

yielded the usual mixture; the identity of amines prepared from either the pure compound or mixtures; and the deamination of the amines to the less common of the original compounds.

The absorption of ammonia is typical of cobalt(II) compounds.⁷ The metastable compound observed in the low pressure region—possibly a second form of the diammine—probably is responsible for the lack of sharpness in the break between the diammine and hexammine in Fig. 1. Its disappearance (patterns D, E, and F) may be simple aging or an irradiation-accelerated process. The hexammine is formulated as $[\text{Co}(\text{NH}_3)_6](\text{N}_3)_2$ (instead of, for instance, $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2 \cdot 2\text{NH}_3$) on the basis of the ammonia absorption studies and the known structure of the hexamminecobalt(II) halides.⁸

The products of the thermal decomposition of $[\text{Co}(\text{NH}_3)_6](\text{N}_3)_3$ are clearly linked to the

(7) "Gmelins Handbuch der anorganischen Chemie, System Number 58: Kobalt, Teil B: Die Ammine des Kobalts," Verlag Chemie, Berlin, 1930, p. 9f.

(8) R. W. Parry, *Chem. Rev.*, **46**, 507 (1950).

cobalt(II) azide system by the ability of the diammine to absorb ammonia and form the customary hexammine. The relation of the sharpness of the powder pattern and the physical appearance of the diammine to ammonia pressure suggests that the reaction initially produces a finely divided compound with higher pressures favoring the growth of crystals. The tetrammine formed by decomposition persists at room temperature; however, the absence of a corresponding plateau in Fig. 1 or X-ray evidence from the cobalt(II) azide preparations indicates instability at the lower temperatures. It probably is more sensitive than the diammine since decompositions at 140° producing the tetrammine exploded (Fig. 3), while the diammine was formed without difficulty. The unknown compound appears in runs with the stoichiometry of eq. 1 and thus may be still another form of the diammine. However, since it is observed in mixtures, usually in small amounts judging by powder pattern intensities, a certain identification is not now possible.

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A Potentiometric Study of the Reaction between Halides and Divalent Zinc, Cadmium, Mercury, and Lead in Glacial Acetic Acid

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Bivalent zinc, cadmium, mercury, and lead acetates react with potassium halides in glacial acetic acid to form MX_2 as the predominant species in solution. Only in the reaction between cadmium(II) and potassium bromide is there evidence of fourfold coordination of the metal. The potential difference of the glass-calomel electrode pair as a function of concentration of solution was used to determine the dissociation constants for the soluble reactant metal acetates. The order of decreasing dissociation of the acetates is $\text{Cd} > \text{Pb} \gg \text{Hg}$. The molar solubilities of the slightly soluble halides of cadmium and lead follow an order of increasing solubility in acetic acid with increasing molecular weight.

The divalent metals of periodic group IIB, possessing complete electronic d-levels, exhibit coordination numbers of two, three, four, and six with ligands in aqueous solutions, and covalently bonded weak electrolytes may be formed. The polarographic behavior of divalent zinc, cadmium, and mercury in acetonitrile as a solvent indicates that the most stable metal halide complexes are identical to those found in aqueous solutions.¹

(The dielectric constant of acetonitrile is 38 at 25°.) However, in glacial acetic acid as the solvent, the reaction of mercury(II) with halides forms non-ionic HgX_2 as the predominant species.² No clear potentiometric evidence has been found for tetrahedral complexes with halides, although the solvate, $\text{HgCl}_2 \cdot 2\text{HOAc}$, reported by Davidson and Chappell may have such a structure.³ Sol-

(1) I. M. Kolthoff and J. Coetzee, *J. Am. Chem. Soc.*, **79**, 870 (1957).

(2) O. W. Kolling, *ibid.*, **79**, 2717 (1957).

