CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF ARIZONA, TUCSON, ARIZONA 85721

Electronic Properties of Some Aromatic Amine Ligands and Their Abilities to Enhance Metal Ion Catalysis of the Decarboxylation of β-Keto Acids

BY JOHN V. RUND AND KENNETH G. CLAUS

Received October 27, 1967

A tentative explanation is offered of the fact that complexes of metal ions with aromatic amine ligands are better catalysts than aqueous metal ions for the decarboxylation of β-keto acids. Some aliphatic amines are tested and found not to give increased catalysis rates when coordinated to metal ions. It is suggested that the π orbitals of the ligands are involved in catalytic enhancement. Several electronic properties of a series of substituted 1,10-phenanthroline molecules are examined and correlated with the ability of these molecules to increase the rate of Mn^{2+} and Zn^{2+} catalysis. Enhancement of Mn^{2+} catalysis seems to depend on the electron availability at the nitrogens, and that of Zn^{2+} is related to the energy of the first $\pi \rightarrow \pi^*$ transition of the phenanthroline.

Introduction

When a metal ion is a reaction catalyst, its catalytic ability is sometimes found to be strongly dependent on the ligands attached to it. In some cases, the ligands participate chemically in the catalysis and form bonds with the reacting substrate. In others, the ligands affect the rate by causing changes in the metal ion. The latter situation occurs in the decarboxylation of β-keto acids. The reaction is catalyzed by the ions of several metals, the catalytic abilities of which are influenced by their ligands. Increases in catalytic rates (compared with that for the aqueous metal ion) have been observed when the ligands are pyridine,[1] 1,10-phenanthroline[2] or its derivatives,[3] bipyridyl,[4] and terpyridyl.[2]

The reason for this enhancement of catalytic ability has not been established. Because all of the ligands which are catalytic promoters bind to metals through aromatic nitrogens, delocalized electron density may play an essential part. The purposes of the research reported in this paper are: (1) to establish whether the metal ion catalyzed decarboxylation of β-keto acids could be promoted by ligands containing aliphatic nitrogens, (2) to determine whether there was any simple correlation between electronic properties of a series of aromatic amines and their ability to promote catalysis, and (3) to offer tentative explanations for catalytic enhancement based on the correlation just mentioned. An investigation of the electronic properties of the metal complexes of these aromatic amines is in progress.

Experimental Section

Chemicals.—3,4,7,8-Tetramethyl-1,10-phenanthroline, 3,5,6,8-tetramethyl-1,10-phenanthroline, and 5,6-dimethyl-1,10-phenanthroline were purchased from the G. Frederick Smith Chemical Co. The first two were used as received. The last was recrystallized from aqueous ethanol. The aliphatic amines were obtained from the Aldrich Chemical Co. and used as received. All other chemicals and reagents were prepared as previously reported.[2,3]

Rates.—Some of the decarboxylation rates which are cited have been reported before. A number of rates for other catalysis are given here, and these were determined and corrected by methods noted in previous papers.[2,3]

Acid Dissociation Constants.—The pK_a's of the phenanthrolines which have not appeared in the literature were measured by the method of Smith.[5] A weighed amount of the base was mixed with a measured weight or volume of standardized strong acid. The solution was diluted to a known volume, and its pH was measured at 25° with a Beckman Model G pH meter. Care was taken to keep the solutions free from CO_2 contamination. Since the bases are not soluble enough for the measurements to be made in water, they were dissolved in water–dioxane and extrapolated to pure water. Measurements were found to be reproducible to 0.02 pH unit, and the graphs gave good straight lines.

Nmr Spectra.—The proton magnetic resonance spectra were recorded with a Varian A-60 spectrometer, using tetramethylsilane as an external standard. Peak locations could be read to within ±0.5 cps. Solutions (5%) of the phenanthrolines in $CDCl_3$ were used for spectral measurements. The chemical shifts were calculated from the resonance frequencies on an IBM 7072 digital computer with the program LAOCOON II, part I.[6]

Ultraviolet Spectra.—The ultraviolet spectra of the phenanthrolines were measured on a Cary Model 14 spectrophotometer between 200 and 400 mμ. Methanol and cyclohexane were used as solvents, and the solutes were varied over a 100-fold concentration range.

