

quinones has also been measured.<sup>17,18</sup> One mechanism which is consistent with the acid-dependence observed in the latter studies involves the ionization of  $\text{QH}_2$  to  $\text{QH}^-$  followed by the oxidation of  $\text{QH}^-$  by  $\text{Fe}(\text{H}_2\text{O})_6^{+3}$ . The standard free energy change of this reaction has been calculated,<sup>19</sup> and this value, combined with the free energy of activation of the reaction can be used to calculate the free energy of activation of the  $\text{Fe}(\text{H}_2\text{O})_6^{+2}$ - $\text{QH}$  reaction. The free energy of activation calculated in this way, together with the appropriate data on some  $\text{Fe}(\text{H}_2\text{O})_6^{+2}$ - $\text{Fe}(\text{III})$  reactions, is plotted in Fig. 2.

A linear relation appears to exist between  $\Delta G^*$  and  $\Delta G^0$  for the reactions of  $\text{Fe}(\text{H}_2\text{O})_6^{+2}$  with  $\text{Fe}(\text{phen})_3^{+3}$ ,  $(\text{H}_2\text{O})_5\text{FeCl}^{+2}$  and the semiquinones. On this basis, the reaction of  $\text{Fe}(\text{H}_2\text{O})_6^{+2}$  with  $\text{Fe}(\text{H}_2\text{O})_6^{+3}$  seems somewhat slower than expected, while its reaction with  $(\text{H}_2\text{O})_5\text{FeOH}^{+2}$  seems considerably faster. The work required to bring the reactants from infinity to the distance they occupy in the activated complex is different in the various reactions. While the amount of this work is probably small at the distances and ionic strengths involved, it may be partly responsible for the relative slowness of the  $\text{Fe}(\text{H}_2\text{O})_6^{+2}$ - $\text{Fe}(\text{H}_2\text{O})_6^{+3}$  reaction. In addition, the free energy required to reorganize the inner coordination shell of the  $\text{Fe}(\text{H}_2\text{O})_6^{+3}$  ion before electron transfer can occur<sup>20</sup> is probably larger than that required for the other species.

The very rapid rate of the  $\text{Fe}(\text{H}_2\text{O})_6^{+2}$ - $(\text{H}_2\text{O})_5\text{FeOH}^{+2}$  reaction may indicate that this reaction proceeds by a different type of mechanism. Such a mechanism may involve hydrogen atom transfer as has been suggested.<sup>21</sup> However, measurements of the rates of the exchange reactions of  $\text{Fe}(\text{H}_2\text{O})_6^{+2}$  with  $\text{Fe}(\text{H}_2\text{O})_6^{+3}$ ,  $(\text{H}_2\text{O})_5\text{FeOH}^{+2}$  and  $(\text{H}_2\text{O})_5\text{FeCl}^{+2}$

in  $\text{D}_2\text{O}$ ,<sup>22,23</sup> as well as those of other oxidation-reduction reactions in this solvent, do not support the interpretation that the hydroxide-catalyzed exchange proceeds uniquely *via* a hydrogen atom transfer mechanism.

In view of the above linear relation between  $\Delta G^*$  and  $\Delta G^0$  for the oxidation-reduction reactions, it is likely that a similar relation exists between the  $\Delta H^*$  and  $\Delta H^0$  for the oxidation-reduction reactions. The small value of the heat of activation (0.2 kcal./mole) found for the ferrous-ferric phenanthroline reaction suggests that the  $\Delta H^0$  of this reaction has a large negative value. Unfortunately the value of  $\Delta H^0$  has not been determined, but it may be estimated from the known value of  $\Delta G^0$  and an estimate of  $\Delta S^0$  for the reaction. The difference in the entropies of  $\text{Fe}(\text{H}_2\text{O})_6^{+2}$  and  $\text{Fe}(\text{H}_2\text{O})_6^{+3}$  is 43.0 cal./deg. mole with that of  $\text{Fe}(\text{H}_2\text{O})_6^{+3}$  more negative.<sup>24</sup> Irvine<sup>13</sup> has measured the difference in the entropies of the tris-(4,4'-dimethylbipyridyl)-iron(II) and tris-(4,4'-dimethylbipyridyl)-iron(III) ions to be 1.9 cal./deg. mole with that of the tripositive ion more positive. Because the sizes of the 4,4'-dimethylbipyridyl and 1,10-phenanthroline complexes are similar, the entropy difference of 1.9 cal./deg. mole measured for the 4,4'-dimethylbipyridyl complexes will be assumed also for the 1,10-phenanthroline complexes. This assumption is supported by unpublished measurements on a number of bipyridyl and phenanthroline complexes.<sup>13</sup> The value of  $\Delta G^0$  for the oxidation-reduction reaction is -9.2 kcal./mole.<sup>15</sup> This, together with the  $\Delta S^0$  estimate, gives a value of  $\Delta H^0 = -22.6$  kcal./mole.

