

# Lawrence Berkeley National Laboratory

## Recent Work

### Title

CORE BINDING ENERGIES OF SOME METAL B -DIKETONATES AND B-DIKETONES IN THE VAPOR PHASE

### Permalink

<https://escholarship.org/uc/item/4xq6w8w1>

### Author

Schaaf, Theodore F.

### Publication Date

1975-09-01

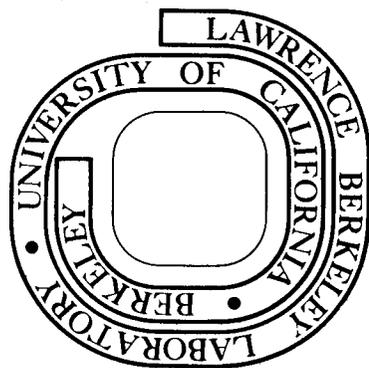
CORE BINDING ENERGIES OF SOME METAL  $\beta$ -DIKETONATES  
AND  $\beta$ -DIKETONES IN THE VAPOR PHASE

Theodore F. Schaaf, Steven C. Avanzino, and  
William L. Jolly

September 29, 1975

Prepared for the U. S. Energy Research and  
Development Administration under Contract W-7405-ENG-48

DOCUMENTS  
**For Reference**  
Not to be taken from this room



LBL-4176  
c.1

## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

CORE BINDING ENERGIES OF SOME METAL  $\beta$ -DIKETONATES  
AND  $\beta$ -DIKETONES IN THE VAPOR PHASE

THEODORE F. SCHAAF, STEVEN C. AVANZINO and WILLIAM L. JOLLY

Department of Chemistry, University of California, and Inorganic Materials  
Research Division, Lawrence Berkeley Laboratory, Berkeley, California  
94720 (U.S.A.)

ROBERT E. SIEVERS

Department of Chemistry, University of Colorado, Boulder, Colorado 80302  
(U.S.A.)

ABSTRACT

The vapor-phase core binding energies of some tris  $\beta$ -diketonates of Al(III), V(III), Cr(III), and Fe(III) and of two  $\beta$ -diketones have been measured. The rather large shifts observed for the Al 2p energies are believed to be caused mainly by changes in the electrostatic potential at the Al atom due to changes in the charges of the ligand atoms. Considerable resonance relaxation energy is associated with the core ionization of the carbonyl carbon atoms and the CH carbon atoms. The data for the metal hexafluoroacetylacetonates show that the metal d orbitals are not significantly involved in the bonding and suggest that there is no strong ligand-metal donor bonding.

2 2 6 0 0 7 6 0 0 0 0

## INTRODUCTION

X-ray photoelectron spectroscopy has been shown to be a useful technique for determining atomic charge distributions within molecules, particularly when applied to molecules in the gas phase<sup>1,2</sup>. We have used this technique to obtain the core electron binding energies of a series of volatile tris  $\beta$ -diketonate complexes in order to study the valence electron distribution and bonding in these compounds. The  $\beta$ -diketonate ligands studied were hexafluoroacetylacetonate (hfa), trifluoroacetylacetonate (tfa), acetylacetonate (acac), and 2,2,6,6-tetramethyl-3,5-heptanedionate (thd). The compounds and measured core binding energies are listed in Table 1. We shall separately discuss three aspects of the data: (1) the trend in the aluminum binding energies, (2) the ligand atom binding energies of the aluminum complexes, and (3) the ligand atom binding energies of all the hfa complexes.

## DISCUSSION

### The Aluminum Binding Energies

A chemical shift in core binding energy can be equated to the sum of three terms: (1) a term proportional to the change in the charge of the atom that undergoes core ionization, (2) the change in electrostatic potential at the site of the core ionizing atom due to the charges of the other atoms in the two molecules, and (3) the change in the relaxation energy associated with core ionization<sup>1,2</sup>.