Overlap Integrals.—Overlap integrals for σ and π bonds between the metal ions and the 1,10-phenanthroline ligands were calculated using values which appear in the literature. The Slater parameters[7] are calculated for a given electronic distribution and internuclear separation. The overlap integrals corresponding to these parameters are read from published tables.[8-11] The integrals (2s, $3d_{z^2}$) and ($2p_\sigma$, $3d_{z^2}$) with the internuclear direction along the x axis have not been published, but they were easily calculated by the method suggested by Roberts and Jaffé.[12] Nor are the ($2p_\pi$, $4p_\pi$) integral values available, and these were estimated from tables of (p_π, p_π) integrals for other quantum numbers. The metal–nitrogen distances of the compounds have not been measured. The Zn–N distances in dichlorodiammine-

---

(1) R. Steinberger and F. H. Westheimer, *J. Am. Chem. Soc.*, **73**, 429 (1951).

(2) J. V. Rund and R. A. Plane, *ibid.*, **86**, 367 (1964).

(3) J. V. Rund and K. G. Claus, *ibid.*, **89**, 2256 (1967).

(4) R. W. Hay and K. N. Leong, *Chem. Commun.*, 800 (1967).

(5) A. A. Schilt and G. F. Smith, *J. Phys. Chem.*, **60**, 1546 (1956).

(6) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964).

(7) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

(8) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

(9) H. H. Jaffé, *ibid.*, **21**, 258 (1953).

(10) H. H. Jaffé and G. O. Doak, *ibid.*, **21**, 196 (1953).

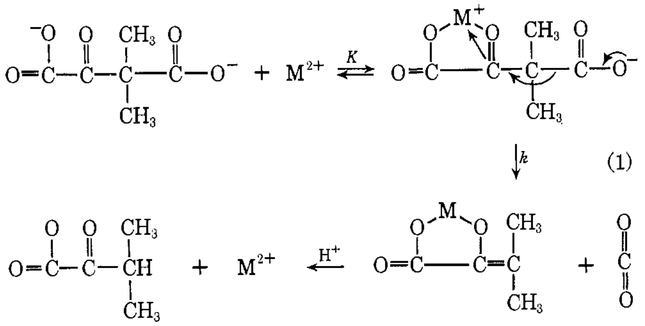
(11) L. Leifer, F. A. Cotton, and J. R. Leto, *ibid.*, **28**, 364 (1958).

(12) J. L. Roberts and H. H. Jaffé, *ibid.*, **27**, 883 (1957).

zinc(II)[13] and bis(8-quinolinol)diaquozinc(II),[14] however, are in the range of 2.0–2.1 Å, and this is probably about the bond distance in the zinc–phenanthroline complexes. Comparison of the isostructural compounds MnF_2[15] and ZnF_2[16] indicated that the radius of Mn^{2+} is about 0.05 Å larger than that of Zn^{2+}, although in the phenanthroline complex this difference may be less because of the ability of manganese to participate in π bonding with the ligand. The accuracy of the interatomic distances is not critical to the conclusions, so long as they are in reasonable agreement with reality.

Results

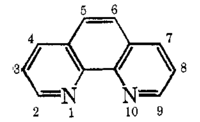
The Reaction.—The rate constants in this paper are those of the decarboxylation of dimethyloxaloacetic acid. Catalysis by a metal ion proceeds as



(1)

The corrected constants, k_c, for various catalysts, appear in Tables I and II and are the observed rate constants corrected for autodecarboxylation of the substrate and for decarboxylation by other catalysts. These constants are functions of both k and K in the above mechanism.[3]

The catalysts were 1:1 metal–ligand complexes. Two types of ligands were used: aliphatic, chelating amines and substituted 1,10-phenanthrolines. The



1,10-phenanthroline

substituents were sufficiently remote from the site of reaction that it is unlikely that any steric interaction occurred between them and the substrate.

Aliphatic Amines as Ligands.—Table I lists the rate constants for the decarboxylation catalyzed by manganese and zinc ions coordinated with N,N′-dimethylethylenediamine, N,N,N′,N′-tetramethylethylenediamine, tris(diethylaminomethyl)phosphine, and biuret. The rate constants for catalysis by the aqueous metal ions are included for comparison. It may be seen that the aliphatic amines had an inhibiting effect on the catalysis. This result is easily rationalized on the basis of the mechanism. Catalysis by the metal ion results from its positive charge, which helps to draw electrons toward the carbonyl group of the substrate and promotes the second step of the reaction. Because amines are more basic than water, the metal in the amine complex appears to the substrate to be less positive than the metal ion in the aquo complex.