**Acknowledgments.**—We wish to thank Dr. R. W. Dodson for helpful discussions. One of us (B. M. G.) is grateful for the hospitality extended him by the Chemistry Department, Brookhaven National Laboratory.

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## Stabilities of Bivalent Metal Complexes of Some B-Ketoimines

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Acid dissociation constants of several B-ketoimines and formation constants of some of their metal derivatives have been determined.

### Introduction

The chelating tendencies of  $\beta$ -diketones have been studied extensively.<sup>1</sup> However, the properties of  $\beta$ -ketoimines, Schiff-base derivatives of  $\beta$ -diketones, are less well known. Cromwell<sup>2</sup> has written an excellent review of the organic chemistry of  $\beta$ -

ketoimines. More recently, Holtzclaw, *et al.*,<sup>3</sup> described the synthesis and infrared spectra of these ligands and their copper derivatives. Hovey, *et al.*,<sup>4</sup> have reported the preparation and absorption spectra of analogs of bisacetylacetonethylenediimine and its metal chelates. The dissocia-

(1) J. Bjerrum, G. Schwarzenbach and L. G. Sillen, "Stability Constants," Part I, Special Publication No. 6, The Chemical Society, London, 1957.

(2) N. H. Cromwell, *Chem. Revs.*, **38**, 83 (1946).

(3) H. F. Holtzclaw, Jr., J. P. Collman and R. M. Alire, *THIS JOURNAL*, **80**, 1100 (1958).

(4) R. J. Hovey, J. J. O'Connell and A. E. Martell, *ibid.*, **81**, 3189 (1959).

TABLE I  
 $\beta$ -KETOIMINES<sup>10</sup> OF THE TYPE  $\text{RCOCH}_2\text{C}(=\text{NAr})\text{R}'$ 

Compound No.	R	R'	Ar	Yield, %	M.p., °C.	Recrystn. solvent <sup>a</sup>	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
I	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	50	45 <sup>b</sup>	A	75.40	75.78	7.48	7.55
II	CH <sub>3</sub>	CH <sub>3</sub>	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	93	145.5-146	A + B	59.99	60.00	5.49	5.53
III	CH <sub>3</sub>	CH <sub>3</sub>	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	50	50-52 <sup>c</sup>	A	70.22	69.94	7.37	7.65
IV	CH <sub>3</sub>	CH <sub>3</sub>	2,6-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	60	52.5-54	A	76.84	76.96	8.43	8.59
V	CH <sub>3</sub>	CH <sub>3</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	48	61-62 <sup>d</sup>	A	62.99	63.24	5.73	6.03
VI <sup>e</sup>	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	93	109-110 <sup>f</sup>	C	80.99	80.94	6.37	6.32
VII	CH <sub>3</sub>	CH <sub>3</sub>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	56	67-68 <sup>g</sup>	A	76.15	76.34	7.99	8.11
VIII	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	38	98.5-100 <sup>h</sup>	A + B	84.25	84.57	5.72	5.72

<sup>a</sup> A, petroleum ether (30-60°); B, benzene; C, dil. ethanol. <sup>b</sup> Reported m.p. 47°; ref. 3. <sup>c</sup> Reported m.p. 51-52.5°; ref. 6. <sup>d</sup> Reported m.p. 60-61°; ref. 6. <sup>e</sup> Cf. ref. 2 for discussion of structure. <sup>f</sup> Reported m.p. 110° [C. Beyer, *Ber.*, 20, 1767 (1887)]. <sup>g</sup> Reported m.p. 68-69°; ref. 6. <sup>h</sup> Reported m.p. 102-103; ref. 6.

tion constants and formation constants of  $\beta$ -ketoimines seem never to have been determined.