Table 1. CORE BINDING ENERGIES OF METAL  $\beta$ -DIKETONATES AND  $\beta$ -DIKETONES

Compound	Binding Energy, eV						
	Metal 2p	O 1s	F 1s	C 1s			
				CF <sub>3</sub>	CO	CH	CH <sub>3</sub>
Al(thd) <sub>3</sub>	79.03	536.46			291.0		289.83 <sup>a</sup>
Al(acac) <sub>3</sub>	79.33	536.70			291.93	289.24	290.31
Al(tfa) <sub>3</sub>	80.36	537.75	693.72	298.05	293.00	290.30	291.09
Al(hfa) <sub>3</sub>	81.44	538.77	694.27	298.66	293.89	291.2	
V(hfa) <sub>3</sub>	522.34 <sup>b</sup>	538.64	694.29	298.64	293.74	290.93	
Cr(hfa) <sub>3</sub>	584.0 <sup>b</sup>	538.72	694.33	298.69	293.81	290.99	
Fe(hfa) <sub>3</sub>	---	538.75	694.37	298.94	294.14	291.33	
H(hfa)		{ 539.01 <sup>c</sup> 540.30	694.55	298.90	294.22	291.5	
H(acac)		{ 537.51 <sup>d</sup> 538.55			292.80		290.75 <sup>a</sup>

<sup>a</sup>Combination peak due to all non-carbonyl carbon atoms. <sup>b</sup>2p<sub>3/2</sub> level. <sup>c</sup>Assuming equal intensities for the two lines, the FWHM values were 1.4 and 1.2 eV for the lower and higher E<sub>B</sub> lines, resp.

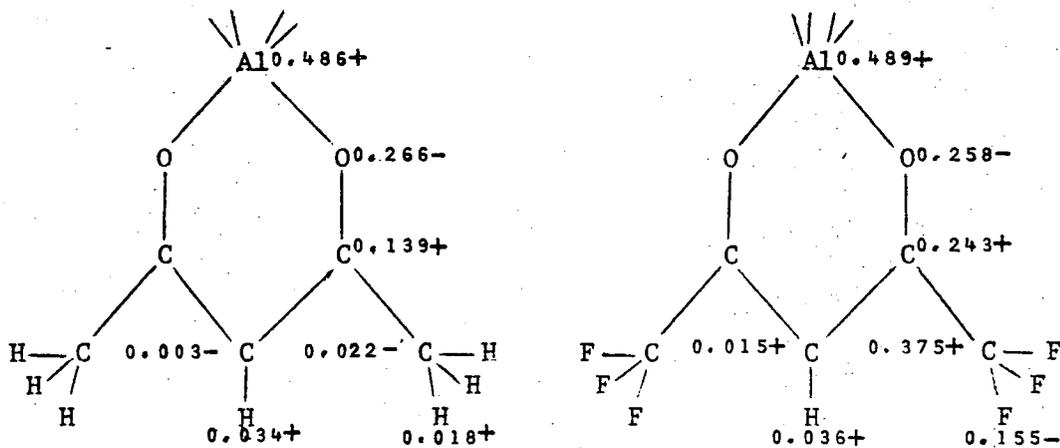
<sup>d</sup>The line of lower E<sub>B</sub> (FWHM = 1.3 eV) was about 0.7 as intense as the other (FWHM = 1.5 eV).

