Acid Dissociation Constants of Some 3-Substituted 2-hydroxy-5-methylacetophenones and the Formation Constants of their Metal Complexes

C. B. PATEL and R. P. PATEL

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar-388120

Acid dissociation constants of some 3-substituted 2-hydroxy-5-methylacetophenones and the formation constants of their complexes with Cu(II), Ni(II), Co(II) and Zn(II) have been determined at 40° in aqueous dioxane medium containing 50% dioxane by volume and 0.1M KNO₃ using Calvin-Bjerrum technique as applied by Irving and Rossotti. The stability constants follow the usual stability order.

IN continuation of our earlier studies[1-9] on complexes of 2-hydroxyphenones we report here the stability constants of Cu(II), Ni(II), Co(II) and Zn(II) with 2-hydroxy-5-methyl-acetophenone (5-CH₃-OHA), 2-hydroxy-3-nitro-5-methylacetophenone (3-NO₂-5-CH₃-OHA), 2-hydroxy-3-chloro-5-methylacetophenone (3-Cl-5-CH₃-OHA), 2-hydroxy-3-bromo-5-methylacetophenone (3-Br-5-CH₃-OHA) and 2-hydroxy-3,5-dimethylacetophenone (3-CH₃-5-CH₃-OHA). The data reported here are obtained for the first time at 40° in aqueous dioxane medium containing 50% dioxane (v/v) at an ionic strength $0.1M$ with respect to KNO₃ following the technique of Calvin-Bjerrum as applied by Irving and Rossotti[10].

Experimental

All the ligands were prepared by the known methods of synthesis[11-15]. All chemicals used were of AnalaR grade. All solutions and pH-measurements were made as described earlier[16].

The following solutions (total volume 40 ml) were prepared and titrated against ~0.31M NaOH : (i) 2 ml 0.148M HNO₃+5 ml 0.8M KNO₃+13 ml water and 20 ml dioxane; (ii) 2 ml 0.148M HNO₃ +5 ml 0.8M KNO₃+13 ml water+ 10 ml ~0.025M reagent and 10 ml dioxane; (iii) 2 ml 0.148M HNO₃ +5 ml 0.8M KNO₃+11 ml water+2 ml ~0.02M metal nitrate solution+10 ml ~0.025M reagent solution and 10 ml dioxane.

Results and Discussion

Proton-Ligand Formation Constants :

The practical proton-ligand formation constants were calculated using the following equation

$$\log {}^{P}K^{H} = B + \log \frac{\bar{n}_H}{1 - \bar{n}_H} \qquad \ldots \quad (1)$$

where B is meter reading.

From the several log ${}^{P}K^{H}$ values calculated for each system the average values were obtained and these are given in Table 1. The log ${}^{P}K^{H}$ values for these chelating agents have also been obtained as Bjerrum's half-integral values. The half-integral values are found to be in fairly good agreement with the values obtained as above (Table 1).

The ligands under study may be treated as 3-substituted derivatives of 5-CH₃-OHA. The data reported in Table 1 show that introduction of an electronegative group like -Cl, -Br, or -NO₂ increases the acid strength of the parent compound, just as might be anticipated. The effect of 3-NO₂ group is particularly noticeable. 3-Methyl group weakens the acid noticeably. The methyl group in a position ortho to the -OH of 2-hydroxyketone has two effects : (i) it is expected to exert higher inductive effect on the electron density at phenolic oxygen because of the short distance over which it has to operate and (ii) it would force the -OH group to form H-bond with the keto group in all the molecules and thus increase the H-bond strength. Such a steric facilitation to H-bonding has been noted in the case of o-nitrophenols with alkyl groups ortho to the -OH group[17]. The prominent acid weakening effect of 3-methyl group in 2-hydroxyacetophenones has been similarly interpreted[18].

Metal-Ligand Stability Constants :

The formation curves for the systems under consideration are found to be incomplete since precipitates appear at $\bar{n} \approx 1$. Assuming that only 1 : 1 complexes are formed in these systems the log K_1 values were obtained by Bjerrum-half-integral method and

TABLE 1—METAL-LIGAND STABILITY CONSTANTS

$t = 40° \pm 0.1°$ $\mu = 0.1M$ (KNO₃);   50% Dioxane

Reagent →	5-CH₃-OHA			3-NO₂-5-CH₃-OHA			3-Cl-5-CH₃-OHA			3-Br-5-CH₃-OHA			3-CH₃-5-CH₃-OHA			
Method →	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	
Metal																
	11.42	11.45	—	7.60	7.64	—	10.15	10.12	—	10.05	10.05	—	12.25	12.22	—	$\log p_k{}^{ff}$
Cu(II)	8.10	8.10	8.05	5.60	5.60	5.52	7.33	7.27	7.23	7.28	7.28	7.24	8.60	8.61	8.57	$\log K_1$
	—	—	6.43	—	—	4.31	—	—	5.96	—	—	5.53	—	—	7.17	$\log K_2$
	—	—	14.48	—	—	9.83	—	—	13.19	—	—	12.77	—	—	15.74	$\log \beta_2$
Ni(II)	5.45	5.48	5.19	3.92	3.89	3.92	4.80	4.84	4.83	4.98	4.90	4.75	6.52	6.40	6.14	$\log K_1$
	—	—	4.99	—-	—	—	—	—	2.85	—	—	4.27	—	—	6.13	$\log K_2$
	—	—	10.18	—	—	-ve	—	—	7.68	—	—	9.02	—	—	12.27	$\log \beta_2$
Co(II)	5.55	5.56	4.79	3.70	3.75	3.80	4.67	4.64	4.59	4.64	4.61	4.54	6.48	4.46	6.38	$\log K_1$
	—	—	5.76	—	—	—	—	—	3.54	—	—	3.68	—	—	5.50	$\log K_2$
	—	—	10.55	—	—	-ve	—	—	8.13	—	—	8.22	—	—	11.88	$\log \beta_2$
Zn(II)	6.24	6.25	6.17	3.07	3.08	3.07	—	5.68	5.68	5.65	5.66	5.67	6.97	6.95	6.95	$\log K_1$
	—	—	5.33	—	—	0.69	—	—	3.87	—	—	—	—	—	—	$\log K_2$
	—	—	11.50	—	—	3.76	—	—	9.55	—	—	-ve	—	—	-ve	$\log \beta_2$

