is shown in Table VI. The results of Table IV reveal that a general decrease in values of $AE(L)$ (and hence a decrease of stability of the molecular ion) occurs on proceeding to the right of Table VI, which for the transition metals parallels the increasing stability of the +2, and the decreasing stability of the +4 oxidation state, relative to the +3 state. For all complexes, initial loss from the molecular ion of the odd-electron species acac^\cdot is a prominent process. In agreement with generalization 1, the titanium complex has the most abundant molecular ion, and the species $(L_3M - 82)^+$ and $(L_3M - 100)^+$ formed by successive losses of even-electron species of 82 and 18 amu from the molecular ion are also prominent. On the other hand, loss of an odd-electron species CH_3^\cdot or acac^\cdot from $M(\text{acac})_2^+$ (resulting in ions in which a formal decrease of metal ion valency has occurred, and which are placed in the lower part of Table VI below the broken line for emphasis) occurs more readily from the later members of the series, reflecting the increased stability of the +2 oxidation state. Loss of an even-electron fragment of 82 amu from $M(\text{acac})_2^+$ occurs more readily for the less readily reducible earlier transition elements, especially for $M = \text{Ti}$.

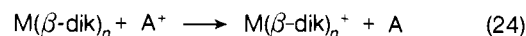
The relative intensities of the $(P - L)^+$ and $(P - \text{CH}_3)^+$ ions ($L = \text{acac}$ in Table VI) can also be rationalized if $(P - L)^+$ is formed from $(P - \text{CH}_3)^+$ as indicated in section V.C. The energetic studies pointed to a parallel between the energies required for the formation of these two ions. When the activation energies required are low, the $(P - \text{acac})^+$ ion would be formed rapidly, to the exclusion of significant steady-state concentrations of $(P - \text{CH}_3)^+$ in the ion source. When the activation energies are higher, then formation of $(P - \text{acac})^+$ is slowed down and steady-state concentrations of $(P - \text{CH}_3)^+$ can increase. Thus, $M(\text{acac})_3$ complexes, for which $AE(L)$ values are generally low, show little tendency to form $(P - \text{CH}_3)^+$ ions, while $M(\text{acac})_2$ complexes, having significantly greater $AE(L)$ values, often show abundant $(P - \text{CH}_3)^+$ ions.^{10,87}

Direct experimental evidence for the valence change concept has also been obtained from the mass spectra of certain complexes. For example, in the mass spectra of $M(\text{hfacac})_3$ complexes metastable peaks were observed for eliminations of the neutral metal fluorides AlF_3 ,¹¹⁸ CrF_3 ,^{118,127} FeF_3 ,¹²⁷ FeF_2 ,¹²⁷ and CoF_2 ¹²⁷ from appropriate metal-containing fragment ions. Reduction of the metal occurs in the formation of FeF_2 and CoF_2 from $M(\text{hfacac})_3$. Similar evidence for reduction of copper(II) was given by the observation of a metastable peak for elimination of neutral CuCH_3 in the mass spectrum of $\text{Cu}(\text{tfacac})_2$.¹¹⁸

VII. Suggestions for Future Research

In the summary to section IV the proposal was made that, for

β -diketonate complexes, ionization from metal orbitals to the ground state of the molecular ion by electron or photon impact was a process of significantly lower probability than ionization from ligand orbitals, and that IP's measured by electron impact corresponded to ionization energies from ligand π orbitals; i.e., vertical transitions from the ground state of the neutral complex led, in many cases, to electronically and/or vibrationally excited states of the molecular ion. Thus, true IP's would be lower than those recorded by the electron impact method. An alternative method of ionization might provide a way of substantiating this proposal. An approach which seems attractive is by a charge-transfer reaction, as represented by eq 24. Since the ion-mol-



ecule interaction is much slower than an electron-molecule or photon-molecule interaction, then adjustments of bond lengths in the metal-containing species during the interaction should give a higher probability of producing a molecular ion in its ground state. The species A should be chosen such that it has a lower IP than the instrumentally recorded IP of $M(\beta\text{-dik})_n$. Thus, if both $M(\beta\text{-dik})_n$ and A are present in the ion source, the electron energy can be set to values adequate to cause ionization of A but not of $M(\beta\text{-dik})_n$. If such charge-transfer reactions are, in fact, observed, then selection of a series of compounds A, covering a range of IP's, would place limits on the true IP of $M(\beta\text{-dik})_n$. Proton transfer reactions, frequently observed in chemical ionization, should be avoided. Suggestions for A are the aromatic hydrocarbons benzene, naphthalene, anthracene, and suitable derivatives. For success in this approach it will be necessary to work at ion source pressures high enough for ion-molecule reactions to occur, and using a many-fold excess of A. A drawback when using conventional electron impact sources at such pressures is potential high voltage breakdown, and it may prove necessary to use a modified ion source or a chemical ionization source.

