

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N. Y.]

Catalysis of the Decarboxylation of Dimethyloxaloacetate by Manganese(II), Nickel(II), and Their Complexes¹

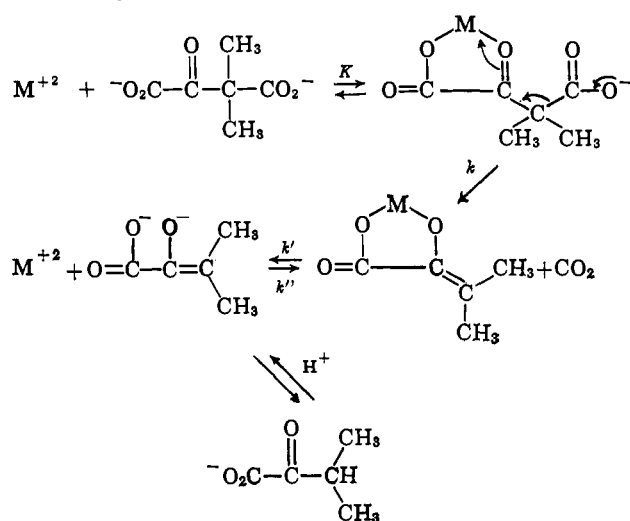
BY JOHN V. RUND AND ROBERT A. PLANE

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Kinetics were measured for the decarboxylation of dimethyloxaloacetate as catalyzed by Mn^{+2} and Ni^{+2} in aqueous solution in the presence and absence of dioxane and of various chelating ligands in an attempt to prepare enzyme models. The first-order rates were found, except in quite high dioxane concentration, to be proportional to the catalyst concentration and increased by as much as three orders of magnitude on addition of dioxane owing to an increased association constant for the catalyst-substrate complex. Certain complex ions of Mn^{+2} and Ni^{+2} also catalyzed the decarboxylation. If the complex was hexadentate, it showed no catalytic activity. For lower complexes, anionic oxygen base ligands such as 8-hydroxyquinoline-5-sulfonate lowered the catalytic activity of the metal ions; other ligands such as *o*-phenanthroline enhanced the catalytic activity of Mn^{+2} greatly (16 times) and that of Ni^{+2} slightly (2 times). This enhancement quantitatively resembles that caused by the enzyme oxaloacetate decarboxylase, and was found to be an effect on the specific rate of decarboxylation of the active complex.

The decarboxylation of β -keto acids, a reaction of biological importance, is catalyzed by metal-containing enzymes. The enzyme protein with the metal ion removed does not appreciably catalyze the reaction² but the metal ion (Mn^{+2} , Mg^{+2}) by itself possesses some catalytic power. It has been shown that several bivalent and trivalent ions in aqueous solution increase the rate of decarboxylation.³ Their catalytic ability is generally enhanced by the addition of enzyme protein. In separate studies^{4,5} using two different sources of enzyme it has been found that the coordination of a nickel(II) ion with enzyme protein increased its ability to catalyze the decarboxylation of oxaloacetic acid by less than a factor of 2 and increased the ability of manganese(II) by a factor of about 20.

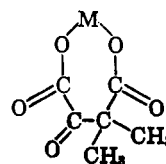
Westheimer and co-workers^{6,7} have given strong evidence that the decarboxylation of dimethyloxaloacetic acid, and presumably other β -keto acids as well, proceeds by the mechanism



where M^{+2} is the metal ion either in aqueous solution or complexed with the enzyme protein. For the aqueous metal ion, k is the rate constant of the rate-determining step. When the metal is complexed by

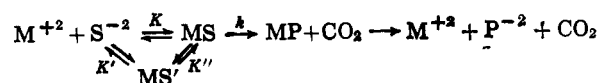
the protein, it is thought that this decarboxylation step is increased by a factor of 10^8 , and that it is the succeeding reaction, in which the catalyst is regenerated, which then determines the rate.⁷ For a similar enzymatic reaction, Westheimer has demonstrated the formation of a Schiff base.⁸

Williams⁹ suggested that two kinds of complex could be formed between the metal and the substrate. In addition to the one in Westheimer's mechanism, there could be an inactive complex of the sort



Further, equilibrium constants measured for the metal-substrate complex¹⁰ are of the size expected for this complex, which are an order of magnitude too large for the other. It was concluded that at a pH where substrate is in the form of the dianion, the predominant complex is this inactive form.

