Figure 1.—Electronic absorption spectra (in isooctane solution) and experimental term level diagrams of complexes I and II.

no doubt that structure II overemphasizes the effects of the nonplanarity of the dienone ring and strongly suggests that both complexes must have analogous electronic structures. The electronic spectrum of I has already been interpreted in terms of simple MO theory.[3] Three characteristic absorptions of the metal–cyclopentadienone system are to be expected, namely the $n_{=\ddot{o}}:-\pi^*$, the $3d-\pi^*$, and the first $\pi-\pi^*$ transition. The experimental term level schemes are also shown in Figure 1. The only difference in the spectrum of II arises from the appearance of a band at 242 mμ (log ϵ 4.14) which because of its solvatochromic behavior is assigned to a second metal–cyclopentadienone $(3d-\pi^*)$ transition.[4] It must also be pointed out that the π-bonded duroquinone is nonplanar as well, with the two carbonyl groups pointing away from the metal.[5] This ring distortion has been explained without invoking the formation of metal–carbon σ-bonds as the result of repulsive conditions in certain metal–quinone orbital interactions.[6] The distortion of the cyclopentadienone ring may be at least in part caused by a similar effect. Since CF_3 substitution will increase the effective Coulomb terms of the ring carbon atoms, this will lead primarily to stronger backbonding interactions. In the lowest unoccupied MO of cyclopentadienone a node passes between the atoms of the carbonyl group, leading to a repulsive condition just as in the case of duroquinone. Inspection of the charge density map calculated for cyclopentadienone by simple MO theory furthermore shows that the sites of greatest π-electron density on the ring are at the two carbon atoms next to the carbonyl group. This may indeed lead to a small degree of localization in the metal–

(3) G. N. Schrauzer and G. Kratel, *J. Organometal. Chem.*, **2**, 336 (1964).

(4) In 70% $HClO_4$ this band is shifted to 237 mμ, with a loss in intensity to log ϵ 3.63. Similarly, the first metal–ligand charge-transfer band in II at 358 mμ (log ϵ 3.54) in $HClO_4$ is shifted to 344 mμ (log ϵ 3.33).

(5) In cyclooctadiene(1,5)duroquinonenickel the distortion of the duroquinone carbonyl groups amounts to 8° (L. F. Dahl, private communication). For spectroscopic evidence for the nonplanarity of π-bonded duroquinone see ref. 6.

(6) G. N. Schrauzer and K. C. Dewhirst, *J. Am. Chem. Soc.*, **86**, 3265 (1964).

dienone interactions and to a partial rehybridization of the relevant carbon atoms. The combined effects of ring deformation and bond localization do not cause a sufficient loss of conjugation in the dienone ring as to justify the exclusive use of valence bond formulas such as II.

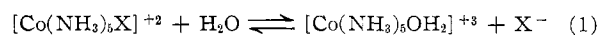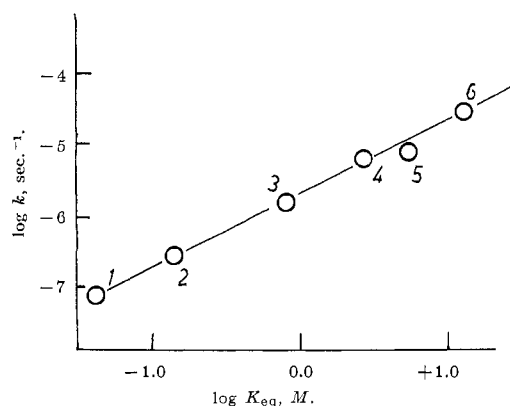(7) Shell Development Co., Emeryville, Calif.

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On the Acid Hydrolysis of $[Co(NH_3)_5X]^{+2}$ Ions and the Mechanism of Interchange

Sir:

Three recent papers[1-3] remind us that the mechanism of reaction 1 (X = F⁻, Cl⁻, Br⁻, I⁻, NO_3^-, and $H_2PO_4^-$) remains a lively issue. Data have now ac-

$$[Co(NH_3)_5X]^{+2} + H_2O \rightleftharpoons [Co(NH_3)_5OH_2]^{+3} + X^- \quad (1)$$

cumulated which permit application of the "Linear Free Energy Relation" tool to the analysis of this problem. Figure 1 shows a plot of the log of the first-order acid hydrolysis rate constant for the forward reaction of equilibrium 1 vs. the log of the equilibrium constant for (1) at a single ionic strength ($\mu = 0.50$). The data are found in ref. 2, 3, and 4. (The equilibrium constant for the hydrolysis of $[Co(NH_3)_5F]^{+2}$ may be estimated with sufficient accuracy from results given in ref. 3.)