In this communication, the acid dissociation constants of some  $\beta$ -ketoimines and formation constants of some metal derivatives are reported.

### Experimental<sup>5</sup>

**Synthesis of  $\beta$ -Ketoimines.**—(Table I) The ligands were prepared by a modification of the method of Roberts and Turner.<sup>6</sup> The condensation of acetylacetone and *p*-nitroaniline represents a typical synthesis. The reaction of aniline with benzoylacetone or dibenzoylmethane was exceptional inasmuch as the amine-( $\beta$ -diketone) molar ratio was 1:1. The  $\beta$ -ketoimines are white crystalline solids with the exception of compounds VI, VIII (yellow) and II (orange).

**CH<sub>3</sub>(4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>N=)CCH<sub>2</sub>COCH<sub>3</sub>.**—A solution of acetylacetone (11.0 g., 0.11 mole), *p*-nitroaniline (13.8 g., 0.1 mole) and 2 drops of concd. H<sub>2</sub>SO<sub>4</sub> in 150 ml. of benzene was refluxed. Water was removed as formed (water separator), the theoretical amount being formed within 2-3 hr. The product, which crystallized on cooling, was filtered and air dried (13 g.). An additional 7.4 g. was obtained by evaporation of the solvent. The product was recrystallized from benzene-petroleum ether.

**Potentiometric Titrations.**—The acid dissociation constants in dioxane-water mixtures were determined according to the method of Van Uitert<sup>7</sup> using tetramethylammonium hydroxide as the base. The potentiometric titrations were performed as previously described.<sup>8</sup> Formation constants were calculated using the method of Block and McIntyre.<sup>9</sup>

TABLE II

$pK_D$ EQUATIONS ( $pK_D = a + bN_2$ ) <sup>a</sup> OF SOME $\beta$ -KETOIMINES			
Compound	a	b	N <sub>2</sub> range
I	13.80	10.67	0.077-0.173
II	14.15	10.70	.077- .173
III	13.50	10.80	.095- .173
IV	13.92	10.73	.077- .173
V	13.42	10.84	.077- .173
VI	14.55	10.65	.0875- .173
VII	13.55	10.92	.077- .173
VIII	15.72	10.68	.143- .173

<sup>a</sup> Reliable within  $\pm 0.05$ .

(5) Microanalyses were performed under the direction of Mr. Joseph Nemeth at the University of Illinois.

(6) E. Roberts and E. E. Turner, *J. Chem. Soc.*, 1832 (1927).

(7) L. G. Van Uitert, *et al.*, *THIS JOURNAL*, **75**, 455 (1953); *ibid.*, **76**, 5887 (1954).

(8) L. G. Van Uitert, *et al.*, *ibid.*, **75**, 457 (1953).

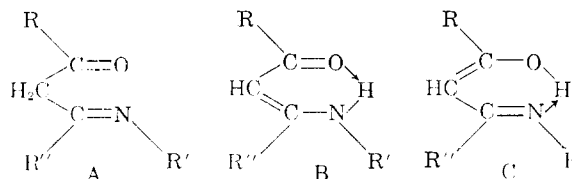
(9) B. P. Block and G. H. McIntyre, Jr., *ibid.*, **75**, 5667 (1953).