00004400934

$$\Delta E_B = k\Delta Q + \Delta V + \Delta E_R \quad (1)$$

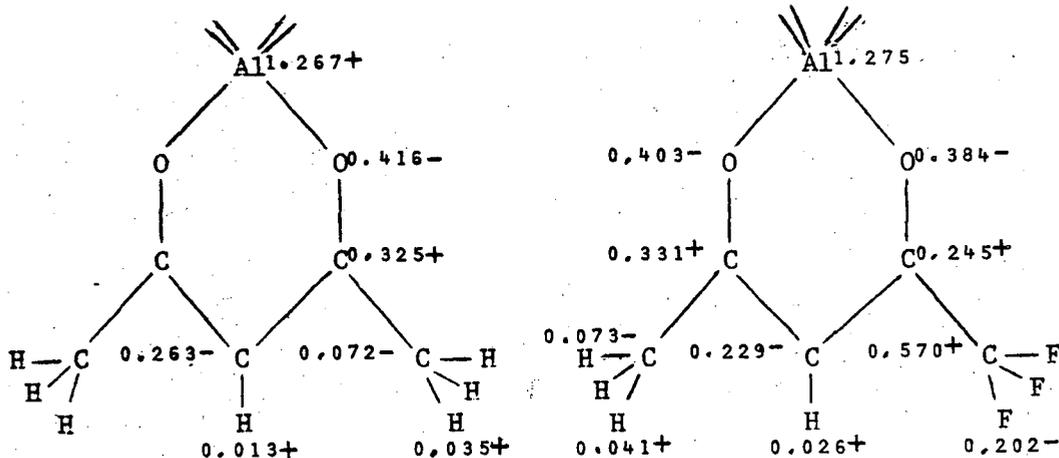
In the case of the tris  $\beta$ -diketonates of aluminum, the molecular structure in the vicinity of the aluminum atoms is unchanged, and we believe it is a good approximation to assume that changes in the relaxation energy are zero for the aluminum 2p binding energies. Thus in this case we may write  $\Delta E_B \approx k\Delta Q + \Delta V$ .

One method for estimating the atomic charges in such complexes is the CHELEQ electronegativity equalization method<sup>2</sup>. We have used this method to calculate the atomic charges in  $\text{Al}(\text{hfa})_3$  and  $\text{Al}(\text{acac})_3$  by making the assumptions that the aluminum atom uses only s and p valence orbitals, that the ligand atoms in the rings use  $sp^2$  hybrid orbitals in their sigma bonds, and that the bond order between the ligand atoms in the rings is 1.5. We found that we could obtain exact agreement between the calculated and observed shift (2.11 eV) by assuming that the  $\text{CH}_3$  carbon atoms in  $\text{Al}(\text{acac})_3$  use  $sp^3$  hybrid orbitals and that the  $\text{CF}_3$  carbon atoms in  $\text{Al}(\text{hfa})_3$  use orbitals with 10% s character in the C-F bonds and orbitals with 70% s character in the C-C bonds. The calculated CHELEQ charges are shown in the following structures.



The change in the CHELEQ aluminum atom charge is so small that a reasonable  $k$  value\* of 10.4 corresponds to a negligible value (0.03 eV) for  $k\Delta Q$ . (The value of 10.4 is estimated from the first ionization potential of aluminum and the second ionization potential of silicon, using the equivalent cores approximation.)

A second method which we have used for estimating atomic charges is the CNDO/2 method<sup>3</sup>. Our CNDO/2 computer program cannot be used to make calculations on molecules having more than 35 atoms or more than 80 valence atomic orbitals; therefore we approximated the desired calculations by calculating the atomic charges for the following bis(formato)-mono( $\beta$ -diketonato) complexes:  $(\text{HCO}_2)_2\text{Al}(\text{acac})$  and  $(\text{HCO}_2)_2\text{Al}(\text{tfa})$ . The calculated CNDO/2 atomic charges in the  $\beta$ -diketonate rings of these hypothetical complexes are shown in the following structures.



By assuming that the atomic charges in  $\text{Al}(\text{acac})_3$  and  $\text{Al}(\text{tfa})_3$  are the same as those indicated in the appropriate structures above (but using three times the indicated change in charge for the aluminum atom), and by estimating  $k = 10.4$  for aluminum, we calculate

5 2 6 0 0 7 0 0 0 0

$$\Delta E_B = k\Delta Q + \Delta V = 0.25 + 0.69 = 0.94 \text{ eV}$$

This calculated value is remarkably close to the observed shift, 1.08 eV. In this case the change in the aluminum atom charge is not negligible; nevertheless the  $\Delta V$  term is almost three times as large as the  $k\Delta Q$  term.

