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Neighboring-Group Effects on the Rate of Metal Ion Catalyzed Decarboxylation of Dimethyloxaloacetic Acid[1]

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Some rates of the metal ion catalyzed reaction of dimethyloxaloacetic acid to give 2-oxo-3-methylbutanoic acid and carbon dioxide are reported. The catalysts are 1:1 complexes of 2-substituted 1,10-phenanthrolines with zinc(II) and manganese(II). In the complexes, the substituents are quite close to the metal ions and could affect the reaction rate by several modes of interaction with the metal or the substrate. The principal effect in zinc complexes is the result of the electron-donating power of the substituent. For manganese complexes, steric inhibition of the approach of the substrate to the metal ion seems to be more important. Some amine substituents are examined to see whether they may be able to react directly with the substrate. The syntheses for some new phenanthroline derivatives are reported.

Introduction

It has been shown that the decarboxylation of β-keto acids is catalyzed by metal ions,[2] that the catalytic abilities of some metal ions can be enhanced by coordinating them with 1,10-phenanthroline,[3] and that the enhancing ability of the phenanthroline is affected by substituents at positions remote (3 through 8 in Figure 1) from the site at which the metal ion is coordinated.[4] No study has yet been published of the effect of placing substituents at the 2 position (or the 2 and 9 positions) on the phenanthroline, where they can interact directly with the metal ion or with the substrate coordinated to it. The substituent could affect the catalysis by a number of interactions. (1) It could cause a change in the electron density at the metal ion by resonance or induction through the phenanthroline. For simplicity, this interaction will be referred to throughout the paper as the *electronic effect.* (2) It could cause crowding in the region around the metal ion and hinder the approach of the β-keto acid. This will be referred to as the *steric effect.* (3) It could coordinate with the metal ion and, in the case of a basic or negatively charged substituent, decrease the rate by lowering the apparent charge on the metal ion. (4) It could interact chemically with a substrate that is not coordinated to the metal ion. (Amines, in particular, are known to react readily with β-keto acids to form Schiff bases[5] and carbinolamines.[6]) (5) It could interact chemically in concert with the metal ion to decarboxylate the substrate.

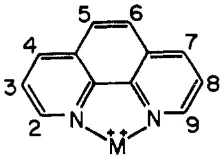

Figure 1.—The structure of 1,10-phenanthroline. The system of numbering is indicated.

The purpose of this research was to determine how a neighboring group influences the catalytic ability of a metal ion. Some metal–2-substituted-1-10-phenanthroline complexes, which have substituents near the metal ion, have been produced, and their catalytic abilities have been tested. On the basis of these data, an attempt was made to assess the relative importance of the steric and electronic effects of the 2-substituents. Interaction 3 (see above) was eliminated in these tests by restricting the size of the substituents. With one exception, no group was tested that was capable of being coordinated by a metal ion that was already bound to the phenanthroline nitrogens. The effect of interaction 4 was eliminated by appropriate rate corrections.

A particular interest of ours was to find a synthetic route to 2-amino-1,10-phenanthroline and to test its complexes. It seemed possible that these could promote rapid decarboxylation as the result of interaction 5. A mechanism may be written that combines the features of metal ion catalysis and aromatic amine catalysis.[6] These catalysts might be very effective in decarboxylating the substrate, first, because of possible reduced crowding in the catalyst–substrate complex and, second, because of the combined positive charges on the metal and nitrogen. Both metal ions[7] and amine groups[8] have been implicated in the very efficient decarboxylation of β-keto acids by metalloenzymes. Although no decarboxylase has been shown to have both a metal ion and an amine group at the active site, the mechanisms of these reactions are not well worked out, and the possibility cannot be dismissed.

Experimental Section

Chemicals.—The dimethyloxaloacetic acid, metal ion solutions, and buffers were prepared as previously described.[3,4] The following compounds were synthesized by procedures in the

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[1] Presented before the Division of Inorganic Chemistry, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

[2] L. O. Krampitz and C. H. Werkman, *Biochem. J.*, **35**, 595 (1941).

[3] J. V. Rund and R. A. Plane, *J. Am. Chem. Soc.*, **86**, 367 (1964).

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

[5] K. J. Pederson, *J. Phys. Chem.*, **38**, 559 (1934).

[6] R. W. Hay, *Australian J. Chem.*, **18**, 337 (1965).

