Ligand Field Activation Energy for Ligand Substitution in Octahedral Complexes

Hideo YAMATERA

Department of Chemistry, Nagoya University, Chikusa-ku, Nagoya

(Received August 23, 1968)

Crystal field theory has been successful in interpreting the relative rate of ligand substitution of transition-metal octahedral complexes, especially the relative inertness of the d^3, d^8 and low-spin d^6 complexes.1) However, there has been disagreement between the crystal field prediction and observation in a few cases.

(1) In the series Mn^{2+}, Fe^{2+} and Co^{2+}, the observed rate of water exchange was $Mn^{2+} > Fe^{2+} > Co^{2+}$ (the activation energy remains nearly unchanged).2) However, the crystal field activation energy (CFAE) was predicted to become more negative in going along the above series.

(2) Low-spin d^5 complexes, *e.g.*, $[Fe(CN)_6]^{3-}$, are known to be the most inert next to d^6 complexes, and are much more inert than predicted.3)

In the present communication, the ligand field activation energy (LFAE) is predicted on the basis of molecular orbital theory. The calculation is based on second-order perturbation theory, like that previously reported in connection with the interpretation of the splitting of absorption bands of cobalt(III) complexes.4) This approach is essentially equivalent to "the angular overlap model" proposed by Schäffer and Jørgensen.5) Using the latter model, Yatsimirski *et al.*6) calculated σ- and π-antibonding effects. The present calculation also led to similar results, which were then used to obtain LFAE.

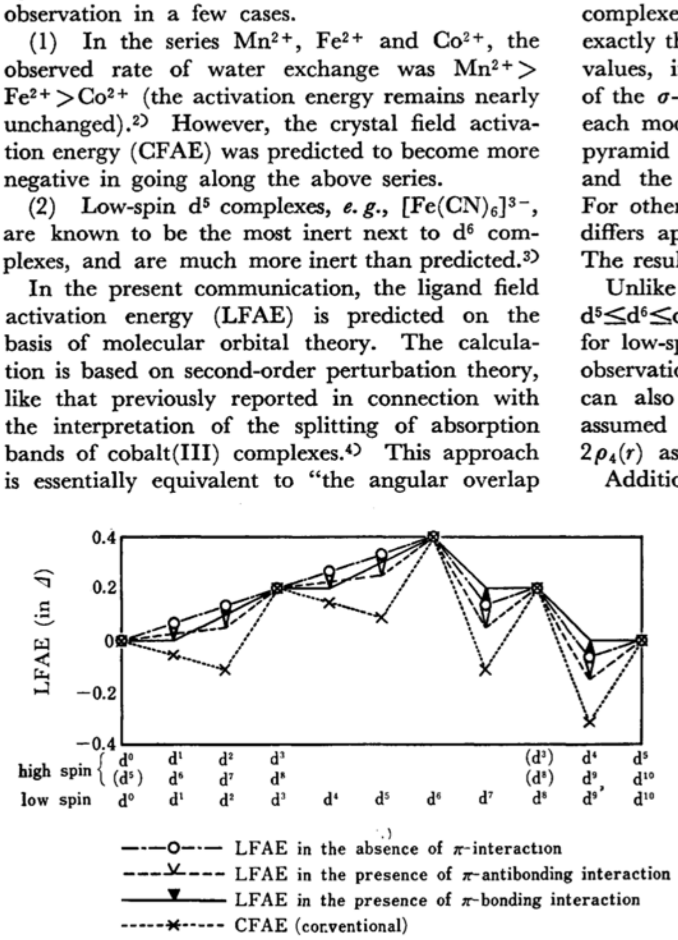

Fig. 1. LFAE and CFAE for the tetragonal pyramid (C_{4v}) model.

For high-spin d^3, d^5 and d^8 and low-spin d^6 complexes, the present calculation of LFAE gives exactly the same values as the conventional CFAE values, irrespective of the relative contributions of the σ- and π-interactions. This is the case for each model of the transition state: the tetragonal pyramid (C_{4v}), the trigonal bipyramid (D_{3h}) and the pentagonal bipyramid (D_{5h}) models. For other complexes, however, the present LFAE differs appreciably from the conventional CFAE. The results for the C_{4v} model are given in Fig. 1.

Unlike CFAE, LFAE increases in the order $d^5 \leq d^6 \leq d^7 < d^8$ for high-spin and $d^3 \leq d^4 < d^5 < d^6$ for low-spin complexes. This explains the above observations (1) and (2) (crystal field calculations can also explain these observations, if $\rho_2(r)$ is assumed approximately equal to $\rho_4(r)$ instead of $2\rho_4(r)$ as in the conventional calculation).7)

Additional spin-pairing may occur, in some transition states. Quantitative calculations showed that this is possibly the case for pentagonal bipyramidal transition states of some low-spin d^4 complexes. This gives a molecular orbital version of Adamson's mechanism8) that $[Mn(CN)_6]^{3-}$—CN^- exchange should proceed through hepta-coordinated, spin-paired $[Mn(CN)_6H_2O]^{3-}$.

Full theoretical results, including those for other models, and detailed discussions on particular cases will be given elsewhere.

---

1) *E. g.*, F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York (1967), p. 145.

2) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

3) A. C. MacDiarmid and N. F. Hall, *J. Am. Chem. Soc.*, **76**, 4222 (1954).

4) H. Yamatera, This Bulletin, **31**, 95 (1958).

5) C. E. Schäffer and C. K. Jørgensen, *Mol. Phys.*, **9**, 401 (1965).

6) K. B. Yatsimirski, T. V. Mal'kova and L. I. Budarin, "Proceedings 10 th I.C.C.C.," Chem. Soc. Japan, Tokyo (1967), p. 290.

7) S. T. Spees, Jr., J. R. Perumareddi and A. W. Adamson, *J. Phys. Chem.*, **72**, 1822 (1968).

8) A. W. Adamson, J. P. Welker and W. B. Wright, *J. Am. Chem. Soc.*, **73**, 4786 (1951).