It is interesting that these two very different methods can give atomic charges consistent with the observed chemical shifts, even though the calculated charge distributions are very different. According to the CNDO/2 calculations, replacement of a  $\text{CH}_3$  group by a  $\text{CF}_3$  group causes the carbon atom to which the group is attached to become less positive and the other atoms of the ring to become more positive or less negative. Results of this type have been previously noted in CNDO calculations<sup>4</sup>, ab initio calculations<sup>5</sup>, and XPS-derived charges<sup>6</sup>. On the other hand, the CHELEQ atomic charges show the classical inductive effect upon replacement of a  $\text{CH}_3$  group by a  $\text{CF}_3$  group. Probably the only clear-cut lesson to be learned from the aluminum binding energy data is that, even if large chemical shifts in the binding energy of a metal are observed on going from one compound to another, the change in the metal atom charge may be very small.

It has been well documented that core electron binding energy shifts can be closely correlated with chemical reaction energies<sup>7,8</sup>. One might expect a good correlation between the aluminum binding energies in these chelates and the aqueous pK values of the corresponding  $\beta$ -diketones<sup>9-12</sup>.

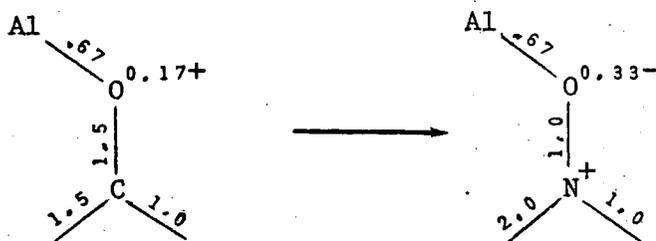
$\text{no } \text{H}$  A plot of these two quantities against one another is shown in Figure 1. The point for thd lies off the straight line because of what we believe is an abnormally high aqueous pK value for H(thd). This diketone has two bulky t-butyl groups which may hinder hydration of the

anion. Presumably a correlation of the binding energies with gas-phase pK values would not show this anomaly.

#### The Ligand Atoms of the Aluminum Complexes

Among the aluminum complexes, the binding energies of a ligand atom of a particular type qualitatively follow the same trend as the binding energies of the aluminum atom, i.e.,  $\text{Al(hfa)}_3 > \text{Al(tfa)}_3 > \text{Al(acac)}_3 > \text{Al(thd)}_3$ . This trend is that expected when one stepwise replaces the fluorine atoms of the  $\text{CF}_3$  groups with the more electropositive hydrogen atoms and then with the more polarizable  $\text{CH}_3$  groups. The decrease in binding energy is undoubtedly due to a reduction of both the absolute atomic charge and the electrostatic potential term and, in some cases, to increased relaxation (more negative  $E_R$ ).

We have used the CHELEQ method (assuming the bonding in the chelate rings to be as we have described above), and equation 1 (using  $k$  and  $l$  values empirically evaluated from data for compounds with unambiguous structures<sup>13</sup>) to calculate the absolute values of the ligand atom binding energies for the aluminum complexes. We obtained fairly good agreement for the fluorine atoms (deviation  $\sim 0.14$  eV), the oxygen atoms (deviations  $< 0.5$  eV), and the  $\text{CX}_3$  carbon atoms (deviations  $\leq 1.08$  eV), but the calculated values for the carbonyl and CH carbon atoms were much too high (by as much as 3.0 eV in the case of  $\text{Al(hfa)}_3$ ). We believe the latter discrepancies were due to unaccounted-for relaxation in the core-ionized molecules. In the case of the core ionization of the carbonyl carbon atom (in which the core is effectively converted to that of a nitrogen atom), the resonance structure weighting probably changes in the direction indicated:



This relaxation process corresponds to a shift of negative formal charge to the oxygen atom bonded to the core-ionized carbon atom. In the case of the CH carbon atom, the resonance structure weighting probably changes in the following direction:



The latter relaxation process corresponds to putting lone pair electron density on the core-ionized atom.

