it is seen that as k_3 increases, the shape of the rate curve, NiL^{-2} *vs. t*, changes until a limiting "wall" is reached at $k_3 \sim 0.08$ l. mole^{-1} sec.$^{-1}$. Thus, if the catalytic paths (2) and (3) are operating it is possible, using this indirect approach, either to evaluate k_3 or at least to establish its lower limit.

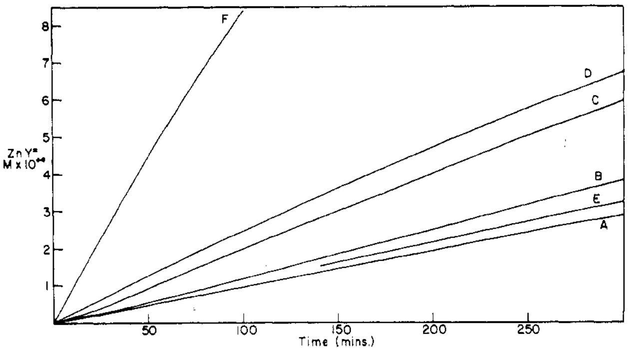

Figure 2.—The rate of formation of ZnY^{-2}: curve A, $k_3 = 0$, $Cu_t = 0, 1.34 \times 10^{-4}$ *M;* B, $k_3 = 1.67 \times 10^{-4}$, $Cu_t = 1.34 \times 10^{-4}$ *M;* C, $k_3 = 16.7 \times 10^{-4}$, $Cu_t = 1.34 \times 10^{-4}$ *M;* D, $k_3 = 833, 1667 \times 10^{-4}$, $Cu_t = 1.34 \times 10^{-4}$ *M;* E, $k_3 = 1667 \times 10^{-4}$, $Cu_t = 1.00 \times 10^{-5}$ *M;* F, $k_3 = 1430 \times 10^{-4}$, $Cu_t = 1.34 \times 10^{-3}$ *M;* other quantities the same as in Figure 1.

All the curves shown in Figure 1 have the same initial slope, which is determined by the sum of the initial velocities of the Zn^{+2} and Cu^{+2} reactions with NiL^{-2}. Thus, zero-time data do not experimentally demonstrate catalysis although, if some knowledge of k_3 is had, catalysis may be deduced, as was done in ref. 1.

The results of Bydalek and Margerum[3] obtained for experiments with Cu^{+2} give a straight line having a slope $3.0_8 \times 10^{-6}$ sec. when plotted as $-\ln (NiL^{-2})$ *vs.* time for the first 400 min. The computed values in Figure 1 for the curve $k_3 \geqslant 0.083$ l. mole^{-1} sec.$^{-1}$ plotted similarly give a straight line with a slope 3.0×10^{-6} sec.$^{-1}$. Thus, the data of Margerum and Bydalek conclusively show the effect of a catalytic path with a rate constant k_3 of at least 0.083 l. mole^{-1} sec.$^{-1}$.

A variation of concentrations shows that this indirect method is most sensitive to k_3 when conditions are arranged so that the velocities of the competing paths (1) and (2) are nearly identical: when the rate of either of the paths (1) or (2) becomes dominant over the other the catalytic path (3) exerts a relatively smaller effect on the rate of the NiL^{-2} disappearance. Under these latter conditions the concentration of the product of the catalyzed reaction is best measured directly. The advantage of a direct approach can be seen by comparing the computed curves given in Figure 2, where the effect of a variation in Cu(II) on the rate of ZnL^{-2} formation is also shown. The effect is seen to be quite large, although at both the high and low Cu(II) levels the rate of disappearance of NiL^{-2} is relatively insensitive to k_3.

Acknowledgment.—We wish to thank the staff of the numerical computation laboratory of The Ohio State University for the kind use of their facilities, and Professor Margerum for valuable discussions.

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(3) Private communication.

Kinetics and Mechanism of the Acid Hydrolysis of Carbonatobis(ethylenediamine)cobalt(III) Ion

Sir:

A paper under the above title appeared in a recent issue of this journal[1] in which an attempt was made to deduce the mechanism of the process from somewhat limited data. The authors found it impossible to choose between two suggested mechanisms based on a protonated intermediate, one involving direct reaction of the intermediate with water, the other with hydronium ion. We wish to report our studies of the same reaction which are now in progress, and which we have extended to the closely similar propylenediamine and trimethylenediamine analogs. These studies developed from our earlier conclusions[2] concerning the acid hydrolysis reaction, which were based on carbonate exchange experiments, and which Tong and co-workers seem to have overlooked. Our new data on the acid hydrolysis reactions embrace the range $1 < pH < 5$ (as compared to the $2.4 < pH < 3$ range of Tong's work), and were obtained by a spectrophotometric technique utilizing phosphate–citric acid buffering. Since (H^+) was effectively kept constant in our work, pseudo-first-order kinetics were observed in individual runs. The mechanism now proposed, which is slightly modified from our previous suggestions,[2] is as follows (L = chelated diamine ligand).