[7] J. F. Speck, *J. Biol. Chem.*, **178**, 315 (1949).

[8] I. Fridovich and F. H. Westheimer, *J. Am. Chem. Soc.*, **84**, 3208 (1962).

Table I

Rate Constants for Catalysis by 1:1 Metal–Phenanthroline Complexes[a]

	Zinc(II)		Manganese(II)		Substituent constants[c]		
Substituent[b]	$10^5 k_{obsd}$, sec^{-1}	Normalized k_{cor}	$10^5 k_{obsd}$, sec^{-1}	Normalized k_{cor}	σ	σ^+	σ^*
CH_3[d]	4.96	~0	10.5	0.23	−0.34[e]	−0.62[e]	−0.20[e]
OC_6H_5	6.14	0.16	10.2	0.33	−0.32	−0.5	+0.85
CO_2^-	32.4	0.88	8.87	0.26	0.00	−0.02	. . .
H	36.5	1.00	21.6	1.00	0.00	0.00	0.00
Br	36.9	1.0	9.29	0.28	+0.23	+0.15	+1.00
$CO_2C_2H_5$	40.1	1.1	14.0	0.56	+0.45	+0.48	~+1
OCH_3	44.2	1.2	13.3	0.62	−0.27	−0.78	+0.52
CN	47.4	1.3	10.2	0.33	+0.66	+0.66	+1.30
Cl	59.4	1.8	14.1	0.57	+0.23	+0.11	+1.05
$CONH_2$	69.3	2.0	13.4	0.52	. . .	. . .	. . .

[a] Catalyst concentrations were 6.73×10^{-3} *M* for zinc and 16.7×10^{-3} *M* for manganese. [b] Substituents at the 2 position of 1,10-phenanthroline. [c] See ref 13. [d] 2,9-Dimethyl-1,10-phenanthroline. [e] Derived by doubling the constant for a single substituent.

literature: 2-chloro-1,10-phenanthroline (mp 130–130.5°, lit.[9] 129–130°); 2-cyano-1,10-phenanthroline (mp 233–235°, lit.[10] 233–234°); 2-carbonamide-1,10-phenanthroline, $C_{12}H_7N_2CONH_2$ (mp 302–303°, lit.[11] 304.5–305°, additional recrystallization did not change the melting point); 2-carboxy-1,10-phenanthroline (mp 210.5–211.5°, lit.[10] 209–210°). 2-Piperidino-1,10-phenanthroline was prepared by the method of Halcrow.[9] Because it is not a crystalline substance, it was converted to the dihydrobromide and recrystallized from ethanol. During the purification, some of the HBr was lost, giving a product with 1.87 mol of HBr/mol of phenanthroline. *Anal.* Calcd for $C_{12}H_7N_2NC_5H_{10} \cdot 1.87HBr$: C, 49.19; H, 4.55. Found: C, 49.19; H, 4.71. The compound was also characterized as the picrate (mp 213–215°, lit.[9] 213–217). 2-Diethylaminoethylamino-1,10-phenanthroline is also not crystalline[9] and was isolated as the dihydrobromide (upon being heated, the compound darkened at 185° and melted at 244°). *Anal.* Calcd for $C_{12}H_7N_2NHCH_2CH_2N(C_2H_5)_2 \cdot 2HBr$: C, 47.3; H, 5.27; N, 12.21. Found: C, 47.16; H, 5.32; N, 12.29. 2,9-Dimethyl-1,10-phenanthroline was purchased from the G. Frederick Smith Chemical Co. and used as obtained.

2-Bromo-1,10-phenanthroline.—1-Methyl-2-*o*-phenanthrolone[9] (9.0 g), PBr_3 (220 g), and $POBr_3$ (13.5 g) were heated with stirring at 120° for 16 hr. The PBr_3 was removed under reduced pressure. Ice was added to the residue, and the resulting solution was filtered. The crude product precipitated from the filtrate upon addition of ammonia. It was purified by recrystallization from water (decolorizing charcoal), followed by recrystallization from methanol. The yellow product had a melting point of 161–162°. *Anal.* Calcd for $C_{12}H_7N_2Br$: C, 55.6; H, 2.70; N, 10.80. Found: C, 55.59; H, 2.72; N, 10.85.