(3) A. W. Davidson and W. Chappell, *ibid.*, **60**, 2043 (1938).

vates have not been obtained with HgBr_2 or HgI_2 . Davidson and McAllister demonstrated the amphoteric character of zinc acetate in glacial acetic acid and isolated a solvated sodium zinc acetate with an empirical formula of $\text{Na}_2\text{Zn}(\text{OAc})_4$.⁴

In the present study, the reactions of glacial acetic acid solutions of divalent zinc, cadmium, mercury, and lead acetates with hydrochloric acid and potassium chloride, bromide, and iodide were investigated potentiometrically, by means of the glass-calomel electrode pair. The stoichiometry of each reaction was determined by volumetric methods. Over-all dissociation constants for the reactant metal acetates were calculated from the measured e.m.f. values of the electrode pair in contact with solutions of known composition. The quantitative solubilities at 25° of all slightly soluble products of the reactions were determined gravimetrically.

Experimental Details

All chemicals for this study were reagent grade quality and were used without additional purification. The glacial acetic acid contained 0.009% water, as determined by Karl Fischer titration, and since water present in amounts less than 0.4% is without effect upon potentiometric measurements,⁵ the glacial acetic acid was used without added treatment.

Preparation of Solutions in Glacial Acetic Acid.—Standard solutions of 0.0834 *M* perchloric acid and 0.00784 *M* hydrochloric acid in glacial acetic acid were prepared and potentiometrically standardized as described earlier.²

The 0.100 *M* solutions of sodium salicylate and potassium acid phthalate, and the 0.010 *M* solutions of potassium halides, were prepared from finely ground and dried (110°) samples of the salts. Potassium iodide solutions were prepared immediately prior to their use, because of the rather rapid release of the triiodide in acetic acid media. Approximately 0.01 *M* solutions of the acetates of cadmium, mercury, and lead were made by dissolving the crystalline hydrates in glacial acetic acid containing sufficient acetic anhydride to consume the water present in the solutes. Each acetate solution was standardized potentiometrically against perchloric acid. All stock solutions and dilutions from these were thermostated at 25.0 ± 0.1°.

Volumetric Methods in Glacial Acetic Acid.—All titrations were performed potentiometrically with the Beckman Model H-2 pH meter, equipped with the usual glass and calomel electrodes.

Direct titrations of 5.00-ml. aliquots of the acetates of lead, mercury, and cadmium in 10 ml. of solvent were attempted with solutions of hydrochloric acid and with the potassium halides (chloride, bromide, and iodide). Indirect titrations were made by adding to aliquots of the

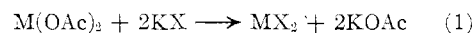
metal acetate solution known excesses of the potassium halide salt solution, and then titrating the released potassium acetate with standard perchloric acid. Portions of the insoluble zinc acetate were placed in 25-ml. aliquots of the potassium halide solution and warmed at 60° until solution was complete. The solution was cooled immediately and the released potassium acetate titrated with perchloric acid. (Prolonged heating at or near the boiling point of acetic acid was avoided to prevent significant solvolysis of the potassium halide solution.) All titration equivalence points were determined from the second derivative of potential difference with respect to volume increment.

Potential Difference-Dilution Measurements.—The procedure for measurement of the potential difference between the glass-calomel electrode pair as a function of the solution concentration in acetic acid was that used by Higuchi, Danguilan, and Cooper.⁶ The e.m.f. for a 0.100 *M* sodium salicylate reference solution was measured before and after each unknown solution, with a resulting over-all precision of ±1.5 mv. in these measurements. Measurements made on the reference solution with three different glass electrodes did not vary by more than 2 mv. in absolute magnitude, thereby suggesting a greater reproducibility of potential values for the glass-calomel electrode pair than usually is assumed.

Solubility Determinations.—Anhydrous chlorides, bromides, and iodides of cadmium and lead were prepared in glacial acetic acid by allowing stoichiometric amounts of the metal acetate to react with the corresponding potassium halide. A 2.0×10^{-4} mole portion of solid was suspended in 100 ml. of glacial acetic acid at a temperature of 25 ± 0.1°. After intermittent shaking for three days, the undissolved precipitate was filtered on fine porosity, tared filter crucibles, washed with solvent, and dried at 100° for 30 min. The solubility was computed as the difference between the amount of solid suspended in the initial volume of solvent and the amount remaining undissolved after three days. Six determinations were made on each halide.

Results and Discussion

Mole Ratios of Reactants.—The stoichiometry of the reaction between the divalent metal acetate and the potassium halides was determined by both direct and indirect potentiometric titrations with solutions of hydrochloric acid and the potassium halides.