(10) The names and corresponding numbers of the ligands are: 2-(phenylimino)-pentane-4-one, I; 2-(4-nitrophenylimino)-pentane-4-one, II; 2-(2-methoxyphenylimino)-pentane-4-one, III; 2-(2,6-dimethylphenylimino)-pentane-4-one, IV; 2-(4-chlorophenylimino)-pentane-4-one, V; 2-(phenylimino)-4-phenylbutane-4-one, VI; 2-(4-methylphenylimino)-pentane-4-one, VII; 1-(phenylimino)-1,3-diphenylpropane-3-one, VIII.

### Discussion

**Acid Dissociation Constants.**—The  $pK_D$  values of the  $\beta$ -ketoimines were determined as a function of mole fraction of dioxane ( $N_2$ ) at 30°. The  $pK_D$ - $N_2$  relationship is approximately linear. Table II lists mathematical expressions for the linear portions which fit the data within  $\pm 0.05$ .

All the  $pK_D$  values deviate from linearity at lower values of  $N_2$ , and the deviation is toward lower values of  $pK_D$ . The comparable deviation observed with  $\beta$ -diketones<sup>7a</sup> is in the opposite direction and is attributed to an increase in the keto-form content at lower values of  $N_2$ . A different explanation may be required for the  $\beta$ -ketoimines. Possibly the ketoimino form (A) predominates at lower  $N_2$  regions. However, the deviations may



arise from a shift in the tautomeric equilibrium between forms B and C.

The actual structure of the  $\beta$ -ketoimines is not established. Cromwell, *et al.*,<sup>11</sup> present evidence in favor of structure B. However, two observations suggest that structure C is of major importance in dioxane-water: The ligand  $pK_D$  is relatively insensitive to nitrogen-atom substituents; the variation of  $pK_D$  (at  $N_2 = 0.173$ ) with substitution for three  $\beta$ -diketones (acetylacetone, benzoylacetone, dibenzylmethane) closely parallels the variation noted for their aniline derivatives (compounds I, VI, VIII, respectively).<sup>12</sup>

**Formation Constants.**—The formation constants, obtained in 59 volume % dioxane ( $N_2 = 0.173$ ) are listed in Table III. The data clearly show that the beryllium, copper and uranyl chelates are very stable, though the stabilities are less than might be expected of  $\beta$ -diketones having comparable  $pK_D$  values. The positions of the three bivalent metal ions in a stability series varies from ligand to ligand.

That the stabilities of beryllium and copper chelates are comparable is surprising because the

(11) N. H. Cromwell, *et al.*, *THIS JOURNAL*, **71**, 3337 (1949).

(12) A plot of  $pK_D$  of  $\text{RCOCH}_2\text{C}(=\text{NC}_6\text{H}_5)\text{R}^1$  vs.  $pK_D$  of  $\text{RCOCH}_2\text{COR}^1$  ( $N_2 = 173$ ) suggests that the relationship is linear.

TABLE III

FORMATION CONSTANTS ( $\log K_n$ )<sup>a</sup> OF SOME BIVALENT-METAL CHELATES OF SOME  $\beta$ -KETOIMINES IN 50 VOLUME % DIOXANE ( $N_2 = 0.173$ ) AT 30°

Compound <i>n</i>		Cu	Be <sup>b</sup>	UO <sub>2</sub> <sup>b</sup>	Ni	Co	Zn	Mn
I	1	10.84 ± 0.03 <sup>c</sup>	10.87 ± 0.02	10.97 ± 0.02	9.77 ± 0.02	9.08 ± 0.02	Ppt.	Ppt.
	2	10.93 ± .03	10.49 ± .01	10.00 ± .02	6.43 ± .02	6.68 ± .01		
II	1	.....	12.04 ± .04	10.56 ± .03	10.30 ± .01	9.64 ± .01	9.37 ± 0.03	Ppt.
	2	.....	10.63 ± .02	10.52 ± .05	8.16 ± .01	7.59 ± .02	7.86 ± .05	
III	1	.....	10.90 ± .03	.....	.....	Ppt.	Ppt.	Ppt.
	2	.....	10.63 ± .02	.....	.....	.....	.....	.....
IV	1	9.80 ± .02	9.98 ± .04	11.44 ± .01	Ppt.	Ppt.	Ppt.	Ppt.
	2	9.09 ± .03	10.30 ± .03	9.74 ± .02				
V	1	11.75 ± .04	11.47 ± .02	11.67 ± .06	9.97 ± 0.02	Ppt.	Ppt.	Ppt.
	2	11.29 ± .04	10.75 ± .02	10.63 ± .02	7.13 ± .06			
VI	1	.....	10.97 ± .04	11.32 ± .02	Ppt.	Ppt.	Ppt.	Ppt.
	2	.....	10.87 ± .02	10.42 ± .05				
VII	1	10.71 ± 0.03	10.43 ± .03	.....	.....	8.71 ± 0.04	Ppt.	Ppt.
	2	10.71 ± .03	10.61 ± .01	.....	.....	7.28 ± .03		
VIII	1	Ppt.	10.55 ± .02	11.59 ± .01	Ppt.	Ppt.	Ppt.	Ppt.
	2		10.34 ± .03	10.49 ± .02				