#### The Ligand Atoms of the hfa Complexes

The binding energies of the carbon, oxygen, and fluorine atoms in the several hfa complexes change very little on going from one metal complex to another. Thus there is no evidence for participation of metal d orbitals in the bonding of the transition metal complexes. The same conclusion has been reached by other investigators with respect to acetylacetonate complexes on the basis of structural<sup>15</sup>, magnetic<sup>15,16</sup>, and spectroscopic<sup>15,17</sup> data. The carbon 1s binding energies of the hfa complexes are not much shifted from those of H(hfa), which exists entirely in the enol form<sup>14</sup>. However the fact that the H(hfa) oxygen

1s binding energies are greater than that of the metal hfa complexes suggests that there is no strong ligand-metal donor bonding in the hfa complexes.

#### EXPERIMENTAL

Spectra were obtained using the Berkeley iron-free double-focusing magnetic spectrometer<sup>18</sup>. The  $\beta$ -diketones and the metal hexafluoroacetylacetonates were placed in a glass vessel connected to the irradiation chamber by a short length of stainless steel tubing. The other metal complexes were placed in a copper chamber which was heated just enough to provide sufficient vapor pressure (ca  $2 \times 10^{-2}$  torr) to obtain a good spectrum. Magnesium  $K_{\alpha}$  X-rays (1253.6 eV) were used. Either neon or argon was introduced with the samples, and the Ne 1s line ( $E_B = 870.23$  eV) and the Ar  $2p_{3/2}$  line ( $E_B = 248.45$  eV) were used as references. Binding energies were determined by a least-squares fitting of the data to Lorentzian line shapes. The relative accuracies of the peak positions are generally about  $\pm 0.05$  eV, however the data in Table 1 given to only one decimal place are believed to be accurate to  $\pm 0.1$  eV. The reported binding energies are absolute free-molecule ionization potentials, with absolute uncertainties of  $\pm 0.1$  eV, or, in a few cases,  $\pm 0.2$  eV.

V(hfa)<sub>3</sub> was prepared by a method analogous to that for Al(hfa)<sub>3</sub>, described by Morris, et al.<sup>19</sup>. Al(hfa)<sub>3</sub> was prepared by the reaction of anhydrous aluminum chloride with H(hfa) in CCl<sub>4</sub> and was recrystallized from the same solvent. Fe(hfa)<sub>3</sub> was prepared by reaction of aqueous iron(II) chloride with a hexane solution of H(hfa). The products were purified by

sublimation.  $\text{Cr}(\text{hfa})_3$  was synthesized by the method of Sievers, et al.<sup>20</sup> by heating chromium(III) nitrate nonahydrate and  $\text{H}(\text{hfa})$  in ethanol. The product was recrystallized from  $\text{CCl}_4$ .  $\text{Al}(\text{acac})_3$  was prepared as described by Young<sup>21</sup> and the product was recrystallized from benzene by the addition of hexane.  $\text{Al}(\text{tfa})_3$  and  $\text{Al}(\text{thd})_3$  were synthesized by analogous methods except that they were purified by fractional sublimation in vacuo. The  $\text{H}(\text{hfa})$  and  $\text{H}(\text{acac})$  were purified by fractional distillation immediately before obtaining their spectra.

The CNDO/2 calculations were made using the parameters for hydrogen and the first-row elements given by Pople and Beveridge<sup>3</sup>. For aluminum we used Santry and Segal's<sup>22</sup> method of parameterization, Hinze and Jaffé's<sup>23</sup> orbital ionization energies and electron affinities, and Cusachs and Corrington's<sup>24</sup> valence s orbital wavefunctions. Structural data required in the CNDO/2 and CHELEQ calculations were estimated from the parameters given for  $\text{Al}(\text{acac})_3$ <sup>15</sup>.

#### ACKNOWLEDGEMENTS

We are grateful to Mr. Albert Bakke for assistance in obtaining the spectrum of  $\text{H}(\text{hfa})$ . This work was supported by the National Science Foundation (Grant GP-41661X) and the U. S. Energy Research and Development Administration.