Only the acetates of cadmium and mercury can be titrated directly with hydrochloric acid. No inflection point was observed in the attempted titration of lead acetate with the same titrant, and zinc acetate is too insoluble to permit direct titration. (Slow titrations of stirred suspensions of zinc acetate during 2–4 hr. intervals were not successful.)

(4) A. W. Davidson and W. McAllister, *J. Am. Chem. Soc.*, **52**, 519 (1930).

(5) O. W. Kolling, *Trans. Kansas Acad. Sci.*, **59**, 422 (1956).

(6) T. Higuchi, M. Danguilan, and A. Cooper, *J. Phys. Chem.*, **58**, 1167 (1954).

Indirect titrations were made by adding potassium halides to the metal acetates in mole ratios up to a maximum of 8:1 for KX to $M(OAc)_2$. In each case the released potassium acetate corresponded to that given in eq. 1, in which the mole ratio of potassium chloride, bromide, and iodide to divalent metal is 2:1. The chloride and bromide of cadmium and the lead halides precipitate as insoluble products during the reaction.

Since it has been observed that mercury(II) acetate can be titrated directly with potassium halides,² the analogous titration was attempted with the acetates of cadmium and lead. No potentiometric inflection occurred for lead acetate. For cadmium, an equivalence point at the ratio of 1:2 for $Cd:X$ was found with potassium chloride and iodide as titrants. However, the reaction of bromide with cadmium gave two inflections, the first at the 1:2 ratio for insoluble $CdBr_2$, and a second at a ratio of 1:4 for a soluble product, presumably K_2CdBr_4 . In contrast to the corresponding titrations with mercury(II), the total magnitude of the inflection in the titration of cadmium(II) with the potassium halides is small, ranging from 10 to 15 mv. That for the second bromide equivalence point is only 5 mv. These small changes indicate that the base strengths of potassium acetate and cadmium acetate differ very little in glacial acetic acid, whereas potassium acetate is a much stronger base than mercury(II) acetate in the same solvent. The recent study of Raman spectra of cadmium bromide complexes has shown that $CdBr_4^{-2}$ species predominate in methanol and acetone solutions.⁷

Base Strengths from E.m.f. vs. Concentration.—The glass-calomel electrode pair, functioning as a concentration cell, demonstrates the qualitative acid-base behavior of solutes in glacial acetic acid.⁸ The appropriate form of the Nernst equation for solutions of bases, as derived by Bruckenstein and Kolthoff,⁸ is shown in eq. 2.

$$E_B = E^0 + \frac{RT}{F} \ln K_s - \frac{RT}{2F} \ln C_B K_B \quad (2)$$

Here, C_B is the concentration of the base, K_s the autoprotolysis constant of the solvent, and K_B the over-all dissociation constant of the base. If the potential difference of the cell is plotted as a function of $\log C_B$, a linear graph is obtained. Such plots are shown in Fig. 1 for the soluble bases used in this study. For the acetates of

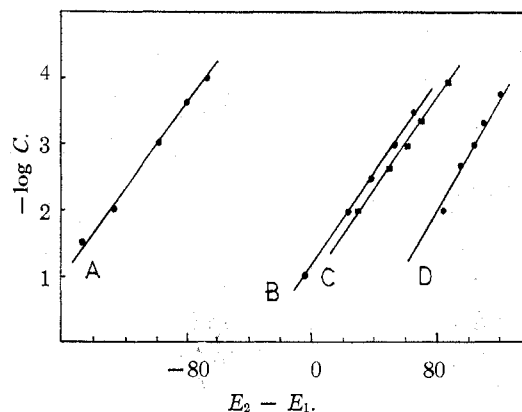


Fig. 1.—Effect of solution concentration (molarity) on potential difference between the glass-calomel electrode pair in glacial acetic acid at 25°. E_1 is the e.m.f. (in mv.) for the reference solution (sodium salicylate) and E_2 is that for the unknown solution. The curves are: (A) $Hg(OAc)_2$; (B) $NaOAc$; (C) $Pb(OAc)_2$; (D) $Cd(OAc)_2$.

lead, cadmium, and mercury, the e.m.f. of the cell follows the predicted 0.0295 v. decrease for each tenfold increase in concentration of base. Likewise, the slope conforms to the behavior of the bases as 1-1 weak electrolytes, according to eq. 3. The order of decreasing strength as bases is $Cd > Pb \gg Hg$.