2-Carbethoxy-1,10-phenanthroline.—2-Cyano-1,10-phenanthroline (4 g), 95% ethanol (8 ml), and sulfuric acid (8 ml) were refluxed together for 5 hr. The solution was poured onto crushed ice, made basic with aqueous ammonia, and cooled. A tarry precipitate resulted, which was extracted with a few small portions of acetone until no more went into solution. After the extracts were combined and their volume reduced to half, water was added to precipitate the ester. It was purified by recrystallization from water–acetone, using decolorizing charcoal; mp 132–133°. *Anal.* Calcd for $C_{12}H_7N_2CO_2C_2H_5$: C, 71.4; H, 4.77; N, 11.11. Found: C, 71.46; H, 4.74; N, 10.93.

2-Methoxy-1,10-phenanthroline.—A solution of 2-chloro-1,10-phenanthroline (2.0 g) and sodium methoxide (2.0 g) in methanol (85 ml) was refluxed for 20 hr. Half of the solvent was pumped off, and the precipitated sodium chloride was filtered out. Water was added to the filtrate to precipitate the product. Two recrystallizations from water–ethanol produced the white monohydrate; mp 74–76°. *Anal.* Calcd for $C_{12}H_7N_2OCH_3 \cdot H_2O$: C, 68.5; H, 5.27; N, 12.28. Found: C, 68.48; H, 5.21; N, 12.41.

2-Phenoxy-1,10-phenanthroline.—An intimate mixture was made of 2-chloro-1,10-phenanthroline (8.3 g), phenol (12.2 g), and finely powdered KOH (4.4 g). The mixture was heated at 115° for 40 hr. A 100-ml sample of 20% KOH was added, and heating was continued for 1 hr more. After the mixture was cooled to room temperature, the solid was washed several times with water by decantation. It was recrystallized from water–ethanol and, after preliminary drying in air, heated to 110° for 1 hr; yield 8.4 g; mp 160–161°. *Anal.* Calcd for $C_{12}H_7N_2OC_6H_5$: C, 79.4; H, 4.44; N, 10.29. Found: C, 79.48; H, 4.38; N, 10.07.

2-Amino-1,10-phenanthroline.—A mixture of 2-phenoxy-1,10-phenanthroline (2.6 g) and NH_4Cl (15 g) was heated at 320–340° in a Wood's metal bath for 40 min. The resulting solid was treated with 50 ml of water and filtered. When aqueous ammonia (50 ml) was added to the filtrate, a resinous brown mass precipitated. The mixture was cooled in ice for 1 hr, and the liquid was decanted. The solid was dissolved in ethanol (50 ml), boiled with decolorizing charcoal, and filtered. After being dried with molecular sieves, the filtrate was saturated with HBr. The yellow dihydrobromide that precipitated was filtered out and dried under vacuum; mp 281°. *Anal.* Calcd for $C_{12}H_7N_2NH_2 \cdot 2HBr$: C, 40.4; H, 3.08; N, 11.76. Found: C, 40.52; H, 3.40; N, 11.46. When the above material sat under vacuum for 2 days at 100°, 1 mol of HBr was lost giving a yellow monohydrobromide; mp 302–304°. *Anal.* Calcd for $C_{12}H_7N_2NH_2 \cdot HBr$: C, 52.3; H, 3.62; N, 15.20. Found: C, 52.17; H, 3.42; N, 15.14.

Rates.—The reaction employed in this research was the decarboxylation of dimethyloxaloacetic acid, $HO_2CCOC(CH_3)_2CO_2H$, to give 2-oxo-3-methylbutanoic acid, $HO_2CCOCH(CH_3)_2$, catalyzed by various 1:1 metal–phenanthroline complexes. The reactants were thermostated at 25° and mixed in a sealed vessel equipped with a manometer.[3] The progress of the reaction was monitored by following the rise in pressure due to the carbon dioxide evolution. The rates of three to five reactions were measured at each set of conditions. The rate data followed first-order kinetics well. The values of the observed rate constant, k_{obsd}, in Table I are $(d \ln (P_\infty - P))/dt$, where P is the pressure at time t and P_∞ is the pressure at the end of the reaction. Standard deviations were generally less than 5%.

In order to calculate the corrected rate constant, k_{cor}, the concentrations of free metal ion, free substrate, and bis(phenanthroline)metal complex were calculated. For some phenanthrolines, the association constants with metal ions have not been measured and were estimated from the large body of published constants for other phenanthroline complexes.[12] The cor-

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(9) B. E. Halcrow and W. O. Kermack, *J. Chem. Soc.*, 155 (1964).