TABLE I

CATALYSIS BY ALIPHATIC AMINE COMPLEXES

Catalyst	Total metal concn × 10^3, M	Catalyst concn × 10^3, M	10^5k_o, obsd rate constant, sec^{-1}	10^5k_c, cor rate constant, sec^{-1}
Zn^{2+}–aqueous	4.31	4.31	26.7	24.6
Zn^{2+}–N,N′-dimethylethylenediamine	4.40	4.31	23.8	21.2
Zn^{2+}–N,N,N′,N′-tetramethylethylenediamine	4.57	4.31	24.1	20.0
Zn^{2+}–biuret	4.35	4.31	23.7	21.1
Zn^{2+}–tris(dimethylaminomethyl)phosphine	4.31	. . .[a]	22.84	. . .
Mn^{2+}–aqueous	7.25	7.25	8.00	6.50
Mn^{2+}–N,N′-dimethylethylenediamine	13.28	7.25	8.38	1.88
Mn^{2+}–N,N,N′,N′-tetramethylethylenediamine	15.80	7.25	7.96	0.1
Mn^{2+}–biuret	9.43	7.25	11.42	7.54
Mn^{2+}–tris(dimethylaminomethyl)phosphine	24.7	. . .[a]	~0	. . .

[a] Corrections have not been made because association constants for these ligands are now known.

Phenanthrolines as Ligands.—1,10-Phenanthroline and its derivatives are also more basic than water. Coordination of a metal ion with these ligands, however, usually improved its catalytic ability. The corrected rate constants for decarboxylation catalyzed by 1:1 metal–phenanthroline complexes are reported in Table II. These are pseudo-first-order rate constants and are dependent on the concentration of the catalyst. The catalyst concentrations for which the rates are cited, 2.08×10^{-2} M for manganese and 4.18×10^{-3} M for zinc, are chosen to give rates for the various 1:1 metal–phenanthroline catalysts which are well separated (see Figures 1 and 2 in ref 3).

Acid Dissociation Constants and Hammett Substituent Constants.—The pK_a's of the monoprotonated phenanthroline molecules and the Hammett σ values for the substituents are listed in Table I. The pK_a's of the 4,7-dimethyl and 5,6-dimethyl derivatives have not been previously reported. Both determinations were carried out in 15–40% aqueous dioxane. The respective changes in pK_a value with changes in weight fraction of dioxane, given the symbol m by Smith,[5] were −0.68 and −1.58.

When the pK_a's are compared with the rate constants of decarboxylation by the manganese–phenanthroline catalysts, a general rise in catalytic ability is observed with increasing basicity of the ligand. The logarithm of the rate constant is plotted as a function of the pK_a in Figure 1 and as a function of the Hammett substituent constant in Figure 2. Both of these graphs show an initial slight rise in rate constant with increasing availability of the electrons on the nitrogens. The upward turn of the line at high values of σ and pK_a is consistent with a change in mechanism (but not with a change in the rate-determining step of the same mechanism).[17] This change had previously

---

[13] C. H. MacGillavry and J. M. Bijvoet, *Z. Krist.*, **94**, 249 (1936).

[14] L. Merritt, R. T. Cady, and B. W. Mundy, *Acta Cryst.*, **7**, 473 (1954).

[15] P. A. Akishin, V. P. Spiridonov, and V. A. Naumov, *Zh. Fiz. Khim.*, **30**, 951 (1956).

[16] W. H. Baur, *Acta Cryst.*, **11**, 488 (1958).

[17] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 187–191.

TABLE II

Derivative	pK_b	σ^a	Mn rate[b] constant × 10^5, sec^{-1}	Zn rate[c] constant × 10^5, sec^{-1}	Electron density at position			
					2,9	3,8	4,7	5,6
4,7-Dichloro	3.03[d]	+0.226	14.2	17.7	1.008	0.982	...	0.952
5-Nitro	3.57[e]	+0.17[i]	14.4	30.9	0.982[k]	0.975[k]	0.946[k]	0.907[l]
4,7-Dibromo	3.8[f]	+0.232	18.1	22.5				
5,6-Dimethyl	4.26[g]		9.5[j] 29.1	7.1[j] 28.9	1.004	1.002	0.979	...
4,7-Diphenyl	4.84[d]	+0.009	18.1	32.0	0.999	1.004	...	0.994
Unsubstituted	4.96[h]	0.000	19.9	26.6	1.000	1.000	1.000	1.000
4,7-Dimethyl	5.97[g]	−0.170	106	2.7	1.016	1.017	...	0.979
3,4,7,8-Tetramethyl	6.31[d]	−0.239	123	14.9	1.026	...	...	0.979
4,7-Dimethoxy	6.45[d]	−0.268	121	97.3	1.011	1.051	...	0.952