Equation 2 also may be used for determining the comparative strengths of pairs of acetates. If bases 1 and 2 are compared, and their corresponding e.m.f. values, concentrations, and dissociation constants are designated by the added subscripts 1 and 2, eq. 4 may be easily derived.

$$\frac{2F}{RT}(E_{B_1} - E_{B_2}) = \ln C_{B_2} K_{B_2} - \ln C_{B_1} K_{B_1} \quad (4)$$

If solutions are prepared so that $C_{B_2} = C_{B_1}$, then eq. 5 follows, and pK_{B_1} can be calculated by comparison to a standard reference base.

$$\frac{2F}{RT}(E_{B_1} - E_{B_2}) = pK_{B_1} - pK_{B_2} \quad (5)$$

In Table I the values for the dissociation constants for the reactant bases are given. Since a

TABLE I
DISSOCIATION CONSTANTS FOR REACTANT BASES AT 25°

Compound (0.001 M)	$E_2 - E_1$, mv. ^a	$M(OAc)_2$ pK_B in HOAc	$M(OH)^+$ pK_B in H_2O
Sodium acetate	57	6.58 ± 0.02	...
Cadmium acetate	104	5.02 ± 0.05	5.0
Mercuric acetate	-105	12.0 ± 0.1	10.3
Lead acetate	64	6.35 ± 0.06	6.2

^a $E_2 - E_1$ has the same meaning as in Fig. 1.

(7) W. Yellin and R. Plane, *J. Am. Chem. Soc.*, **83**, 2448 (1961).

(8) S. Bruckenstein and I. M. Kolthoff, *ibid.*, **78**, 2975 (1956).

reliable constant for sodium acetate has been determined from both spectrophotometric and potentiometric methods,⁸ this solute was selected as the reference base. The solute concentration of 0.001 *M* was selected as a suitable level, because measured e.m.f. values are more precise than at lower molarities and yet solutions are sufficiently dilute for the Nernst equation to be valid as expressed in concentration units. The pK_B values for the bases in water solutions were calculated from the literature values for the first acid ionization constants (K_A conj.) as summarized by Basolo and Pearson.⁹ The same general trend in the dissociation of the M:O bond is observed in the pK_B values for the three solvo bases in aqueous media as is found for the acetates in acetic acid. The constants for the acetates in acetic acid parallel the dilution plots, and indicate that cadmium acetate is a stronger base than lead acetate, while mercuric acetate is a weaker base than urea in glacial acetic acid.

Solubilities of Slightly Soluble Products.—

The molar solubilities of the three halides of lead and the two halides of cadmium at 25° are listed in Table II. For both metals, it will be noted

TABLE II
SOLUBILITY VALUES FOR SLIGHTLY SOLUBLE METAL HALIDES

Compound	Molar solubility	
	in HOAc (25°)	in H ₂ O (20°) ^a
Cadmium chloride	$4.3 (\pm 0.1) \times 10^{-5}$	
Cadmium bromide	$1.07 (\pm 0.05) \times 10^{-4}$	
Lead chloride	$1.2 (\pm 0.1) \times 10^{-5}$	3.6×10^{-2}
Lead bromide	$1.3 (\pm 0.1) \times 10^{-5}$	2.3×10^{-2}
Lead iodide	$5.5 (\pm 0.1) \times 10^{-5}$	1.4×10^{-3}

^a Calculated solubility based upon values given by M. Sneed and R. Brasted, "Comprehensive Inorganic Chemistry," D. Van Nostrand Co., Princeton, N. J., 1958, vol. 7, p. 241.

that solubility in glacial acetic acid increases with increasing molecular weight of the solute, in contrast to aqueous solutions in which the corresponding solutes show decreasing solubility with increasing molecular weight.