(10) E. J. Corey, A. L. Borror, and T. Foglia, *J. Org. Chem.*, **30**, 288 (1965).

(11) R. Breslow, R. Fairweather, and J. Keana, *J. Am. Chem. Soc.*, **89**, 2135 (1967).

(12) "Stability Constants of Metal Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964; H. Irving and D. H. Mellor, *J. Chem. Soc.*, 5222, 5237 (1962).

rections involving these constants were generally minor and could be made satisfactorily from approximate values. The rate constant due to free metal ion was read from the linear graph of $1/k$ *vs.* $1/[\mathrm{M}^{2+}]$ for the particular metal[3,4] and subtracted from k_{obsd}. In the same way, the rate constant for the autodecarboxylation of dimethyloxaloacetate was determined for the substrate in the presence of all of the reactants except the metal ion. An appropriate correction for the decarboxylation of the substrate that existed uncomplexed in solution was then applied to the reaction that contained the metal. Corrections for catalysis by bis(phenanthroline)metal catalysts were found to be insignificant.

An illustrative sample correction of k_{obsd} to k_{cor} will be made for a Zn^{2+}–phen catalyst. At $[\mathrm{Zn}^{2+}] = [\mathrm{phen}] = 7.00 \times 10^{-3}\ M$ and $[\mathrm{substrate}] = 7.81 \times 10^{-3}\ M$, the observed rate constant was $38.2 \times 10^{-5}\ \mathrm{sec}^{-1}$ (see Figure 2 for a plot of this run). The concentration of free metal ion was calculated to be $0.17 \times 10^{-3}\ M$ and contributed $1.15 \times 10^{-1}\ \mathrm{sec}^{-1}$ to the rate constant. Since the 2:1 metal–phenanthroline catalyst was virtually absent, the concentration of the 1:1 catalyst was $6.83 \times 10^{-3}\ M$. The amount of free substrate was $2.35 \times 10^{-3}\ M$ and contributed $1.36 \times 10^{-5}\ \mathrm{sec}^{-1}$ to k_{obsd}. When these contributons were removed, k_{cor} was obtained as $35.7 \times 10^{-5}\ \mathrm{sec}^{-1}$. Corrections for k_{obsd} in Table I are on file with the ASIS.[13]

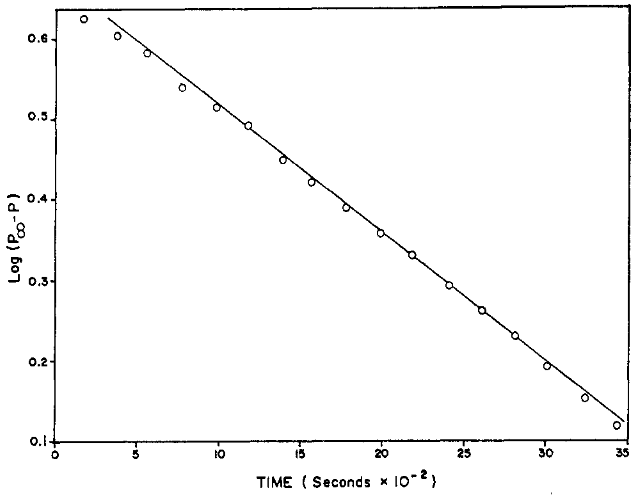

Figure 2.—Sample kinetic run for the decarboxylation of dimethyloxaloacetic acid by 1:1 Zn^{2+}–phen catalyst.

For each metal, the values of k_{cor} were all determined at the same concentration of 1:1 catalyst. This was done either by adjusting the initial concentrations of metal and phenanthroline to give that concentration of catalyst or by interpolating the linear plot of $1/k_{\mathrm{cor}}$ *vs.* $1/[\mathrm{catalyst}]$. The corrected rate constants were then divided by the rate constant for decarboxylation by 1:1 metal–phenanthroline (unsubstituted) catalyst at the same concentration to give "normalized k_{cor}" in Table I.

Molecular Models.—Models for the catalytic species were made from CPK atomic models purchased from the Ealing Corp. The scale of the models was 1.25 cm/Å.