$$CoL_2CO_3^+ + H_2O \rightleftarrows CoL_2(OH_2)(OCO_2)^+ \qquad (1)$$

$$CoL_2(OH_2)(OCO_2)^+ + H^+ \rightleftarrows CoL_2(OH_2)(OCO_2H)^{+2} \quad 1/K \qquad (2)$$

$$CoL_2(OH_2)(OCO_2)^+ + H_2O \longrightarrow CoL_2(OH)(H_2O)^{+2} + HCO_3^- \quad k_1 \qquad (3)$$

$$CoL_2(OH_2)(OCO_2H)^{+2} + H_2O \longrightarrow CoL_2(OH_2)_2^{+3} + HCO_3^- \quad k_2 \qquad (4)$$

$$CoL_2(OH_2)(OCO_2H)^{+2} + H_3O^+ \longrightarrow CoL_2(OH_2)_2^{+3} + H_2CO_3 \quad k_3 \qquad (5)$$

This is similar to Tong's suggestions in that, except for our assumption of opening of the carbonato chelate by inclusion of a water molecule in the coordination sphere, his reactions 1a, 2a, and 2b correspond to our reactions 3, 4, and 5. We differ, however, in our inter-

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[1] J. Y. Tong, E. St. A. Kean, and B. B. Hall, *Inorg. Chem.*, **3**, 1103 (1964).

[2] G. Lapidus and G. M. Harris, *J. Am. Chem. Soc.*, **85**, 1223 (1963).

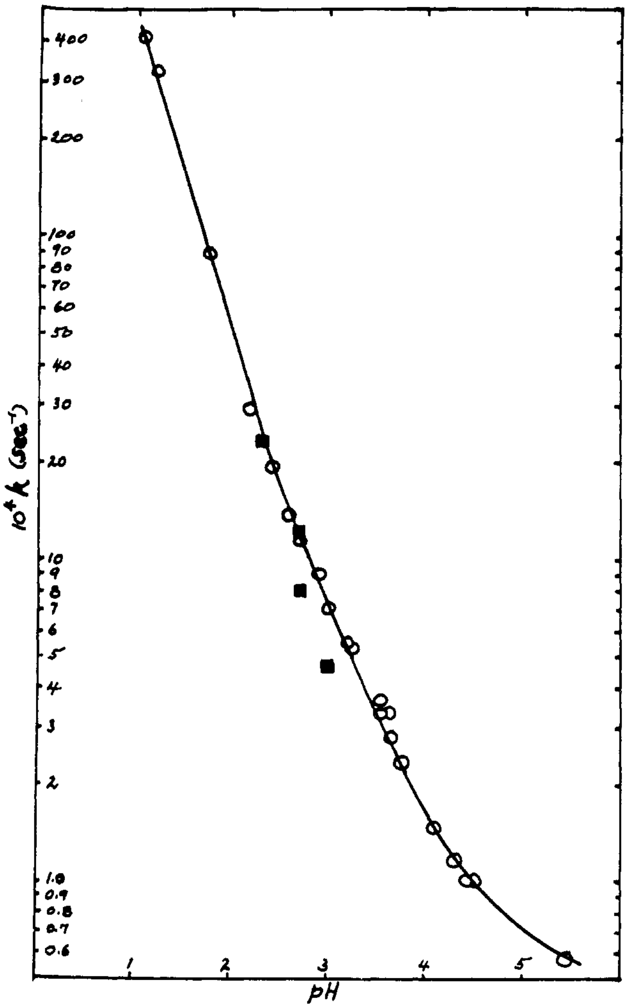

Figure 1.—Acid hydrolysis rate of carbonatobis(ethylenediamine)cobalt(III) ion as a function of pH in aqueous solution: (complex ion) = 5 × 10^{-3} *M;* ionic strength ~ 0.25 *M;* temperature 25°.

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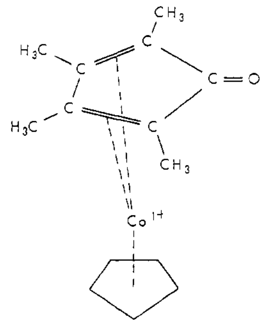
[3] We are grateful to Dr. H. F. King of this laboratory for his assistance in the computer application.

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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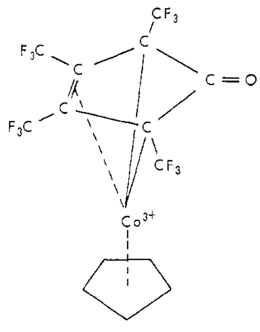

II

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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).