Bipyridine Complexes

Sir:

We have been determining[1] and collecting stability constants of metal complexes with pyridine and its derivatives for many years. The paper of Atkinson and Bauman[2] on the thermodynamics of transition metal complexes with 2,2′-bipyridine therefore received our special attention. We note that even the second decimal for the logarithm of each stability constant is given in this paper. However, there is little agreement between these constants and the values found by other authors[3] or obtained in our own laboratory.[4] The discrepancies are in some cases higher than one log K unit, which make it obvious that they could not be due to differences in ionic strength. An inspection of the dissertation[5] from which the data of ref. 2 have been extracted made it clear that the authors have underestimated the large errors which arise if a pH method is used in strongly acid solutions. The classical Bjerrum method for determining stability constants is unsuitable for very weakly basic ligands which form metal complexes of considerable stability, such as bipyridine. The findings of Bauman and Atkinson that the degree of complex formation with Mn^{2+} and Zn^{2+} rises up to $\bar{n} = 5.87$ and 6.09, respectively, should have made the authors suspicious of the usefulness of their experimental method. A collection of the more trustworthy stability constants of the bipyridine–transition metal complexes has recently been given by Irving and Mellor.[6]

(1) G. Anderegg, *Helv. Chim. Acta*, **43**, 414, 1530 (1960); **45**, 1643 (1962).

(2) G. Atkinson and J. E. Bauman, Jr., *Inorg. Chem.*, **1**, 900 (1962).

(3) H. Irving, private communication. Cited in ref. 2 and Proc. of 1959 Intern. Conf. on Coordination Compounds, London.

(4) Unpublished results. For instance: Mn^{2+}, log K_1 = 2.5; Cu^{2+}, log K_1 = 8.0 at 20° and μ = 0.1.

(5) J. E. Bauman, Thesis, University of Michigan, 1962.

(6) H. Irving and D. H. Mellor, *J. Chem. Soc.*, 5222 (1962).

LABORATORIUM FÜR ANORGANISCHE CHEMIE — G. ANDEREGG
EIDG. TECHNISCHEN HOCHSCHULE
ZÜRICH, SWITZERLAND

RECEIVED MARCH 27, 1963

Bipyridine Complexes

Sir:

Our recent papers[1,2] presented a consistent set of ΔF and ΔH values for pyridine and bipyridine complexes of Mn^{+2}, Ni^{+2}, Cu^{+2}, and Zn^{+2}. We did not feel then nor do we feel now that this work represents the final word on the thermodynamics of these systems. Nor do we feel that the classical Bjerrum method is totally free of error in log K_i determinations in these systems. We do feel that the thermodynamic data show an internal consistency that is encouraging and that no other method yet proposed is superior to the Bjerrum technique for these systems.

The letter of Anderegg[3] refers to unpublished data from his laboratory. Since we have not been so priviliged as to see this data nor been informed as to how it was obtained, we must reserve comment on it.

The Irving–Mellor data referred to by Anderegg have been examined[4] and there are some doubts about the validity of the distribution method used by the authors and apparently proposed as a standard by which all other methods and data are to be judged. The method used involved the extraction of free ligand from an aqueous solution containing ligand and metal, buffered with sodium acetate and HCl and containing KCl to bring it to what is supposed to be an ionic strength of 0.1. First of all, the authors make no mention of the fact that acetate complexes and chloride complexes of divalent transition metals are well known and, in quite a few cases, their stability constants have been measured.[5] They also ignore the strong possibility of mixed ligand complexes as well as passing over the real problem of knowing or calculating the ionic strength in such a mixture. Examination of the log k_n/k_{n+1} values obtained shows curious inconsistencies not related to obvious problems such as Fe^{+2} spin-pairing and Cu^{+2} coordination changes.

To propose this technique as an interesting and useful approach is certainly valid. To propose it as a standard by which to judge all others is not justified by their work as presented. Their "recommended values" seem to be only their own data rounded off to two significant figures.

(1) G. Atkinson and J. Bauman, *Inorg. Chem.*, **1**, 900 (1962).

(2) G. Atkinson and J. Bauman, *ibid.*, **2**, 64 (1963).

(3) G. Anderegg, *ibid.*, **2**, 1082 (1963).

(4) H. Irving and D. H. Mellor, *J. Chem. Soc.*, 5222 (1962).

(5) "Stability Constants," The Chemical Society, London, 1957.