The IP's of mixed β -diketonate complexes, $ML_nL'_{3-n}$ ($n = 0-3$) and $ML_nL'_{2-n}$ ($n = 0-2$) of Cr^{III} , Co^{III} , Rh^{III} , and Cu^{II} were shown to vary with n in a linear fashion.⁸⁸⁻⁹⁰ This type of experiment should be extended to other identities of M to establish the importance of the d electron configuration to this observation. In particular, it would be of interest to determine the IP's of mixed β -diketonate complexes, $ML_nL'_{3-n}$, of Al^{III} (no low-lying d orbitals) and Sc^{III} (vacant 3d orbitals) where, for example, $L = \text{acac}$ and $L' = \text{hfacac}$ (or any other combination of ligands with significantly different influences on the IP) to see whether a linear dependence of IP on n is still observed, or whether a discontinuity occurs when the ligand of higher energy π orbitals is no longer present. Lack of d electrons simplifies the energy level scheme, and consequently some structure might become apparent in the ionization efficiency curves of the mixed complexes.

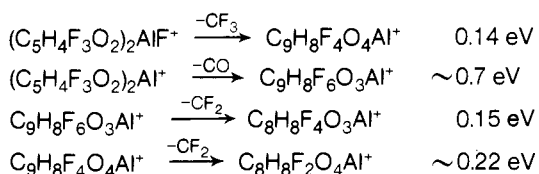
Further determinations of the electron impact IP's of β -diketonate complexes of several metals are desirable to improve knowledge of the extent to which metal and ligand influence the ionization potential. In particular, additional comparisons with the PES data in Table III could be made. Further experiments could be directed toward determination of the electronic influ-

ence of the metal ion via correlations of IP with σ_p^+ as in Figures 5 and 6, which could then, perhaps, be related to other parameters describing the properties of the metal ion.

In section IV.B, it was pointed out that variations in IP of acetylacetonates of trivalent transition metals could not be correlated with the theoretical molecular orbital description of the complexes. A weakness in the theoretical treatments was inadequate allowance for changes in bond length on electron removal from various orbitals. The differences between theory and experiment could, perhaps, be largely reconciled by theoretical estimates of changes of bond lengths, and of potential energy surfaces for the normal vibrational modes, between the parent molecule and molecular ion, to evaluate ionization probabilities and Franck-Condon parameters, for electron removal from orbitals of various types.

For none of the AP determinations reported in this review were measurements made of kinetic shifts or kinetic energy release on fragmentation. The contribution of an appreciable kinetic shift to an AP can be inferred if the AP of the metastable peak (if detectable) corresponding to the particular fragmentation is significantly lower than that of the daughter fragment ion (see section II.C). The β -diketonate complexes usually show many metastable peaks in their mass spectra. If necessary, relative intensities of metastable ions can be enhanced by the "defocusing" technique using a double-focusing mass spectrometer.

Kinetic energy release on the decomposition of a metastable ion can be measured by analysis of the metastable peak shape. A more precise method is to use the electrostatic sector of a double-focusing mass spectrometer (IKES technique) of the usual Nier-Johnson geometry, or with mass analysis using an instrument of reversed Nier-Johnson geometry (MIKES technique). The IKES technique has been used¹²⁸ to measure kinetic energy release only for some of the metastable decompositions observed in the mass spectrum of Al(tfacac)₃, as follows:



Of particular interest here is kinetic energy release for simple fragmentations of the molecular ion just above threshold, but such measurements are not, so far, available. It is doubtful that kinetic energy release would have a marked influence on variations in AE values of the magnitude observed. It has been stated¹²⁹ that it is seldom that fragment ions from polyatomic molecules are observed with appreciable amounts of kinetic energy, radiationless transitions, and predissociations being preferred processes.

Further determinations of AP's for simple fragmentations of the molecular ion are desirable to extend data for evaluation of relative stabilities of metal oxidation states and their relationship to the concept of valency change of the metal.

The use of an ion cyclotron (ICR) spectrometer has been suggested¹³⁰ as a suitable method for AP determinations. Because of the long time interval between ion formation and mass analysis, typically several milliseconds compared with several microseconds in a conventional electron impact mass spectrometer, kinetic shifts can be minimized, or, at least, assessed more accurately. ICR spectrometry is also a powerful tool for the study of ion-molecule reactions (including charge exchange reactions referred to above) and is also a complementary approach to energetic studies for deduction of ion structures. Until recently, the main drawback of the method was the limitation of the mass range to ≈ 200 , far below the masses of the ions of interest from the metal complexes discussed here. These

limitations should be overcome by the developments in Fourier transform ICR spectrometry.¹³¹

Although the remarks in this section have been made mainly with reference to β -diketonate complexes, it is hoped that the suggestions will prove useful in studies of other types of metal complex and stimulate further research in this still only slightly explored area of chemistry.

VIII. Addendum

Recently, in agreement with the observations recorded in section IV, linear correlations of ionization energies of copper¹³² and chromium¹³³ β -diketonates with Hammett substituent constants were made. These were based on some (but not all) of the earlier results, and no new experimental data were obtained.

IX. References

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