In the present research, nickel(II) and manganese(II) were studied as catalysts for dimethyloxaloacetic acid decarboxylation, assuming the mechanism



where M^{+2} is a metal ion, S^{-2} is the substrate, dimethyloxaloacetate, MS is the metal-substrate complex which can decarboxylate, MS' is the complex which cannot, and MP is the decarboxylated complex. The reaction constants could be separated into $(K' + K)$ and kK under various reaction conditions. By finding limiting ratios of K' to K , limits could be set on the constants k and K .

The research centered around finding possible processes by which the enzyme protein enhanced the catalytic ability of the metal ion. The possibility that in the enzyme the metal might exist in a region of low microscopic dielectric constant suggested a study of the catalysis by the metal ion in solutions of various dielectric constants. Though it was realized that the macroscopic dielectric constant of the solution was probably not the same as that of the microscopic region in which the metal ion existed, and that the ion could probably surround itself preferentially with molecules of solvent which did not represent the average composition of the solution, it was expected that changes

(1) From the thesis submitted by John V. Rund to the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.

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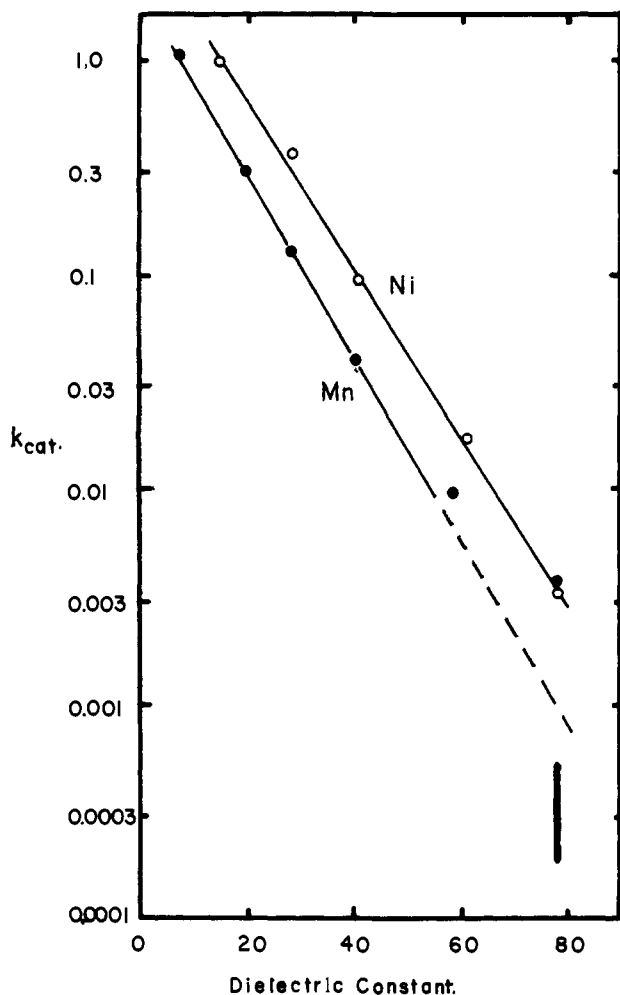


Fig. 1.—Change of catalytic rate constants with macroscopic dielectric constant.

in macroscopic dielectric constant would generally cause parallel changes in the microscopic one. A second line of inquiry was suggested by the general belief that the metal is held in the enzyme by coordination to atoms on the surface of the enzyme protein. The catalytic ability of metal ions coordinated to various organic ligands was measured. The criteria for judging whether or not the modification of a metal ion made it more like the metal in the enzyme were these: whether the rate of the over-all decarboxylation was increased, whether it was increased much more for manganese than for nickel ions, and whether the increase was due to an increase in k rather than in K . These criteria allow certain tentative suggestions to be made about the function of the enzyme protein in enhancing the catalysis rate.

