TABLE I

FORMATION CONSTANTS OF $(H_2NCH_2)_2CHOH$ WITH VARIOUS METALS IN 1.0 M KNO_3 SOLUTION

Values for $(H_2NCH_2)_2CH_2$ and $(H_2NCH_2)_2C(CH_3)_2$ included for comparison.

	$(H_2NCH_2)_2CHOH$		$(H_2NCH_2)_2CH_2$[6]		$(H_2NCH_2)_2C(CH_3)_2$[6]	
	log K_1	log K_2	log K_1	log K_2	log K_1	log K_2
H^+, 0°	10.65	9.14	11.60	9.95	11.22	9.07
30°	9.68	8.23	10.54	8.95	10.22	8.18
50°	9.11	7.69	9.92	8.38	9.65	7.55
Ag^{++}, 30°	5.80				4.66	
Co^{++}, 30°	3.90	3.24			4.88	3.07
Ni^{++}, 0°	6.19	4.88	7.00	4.92	7.22	4.99
30°	5.64	4.38			6.59	4.41
50°	5.37	4.01			6.23	4.15
Zn^{++}, 30°	4.60	4.42			5.21	5.20

stants are those given by Carlson, McReynolds and Verhoek.[5] The calculated constants are given in Table I.

1,3-Diamino-2-propanol is a somewhat weaker base than either 1,3-diaminopropane or 2,2-dimethyl-1,3-propanediamine. The complete agreement in the N values for all three amines (except for Cu^{++}) indicates that the –OH group is not active in coördination. The complexes of 1,3-diamino-2-propanol with Co^{++}, Ni^{++} and Zn^{++} are less stable than those of 2,2-dimethyl-1,3-diaminopropane with the same ions. Similarly, the Ni^{++} complexes are less stable than those of 1,3-diaminopropane. The system Cu^{++}–1,3-diamino-2-propanol is anomalous in that $\bar{n}$ reaches a maximum value of 1.5.

(5) C. A. Carlson, J. P. McReynolds and F. H. Verhoek, THIS JOURNAL, **67**, 1334 (1945).

(6) G. B. Hares, W. C. Fernelius and B. E. Douglas, *ibid.*, accepted.

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The Preparation of *cis*- and of *trans*-Dichloro-bis-*l*-propylenediaminecobalt(III) Chloride[1,2]

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The preparation of *cis*- and of *trans*-dichloro-bis-*l*-propylenediaminecobalt(III) chloride was first reported by Werner and Fröhlich.[3] This method was later modified by Bailar and co-workers.[4] We wish to report a semi-micro preparation which is a further modification of the original procedure. By making a careful study of the acidity requirements and of the procedure for oxidizing cobalt(II) to cobalt(III) the time required has been greatly diminished and the product is obtained without difficulty. The original method often yielded a product which could not readily be converted from *trans* to *cis*, possibly because of a residual acid condition; consequently the product was of questionable purity. The ready conversion from *trans* to *cis* has been considered a good index of purity. Use of 30% H_2O_2 cuts down the original 16 hours of aeration time to about 10 minutes. The original method gave yields from 35 to 45%. This method gives yields of from 45 to 55%.

Experimental

Preparation of the *trans* Form.—A flask containing 3.8 ml. of *l*-propylenediamine (resolved by the method of Baumann[5] as modified by Bailar and co-workers[4] and further modified by Jonassen[6]) and 4.76 g. of $CoCl_2 \cdot 6H_2O$ was immersed in an ice-bath. While swirling the solution in the reaction vessel 3 ml. of 30% H_2O_2 was added cautiously. On removal from the ice-bath, 25 ml. of concd. HCl (sp. gr. 1.18, 34% HCl) was added slowly. The resulting solution was concentrated to one-third of its original volume by passing a stream of air over it, keeping the temperature below 80°. The green crystals formed, *trans*[Co-*l*-pn_2Cl_2]Cl, were separated from the solution by filtration, washed with ether and dried in an oven below 80°.

Conversion to the *cis* Form.—The dried crystals of the *trans* salt were dissolved in a minimum of water and the solution carefully neutralized with dilute (1:4) NH_4OH to a *p*H of approximately 7. On evaporation of this solution on a steam-cone, purple *cis*-[Co-*l*-pn_2Cl_2]Cl formed as a glassy solid. The extreme solubility of the compound in water and the fact that it must be converted to the *cis* form in a neutral solution seems to make the preparation as a glassy solid imperative. Solubility studies made in this Laboratory have failed to yield any solvent from which it may be crystallized. This entire preparation was carried out in less than 4 hours.

(1) From the B.S. theses of Misses Joan Busch and Milda Gulbinskas.

(2) Aided by a grant from Research Corporation.

(3) A. Werner and A. Fröhlich, *Ber.*, **40**, 2225 (1907).

(4) J. C. Bailar, Jr., C. A. Stiegman, J. H. Balthis, Jr., and E. H. Huffman, THIS JOURNAL, **61**, 2402 (1939).

(5) G. Baumann, *Ber.*, **28**, 1180 (1895).

(6) H. B. Jonassen, Thesis, University of Illinois, 1946.