DEPARTMENT OF CHEMISTRY — G. ATKINSON
UNIVERSITY OF MARYLAND
COLLEGE PARK, MARYLAND
DEPARTMENT OF CHEMISTRY — J. BAUMAN
UNIVERSITY OF MISSOURI
COLUMBIA, MISSOURI

RECEIVED APRIL 25, 1963

The Electronic Spectra of α-Silyl Ketones

Sir:

In 1957 Brook synthesized the first α-silyl ketone, triphenylsilyl phenyl ketone, and established that this compound was yellow in color.[1] This striking observation was followed by an investigation of the electronic spectra of a number of silyl ketones, which showed that in every case the long wave length carbonyl transition was shifted to the visible region.[2] Brook attributed the large spectral shift to interaction between lone-pair electrons on the carbonyl *oxygen* and 3d orbitals of the

(1) A. G. Brook, *J. Am. Chem. Soc.*, **79**, 4373 (1957).

(2) A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz, and C. M. Warner, *ibid.*, **82**, 5102 (1960).

silicon atom.[2] We now wish to submit an alternative explanation for the observed shift, based on qualitative molecular orbital theory, which does not involve such "β π-bonding."

The electronic configuration of the carbonyl group may be simply designated as $s_0{}^2\pi^2p_0{}^2$, where s_0 and p_0 are atomic orbitals localized on the oxygen atom and π is the bonding π-orbital between the carbon and oxygen atoms. The long wave length (n → π^*) electronic transition in question is considered to result from the transition $s_0{}^2\pi^2p_0{}^2 \rightarrow s_0{}^2\pi^2p_0\pi^*$, where π^* is the antibonding π-level.

Table I lists the absorption maxima of the n → π^* transition for several ketonic compounds with the general formula R(C=O)A. The substituents A may be divided into two classes, A1 and A2. Class 1 substituents possess relatively high electronegativities and unshared pairs of electrons and cause shifts to shorter wave length (–Cl, –OH, –NH_2); class 2 substituents have low electronegativities and vacant π-type orbitals, and cause shifts to longer wave length (($(CH_3)_3Si$–, $(C_6H_5)_3Si$–, $(C_6H_5)_3Ge$–). It is somewhat surprising that the shifts caused by class 2 substituents are about as large as those brought about by the strongly-interacting type 1 sustituents.

TABLE I

LONG WAVE LENGTH ABSORPTION MAXIMA FOR SOME CARBONYL COMPOUNDS

Compound	ν_{max}, cm.$^{-1}$	Ref.
CH_3COOH	49,000	3
CH_3CONH_2	46,700	3
CH_3COCl	42,600	3
CH_3COCH_3	35,800	2
$CH_3C_6H_5$	30,800	2
t-$C_4H_9COC_6H_5$	31,000	4
$C_6H_5COC(C_6H_5)_3$	30,400	3
$CH_3COSi(C_6H_5)_3$	26,900	2
$C_6H_5COSi(CH_3)_3$	24,200	2
$C_6H_5COSi(C_6H_5)_3$	24,000	2
$C_6H_5COGe(C_6H_5)_3$	24,100	2

The influence of substituents of class 1 has been well explained previously.[3] Figure 1 is a simplified, generalized energy level diagram showing the effect of resonant interaction of a class 1 substituent (A1) on the carbonyl transitions. Interaction takes place with both levels π and π^*, but most strongly with the bonding level π, because it is closest in energy to π_{A1}. The lowest resultant level π_1 is largely localized on A1, so the effect can be viewed as a shifting upward of π and π^*. Because p_0 is left essentially unaffected, the net result is to increase the energy of the $p_0 \rightarrow \pi^*$ transition.

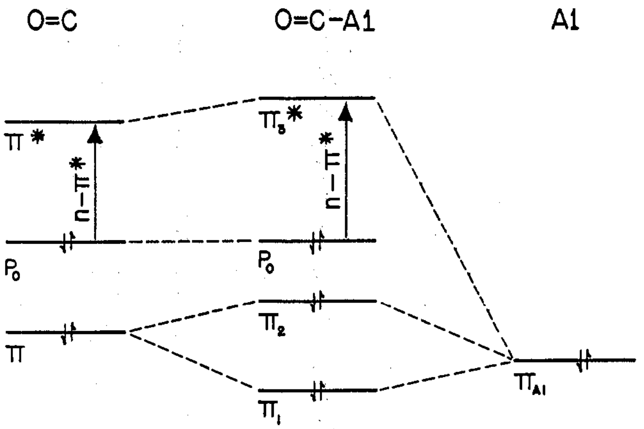

Fig. 1.—Perturbation of energy levels of a carbonyl chromophore by a class 1 substituent, A1.