[a] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23,** 420 (1958). [b] Catalyst concentration 0.0208 *M*. [c] Catalyst concentration 4.18×10^{-3} *M*. [d] See ref 5. [e] W. W. Brandt and D. K. Gullstrom, *J. Am. Chem. Soc.*, **74,** 3532 (1952). [f] Not measured because of insolubility. Estimated by comparison of the 4-bromo and other derivatives.[5] [g] Present work. [h] C. H. Cook and F. A. Long, *J. Am. Chem. Soc.*, **73,** 4119 (1951), and present work. [i] By interpolation of a plot of pK_b *vs.* σ. [j] Kinetic plots have two linear portions corresponding to these two rates. [k] Average of the two positions. [l] Position 6 only.

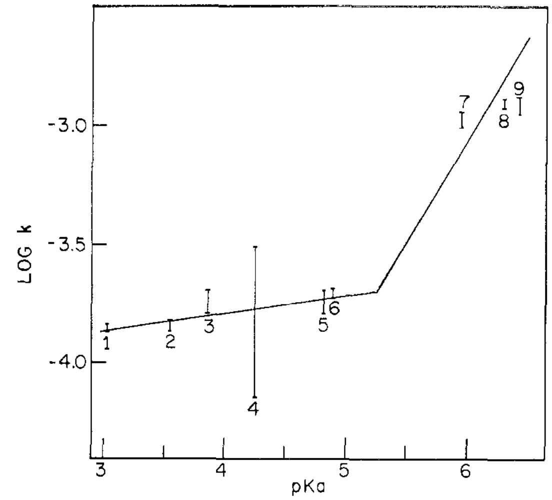
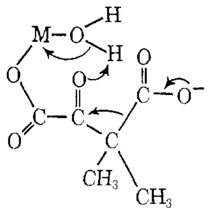


Figure 1.—Logarithms of the decarboxylation rate constants for the reaction catalyzed by 1:1 manganese–phenanthroline complexes as a function of the pK_a's of the monoprotonated phenanthrolines. Both the slow and fast rates are plotted for the 5,6-dimethyl derivative. Phenanthroline derivatives: (1) 4,7-dichloro, (2) 5-nitro, (3) 4,7-dibromo, (4) 5,6-dimethyl, (5) 4,7-diphenyl, (6) unsubstituted, (7) 4,7-dimethyl, (8) 3,4,7,8-tetramethyl, (9) 4,7-dimethoxy.

been detected from internal kinetic evidence,[3] although it was interpreted in terms of a change in the rate-determining step.

The new mechanism might involve a transition state in which the substrate is coordinated to the metal through only the carboxyl group



The results for the zinc complexes are more difficult to understand. Figure 3 shows the logarithm of their rate constants plotted as a function of the phenanthroline pK_a's. A graph of log *k vs.* σ looks similar. There is considerable scatter in the data, but the rate con-

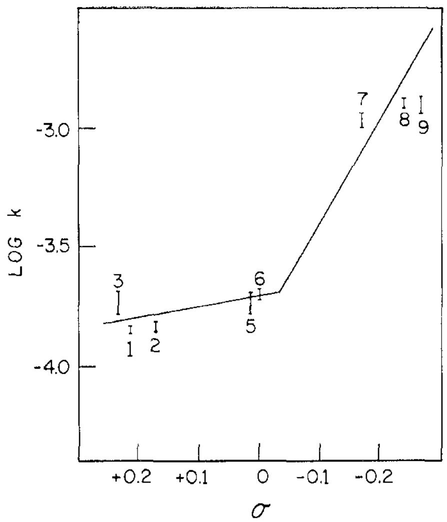


Figure 2.—Logarithms of the decarboxylation rate constants for the reaction catalyzed by 1:1 manganese–phenanthroline complexes as a function of the Hammett substituent constants for the phenanthrolines. The derivatives are numbered the same as in Figure 1.