Experimental

Materials.—Dimethylaloacetic acid was synthesized by the method of Steinberger and Westheimer⁶; m.p. 106.5–107°. Solutions of metal ions were made up from reagent grade perchlorate, chloride, and sulfate salts, and the concentrations determined by standard gravimetric techniques (Mn by oxidation with NaBiO_3 ; Ni by precipitation with dimethylglyoxime), and subsequent solutions standardized by use of a Beckman DU spectrophotometer. Reagent grade coordinating agents were weighed out directly. Buffers were made from sodium hydroxide solution and acetic or butyric acid. The pH of the buffer was adjusted to 4.6 at the proper dilution, using a pH meter.

p -Dioxane was purified by refluxing several hours with sodium and distilling at atmospheric pressure. It could be kept about a week without apparent contamination by peroxides.

Dielectric Constants.—The dielectric constants of the dioxane-water solutions quoted are from the "International Critical Tables" and do not take into account the effect on the dielectric

constant of the buffer, substrate, and catalyst which were added to the solution.

Rates.—The rate of decarboxylation of dimethylaloacetic acid was determined by measuring the pressure of CO_2 evolved. A freshly prepared solution of acid was introduced into an all-glass reaction vessel equipped with a negligible-volume mercury manometer. The catalyst was added, and the vessel quickly evacuated and sealed, the temperature being regulated to $25.00 \pm 0.01^\circ$ by a water bath. The solution was stirred, and pressure readings were made at regular intervals.

The reactions were all first order in dimethylaloacetic acid, and the data were treated in the usual manner to determine the observed first-order rate constants, k_0 . Finding the rate constant for the catalytic reaction, k_{cat} , involved subtracting the rate constant for the autodecarboxylation of the acid from k_0 . For this purpose, autodecarboxylation rates were measured at various dielectric constants in the absence of the catalyst.

Neither the pH nor the ionic strength could be kept constant over a wide range of dielectric constant. The best that could be done was to add a constant amount of buffer (to make the reaction solution 0.025 M in both acid and conjugate base) to each reaction. It was thus assumed that the dielectric effect on buffer was the same as it was on the dimethylaloacetic acid. Initially each reaction was $6.25 \times 10^{-3} M$ in dimethylaloacetic acid.

Results

The catalytic rate constant, k_{cat} , was determined as a function of dielectric constant in dioxane-water solutions for constant total concentrations of metal ion. The data found are presented in Table I and Fig. 1.

TABLE I
CATALYTIC RATE CONSTANTS

Metal ion, M	Dielectric constant	k_{cat} , min.^{-1}
Ni, 5×10^{-4}	78	0.00343 ± 0.00011
Ni, 5×10^{-4}	61	$.0180 \pm 0.0005$
Ni, 5×10^{-4}	40	$.095 \pm 0.003$
Ni, 5×10^{-4}	28	$.367 \pm 0.025$
Ni, 5×10^{-4}	14	~ 1.0
Mn, 1×10^{-2}	78	0.00383 ± 0.00019
Mn, 1×10^{-2}	78	$(.00036 \pm 0.00019)^a$
Mn, 1×10^{-2}	58	$.0099 \pm 0.0004$
Mn, 1×10^{-2}	40	$.0406 \pm 0.0009$
Mn, 1×10^{-2}	28	$.133 \pm 0.007$
Mn, 1×10^{-2}	19	$.326 \pm 0.002$
Mn, 1×10^{-2}	7	1.14 ± 0.04

^a Extrapolated from a linear plot of data taken at higher manganese concentrations.

For the purpose of separating the reaction constant ($K' + K$) and kK , k_{cat} was determined at various concentrations of catalyst at each dielectric constant. Graphs of k_{cat}^{-1} as a function of M_T^{-1} , where M_T is the total metal concentration, were found to be straight lines for dielectric constants as low as 28. Table II gives the data for which the separation of constants could be made and Fig. 2 is a sample plot of the data for the catalysis of nickel in aqueous solution.