Results and Discussion

Table I presents the catalytic rate constants for 1:1 phenanthroline–metal complexes. The observed rate constants, k_{obsd}, are the pseudo-first-order constants for the evolution of CO_2. The concentrations of 1:1 complexes were the same for all phenanthrolines. The rate constants k_{cor} were corrected for catalysis by metal-containing complexes other than the 1:1 catalysts and for autodecarboxylation of the substrate. The numbers in the table have been divided by k_{cor} for the unsubstituted phenanthroline catalyst for convenience. Also given in the table are the substituent constants σ, σ^+, and σ^*.[14] The first of these is the ordinary Hammett constant, quoted for a substituent in the *para* position on an aromatic ring. The substituent in this research was *ortho* to the phenanthroline nitrogen, which means that the parameter will somewhat overemphasize the resonance effects with respect to the inductive effects. The parameters σ^+ and σ^* may be considered to approximate division of σ into its resonance and inductive parts.

Catalysis by Zinc(II) Complexes.—The rate constants for zinc catalysts correlate fairly well with σ. Substituents which, compared to hydrogen, withdraw electron density from the nitrogens cause an increase in the rate, and those which donate electrons cause a decrease. This trend is in the expected direction, for the catalytic power of the metal ion depends on its positive charge, which in turn depends to some extent on the electron density of the nitrogens coordinated to it. Two anomalies are apparent in the table. The more pronounced is the rate produced by the methoxy substituent. Of the substituents, only two, methoxy and phenoxy, have the resonance and inductive parts of their electronic effects in opposing directions. The inductive withdrawal of electrons by the methoxy group seems to have outweighed the resonance donation in influencing the rate. As just explained, σ tends to overemphasize the resonance contribution, so that for this case it probably does not reflect the electronic effect of the substituent very well. From an electronic point of view, the methoxy and phenoxy groups should be similar. That the latter group causes an inhibition of the reaction must then be assigned to its steric effect. The other anomalous substituent is the chloro group, its rate being greater than would be predicted from σ. Chloride is a rather small substituent,[15] and its catalysis may not suffer as much from steric inhibition as does that of the cyano and carbethoxy derivatives. It is more likely that it is the bromo complex that is out of place. Some difficulty was encountered with the insolubility of this catalyst, which may have caused a decreased rate. It might be wondered whether groups like the carboxylate can coordinate to the metal ion when the latter is already bound to the phenanthroline nitrogens. We were not able to make a molecular model in which such bonding occurred. Goodwin and Silva[16] have isolated a number of metal complexes with the 1,10-phenanthroline-2-carboxylate anion. It is not possible to decide from the stoichiometry of the compounds whether the carboxylate is coordinated. On the basis of the shift

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[13] These data have been deposited as Document No. NAPS-00144 with the ASIS National Auxiliary Publication Service, c/o CCM Information Sciences, Inc., 22 W. 34th St., New York, N. Y. 10001. A copy may be secured by citing the document number and by remitting \$1.00 for microfiche or \$3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

[14] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963, pp 173, 204, 222.

[15] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, New York, N. Y., 1956, Chapter 13.

[16] H. A. Goodwin and R. N. Silva, *Australian J. Chem.*, **20**, 217 (1967).

in the antisymmetric COO^- stretching frequency, Goodwin and Silva concluded that it is. We have found, however, that a similar shift is produced merely by ionizing the group with base. Furthermore, coordination of a negatively charged group with the metal ion would be expected to inhibit strongly the catalysis of the decarboxylation of the acid.[3] We are of the opinion that the carboxylate is not coordinated in our catalyst.

Catalysis by Manganese(II) Complexes.—The most obvious feature of the catalysis by manganese–phenanthroline complexes is that all of the substituted ligands slow down the reaction. This suggests that a predominant role is played by the steric effect. Manganese is expected to be more sensitive to the steric effect than zinc because of its relatively small coordinating power. For example, the association constant between dimethyloxaloacetate and the 1:1 metal–phenanthroline complex is about 6 times as great for zinc as for manganese.[4] Anything that further decreases the already low affinity of the manganese for the substrate is likely to have a marked influence on the reaction rate. It does not seem possible to rationalize the rates for individual substituents with respect to either steric or electronic effects. The fastest catalysts do have electron-withdrawing substituents, but the pattern is far from clear.