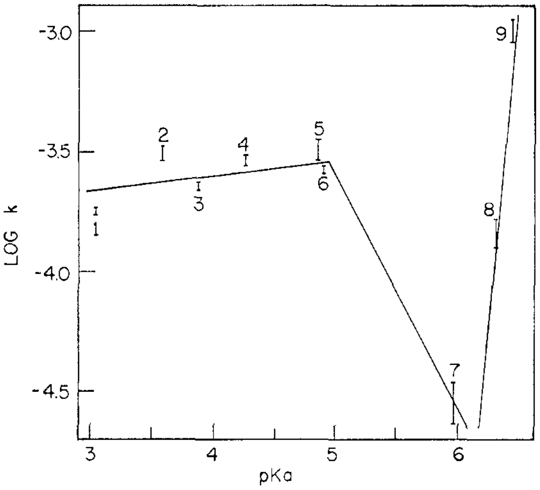


Figure 3.—Logarithms of the decarboxylation rate constant for the reaction catalyzed by 1:1 zinc–phenanthroline complexes as a function of the pK_a's of the monoprotonated phenanthrolines. Only the fast rate is plotted for the 5,6-dimethyl derivative. The derivatives are numbered the same as in Figure 1.

stants probably rise with about the same slope as those of manganese for the less basic phenanthrolines. At higher pK_a's the rate constants fall off and then rise sharply. It is possible to explain data such as these in terms of mechanistic changes but the authors feel that the explanation would be too speculative without more corroborative evidence.

Nmr Spectra.—A method of examining π-electron changes which is more direct than the use of acidities is nuclear magnetic resonance. The chemical shifts of the protons indicate how substituents on the phenanthrolines affect the π-electron densities on the various carbons. They are dependent on the polarization of the C–H bonds, which in turn are related to the electron density at the carbons to which the protons are attached by the equation $\delta_i = K\Delta\rho_i$, where δ_i is the chemical shift to the ith proton from the frequency of the corresponding proton in 1,10-phenanthroline and $\Delta\rho_i$ is the change of electron density at the ith atom.[18] Since relative electron densities were calculated, the value chosen for the proportionality constant, K, had no effect on the results. The calculation was simplified by using 1,10-phenanthroline as the reference, because the need to correct for ring-current effects was eliminated. However, the validity of the electron-density calculations for the protons at the 2 and 9 positions is limited by the magnetic anisotropy of the nitrogens.[19] The chemical shift depends both on the electron density of the carbon to which the proton is attached and on the anisotropy of the neighboring nitrogen. It is not certain to what extent the problem is alleviated by using 1,10-phenanthroline as a reference, and at present no satisfactory method is available to correct for the deshielding due to the nitrogens. The proton chemical shifts are listed in Table III and the relative electron densities in Table II.

TABLE III

NMR CHEMICAL SHIFTS OF 1,10-PHENANTHROLINES[a]

Derivative	Position 2,9	3,8	4,7	5,6
Unsubstituted	−556.5	−460.5	−497.0	−469.0
4,7-Dichloro	+5.2	−11.6	...	−37.8
5-Nitro	−13.0 (2) −10.5 (9)	−17.2 (3) −15.2 (8)	−52.0 (4) −17.6 (7)	−59.5 (6)
5,6-Dimethyl	+1.7	−1.5	−13.2	...
4,7-Diphenyl	−0.7	−4.2	...	−3.9
4,7-Dimethyl	+10.4	+11.0	...	−13.1
3,4,7,8-Tetramethyl	+16.4	...	...	−13.4
4,7-Dimethoxy	+6.8	+33.2	..	−30.8

[a] 1,10-Phenanthroline figures are relative to tetramethylsilane as an external standard. Other numbers are relative to 1,10-phenanthroline.

The electron densities offer little insight into catalytic enhancement beyond what was already apparent from the acidity constants. Although the correlation is not as obvious, it again seems that ligands with more π-electron density are better promoters of catalysis by Mn^{2+}.

Overlap Integrals.—The electronic effect which the phenanthrolines have on the substrate must be transferred to it through the metal ion. The overlaps of the metal–nitrogen π and σ bonds were calculated to find whether back-donation could be playing a predominant part in metal–ligand bonding. The values of the overlap integrals for M–N σ and π bonds are presented as a function of the internuclear separation in Figure 4. For each bond, two electron distributions, N^0–M^{2+} and N^+–M^+, have been used in making the calculations. It can be seen that the results are not very sensitive to the electron distributions chosen.

