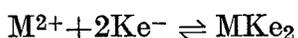


# STABILITY CONSTANTS OF COMPLEXES OF RESACETOPHENONE OXIME\*†

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Resacetophenone oxime (2,4-dihydroxyacetophenone oxime,  $\text{CH}_3\text{C}(=\text{NOH})\text{-C}_6\text{H}_3(\text{OH})_2$ ) forms chelates with many metals. This reagent has been widely employed in these laboratories for the colorimetric, volumetric, amperometric, conductometric, and gravimetric estimation of metals copper,<sup>1</sup> iron,<sup>2</sup> nickel,<sup>3</sup> palladium,<sup>4</sup> niobium,<sup>5</sup> etc. In view of its wide application as an analytical reagent, it is of interest to know the physicochemical properties such as magnetic susceptibility, polarographic behaviour, and stabilities of these metal complexes. Hence the authors have undertaken these studies, and the present investigation deals with the determination of the stability constants of complexes of copper, nickel, cobalt, and manganese with resacetophenone oxime by the pH metric method. Since the chelates were insoluble in water (except manganese) the study was carried out in 60% by volume dioxan-water mixture. The procedure employed was that of Calvin and Wilson, modified by Calvin and Melchior<sup>6</sup> to avoid the difficulties which might be caused by the presence of small amounts of impurities. The stabilities were expressed in terms of the equilibrium constant  $\beta_2$  for the reaction



$$\beta_2 = \frac{[\text{MKe}_2]}{[\text{M}^{2+}] [\text{Ke}^-]^2}$$

as the reagent forms a 1 : 2 complex with the metals studied.

## Experimental

Resacetophenone oxime was prepared by the procedure described in an earlier paper.<sup>7</sup> All the metal salts were of analytical reagent quality.

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<sup>1</sup> Krishna Reddy, Y., *Proc. Indian Acad. Sci.*, 1965, **61**, 368.

<sup>2</sup> Raja Reddy, G., Kadarmandalgi, S. G., and Murthy, A. S. R., *Proc. Indian Acad. Sci.*, 1964, **59**, 159.

<sup>3</sup> Krishna Reddy, Y., unpublished data.

<sup>4</sup> Krishna Reddy, Y., unpublished data.

<sup>5</sup> Raghava Naidu, R., *Curr. Sci.*, 1967, **36**, 150.

<sup>6</sup> Calvin, M., and Melchior, N. C., *J. Am. chem. Soc.*, 1948, **70**, 3270.

<sup>7</sup> Seshagiri, V., Krishna Reddy, Y., and Brahmaji Rao, S., *Proc. Indian Acad. Sci.*, 1965, **62**, 231.

Dioxan was purified by the procedure described in the paper by Naidu and Krishnan.<sup>8</sup> Elico pH meter LI-10A was used for pH measurements.

Comparison titrations were carried out as follows: 50 ml of 0.02M resacetophenone oxime in 60% dioxan was placed in the titration vessel (100-ml beaker) followed by 5 ml of 0.01M nitric acid and 0.5 ml of pure water or 0.001M metal salt solution. The mixture was titrated with 0.1M solution of AnalaR sodium hydroxide prepared in carbon dioxide-free water. The additions were done with a microburette and the pH reading was taken after each addition of 0.02 ml.

### Results

A graph was drawn of pH values against volume of sodium hydroxide added. At any pH the horizontal distance between the reference curve determined without the presence of a metal ion and the curve determined in the presence of metal ion was measured accurately. This divided by the total metal added is  $\bar{n}$  the average number of ligands bound to a metal atom. At any pH the value of total  $\text{Ke}^-$  can be calculated from the known amount of  $\text{HKe}$  and its dissociation constant. The dissociation constant of the chelating agent determined by polarographic method by the authors<sup>9</sup> was used. The formation curves were constructed by plotting  $\bar{n}$  values against  $\log(1/[\text{Ke}^-])$ . Values for  $\log \beta_2$  were obtained by multiplying  $\log(1/[\text{Ke}^-])$  corresponding to  $\bar{n} = 1$ , by 2. The values are as follows:

Metal ion	$\text{Cu}^{2+}$	$\text{Ni}^{2+}$	$\text{Co}^{2+}$	$\text{Mn}^{2+}$
$\log \beta_2$	11.90	8.10	10.50	6.50

### Discussion

The decreasing stability of chelates studied was in the order  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Mn}^{2+}$ . A striking resemblance is seen between the chelate stability and the second ionization potential of the atoms except in the case of cobalt. The above order is not in conformity with the natural Erving-Williams order of stability, since cobalt(II) was found to have a higher stability constant than nickel(II). This difference in the stability constant was also shown by the cobalt complexes of dimethylphenanthrolines as observed by Brisbin and McBryde.<sup>10</sup> The large values for  $\beta_2$  in this case suggests that a very stable complex was formed. This may be due to the oxidation of cobalt(II) to cobalt(III) and the formation of corresponding more stable cobalt(III) complex. Calvin and Melchior<sup>6</sup> in their investigation of the stability of sodium 5-salicylaldehyde sulphonate chelates of transitional elements suggested the involvement of a  $d$  orbital in the chelate formation on the basis of the correlation of the stability constants with the second ionization potential. They also suggested that the replacement of a chelated oxygen atom by a more basic nitrogen atom enhances the tendency for the coordination electron pairs to enter the  $d$  orbital. So the present authors feel that in the case of the complexes investigated the  $d$  orbital is involved, forcing the molecule into the pure  $dsp^2$  coplanar covalent binding.

<sup>8</sup> Naidu, P. R., and Krishnan, V. R., *Trans. Faraday Soc.*, 1965, **61**, 1347.

<sup>9</sup> Seshagiri, V., and Brahmaji Rao, S., *J. electroanal. Chem.*, 1967, **13**, 330.

<sup>10</sup> Brisbin, D. A., and McBryde, W. A. E., *Can. J. Chem.*, 1963, **41**, 1135.