Catalysis by Complexes Containing Amino Substituents.—For metal–2-amino-1,10-phenanthroline complexes, the normalized corrected rate constants under the conditions indicated in Table I were 2.3 for zinc and 1.9 for manganese. These catalysts were more effective than any containing nonamine substituents. Two explanations can be offered for the activating effect of this electron-donating substituent ($\sigma = -0.7$). First, the mechanism shown in Figure 3 could have been operative. If this had been so, the change in the mechanism produced a very undramatic change in the rate. Second, the amino group may have been protonated, in which case it would have been electron withdrawing instead of electron donating. Substituent constants are not available for the ammonium group but quaternary ammonium salts have σ values of about $+0.8$. The strong electron withdrawal would account for the rate of the zinc complex, and this in combination with the fairly small size of the substituent could probably explain the manganese rate as well. The explanation is corroborated by the results for the piperidino substituent, the constants for which were 1.8 for zinc and 0.51 for manganese. The concerted mechanism could not operate, because the nitrogen is tertiary, but the zinc rate was still large. Manganese would not be expected to have a large rate as well, because of the bulky nature of the substituent.

Some interesting results have been obtained for another amino-substituted phenanthroline, the diethylaminoethylamino derivative $C_{12}H_7N_2NHCH_2CH_2(C_2H_5)_2$. This ligand, which might give a concerted mechanism and which can occupy three coordination positions on the metal, had constants of 8.6 and 1.3 for zinc and manganese. The cause of its enhancement has not yet been determined, but this and similar ligands are presently being studied.

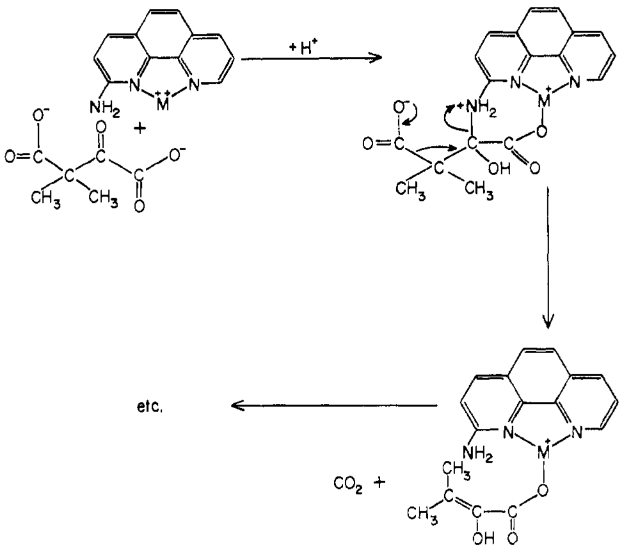

Figure 3.—Carbinolamine mechanism for the metal-catalyzed decarboxylation of dimethyloxaloacetic acid.

Conclusions

The rate of catalyzed decarboxylation of dimethyloxaloacetic acid seemed to be sensitive to both the steric and electronic influences of a group that is located near the site of reaction. The catalysis by a metal ion that complexed weakly with the substrate was consistent with the tendency of the substituent to hinder the approach of the substrate to the metal ion being the dominant effect. The electronic effect was more important for a metal ion which formed a stronger complex, although steric effects were still evident. In a single instance for which the steric effect was weak and the resonance and inductive contributions to the electronic effect were opposed, the inductive effect seemed to have the larger effect on the rate. The change in rate with the change in electron-withdrawing power of the substituent was in a direction that was explicable on the basis of a simple electrostatic model; electron withdrawal increased the charge on the metal ion, and this increased the rate. The trend was in marked contrast to that for the substituents at positions *para* to the nitrogens, for which electron-withdrawing groups were generally deactivating.[17] This had required an explanation based on the transition state for decarboxylation, whereas the present data seem understandable in terms of the substituent influences prior to the transition state.

The amino substituent, which was tested in the hope of finding a catalysis mechanism involving chemical reaction between the neighboring group and the substrate, gave rates that seemed to result from the same steric and electronic interactions that caused rate changes for nonreacting substituents. Certainly a supercatalyst for decarboxylation that resembled an

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[17] J. V. Rund and K. G. Claus, *Inorg. Chem.*, **7**, 860 (1968).

enzyme was not created. One particularly active catalyst was tested, but the mode of catalysis is not yet understood.