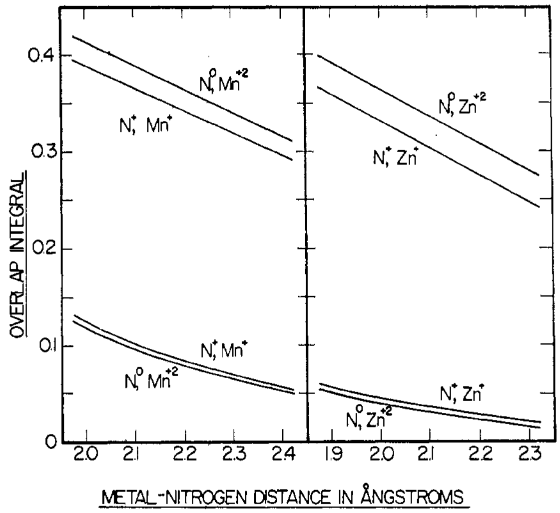


Figure 4.—Values of the overlap integrals as a function of the metal–nitrogen distance.

For both manganese and zinc, the equilibrium M–N separations are near the centers of their respective diagrams.

The overlaps of the σ orbitals are much greater than those of the π orbitals but the latter are increasing proportionately more rapidly with decreasing radius. What is more to the point, at about 2.0 Å, the manganese π-orbital overlap is increasing by a greater absolute amount than is that of the σ orbital. Thus, for a *change* in bond length at this separation, the amount of π overlap changes more than the amount of σ overlap. Based on this calculation, two lines of argument can be advanced to explain catalytic enhancement by phenanthroline ligands. The first is that the more basic phenanthrolines can be assumed to have shorter Mn–N separations and will be better able to remove electron density from the dπ orbitals of the manganese ion, making it a better catalyst. This is not a very appealing argument, because it leads to the conclusion that more basic ligands produce more positive manganese ions. The other argument concerns the transition state for the decarboxylation reaction. If a π molecular orbital which extends over the phenanthroline, the metal, and the carbonyl group of the substrate is considered, it can be seen that a phenanthroline which is closer to the manganese (more basic) would be better able to delocalize the electron

---

[18] (a) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960); (b) J. I. Musher, *J. Chem. Phys.*, **37**, 34 (1962).

[19] T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

pair which moves to the carbonyl as the carbon-to-carbon bond is breaking.

Zinc, on the other hand, has a π overlap which is much smaller than that of manganese and which increases with decreasing radius more slowly than its σ overlap.

Ultraviolet Spectra.—The ultraviolet spectra of the phenanthrolines were examined to find whether there was any relation between catalytic enhancement and the energies of the excited states of the ligands. It was fairly easy to pick out the corresponding absorptions of the various phenanthrolines, since the frequencies and extinction coefficients did not change much from one compound to another. Tentative identification of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions could be made from the frequency shifts which result from changing from polar to nonpolar solvents and from the disappearance of the $n \rightarrow \pi^*$ absorptions associated with the unshared pairs of electrons on the nitrogens upon protonation.[20] The frequency shifts of the absorptions in going from one phenanthroline to another had no understandable relationship to the catalytic ability of the corresponding manganese complex. The change in energy of a transition at about 33,000 cm^{-1}, however, showed a clear, although not linear, correlation with the rates of zinc catalysis for phenanthrolines with low and intermediate pK_a values (see Figure 5). These rates are much better correlated in this way than by a pK_a plot. Among the phenanthrolines whose pK_a's are greater than that of 1,10-phenanthroline, only the 4,7-dimethyl derivative showed a well-defined transition at this energy. For the other derivatives, all of which have slow rates, the transitions are very weak. They appeared only as indistinct shoulders on the strong adjacent absorptions, and their frequencies could not be accurately determined.