The reaction constants were separated by solving eq. 1 by successive approximations for points on the

$$\frac{1}{k_{\text{cat}}} = \frac{1 + K_a/[H^+]}{kK[M^{+2}]} + \frac{(K' + K)}{kK} \quad (1)$$

lines drawn through the data (e.g., Fig. 2). K_a is the second ionization constant of dimethylaloacetic acid, and $[M^{+2}]$ is the concentration of metal ion not complexed by the acid. It can be seen that a plot of k_{cat}^{-1} as a function of $[M^{+2}]^{-1}$ would give a linear plot having an intercept $(K' + K)/kK$ and a slope of $(1 + K_a/[H^+])/kK$. By choosing values for $(K' + K)$, $[M^{+2}]$ values were found from the equation

$$(K' + K) = \frac{[MS] + [MS']}{[M^{+2}][S^{-2}]} = \frac{M_T - [M^{+2}]}{[M^{+2}](S_T - [HS^-] - M_T - [M^{+2}])} \quad (2)$$

These $[M^{+2}]$ values were substituted into eq. 1, and from data plots (e.g., Fig. 2) an apparent value of

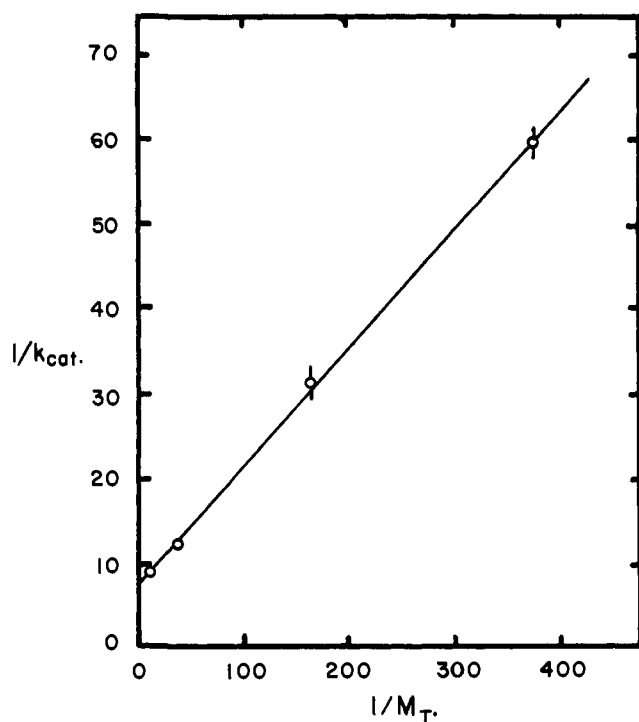


Fig. 2.—Dependence of catalytic rate constant on stoichiometric metal ion concentration; result of typical experiment, Ni^{+2} in H_2O .

$(K' + K)$ was found which was used in eq. 2 and the procedure repeated until a value of $(K' + K)$ was obtained which was equal to the one used. The constants thus derived for $(K' + K)$ and kK , respectively, were $95 M^{-1}$ and $11.8 \text{ min.}^{-1} M^{-1}$ for nickel at D. 78, $1.9 \times 10^3 M^{-1}$ and $3.9 \times 10^2 \text{ min.}^{-1} M^{-1}$ for nickel at D. 61, and $61 M^{-1}$ and $0.40 \text{ min.}^{-1} M^{-1}$ for manganese at D. 78. In the case of the experiments at D. 61 the assumption was made that the ratio of $[\text{S}^{-2}]$ to $[\text{HS}^{-}]$ was the same as in pure water. If anything, this ratio should decrease, making the values found for D. 61 lower limits.

TABLE II
RATE EFFECT OF ADDED DIOXANE

M_T	$k_{\text{cat}}, \text{min.}^{-1}$	M_T^{-1}	k_{cat}^{-1}
Nickel at D. 78			
0.178	0.1125 ± 0.0030	5.62	8.65–9.12
.0285	$.0816 \pm .0012$	35.1	12.1–12.5
.00618	$.0319 \pm .0026$	162	29.0–34.1
.00268	$.0165 \pm .0006$	373	58.5–62.8
Nickel at D. 61			
9.95×10^{-3}	0.181 ± 0.008	1.10×10^2	5.3–6.3
4.03	$.110 \pm .004$	2.48	8.8–9.4
1.16	$.0530 \pm .0015$	6.21	18.4–19.4
0.806	$.0277 \pm .0012$	12.4	34.6–37.7
Manganese at D. 78			
0.200	0.00585 ± 0.00067	5.0	153–193
0.0500	$.00440 \pm .00021$	20.0	217–239

The fact that data plots such as Fig. 2 involving the total metal concentration were straight lines indicated that the concentration of free metal must be proportional to that of total metal at a given dielectric constant. This could be shown mathematically to be true when either the metal or the acid were in great excess, and was found empirically to be true for intermediate concentrations as well.