<sup>a</sup>  $\log K_1$  and  $\log K_2$  for the reactions  $M^{++} + Ch^- \rightarrow MCh^+$  and  $MCh^+ + Ch^- \rightarrow MCh_2$ , respectively. <sup>b</sup> These values were obtained using nitrate rather than perchlorate salts. <sup>c</sup> 95% confidence limits.

coördination of  $Be^{+2}$  is often weak or non-existent with ligands containing nitrogen as a coördinating atom. This was observed by Sen<sup>13</sup> in a study of the chelating tendencies of  $Be^{+2}$  and amino acids (including picolinic acid, glycine,  $\beta$ -alanine and iminodiacetic acid).

The chelating tendency of a related series of  $\beta$ -diketones toward a given metal increases with increasing ligand  $pK_D$ .<sup>14</sup> There appears to be no correlation between  $\beta$ -ketoimine  $pK_D$  and  $\log K_n$  for a given metal chelate. To some extent this might be explained in terms of steric effects:  $\log K_n$  should be far more sensitive to steric restrictions than  $pK_D$ . Thus the lower stability of the beryllium and copper derivatives of compound IV can be attributed to the increased steric requirements of a 2,6-dimethylphenyl group.

Perhaps a  $pK_D$ - $\log K_n$  correlation should not be expected. Jones, *et al.*,<sup>15</sup> present evidence to show that the linear relationship between  $pK_D$  and  $\log K$  has no general validity. The present work would tend to confirm this observation.

Although the  $\beta$ -ketoimine  $pK_D$  is not overly sensitive to nitrogen-atom substitution, the value of  $\log K_n$  for a given metal derivative varies

(13) D. Sen, unpublished results; cited by R. M. Izatt, W. C. Fernelius and B. P. Block, *J. Phys. Chem.*, **59**, 80 (1955).

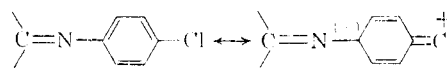
(14) L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, *THIS JOURNAL*, **75**, 2736, 2862 (1953).

(15) J. G. Jones, J. B. Poole, J. C. Tomkinson and R. J. P. Williams, *J. Chem. Soc.*, 2001 (1958).

markedly with such substitution. The effect of *p*-nitro substitution (II) is to increase the value of  $pK_D$  and generally to increase the stability of the metal chelates. This is attributed to the electron-withdrawing action of the nitro group causing an increase in electron density about the imino nitrogen



An electron-donating group, as in compound V, also increases the electron density about the nitrogen atom with similar results



The  $\beta$ -ketoimines are potentially susceptible to acid-catalyzed hydrolysis. This reaction prevented formation constant determinations using the ligands:  $CH_3COCH_2C(=NCH_3)CH_3$ , bisacetylacetonediimine and bisacetylacetonediimine. The  $\beta$ -ketoimines studied were stable to hydrolysis under the conditions employed. Compound III is a possible exception inasmuch as in three instances (copper, nickel and uranyl determinations) reproducible formation constants could not be calculated.