The 33,000-cm^{-1} absorption consistently shifted to higher energy when the solvent was changed from methanol to cyclohexane. On this basis, it was identified as a $\pi \rightarrow \pi^*$ transition, and it is the one of lowest frequency in the phenanthroline spectrum. It appears that the stabilization of the transition state of the reaction and the stabilization of the lowest unoccupied π orbital are related to each other. However, whether this is a cause–effect relationship or one in which both are the effects of a common cause is not clear. A similar relationship between the reactivity of aromatic molecules and the energy of their π orbitals has been noted before and given the name "superdelocalizability."[21] The explanation of the changes in rate of the reaction treated here based on a superdelocalizability argument would be as follows: as the activated complex is approached on the reaction coordinate, the substrate perturbs the π system of the catalyst; there is a second-order effect of stabilization due to mixing of excited-state wave functions with the ground state. This is a nucleophilic reaction, and the most important stabilization of the complex comes from the mixing in of the lowest unoccupied π orbital. Thus, the activation energy is lowered most for the molecule in which this orbital has the lowest energy. This is a possible explanation for the data plotted in Figure 5. It also explains in a qualitative way the slow rates of the methyl-substituted phenanthrolines for which the transition is obscured. Empirical correlations[22] used by spectroscopists indicate that the methyl group has the least ability of any of the substituents treated here to lower the energy of the transition in question. No clear conclusion can be reached about the effect of different numbers of positions of the methyl groups. 4,7-Dimethoxy-1,10-phenanthroline (which is responsible for very fast zinc catalysis) has an anomalous spectrum. Two strong new absorptions, possibly the $n \rightarrow \pi^*$ absorptions of the methoxy groups, occur at the position predicted for the $\pi \rightarrow \pi^*$ absorption, thereby making it impossible to determine the energy of the latter transition.

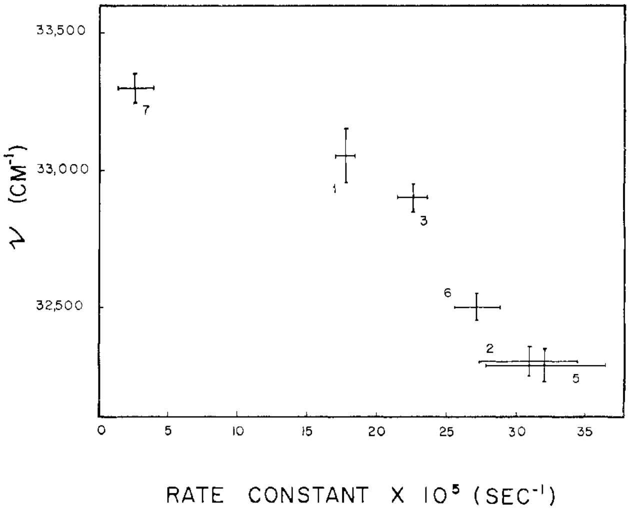


Figure 5.—Frequencies of the lowest lying $\pi \rightarrow \pi^*$ transition of the phenanthrolines as a function of the decarboxylation rate constants for the reaction catalyzed by 1:1 zinc–phenanthroline complexes. The derivatives are numbered the same as in Figure 1.

Conclusion

It has been shown that the coordination of a metal ion to a ligand with aromatic donor atoms enhances its catalytic ability (using the aqueous metal ion as a standard) in the decarboxylation reaction. However, when the ligand does not have aromatic donor atoms, catalysis is inhibited. These observations seem to implicate the π system of the ligands as the source of catalytic enhancement, although other properties of the ligand, such as its size, cannot yet be ruled out. When several electronic properties of the phenanthrolines are compared with the abilities of the phenanthrolines to enhance catalysis by the Mn^{2+} ion, a fairly simple pattern emerges. Catalysis is enhanced more when more electron density is available

---

(20) See, for example, J. G. Calvert and J. N. Pitts, "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, pp 260–262.

(21) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., New York, N. Y., 1966, pp 326–332.

(22) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 189–237.

on the donor nitrogens. Correlations with basicity and with Hammett substituent constants both indicate this, and it is corroborated to some extent by the nmr chemical shifts of the ligand protons. This conclusion is unexpected, since the function of the metal ion in promoting decarboxylation is to serve as a positive center to attract electrons from the substrate, and more basic ligands should decrease the charge on the metal ion. A tentative explanation is suggested from the examination of Mn–N overlap integrals. More basic ligands would be more tightly bound to the metal. If the enhancement of catalytic ability were due to delocalization into the ligand π-system of the negative charge which develops on the oxygen of the substrate during reaction, then the more basic ligands would be the best enhancers.

The rates of zinc catalysis are not easily correlated with the electron availability on the ligand nitrogens, nor can the same argument that was made involving overlap integrals of manganese be used for zinc. The rates do seem well correlated, however, with the energies of the lowest $\pi \rightarrow \pi^*$ transitions of the ligands. Based on previous explanations of similar phenomena, it is possible to argue that low-lying excited states tend to mix with the ground state as the transition state is approached. The free energy of activation would thus be decreased in complexes containing lower lying excited states.

