BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 555 (1969)

Spectrophotometric Determination of a Trace Amount of Cobalt(II) in Nickel(II) Solution

Mutsuo KODAMA

Department of Chemistry, Ibaraki University, Mito, Ibaraki

(Received June 8, 1968)

Previously,[1,2] we studied the substitution reactions of Eriochrom Black T (BT) with cobalt(II)- and nickel(II)-EDTA chelates spectrophotometrically, and determined the reaction mechanism and rate constants.

The reaction of BT with cobalt(II)-EDTA chelate was found to proceed much faster than that with nickel(II)-EDTA chelate. In the mixture of nickel(II)- and coblat(II)-EDTA chelates, the reaction of BT may proceed through both nickel(II)- and cobalt(II)-EDTA chelates. Therefore, in nickel(II)-EDTA solution contaminated with a trace amount of cobalt(II)-EDTA chelate, the rate at which the concentration of BT decreases would be much greater than that in the pure nickel(II)-EDTA chelate solution. Hence, even a trace amount of cobalt(II) in the nickel(II)-EDTA solution may be estimated by determining the increase in the apparent rate at which the concentration of BT decreases.

As stated previously,[1,2] both reactions of BT with cobalt(II)- and nickel(II)-EDTA chelate are first-order in BT and first-order in metal(II)-EDTA chelate. Consequently, the initial rate of the substitution reaction, $-(\mathrm{d[BT]}/\mathrm{d}t)_0$, in the mixed solution of nickel(II)- and cobalt(II)-EDTA chelate containing uncomplexed EDTA can be expressed as,

$$-\left(\frac{\mathrm{d[BT]}}{\mathrm{d}t}\right)_0 = (k_{\mathrm{Ni}}\cdot[\mathrm{NiY^{2-}}] + k_{\mathrm{Co}}[\mathrm{CoY^{2-}}])\cdot[\mathrm{BT}]_0 \quad (1)$$

where k_{Ni} and k_{Co} are the conditional second-order rate constants of the reaction of BT with pure nickel(II)-EDTA chelate and that with pure cobalt(II)-EDTA chelate, respectively. Both k_{Ni} and k_{Co} values increase with increasing pH value of the solution.[1,2]

Alternatively, one can define the initial reaction rate as,

$$-\left(\frac{\mathrm{d[BT]}}{\mathrm{d}t}\right)_0 = k\cdot[\mathrm{MY^{2-}}]_t\cdot[\mathrm{BT}]_0 \quad (2)$$

where $[\mathrm{MY^{2-}}]_t = [\mathrm{NiY^{2-}}] + [\mathrm{CoY^{2-}}]$.

Combining the above two equations, one can derive the following relation.

$$[\mathrm{CoY^{2-}}] = \frac{k - k_{\mathrm{Ni}}}{k_{\mathrm{Co}} - k_{\mathrm{Ni}}}[\mathrm{MY^{2-}}]_t \quad (3)$$

This relation clearly shows that when the total concentration of cobalt(II)- and nickel(II)-EDTA chelates is known, the concentration of cobalt(II)-EDTA chelate in the nickel(II)-EDTA chelate solution, $[\mathrm{CoY^{2-}}]$, can be estimated from k, k_{Ni} and k_{Co} values determined experimentally. The concentration of cobalt(II) in the nickel(II)-EDTA solution was estimated with the aid of Eq. (3) using k, k_{Ni} and k_{Co} values determined at pH 9.60. Typical results are given in Table 1, which can be regarded as satisfactory. k_{Ni} and k's used in the calculation of $[\mathrm{CoY^{2-}}]$ were determined from the initial slope of absorbance *vs.* time curves, because the absorbance decreases almost linearly with time in the reaction of BT with pure nickel(II)-EDTA, and with nickel(II)-EDTA contaminated with a small amount of cobalt(II). On the other hand, k_{Co} was estimated from the slope of the linear relation between $\log(A_{\mathrm{D}}/(A-A_{\mathrm{CoD}}))$[1] and time t, because the reaction of BT with cobalt(II)-EDTA chelate proceeds so rapidly that the initial slope cannot be determined accurately.

TABLE 1. CALCULATION OF $[\mathrm{CoY^{2-}}]$ WITH THE AID OF Eq. (3)

$\mu = 0.30$, 15°C
$\lambda = 630\,\mathrm{m}\mu$, pH = 9.60
$k_{\mathrm{Co}} = 1.74\times10^{1}$, $k_{\mathrm{Ni}} = 3.58\times10^{-2}$

k	$[\mathrm{MY^{-2}}]_t$ mM	$[\mathrm{CoY^{2-}}]$ mM	
		added	found
1.98×10^{-1}	5.05	5.0×10^{-2}	4.7×10^{-2}
3.76×10^{-1}	5.10	1.0×10^{-1}	1.0×10^{-1}
7.22×10^{-1}	5.20	2.0×10^{-1}	2.1×10^{-1}
5.28×10^{-2}	10.46	1.0×10^{-2}	1.0×10^{-2}*
7.10×10^{-2}	10.47	2.0×10^{-2}	2.1×10^{-2}
1.24×10^{-1}	10.50	5.0×10^{-2}	5.3×10^{-2}
2.09×10^{-1}	10.55	1.0×10^{-1}	1.1×10^{-1}

* This value is less accurate.

Apparatus, detailed experimental procedures and the preparation of standard solutions used in this study were as described in previous papers.[1,2]

1) M. Kodama, This Bulletin, **40**, 2575 (1967).
2) M. Kodama, C. Sasaki and M. Murata, *ibid.*, **41**, 1333 (1968).