At low dielectric constants, the catalysis exhibited signs of inhibition. A plot of k_{cat}^{-1} against M_T^{-1} at

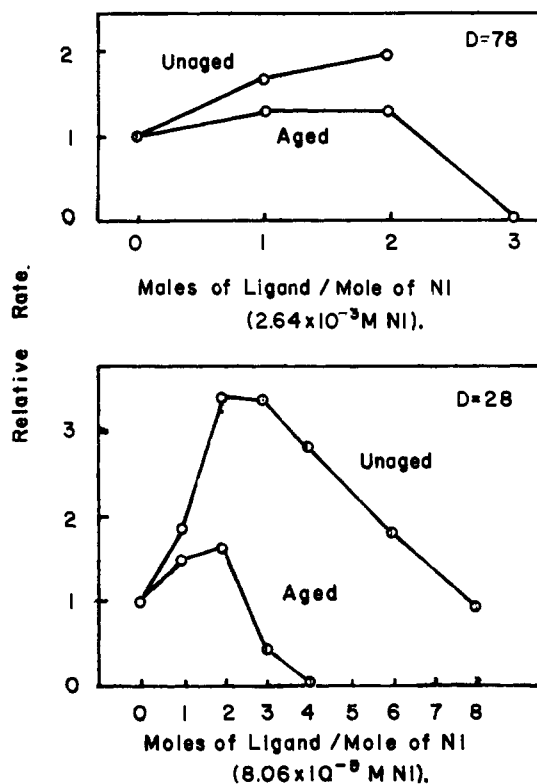


Fig. 3.—Effect of *o*-phenanthroline on nickel catalysis.

D. 14 was curved, indicating that the catalyst was becoming less efficient at high concentrations. Further, with decreasing dielectric constant, the catalysis rate of a constant concentration of metal ion reached a maximum, and then began to decrease. The data in Table III indicate that manganese reaches its maximum rate at a lower dielectric constant than nickel.

TABLE III

RATE DATA SHOWING MAXIMUM AT LOW DIELECTRIC CONSTANT

Metal	Concentration, M	Dielectric constant	$k_{\text{cat}}, \text{min.}^{-1}$
Ni	1.34×10^{-4}	14.0	0.35^a
		10.4	0.108 ± 0.002
		6.7	$.096 \pm .013$
		4.4	$.053 \pm .004$
Mn	1.0×10^{-3}	9.0	$.091 \pm .005$
		6.7	$.134 \pm .012$
		4.4	$.067 \pm .012$
		3.6	$.039 \pm .007$
		5.85×10^{-3}	3.6

^a Extrapolated from a plot of k_{cat}^{-1} against M_T^{-1} at D. 14.

The rates of reaction were also measured using a catalyst of metal ion coordinated with various ligands. These data are presented in Table IV. Numbers in the column headed Relative Rate are the rate constants divided by the rate constants for the reactions with the same concentration of metal ion, but no ligand. Ligands containing primary amine groups could not be used, since the amines themselves are effective catalysts. It was found that catalysts containing *o*-phenanthroline suffered from aging effects. Data are presented for fresh solutions and for solutions which had been allowed to age until they reached a steady catalysis rate (about 1 day). Figure 3 is a graph of relative rate of catalysis of $2.64 \times 10^{-3} M$ nickel at D. 78 and $8.06 \times 10^{-3} M$ nickel at D. 28 in the presence of various quantities of *o*-phenanthroline. Figure 4 is the same sort of graph for fresh *o*-phenanthroline-manganese catalysts at D. 78.

