Note on the Formation Constant of the Mono(ethylenediamine)-chromium(III) Complex

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In a paper in this journal, Tsuchiya and his co-workers[1] have given values for the 1st formation constant in the chromium(III)-ethylenediamine system. Their procedure was as follows: Aqueous solutions of tris(ethylenediamine)chromium(III) perchlorate to which an excess amount of perchloric acid had been added, were maintained at 25°C for one or two months. On the assumption that equilibrium was established, the solutions containing mono(ethylenediamine) and hexa-aqua ions were then analyzed spectrophotometrically. In this way values of the 1st formation constant were found to be about $10^{16.5}$. As this value in our opinion is much too high, we suspected that the solutions examined by Tsuchiya and his co-workers had not been in equilibrium, and we have, therefore, made similar measurements but at a higher temperature in order to reach equilibrium more rapidly. A solution with the following total concentrations of $[\mathrm{Co\ en_3}](\mathrm{ClO_4})_3$ 0.0085M and $\mathrm{HClO_4}$ 0.072M was placed in a thermostat at 50°C, and the advancing hydrolysis was followed spectrophotometrically. In our experiment the spectrum changed relatively little over a long period of time in the "equilibrium" range of Tsuchiya and his co-workers, but after the lapse of about three months the spectrum was indistinguishable from that of a solution of the hexa-aquachromium(III) ion. The same was the case with a 0.0096M solution of $\mathrm{Cr(H_2O)_6(ClO_4)_3}$, 0.032M in $\mathrm{enH_2(ClO_4)_2}$ and 0.022M in $\mathrm{HClO_4}$. These results are also consistent with a kinetic study by Garner and his co-workers[2] which implies that the systems studied by Ohta, Matsukawa, and Tsuchiya were not at equilibrium, and that their "equilibrium constants" are not accurate. According to our findings the amount of mono(ethylenediamine) complex not hydrolyzed must be less than one percent of the total chromium. The hydrogen ion concentration in the aquated solution is 0.020M, that of $\mathrm{enH_2^+}$ 0.026M, and by introducing the acid dissociation constants of the last-mentioned ion at 50°C $K_{\mathrm{A},1}\times K_{\mathrm{A},2}=10^{16.06}$[3] a simple calculation shows that the 1st formation constant in the chromium(III) ethylenediamine system must be smaller than $\sim 10^{12}$. This value is more than 10^4 times smaller than the value $\sim 10^{16.5}$ given by Ohta, Matsukawa, and Tsuchiya.[1] Tsuchiya and his co-workers[4] have published formation constants for many other chromium(III) complexes but have not made sure that equilibrium is reached by approaching it from both sides. A critical revision of their data therefore seems necessary.

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[1] M. Ohta, H. Matsukawa, and R. Tsuchiya, This Bulletin, **37**, 692 (1964).

[2] R. F. Childers, Jr., K. G. Van der Zyl, Jr., D. A. House, R. G. Hughes, and C. S. Garner, *Inorg. Chem.*, **7**, 749 (1968).

[3] F. A. Cotton and F. E. Harris, *J. Phys. Chem.*, **69**, 1203 (1955).

[4] This Bulletin, **38**, 1059, 1235 (1965); **39**, 1589 (1966); **41**, 2416 (1968).