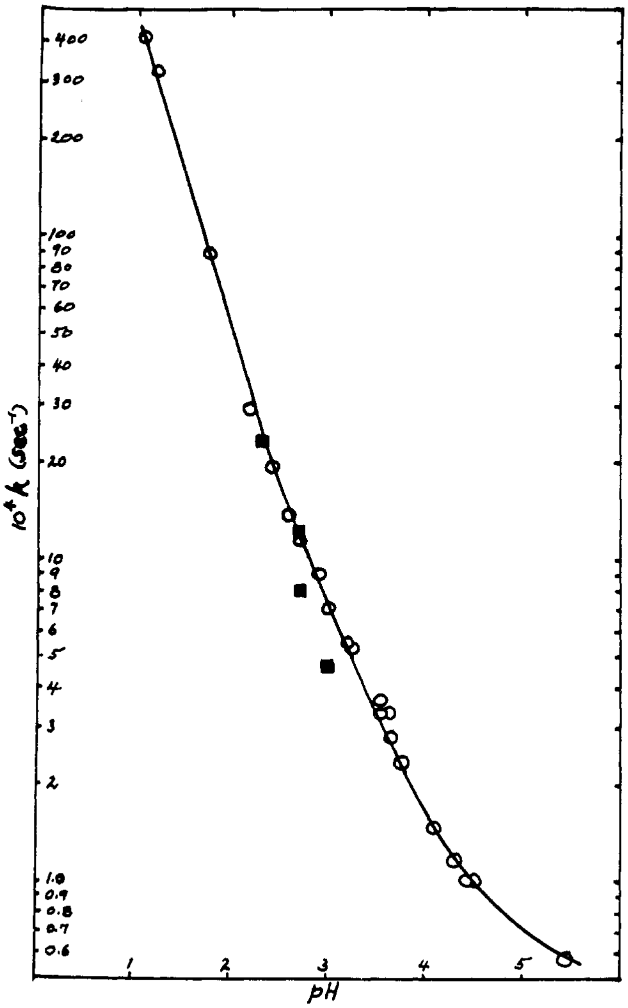

Figure 1.—Acid hydrolysis rate of carbonatobis(ethylenediamine)cobalt(III) ion as a function of pH in aqueous solution: (complex ion) = $5 \times 10^{-3}\ M$; ionic strength $\sim 0.25\ M$; temperature 25°.

pretation of the process in that our data confirm that protonation of the carbonato species is an equilibrium process, as shown in our reaction 2, and that all three of the subsequent aquation reactions contribute to the total process. If it is accepted that the equilibrations are very rapid as compared to any of the aquations, it is readily deduced that the total rate constant for aquation is given by (neglecting the indeterminate constant involved in the water equilibration step)

$$k = \frac{k_1K + k_2(\mathrm{H}^+) + k_3(\mathrm{H}^+)^2}{K + (\mathrm{H}^+)}$$

This formulation has been tested on our aquation data at 25° for the bisethylenediamine species, "best-fit" values for the constants being evaluated by use of an IBM 1620 computer.[3] The values obtained were $k_1 = 5.3 \times 10^{-5}$ sec.$^{-1}$, $k_2 = 5.1 \times 10^{-4}$ sec.$^{-1}$, $k_3 = 4.5 \times 10^{-1}\ M^{-1}$ sec.$^{-1}$, and $K = 3.2 \times 10^{-4}\ M$. The excellent fit of this interpretation to our experimental data (circles in Figure 1) is illustrated by the continuous curve. Tong's k_1 values (squares in Figure 1), which are the only ones strictly comparable to our inclusive k, are seen to be in good agreement at the lower pH values, where (H$^+$) is effectively constant during a run. They deviate, as expected, to smaller values at the higher pH runs, where (H$^+$) falls off appreciably in the absence of buffering.

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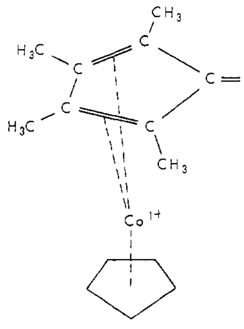
[3] We are grateful to Dr. H. F. King of this laboratory for his assistance in the computer application.

Electronic Transitions and Bonding in Tetrakis(trifluoromethyl)cyclopentadienone-cobalt Cyclopentadienyl

Sir:

The X-ray structural analyses of two cobalt cyclopentadienyl complexes of cyclopentadienone derivatives have revealed varying degrees of distortions of the dienone rings and have led to two different structural proposals. Dahl and Smith conclude that the metal–dienone bonding in tetramethylcyclopentadienone cyclopentadienyl cobalt (complex I) is essentially delocalized as the C–C and the Co–C bond lengths are nearly equal and the bonded cyclopentadienone deviates only little from planarity.[1] In the analogous complex of tetrakis(trifluoromethyl)cyclopentadienone (complex II) the dienone is more strongly distorted. A localized structure II with Co–C σ- and π-bonds has been proposed by Bailey, Gerloch, and Mason.[2] The two formulations imply a fundamental difference in the electronic structures. In I the formal oxidation number of Co is +1 and the ligand retains its basic cyclopentadienone structure. In structure II, however, the cobalt atom would have the formal oxidation number of +3 and the ligand would no longer be conjugated. It therefore appeared to be of interest to compare the electronic spectra of both complexes. In Figure 1 the solution absorption spectra are shown. Solid state reflectance spectra have been measured also but are not included since they are not significantly different. The close similarity of the spectra leaves



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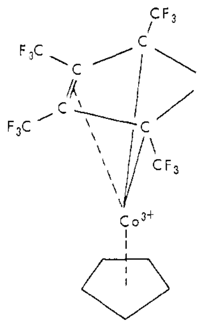

II

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[1] L. F. Dahl and D. L. Smith, *J. Am. Chem. Soc.*, **83**, 752 (1961).

[2] N. A. Bailey, M. Gerloch, and R. Mason, *Nature*, **201**, 72 (1964); also see M. Gerloch and R. Mason, *Proc. Roy. Soc.* (London), **A279**, 170 (1964); M. J. Bennett, M. R. Churchill, M. Gerloch, and R. Mason, *Nature*, **201**, 1318 (1964).

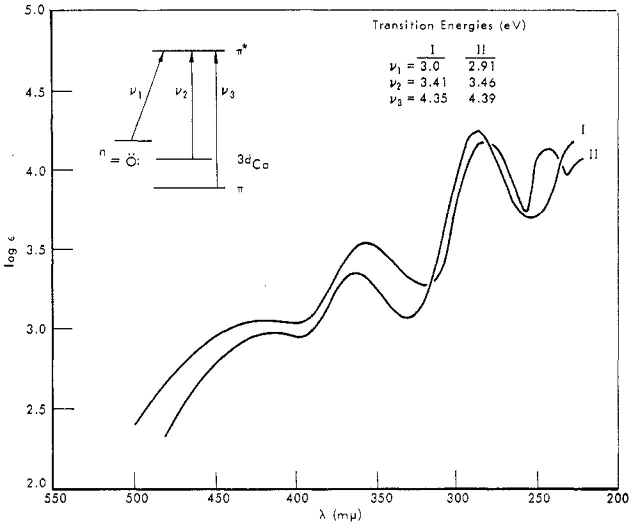

Figure 1.—Electronic absorption spectra (in isooctane solution) and experimental term level diagrams of complexes I and II.

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–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.

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[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).

[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 accumulated 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 (μ = 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.)

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

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 α = 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

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[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).