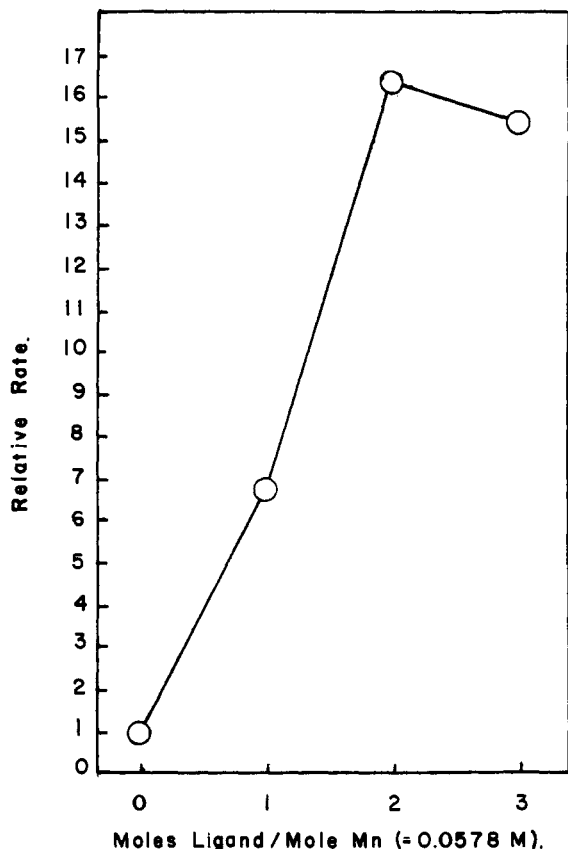


Fig. 4.—Effect of *o*-phenanthroline on manganese catalysis.

The enhancement of activity was for the catalyst containing 2 moles of *o*-phenanthroline per mole of metal ion. The variation in rate constant with catalyst concentration was determined in order to separate the reaction constants for this catalyst. Table V gives the data for reactions where the constants were separable.

The constants ($K' + K$) and kK (min.^{-1}), respectively, are 20.3 and 10.2 for nickel at D. 78, 660 and 248 for nickel at D. 61, and 10.7 and 1.65 for manganese at D. 78.

Discussion

Of the two methods used to enhance the catalytic decarboxylation by metal ions, lowering dielectric constant of the solvent and coordination of the metal ion, the second resembles much closer the action exerted by addition of enzyme protein. Whereas lowering the dielectric constant greatly increases the catalytic activity (by some three orders of magnitude), both Ni^{+2} and Mn^{+2} are enhanced to the same degree. On the other hand, coordination by *o*-phenanthroline enhances Mn^{+2} catalysis by a factor of more than 16 but that of Ni^{+2} by but a factor of 2. It should be noted that these enhancements and in fact the over-all rates are completely comparable to the rates which have been observed in the presence of enzyme.^{4,5} However, the rate in the absence of enzyme does not, even with lowered dielectric constant, increase by the many orders of magnitude estimated by Westheimer⁷ for a change in rate-limiting step for the enzyme system. The model system used here does not include the possibility of Schiff base formation.

In order to assess the roles played by lowered dielectric constant and by coordination, it is instructive to examine separately association constants (K) for formation of the metal-substrate complex and rate constants (k) for its rate of carboxylation. To do this it is necessary to set limits on the ratio of K' (formation