REFERENCES

1. K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Hedén, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, "ESCA Applied to Free Molecules," North-Holland Publ. Co., Amsterdam, 1969; U. Gelius, Physica Scr., 9, 133 (1974).
2. W. L. Jolly and W. B. Perry, J. Amer. Chem. Soc., 95, 5442 (1973); Inorg. Chem., 13, 2686 (1974).
3. J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N.Y., 1970.
4. J. A. Pople and M. Gordon, J. Amer. Chem. Soc., 89, 4253 (1967); R. T. C. Brownlee and R. W. Taft, J. Amer. Chem. Soc., 92, 7007 (1970).
5. W. J. Hehre and J. A. Pople, J. Amer. Chem. Soc., 92, 2191 (1970).
6. D. W. Davis, D. A. Shirley, and T. D. Thomas, J. Amer. Chem. Soc., 94, 6565 (1972); D. W. Davis, M. S. Banna, and D. A. Shirley, J. Chem. Phys., 60, 237 (1974); S. A. Holmes and T. D. Thomas, J. Amer. Chem. Soc., 97, 2337 (1975).
7. W. L. Jolly and D. N. Hendrickson, J. Amer. Chem. Soc., 92, 1863 (1970); W. L. Jolly in "Electron Spectroscopy," D. A. Shirley, Ed., North-Holland Publ. Co., Amsterdam, and American Elsevier, New York, N.Y., 1972, p. 629.