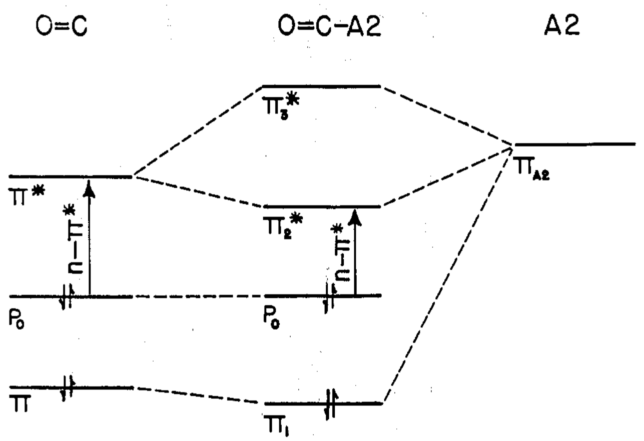

Fig. 2.—Perturbation of energy levels of a carbonyl chromophore by a class 2 substituent, A2.

Substituents of class 2 should interact by resonance with the carbonyl levels as shown in the generalized diagram of Fig. 2. The π_{A2} level of the substituent will again interact with both the bonding and antibonding π-levels, but this time most strongly with π^*. Here, however, $\pi_3{}^*$ is the orbital localized on the substituent, and the effective result is to shift both π^* and π downward in energy. The p_0 level is again largely unaffected and the n → π^* transition should fall at lower energy, as observed.[2] Because it is closest in energy to π_{A2}, the π^* level is the one most strongly affected by class 2 substituents. Therefore, *for a given amount of π-overlap, class 2 substituents will influence the transition energy more than class 1 substituents.* Thus the large spectral shift in the silyl ketones can be accounted for, even though the π–3d overlap is probably not large.

In the simple argument given above, the purely inductive effect of the substituents has been ignored. The effect of this will be to lower the energies of all of the carbonyl levels for class 1 substituents and to raise them all for class 2 substituents. Unfortunately, it is difficult to predict which of the two carbonyl levels, π^* or p_0, will undergo the greatest change. The coulombic interaction of the substituent certainly influences the energy of the n → π^* transition, but there is reason to believe that these inductive effects are less important than resonance effects.[3,5] Other factors will also influence the energies of carbonyl electronic transitions, including steric effects and, for silyl compounds, perhaps

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(3) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp. 175–182. Our explanation of the effects of class 1 substituents follows that of Jaffé and Orchin.

(4) P. Ramant-Lucas, *Bull. Soc. Chim. France*, 259 (1950).

(5) F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5243 (1950).

even the β-O–Si interaction proposed by Brook and co-workers.[2] The latter effect, however, is probably small compared to the C–Si π-bonding considered above. For reasonable values of bond distances and angles in silyl carbonyl compounds, overlap of 3d silicon orbitals is expected to be larger with the carbon π-orbital than with the oxygen lone pairs.[6]

Extension of the approach given above to other chromophoric groups can easily be carried out. For example, class 2 substituents on C=C chromophores should produce a spectral shift of the same type as found for class 1 substituents, decreasing the energy of the π–π^* transitions. A further prediction from our theory is that compounds with a boron atom attached directly to a carbonyl group (such as $R_2BCOC_6H_5$), when they are synthesized, will show transitions above 400 mμ and so will appear visibly colored.[8,9]

Acknowledgments.—The authors thank the Air Force Office of Scientific Research for financial support and the Stauffer Chemical Company for a fellowship (to D. F. H.)

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[6] Such β-interactions may, of course, be important in lowering the energies of transition states, *i.e.*, for rearrangement reactions.[2,7]

[7] A. G. Brook, *J. Org. Chem.*, **25**, 1072 (1960); *J. Am. Chem. Soc.*, **80**, 1886 (1958); A. G. Brook, C. M. Warner, and M. McGriskin, *ibid.*, **81**, 981 (1959); A. G. Brook and W. W. Limburg, *ibid.*, **85**, 832 (1963).

[8] Observations on α-boryl ketones should provide a good test of theory, for β π-bonding of the type suggested by Brook[2] should be negligible to the p-orbital on boron.