Acknowledgment.—This research was carried out under a grant from the National Institutes of Health, GM 11989.

CONTRIBUTION FROM THE ISTITUTO DI CHIMICA GENERALE E INORGANICA,
UNIVERSITÀ DI FIRENZE, FLORENCE, ITALY

Transition Metal Complexes with the Tetradentate Ligand 3,3′,3′′-Triaminotripropylamine: Stability Constants

BY A. DEI, P. PAOLETTI,[1] AND A. VACCA

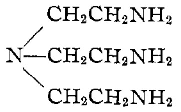
Received November 28, 1967

The four basicity constants of 3,3′,3′′-triaminotripropylamine (tpt) and the formation constants of its complexes with Co(II), Ni(II), Cu(II), and Zn(II) have been determined by potentiometric titration in 0.1 M KCl at 25°. The calculation of the constants and the relative standard deviations was carried out on the IBM 1620 computer, using a FORTRAN program based on the generalized least-squares procedure of "pit mapping" due to Sillén. The following values of the protonation constants of the ligand have been obtained: $\log K_1 = 10.511$, $\log K_{12} = 9.824$, $\log K_{13} \approx 9.129$, and $\log K_{14} = 5.615$. In addition to normal complexes $M(tpt)^{2+}$, Co(II) and Cu(II) give at high pH hydroxo complexes $M(tpt)(OH)^+$. Ni(II) and Cu(II) also form a protonated complex $M(Htpt)^{3+}$. The formation constants of the above complexes have been calculated: $\log K_1$ = 6.360, 8.702, 13.117, and 10.702, for Co(II), Ni(II), Cu(II), and Zn(II), respectively; $\log K(ML^{2+} + OH^- \rightleftarrows ML(OH)^+) =$ 2.990 and 3.991 for M = Co and Cu, respectively; and $\log K(M^{2+} + HL^+ \rightleftarrows MHL^{3+}) = 5.27$ and 10.757 for M = Ni and Cu, respectively. The stability constants of the normal complexes are compared with the corresponding values, from the literature, for 2,2′,2′′-triaminotriethylamine (tren) and 3,3′-diaminodipropylamine (dpt). The lower stability of the tpt complexes compared with those of tren (4.0–6.5 log units) seems to be due to the greater strain present in six-membered chelate rings.

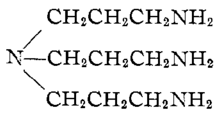
Introduction

2,2′,2′′-Triaminotriethylamine (tren) is able to form metal complexes with different stereochemistry. For example, in a thermochemical study[2] it was shown that in aqueous solution Co(II) forms a high-spin five-coordinated complex $Co(tren)(H_2O)^{2+}$. Structural investigation of the solid complexes of general formula $M(tren)(NCS)_2$ showed that although the Ni(II) complex is octahedral,[3] the Cu(II)[4] and Zn(II)[5] complexes have a trigonal-bipyramidal configuration. Furthermore the visible spectrum of the complex $Co(tren)(NCS)_2$ has been interpreted on the basis of a five-coordinated structure.[6] These results are in agreement with the findings of a calorimetric investigation of two series of polyamine complexes;[7] that is, for Cu(II), Zn(II), and Co(II) the five-coordinated configuration is favored, while for Mn(II), Fe(II), and Ni(II) the octahedral configuration is more stable.

We have presently initiated a study of the complexes formed in aqueous medium by a ligand similar to tren but which has a longer aliphatic chain, namely, 3,3′,3′′-triaminotripropylamine (tpt). This ligand has



tren



tpt

---

[1] Istituto di Chimica Generale ed Inorganica della Università di Cagliari, Cagliari, Italy.

[2] P. Paoletti, M. Ciampolini, and L. Sacconi, *J. Chem. Soc.*, 3589 (1963).

[3] D. Hall and M. D. Woulfe, *Proc. Chem. Soc.*, 346 (1958); S. E. Rasmussen, *Acta Chem. Scand.*, **13**, 2009 (1959).

[4] P. C. Jain and E. C. Lingafelter, *J. Am. Chem. Soc.*, **89**, 724 (1967).

[5] P. C. Jain, E. C. Lingafelter, and P. Paoletti, *ibid.*, **90**, 519 (1968).

[6] M. Ciampolini and P. Paoletti, *Inorg. Chem.*, **6**, 1261 (1967).

[7] P. Paoletti and M. Ciampolini, *ibid.*, **6**, 64 (1967).