TABLE IV

Metal, $M \times 10^5$	D.	Moles of ligand per mole of metal ^a	RATE EFFECT OF ADDED LIGANDS		Relative rate
			k_{cat} , min.^{-1}	k_{cat} (no ligand)	
268 Ni	78	1 EDTA	0	0.0165	0
1000 Ni	78	1 HQ	0.0053	.0418	0.12 ± 0.02
4 Ni	28	1 HQ	.0145	.0337	.43 ± .02
261 Ni	78	1 tP	.0120	.0134	.90 ± .04
8.06 Ni	28	1 tP	.037	.067	.62 ± .02
264 Ni	78	1 Ph ^b	.0171	.0134	1.27 ± .06
264 Ni	78	1 Ph	.0220	.0134	1.64 ± .04
264 Ni	78	2 Ph ^b	.0170	.0134	1.26 ± .04
264 Ni	78	2 Ph	.0262	.0134	1.95 ± .25
264 Ni	78	3 Ph ^b	~0	.0134	0
8.06 Ni	28	1 Ph ^b	0.0910	.0598	1.52 ± .09
8.06 Ni	28	1 Ph	.1905	.0598	1.85 ± .05
8.06 Ni	28	2 Ph ^b	.0983	.0598	1.65 ± .19
8.06 Ni	28	2 Ph	.204	.0598	3.41 ± .28
8.06 Ni	28	3 Ph ^b	.0260	.0598	0.44 ± .04
8.06 Ni	28	3 Ph	.204	.0598	3.40 ± .08
8.06 Ni	28	4 Ph ^b	~0	.0598	0
8.06 Ni	28	4 Ph	0.172	.0598	2.88 ± .08
8.06 Ni	28	6 Ph	.1090	.0598	1.82 ± .06
8.06 Ni	28	8 Ph	.0539	.0598	0.90 ± .07
57.8 Mn	28	1 HQ	.0083	.0204	0.41 ± .02
5000 Mn	78	1 tP	.0306	.00440	6.95 ± .05
57.8 Mn	28	1 tP	.0314	.0204	1.54 ± .01
5780 Mn	78	1 Ph	.0255	.00379	6.72 ± .40
5780 Mn	78	2 Ph	.0621	.00379	16.4 ± .3
5780 Mn	78	3 Ph	.0584	.00379	15.4 ± .2
57.8 Mn	28	1 Ph ^c	.0525	.0204	2.6 ± .3

^a EDTA = ethylenediaminetetraacetic acid; HQ = 8-hydroxyquinoline-5-sulfonic acid; tP = 2,2',2''-terpyridyl; Ph = *o*-phenanthroline. ^b Aged solution. ^c Presumed to be one ligand going on each metal ion, but ligand in considerable excess.

TABLE V

M_T	k_{cat} , min.^{-1}	M_T^{-1}	k_{cat}^{-1}
Nickel at D. 78 (aged)			
5.39×10^{-2}	0.243 ± 0.022	18.5	3.74-4.52
2.16	.119 ± .004	46.3	8.14-8.69
0.720	.0437 ± .0005	139	22.6-23.1
0.288	.0188 ± .0014	347	49.5-57.5
Nickel at D. 61 (aged)			
7.20×10^{-3}	0.217 ± 0.005	139	4.51-4.72
3.46	.123 ± .006	289	7.75-8.55
1.73	.0706 ± .0027	579	13.6-14.7
0.864	.0326 ± .0009	1158	29.8-31.5
0.432	.0175 ± .0011	2310	53.7-61.0
Manganese at D. 78			
0.200	0.0954 ± 0.0045	5.0	10.0-11.0
0.050	.0429 ± .0034	20.0	21.6-25.3

constant of unreactive complex) to K (formation constant of reactive complex). If K' is set equal to zero, the highest possible K and lowest possible k result. Conversely, examination of model compounds for the two metal-substrate complexes (*e.g.*, succinates and pyruvates) suggests that K'/K will not be greater than 15, and assuming this value puts the opposite limits on k and K . Table VI gives the limiting values of the reaction constants, based on the assumptions mentioned above (see Results).

Where $K' = 0$ is assumed, the values of K are of the right order of magnitude for model complexes of this type (*e.g.*, pyruvate complexes have $K = 10^2$) but for $K'/K = 15$, the K found is considerably smaller than the values which would be predicted for it.

TABLE VI
 SEPARATION OF CONSTANTS

Metal	D.	M^{+2}		$M(Ph)_2^{+2}$	
		k , min. ⁻¹	K , M^{-1}	k , min. ⁻¹	K , M^{-1}
Letting $K' = 0$					
Mn	78	6.6×10^{-3}	61	0.15	11
Ni	78	0.124	95	0.50	20.3
Ni	61	0.21	1.9×10^3	0.38	6.6×10^2
Letting $K'/K = 15$					
Mn	78	0.098	4.1	2.3	0.73
Ni	78	1.9	6.3	7.6	1.35
Ni	61	3.0	1.3×10^2	5.6	44

From the limiting values given in Table VI it is seen that lowering of the solvent dielectric constant greatly enhances K , the catalyst-substrate association, but has little effect on k , its rate of decarboxylation. Conversely, the effect of coordination by *o*-phenanthroline has a small effect on K (decreases it slightly as expected from statistics) but in the case of Mn^{+2} , it greatly increases the rate constant k . The fact that k for Ni^{+2} is not so strongly affected suggests that the specific enhancement of Mn^{+2} by enzyme is the result not of just a lowered dielectric constant which would cause a stronger binding of the substrate, but to a specific coordination of the metal by the enzyme such as to greatly speed the decarboxylation of the bound substrate.