[9] Note Added in Proof.—A similar, though less detailed, explanation for the spectral properties of α-silyl ketones has recently been advanced independently by L. E. Orgel, quoted in "Volatile Silicon Compounds," E. B. Ebsworth, Pergamon Press, Ltd., Oxford, 1963, p. 81.

Department of Chemistry
University of Wisconsin
Madison, Wisconsin, 53706

Daniel F. Harnish
Robert West

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Book Reviews

Absorption Spectra and Chemical Bonding. By C. K. Jørgensen. Addison-Wesley Publishing Co., Inc., Reading, Mass., 1962. 347 pp. 14 × 22 cm. Price, $10.00.

Probably the largest amount and certainly the dullest[1] prose being written today is the scientific, so-called "literature." As a notable exception, one might cite the works of Christian Klixbüll Jørgensen. Former astronomer and sometime symbolic logician, he writes in a style unmistakably his own and often refreshing in its dissimilarity to the usual run of insipid syntax. Of course, roses (excepting Zephirine Drouhin and a few others) come equipped with thorns; that is, one seldom finds unadulterated virtue, with no catches, in this world. Some of Jørgensen's prose seems inspired by the stream of consciousness school. Both in his style of writing and in his scientific thinking he is *durchaus eigentümlich,* with all the good *and* bad consequences this may have. In the volume under review, his *Eigentümlichkeit* is much in evidence.

I cannot but applaud Jørgensen's stated purpose of trying "to win over some of the mental inertia which has caused most chemists to think of chemical bonds in terms of a valency-bond and hybridization description." I am afraid, though, that the preaching which follows will be mainly to the already converted, because of the pell-mell attack on the subject matter. The presentation has indeed some logic of its own, but not, I fear, the sort which is appropriate for instructing the uninitiated.

Having offered these animadversions, I hasten to say also that this book has its attractions for the serious (but not entirely naïve) student of coordination chemistry. It contains a great deal of interesting factual information and many stimulating and unusual observations. It is also noteworthy for its eclectic approach; probably no element in the periodic table goes unmentioned, and all aspects of the subject, as summarized in the title, are discussed to some extent.

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[1] Not, however, the most abominable, for which due acknowledgment may be given to the social "sciences" and "communications sciences."

Massachusetts Institute of Technology
Cambridge 39, Massachusetts

F. A. Cotton

Progress in Inorganic Chemistry. Volume 4. Edited by F. A. Cotton. Interscience Publishers, Division of John Wiley and Sons, Inc., New York, N. Y., 1962. 540 pp. 15 × 23 cm. Price, $15.00.

The fourth volume of the series "Progress in Inorganic Chemistry" contains these seven articles: (1) The Polymorphic Modifications of Arsenic Trioxide, by K. A. Becker, K. Plieth, and I. N. Stanski; (2) The Nephelauxetic Series, by C. K. Jørgensen; (3) Peroxides, Superoxides, and Ozonides of the Metals of Groups Ia, IIa, and IIb, by N. Vannerberg; (4) Isopolytungstates, by D. L. Kepert; (5) Phosphonitrile Polymers, by C. D. Schmulbach; (6) The *trans* Effect in Metal Complexes, by F. Basolo and R. G. Pearson; and (7) The Coupling of Vibrational and Electronic Motions in Degenerate Electronic States of Inorganic Complexes. Part II. States of Triple Degeneracy and Systems of Lower Symmetry, by A. D. Liehr.

This reviewer cannot imagine the inorganic chemist capable of digesting the entire seven-course meal. Articles 1, 3, 4, and 5 are mainly descriptive. They are well written and usefully referenced.

Articles 2, 6, and 7 are more theoretical in the order Basolo and Pearson (mildly theoretical), Jørgensen (highly theoretical), and Liehr (whew!). The account of the *trans* effect is very readable and complete in every detail. The article on the nephelauxetic series is well worth reading, although it will be rough going for most inorganic chemists. It is by far the most complete treatment of the subject yet presented. I think it is fair to say that the article overemphasizes many of the author's own prejudices concerning the electronic structures of transition metal complexes. This is not unexpected since he and C. Schäffer gave us the nephelauxetic fever in the first place.

The Liehr article is wasted in this series, being too theoretical for inorganic chemists. It should have been published in one of the volumes read mainly by chemical physicists.

Finally, I should mention that a very useful cumulative index (covering volumes 1–4) appears on p. 577.

In summary, "Progress in Inorganic Chemistry" continues to provide excellent critical reviews of interest to inorganic