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The Fluorosulfuric Acid Solvent System. VI. Solutions of Phosphorus, Arsenic, Bismuth, and Niobium Pentafluorides and Titanium Tetrafluoride

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Conductivity measurements on solutions of PF_5, AsF_5, BiF_5, NbF_5, $PF_5–SO_3$, $NbF_5–SO_3$, and $AsF_5–SO_3$ are reported. Conductometric titrations have been carried out on solutions of AsF_5, BiF_5, and $AsF_5 \cdot SO_3$. The results are compared with those obtained previously for SbF_5 and $SbF_5–SO_3$. It is concluded that acid strength increases in the order: $PF_5 \sim NbF_5 < TiF_4 \sim AsF_5 < BiF_5 < AsF_4(SO_3F) < SbF_5 < AsF_2(SO_3F)_3 < SbF_2(SO_3F)_3$.

It was shown in part II[1] of this series that antimony pentafluoride is a rather weak acid of the fluorosulfuric acid solvent system ionizing according to the equation

$$SbF_5 + 2HSO_3F \longrightarrow H[SbF_5(SO_3F)] + HSO_3F \rightleftarrows H_2SO_3F^+ + SbF_5(SO_3F)^-$$

the acid $H[SbF_5(SO_3F)]$ having a dissociation constant $K = 3.7 \times 10^{-3}$ mol kg^{-1}. Although antimony pentafluoride is not fully ionized, these solutions have an extremely high acidity because of the rather high concentration of the fluorosulfuric acidium ion $H_2SO_3F^+$ and they have been extensively employed for studies of the protonation of very weak bases and for the formation of stable solutions of carbonium ions.[2] Because of the great utility of this medium for the production of new cationic species, it has been termed "magic acid" by Olah and his coworkers.[3] It was also shown in part II[1] that addition of sulfur trioxide to this system still further increases the acidity as SbF_5 is replaced by the fluorosulfates $SbF_4(SO_3F)$, $SbF_3(SO_3F)_2$, and $SbF_2(SO_3F)_3$ which increase in acid strength with increasing number of fluorosulfate groups. Indeed the trifluorosulfate $SbF_2(SO_3F)_3$ forms the strong acid $H[SbF_2(SO_3F)_4]$ in solution in fluorosulfuric acid which is fully ionized according to the equation

$$H[SbF_2(SO_3F)_4] + HSO_3F \longrightarrow SbF_2(SO_3F)_4^- + H_2SO_3F^+$$

Although this $HSO_3F–SbF_5–SO_3$ medium has not been nearly so extensively exploited as the "magic acid" ($HSO_3F–SbF_5$) it is certainly considerably more acidic, at least at low SbF_5 concentrations (0–0.3 *m* SbF_5). The object of the work described in this paper was to investigate the behavior of other fluorides, primarily pentafluorides, in fluorosulfuric acid, to see if they exhibit acid behavior and, in particular, to ascertain if any of them are stronger acids than SbF_5. The effect of sulfur trioxide on the acidity of some of the systems was also studied.

Experimental Section

Niobium Pentafluoride.—Technical grade Ozark-Mahoning material was purified by triple distillation under vacuum at 100–110°, mp 79–81°.

Bismuth Pentafluoride.—Bismuth trifluoride was fluorinated in a flow system at 500°.[4] The crude BiF_5 was purified by sublimation under vacuum in an apparatus made entirely of Vycor glass which is not attacked by BiF_5 at ~100°.

Phosphorus Pentafluoride.—Dry diazonium hexafluorophosphate (Phosfluogen A, Ozark Mahoning Co.) was thermally decomposed at 130° and the resulting PF_5 was purified by trap-to-trap distillation on a vacuum line.

Arsenic Pentafluoride.—The material obtained from a cylinder supplied by the Allied Chemical Co. was purified by trap-to-trap distillation on a vacuum line.

Titanium Tetrafluoride.—Pure material obtained from the Allied Chemical Co. and the Titanium Alloy Manufacturing Co. was used after rigorous drying.

Fluorosulfuric acid and sulfur trioxide were purified as described previously.[1,5] Conductivity measurements were made with the apparatus and technique described previously.[5]

Results and Discussion

The results of conductivity measurements on solutions of phosphorus, arsenic, bismuth, and niobium pentafluorides and titanium tetrafluoride are given in Table I and Figure 1. It may be seen in the figure that all of the fluorides give much smaller conductivities than SbF_5, and, therefore, if they behave as acids at all, they are clearly considerably weaker than antimony pentafluoride. Niobium and phosphorus pentafluorides give an almost negligible increase in the conductivity and must therefore be essentially nonelectrolytes. Arsenic and bismuth pertafluorides and titanium tetrafluoride all cause a rather similar small increase in the

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