Not all ligands enhance the catalytic activity of metal ions. It is seen from Table IV that EDTA, for example, destroys the catalytic activity of Ni^{+2} . This is taken to mean that this ligand, by using all the coordination positions of Ni^{+2} , prevents direct binding to the substrate which is apparently necessary for reaction. Similar results are found for high concentrations of other ligands, even *o*-phenanthroline. Less

obvious is the low reactivity of 8-hydroxyquinoline-5-sulfonic acid complexes. A possible explanation arises from the fact that this negatively charged ligand lowers the effective charge of the metal ion, and it has been found previously that +1 ions do not have catalytic activity.³

The fact that addition of dioxane to the solvent increases the extent of association between positive ions and the substrate anion is easily rationalized in terms of lowered dielectric constant of the medium. The fact that the rate of decarboxylation of the metal ion-substrate complex is increased by the presence of ligands such as *o*-phenanthroline is more unexpected. Apparently, the presence of the *o*-phenanthroline causes an increase in the shift of electron density from the carbonyl oxygen of the dimethylaloacetate ion to the metal ion. The fact that *o*-phenanthroline is generally a better base than water makes this behavior somewhat difficult to understand. It could arise, however, if in the *o*-phenanthroline samples there is some back π -bonding from the metal to the *o*-phenanthroline ring system. This could allow the metal ion to have a higher effective charge when coordinated to *o*-phenanthroline than when coordinated to water. The larger enhancement of Mn^{+2} than of Ni^{+2} could then be accounted for in terms of the smaller nuclear charge of Mn^{+2} which should allow greater back donation. It also might be that there is a finite amount of π -bonding from any coordinated oxygen base to metal. As *o*-phenanthroline is substituted for coordinated water of hydration, the π -bonding from the coordinated oxygens of the substrate increases, thus enhancing the rate of decarboxylation. Whatever the explanation, the results are most suggestive of a type of binding between metal ions and the enzyme, similar to that between metal ions and *o*-phenanthroline, perhaps through appropriately located imidazole rings.

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Organogallium Compounds. IV. Exact Analysis of the Nuclear Magnetic Resonance Spectra of Trivinyl- and Tripropenylgallium-Trimethylamine Adducts^{1,2}

By D. MOY, J. P. OLIVER, AND M. T. EMERSON

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Tri-*iso*-, tri-*cis*-, and tri-*trans*-propenylgallium-trimethylamine derivatives were prepared from the respective dipropenylmercury compounds and gallium metal followed by addition of trimethylamine. The n.m.r. spectra show that these reactions all proceed with complete retention of configuration. Exact analyses of the n.m.r. spectra of these adducts and the trivinylgallium-trimethylamine derivative were carried out giving a consistent set of coupling constants and chemical shifts.

The interest in vinylmetallic compounds has increased rapidly since the discovery of the vinyl Grignard³ and the stereospecific reactions of vinyl lithium⁴ derivatives. This work has been extended to systems containing mercury and thallium by Nesmeyanov and others⁵ who have demonstrated that a number of metal exchange reactions occur with retention of configuration of the vinyl group. In addition, a considerable amount of work has been undertaken to elucidate the mechanisms of cleavage reactions and the stabilities of carbon-metal bonds.⁶ This work, however, has been carried

out primarily on compounds of group II and IV metals because of their stability, with little emphasis placed on compounds of group III except for boron.

Vinyl derivatives of the remaining group III metals have been reported but the work on these has been limited to studies without regard to stereochemistry except for thallium which does not have a stable metal-carbon-metal bridge bond. Thus, there have not been any reports on the stability of isomeric vinyl derivatives of aluminum or gallium. Furthermore, little information is available regarding the effect of the vinyl substituents on the electron density in the metal-carbon bond, although Ritter⁷ has shown by a molecular orbital calculation that this effect should be primarily inductive rather than mesomeric for trivinylborane; and indirect thermodynamic data⁸ has been

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