The figure shows an entirely satisfactory linear relationship[5] implying a relationship between the change of activation free energy and the change of standard free energy of the reaction of the form $\Delta\Delta F^* = \alpha\Delta\Delta F°$, where the parameter $\alpha = 1.0$. The immediately appealing conclusion that α near 1.0 suggests a similarity between the transition state and the products (with respect to the variation in question) has been developed formally by Leffler and Grunwald.[6] The present case is an especially striking one; α is fully 1.0. *The role of the X^- group in the transition state of acid hydrolysis is strongly similar to its role in the product: namely, that of a solvated anion.*

The preceding argument defines only the role of the leaving group in the transition state. It is possible to draw tentative conclusions concerning the role of the entering water using Hammond's analysis[7] of the relationship between the value of α and the magnitude of $\Delta F°$. According to Hammond, the entering group will be strongly bound in a transition state resembling the product only if the reaction is highly endothermic. Explaining this point by inverting the argument, we

(1) R. G. Pearson and J. W. Moore, *Inorg. Chem.*, **3**, 1334 (1964).

(2) A. Haim and H. Taube, *ibid.*, **2**, 1199 (1963).

(3) S. C. Chan, *J. Chem. Soc.*, 2375 (1964).

(4) R. G. Yalman, *Inorg. Chem.*, **1**, 16 (1962).

(5) For X groups not monovalent anions, the rate and equilibrium data fall off the line in Figure 1. See, for example, data on SO_4^{-2} in ref. 2.

(6) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 156 ff.

(7) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

Figure 1.—Plot of log rate constant *vs.* log of equilibrium constant for the acid hydrolysis reaction of $[Co(NH_3)_5X]^{+2}$ ions. Measurements made at 25.0°. Points are designated: 1, $X^- = F^-$; 2, $X^- = H_2PO_4^-$; 3, $X^- = Cl^-$; 4, $X^- = Br^-$; 5, $X^- = I^-$; and 6, $X^- = NO_3^-$. (Data for all X except I^- and F^- appear in ref. 2. Data for I^- are in ref. 4 and F^- in ref. 3.)

expect the transition state to lie at an intermediate point along the reaction coordinate if the molecule derives significant stabilization from a forming bond. The reactions shown in Figure 1 lie in the neighborhood of $\Delta F° = 0$. We may conclude that water is at best weakly bound in the transition state of reaction 1.

The linear free energy relationship suggests a transition state with at most weak bonds to both the entering and the leaving group. The possibility that the entering group is not present at all has been considered by Haim and Taube,[2] and competition factors for a five-coordinate intermediate which are consistent with the equilibria, rates, and water exchange rates have been calculated. Pearson and Moore's[1] experiments failed to verify some of these competition factors. They cited several lines of evidence indicating that there is no five-coordinate intermediate and that both the entering group and the leaving group are stoichiometric components of the transition state. Pearson and Moore discussed a "solvent assisted dissociation" which considers the activation process as primarily bond breaking but with a requirement for a little assistance from some nucleophile in the transition state. This seems a quite reasonable proposal, but it may be useful to compare it to a slightly different formulation.

The "linear free energy relationship" argument places the transition state at a point with weak bonds. Let us consider these *no bonds* for a moment to give the "five-coordinate intermediate." If the activation energy for reaction of this "intermediate" with an entering nucleophile is so low that the reaction rate is higher than the rate of reorganization of solvent molecules around the complex, the "intermediate" must react with a nucleophile already in position in the second coordination sphere. On such a reaction path, the only possible reaction is an interchange between the first and second coordination spheres of the complex. The entering group must be present in advance. But, it is possible for the interchange to take place *without* nucleophilic assistance. This process may have an intermediate in the sense of *transition state theory* (a minimum in the potential surface) but still not have an intermediate in the *phenomenological kinetic* sense of that intermediate being detectable by any sort of competition experiment. Highly charged complex ions interact strongly with their second coordination spheres (contact solvation shells). As Eigen has shown,[8] the reorganization rates are not always close to diffusion control. The above interchange process is most probable in just this circumstance.

In this letter, we suggest that it is possible to formulate a mechanism equivalent in explanatory power to the "solvent assisted dissociation" which does not invoke nucleophilic assistance by the solvent. It is not suggested that a simple experiment will distinguish between the two. Contrarily, the intention is to call attention to the need for *operationally* satisfactory mechanistic categories. Perhaps the best course is to insist on success in competition experiments as the defining criterion for an intermediate (dissociative mechanism) and to use the neutral term "unassisted interchange" for all reactions *failing* to satisfy two opposite operational criteria: (1) presence of an intermediate and (2) well-defined nucleophile order for entering groups.

(8) M. Eigen, *Discussions Faraday Soc.*, **24**, 25 (1957).

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Book Reviews

Reaction Heats and Bond Strengths. By C. T. MORTIMER. Addison-Wesley Publishing Co., Inc., Reading, Mass., 1962. xii + 230 pp. 14.5 × 22 cm. Price, $5.00

This small volume consists of the treatment and use of thermochemical data to generate bond energies for a number of largely organic molecules. Based upon a series of lectures given by the author at the University of Keele (Staffordshire, England) the subject matter seems to be accurately and well explained,

and summarizes a wealth of experimental data. In this respect the effort is of significant value, because bond energies are not normally calculated or compiled in the more standard sources of thermochemical data. Although a number of metallo–organic bonds are discussed, most of the text is oriented toward organic-like species, with a corresponding loss of general interest among inorganic chemists. A notable exception is the chapter on silicon, phosphorus, and sulfur compounds; however, the short chapter on ionization energies in aqueous solution is totally inadequate.