: Half-integral values;   II : Average of the pointwise calculations;   III : Least-squares method.

by pointwise calculation. The pointwise calculation was done using the equation :

$$\log K_1 = pL + \log \frac{\bar{n}}{1-\bar{n}}$$

Finally, the average values were determined (Table 1). In view of very low ($\sim 10^{-3}M$) concentrations of the metal ions used in the titrations, polynuclear complexes may be ignored. In some systems, titrations performed with different ratios of metal to ligand showed that the stability constant is independent of metal ion concentrations.

When an attempt was made to check the validity of the constants calculated as above by substituting them back into the formation functions to calculate $\bar{n}$ it was observed that the $\bar{n}_{calc}$ showed a poor agreement with $\bar{n}_{expt}$ in most cases. The difference was decidedly larger than the estimated experimental error in the $\bar{n}$ values. It was suspected that the maximum coordination number for these systems may not be 1 but may be 2 and that the two steps of coordination are overlapping. Such a suspicion is supported by the results of previous studies[18-19] on systems that are very closely similar to the ones under consideration. Therefore, the $\bar{n}$, pL data were treated by the least-squares method to get the values of $\log K_1$ and $\log \beta_2$. The least-squares values of $\log K_1$ and $\log \beta_2$ were employed to calculate $\bar{n}$. The $\bar{n}_{calc}$ values were in good agreement with $\bar{n}_{expt}$. The standard deviation[20] is found to be quite small (± 0.01], showing the validity of the constants. The values obtained by pointwise calculation, half-integral and least-squares methods are given in Table 1.

Although the least-squares method has been employed to calculate $\log K_1$ and $\log K_2$ only the $\log K_1$ values are regarded as the most representative of experimental data and, therefore the discussion of the metal chelate stability constants has been restricted to the $\log K_1$ values for the systems. The data in Table 1 show that for all the systems except the 3-CH₃-5-CH₃-OHA, the order of stability is Co < Ni < Cu > Zn. This order is found to be in agreement with Irving-Williams order[21]. The system involving 3-CH₃-5-CH₃-OHA deviates from this general observation and gives the order Ni < Co < Cu > Zn. The reversal of positions of cobalt and nickel is rather difficult to account for in absence of other information. There is a relatively large difference between $\log K_1$ values for the copper chelates and those for the chelates of other metal ions in each system. The higher stability of the copper chelates may be due to the formation of a square planar complex, the structure usually found for copper complexes[22]. The higher values of $\log K_1$ of zinc chelates as compared to those for nickel chelates may be due to the greater M–L π-interaction between the π-orbitals of Zn(II) and the ligands.

Acknowledgement

References

1. R. P. PATEL and R. D. PATEL, J. Indian Chem. Soc., 1971, 48, 521.

2. R. P. PATEL and R. D. PATEL, J. Inorg. Nuclear Chem., 1970, 32, 2591.

3. M. N. PATEL and R. P. PATEL, *J. Inorg. Nuclear Chem.*, 1973, **35**, 3023.

4. J. R. SHAH and R.P. PATEL, *J. Indian Chem. Soc*, 1971, **48**, 1177.

5. J. R. SHAH and R. P. PATEL, *J. Indian Chem. Soc.*, 1971, **48**, 169.

6. J. R. SHAH and R. P. PATEL, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2589.

7. M. N. PATEL and R. P. PATEL, *J. Indian Chem. Soc.*, 1971, **48**, 1123.

8. B. B. PATEL, J. R. SHAH and R. P. PATEL, *Indian J. Chem.* (in press).

9. J. R. SHAH and R. P. PATEL, *Indian J. Chem.*, 1973, **11**, 606.

10. H. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1954, 2904.

11. I. M. HEILBORN and H. M. BUNBURY, "*Dictionary of Organic Compounds*", Eyre and Spottiswoode, London, 1953.

12. H. BREDERECK, G. LEHMANN, C. SCHONFELD and E. FRITZSCHE. *Ber.*, **72B**, 1414; *Angew. Chem.*, 1939, **52**, 445.

13. D. CHAKRAVARTI and B. MAJUMDAR, *J. Indian Chem. Soc.*, 1939, **16**, 151.

14. G. WITTING and W. SCHULZE, *J. Prakt. Chem.*, 1931, **130**, 81.

15. N. M. CULLINANE and B. F. R. EDWARDS, *J. Appl. Chem.* (England), 1959, **9**, 133.

16. J. R. SHAH and R. P. PATEL, *Indian J. Chem.*, 1973, **11**, 607.

17. J. C. DEARDEN and W. F. FORBES, *Canad. J. Chem.*, 1950, **38**, 1852.

18. M. N. PATEL and R. P. PATEL, *J. Inorg. Nuclear Chem.*, 1972, **34**, 1891.

19. J. R. SHAH and R. P. PATEL, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2589.

20. H. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1953, 3397.

21. H. IRVING and R. J. P. WILLIAMS, *Nature*, 1948, **162**, 746.

22. R. G. CHARLES and H. FREISER, *Anal. Chim. Acta*, 1954, **11**, 101.