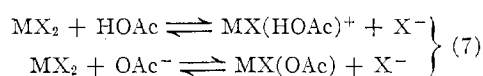
Conclusions

In glacial acetic acid the acetates of divalent cadmium, mercury, and lead dissociate as 1-1 weak electrolytes, yielding MOAc⁺ and OAc⁻ ions, just as is observed in aqueous and methanolic

solutions.¹⁰ The results of isotopic exchange studies on lead(II) acetate in acetic acid have been explained in terms of PbOAc⁺ and Pb(OAc)₃⁻ ions.¹¹ The dissociation constants of the acetates in acetic acid follow the "natural order" of relative stabilities for bivalent metals in aqueous systems, namely: Hg ≫ Pb > Cd.¹²

In the reaction of divalent zinc, cadmium, mercury, and lead with alkali halides in acetic acid the metals show a stoichiometric ratio of 1:2. Only in the case of cadmium is there evidence for fourfold coordination of halide ion as CdBr₄⁻². Although experimental support has been reported for the formation of the tetrahedral ions HgCl₄⁻², CdCl₄⁻², and ZnCl₄⁻² in water solutions,¹³ no potentiometrically detectable amounts of these complexes occur in 0.01 *M* solutions in glacial acetic acid. Studies on the ionization of HgX₂ in dioxane as a solvent have shown no evidence for HgCl₄⁻².¹⁴ However, the ZnCl₄⁻² ion has been postulated for acetic acid solutions of zinc chloride in the presence of hydrochloric acid at the 1-2 *M* level, in order to explain abnormalities in acidity measurements with indicators.¹⁵ The solvates isolated in the solid state studies of Davidson and co-workers^{3,4} suggest that weak complexes with fourfold coordination for zinc and mercury may occur in acetic acid.

The order of increasing molar solubility with increasing molecular weights for the lead and cadmium halides in acetic acid is the reverse of the trend found in aqueous systems. Since other investigators have isolated solvated zinc acetate, and evidence for coordination numbers greater than two has been found for divalent lead and cadmium in acetic acid, the representative equilibria in eq. 6 and 7 may be formulated to account for the observed trend in solubility that occurs for halides of a given metal.



An increase in radius of the halide with increasing atomic number would be expected to have an adverse steric effect upon the reaction in eq. 6,

(10) E. Allen, J. Cartledge, M. Taylor, and C. Tipper, *J. Phys. Chem.*, **63**, 1442 (1959).

(11) E. Evans, J. Huston, and T. Norris, *J. Am. Chem. Soc.*, **74**, 4985 (1952).

(12) F. Basolo and R. Pearson, reference 9, p. 16.

(13) C. Van Eck, *et al.*, *Rec. trav. chim.*, **75**, 802 (1956); L. Woodward and A. Nord, *J. Chem. Soc.*, 3721 (1956).

(14) R. Dessy and Y. Lee, *J. Am. Chem. Soc.*, **82**, 689 (1960).

(15) D. Satchell, *J. Chem. Soc.*, 1916 (1958).

(9) F. Basolo and R. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 387.

in which the metal assumes a higher coordination number without an accompanying dissociation of the solvate into ions. On the other hand, the polarity of the Cd-X and Pb-X bonds decreases with the decreasing electronegativity (and increasing radius) of the halide; this makes the base displacement (eq. 7) of the halide by HOAc

(or by OAc^- from the solvent) become easier with increasing atomic number of the halide. The well known order of decreasing base strength of the halides, *i.e.*, $\text{Cl}^- > \text{Br}^- > \text{I}^-$ in glacial acetic acid, makes the influence of base displacement upon the solubility the more probable mechanism.