REFERENCES, contd.  
~~~~~

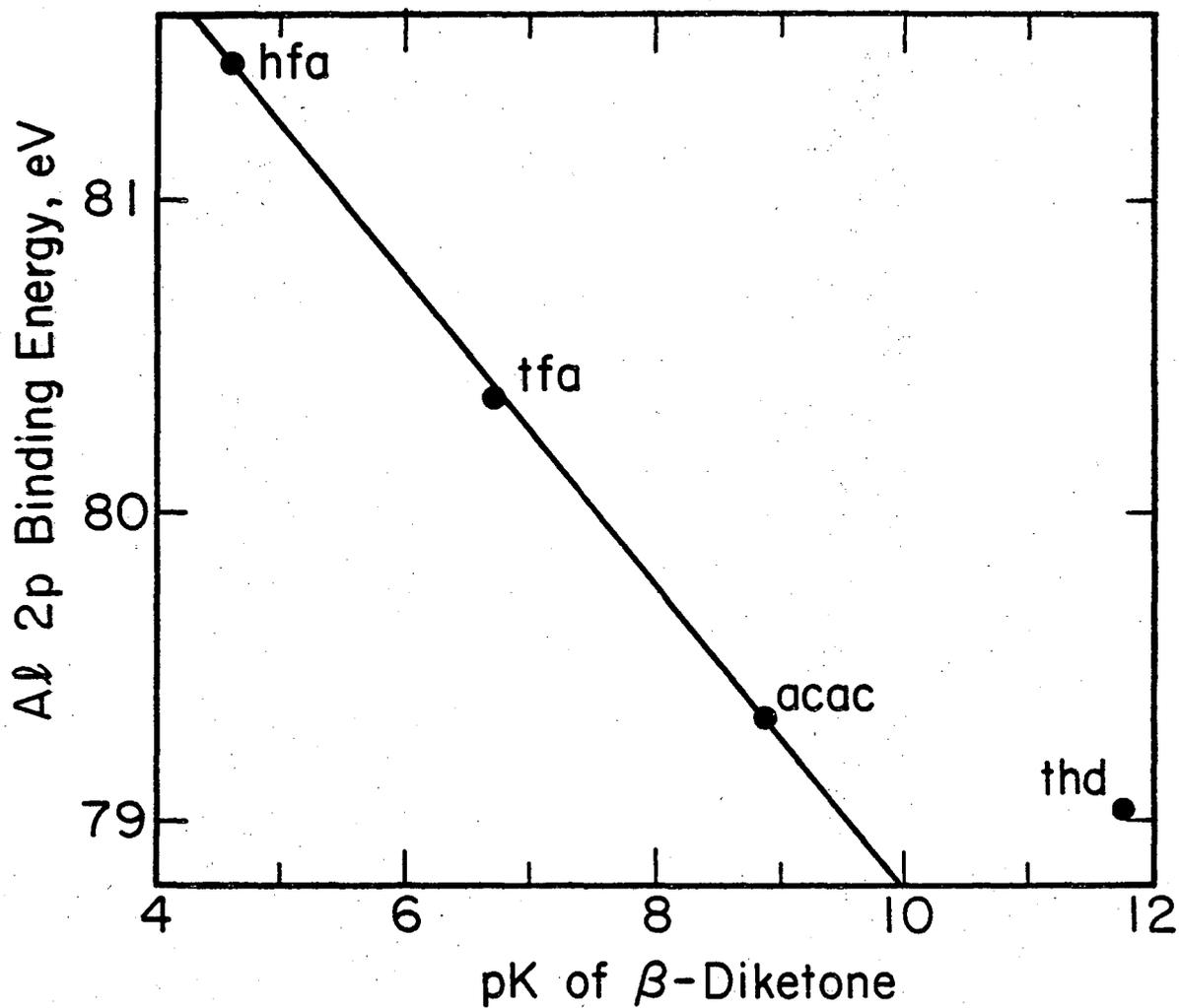
8. R. L. Martin and D. A. Shirley, J. Amer. Chem. Soc., 96, 5299 (1974);  
D. W. Davis and J. W. Rabalais, J. Amer. Chem. Soc., 96, 5305 (1974);  
T. X. Carroll, S. R. Smith, and T. D. Thomas, J. Amer. Chem. Soc.,  
97, 659 (1975).
9. R. L. Belford, A. E. Martell, and M. Calvin, J. Inorg. Nucl. Chem.,  
2, 11 (1956).
10. M. Calvin and K. W. Wilson, J. Amer. Chem. Soc., 67, 2003 (1945).
11. G. Schwarzenbach, H. Suter, and K. Lutz, Helv. Chim. Acta, 23, 1191 (1940).
12. G. A. Guter and G. S. Hammond, J. Amer. Chem. Soc., 78, 5166 (1956).
13. W. L. Jolly, T. F. Schaaf, and W. B. Perry, unpublished calculations.
14. A. L. Andreassen, D. Zebelman, and S. H. Bauer, J. Amer. Chem. Soc.,  
93, 1148 (1971).
15. E. A. Shugam and L. M. Shkol'nikova, Dokl. Akad. Nauk SSSR, 133, 386  
(1960).
16. J. P. Fackler, Prog. Inorg. Chem., 7, 361 (1966).
17. R. H. Holm and F. A. Cotton, J. Amer. Chem. Soc., 80, 5658 (1958).
18. J. M. Hollander, M. D. Holtz, T. Novakov, and R. L. Graham, Ark. Fys.,  
28, 375 (1965).

REFERENCES, contd.

19. M. L. Morris, R. W. Moshier, and R. E. Sievers, Inorg. Syn., 9, 28 (1967).
20. R. E. Sievers, R. W. Moshier, and M. L. Morris, Inorg. Chem., 1, 966 (1962).
21. R. C. Young, Inorg. Syn., 2, 25 (1946).
22. D. P. Santry and G. A. Segal, J. Chem. Phys., 47, 158 (1967)
23. J. Hinze and H. H. Jaffé, J. Amer. Chem. Soc., 84, 540 (1962); J. Phys. Chem., 67, 1501 (1963).
24. L. C. Cusachs and J. H. Corrington in "Sigma Molecular Orbital Theory," O. Sinanoglu and K. Wiberg, Eds., Yale Univ. Press, New Haven, Conn., 1969, p. 256.

FIGURE CAPTION

Fig. 1 - A plot of Al 2p binding energies of tris  $\beta$ -diketonates vs aqueous pK values of the corresponding  $\beta$ -diketones. Data from Table 1 and Refs. 9-12.



XBL 759-7167  
Fig. 1

0 0 0 0 4 4 0 0 9 4 0

LEGAL NOTICE

*This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.*

TECHNICAL INFORMATION DIVISION  
LAWRENCE BERKELEY LABORATORY  
UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA 94720