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Selenocyanate Complexes of Cobalt(II)

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The preparation and characterization of seven selenocyanate complexes of Co(II) are described. It is shown that the compounds $[(\text{CH}_3)_4\text{N}]_2[\text{Co}(\text{NCSe})_4]$ and $[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{Co}(\text{NCSe})_4]$ have the structures implied by the formulas as written. The $[\text{Co}(\text{NCSe})_4]^{2-}$ ion has four N atoms tetrahedrally arranged about Co(II) and it is shown from the spectra and magnetic moments that $-\text{NCSe}$ is very close to but slightly stronger than $-\text{NCS}$ in the spectrochemical series. $\text{HgCo}(\text{NCSe})_4$ is shown by X-ray study to be isomorphous with $\text{HgCo}(\text{NCS})_4$ and it is found that the attachment of Hg to the selenium atoms has the effect of somewhat increasing the strength of the ligand field at the Co, as was the case in the analogous NCS complex. $\text{Co}[(\text{C}_6\text{H}_5)_2\text{PO}]_2(\text{NCSe})_2$ and $\text{Co}(\text{C}_9\text{H}_7\text{N})_2(\text{NCSe})_2$ are also tetrahedral. With pyridine the octahedral complex $\text{Co}(\text{py})_4(\text{NCSe})_2$ has been obtained and is isomorphous with $\text{Co}(\text{py})_4(\text{NCS})_2$, which is known to have a *trans*-octahedral structure. $\text{Co}[(\text{C}_6\text{H}_5)_2\text{P}]_2(\text{NCSe})_2$ has a magnetic moment per Co of only 3.4 B.M. and it is proposed that it has a structure containing equal numbers of octahedrally coordinated, low spin Co(II) ions and tetrahedrally coordinated, high-spin Co(II) ions. The CN stretching frequencies of these complexes also are reported. It appears that the variations parallel those known for the thiocyanate ions, $-\text{NCSe}^-$ groups absorbing in the range 2040–2080 cm^{-1} and bridging, *i.e.*, $-\text{NCSe}^-$ groups absorbing at frequencies well over 2100 cm^{-1} .

Introduction

In view of the results recently reported from this Laboratory on thiocyanate complexes of cobalt(II),² it seemed appropriate to explore the possibility of making their selenocyanate analogs. This paper reports the preparation and properties of seven such compounds. Recently, preliminary communications from other laboratories³ have described several compounds in this class. Turco, *et al.*, reported the isolation and partial characterization of one compound containing the $[\text{Co}(\text{NCSe})_4]^{2-}$ ion and indicated the existence of $\text{HgCo}(\text{NCSe})_4$. Nelson has reported the compounds $\text{Co}(\text{py})_2(\text{NCSe})_2$ and $\text{Co}(\text{py})_4(\text{NCSe})_2$.

(1) (a) Alfred P. Sloan Foundation Fellow; (b) National Science Foundation Predoctoral Fellow.

(2) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Am. Chem. Soc.*, **83**, 4157 (1961).

(3) (a) A. Turco, C. Pecile, and M. Niccolini, *Proc. Chem. Soc.*, 213 (1961); (b) S. M. Nelson, *ibid.*, 372 (1961).

Experimental

Preparation of Compounds.—Potassium selenocyanate was prepared by the method of "Inorganic Syntheses."⁴

$\text{Co}(\text{C}_6\text{H}_5\text{N})_4(\text{NCSe})_2$.—A solution of Co(II) selenocyanate (0.01 mole) in absolute ethanol (50 ml.) was prepared by mixing stoichiometric quantities of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and KNCS and filtering the precipitated KNO_3 . This solution was treated with 3.3 ml. (3.2 g., 0.04 mole) of pyridine and the resulting tan precipitate was filtered, washed with ethyl ether, and dried *in vacuo* over silica gel; yield, 4.8 g. (82%).

$[(\text{CH}_3)_4\text{N}]_2[\text{Co}(\text{NCSe})_4]$.—A solution of Co(II) selenocyanate (0.01 mole) was prepared as above. A solution of $[(\text{CH}_3)_4\text{N}]\text{NCSe}$ was prepared by dissolving $(\text{CH}_3)_4\text{NCl}$ (2.2 g., 0.02 mole) in 40 ml. of hot absolute ethanol, adding a solution of KNCS (3.2 g., 0.02 mole) in 15 ml. of absolute ethanol, and filtering the warm solution. The solution of $[(\text{CH}_3)_4\text{N}](\text{NCSe})$ was added to the cobalt selenocyanate solution and the precipitate, which appeared promptly, was filtered, washed with ethanol and

(4) W. C. Fernelius, Ed., "Inorganic Syntheses," Vol. 2, McGraw-Hill Book Co., New York, N. Y., 1946, p. 186.