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Basic Equilibrium Constants of Nitroguanidine and Nitroaminoguanidine

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The basic equilibrium constants of nitroguanidine and nitroaminoguanidine are extremely small. Consequently accurate determination of these values has not been possible by the usual titrimetric procedures. In connection with a study of the reactions of nitroguanidine in strongly acidic solutions,[1] it was observed that the small peak at 220–225 mμ increased with increasing acidity. The family of curves obtained showed a sharp isosbestic point at 240 mμ between the minor (225 mμ) and major (265 mμ) absorption peaks, Fig. 1. The 265 mμ peak did not shift appreciably

(1) W. W. Brandt, J. E. De Vries and E. St. C. Gantz, *Anal. Chem.* **27**, 392 (1955).

with change in acidity while the 225 mμ peak shifted to longer wave lengths with increasing acidity.

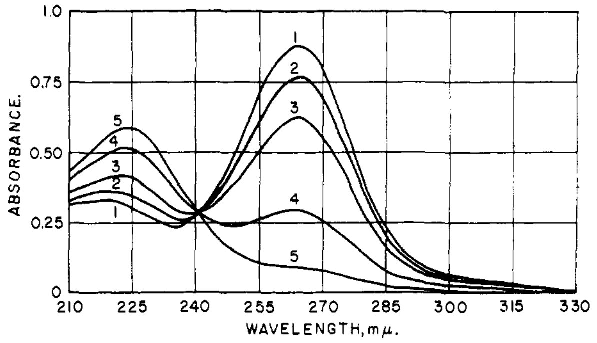

Fig. 1.—Change of absorbance of nitroguanidine with acidity: curve 1, *p*H 7; curve 2, 1.1 *N* HCl; curve 3, 2.07 *N* HCl; curve 4, 4.02 *N* HCl; curve 5, 6.10 *N* HCl. Cary Model 11MS recording spectrophotometer; 1-cm. matched silica cells; temperature 25°.

When the peak absorbance values were plotted against hydrogen ion concentration (*p*H), there was a sharp break in the curve. In the usual application of this method,[2] $pK_b = p\text{OH}$ at the mid-point of the break in the curve. For this experiment conducted in hydrochloric acid solutions, $pK_b = 14.45$ and 14.55 when conducted in sulfuric acid solutions. In these runs there was complete return of the absorption maximum at 265 mμ when the individual strong acid solutions were brought back to *p*H of 7. This indicates complete recovery of the nitroguanidine and that negligible decomposition occurred while the solutions were strongly acidic.

Similar experiments were made with nitroaminoguanidine. In this case the minor peak at about 225 mμ increased very little in absorbance and the decrease in absorbance at 267 mμ was much less than observed for nitroguanidine with increasing acidity. The plot of absorbance *versus* *p*H gave a much smaller break. The $p\text{OH} = pK_b$ for this case was estimated at approximately 15.0.

Previous work has shown that nitroaminoguanidine was the stronger acid of the two compounds, $pK_a = 10.60$ for nitroaminoguanidine and 12.20 for nitroguanidine. This difference in acid strength and similarity in base strength appears to be consistent with the structure of the two compounds.

[2] J. E. De Vries and E. St. C. Gantz, This Journal, **76**, 1008 (1954).

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The Evaluation of the Initial Velocities of Enzyme-catalyzed Reactions that Are Competitively Inhibited by their Reaction Products[1]

By William E. M. Lands[2] and Carl Niemann[3]

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A number of enzyme-catalyzed reactions that are competitively inhibited by their reaction products may be represented by equations 1, 2 and 3 and under certain circumstances, *i.e.*, when $-d[\text{ES}]/dt \doteq 0$, $[\text{S}_f] \doteq [\text{S}]$, $[\text{P}_{1f}] \doteq [\text{P}_1]$ and $[\text{P}_{2f}] \doteq [\text{P}_2]$,

$$\text{E}_f + \text{S}_f \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{ES} \xrightarrow{k_3} \text{E}_f + \text{P}_{1f} + \text{P}_{2f} \ldots \quad (1)$$

$$\text{E}_f + \text{P}_{1f} \underset{k_5}{\overset{k_4}{\rightleftarrows}} \text{EP}_1 \quad (2)$$

$$\text{E}_f + \text{P}_{2f} \underset{k_7}{\overset{k_6}{\rightleftarrows}} \text{EP}_2 \ldots \quad (3)$$

such reactions may be described throughout their course in terms of equation 4

$$-d[\text{S}]/dt = \{[\text{E}][\text{S}](k_3K_\text{P}/(K_\text{P} - K_\text{S}))\}/\{(K_\text{S}(K_\text{P} + [\text{S}]))/(K_\text{P} - K_\text{S}) + [\text{S}]\} \quad (4)$$

where $K_\text{S} = (k_2 + k_3)/k_1$, $K_\text{P} = 1\Big/\sum_{j=1}^{n} 1/K_{\text{P}j}$, $K_{\text{P}_1} = k_5/k_4$ and $K_{\text{P}_2} = k_7/k_6$. While it has been shown[4-7] that the initial velocities of the above reactions may be evaluated by graphical procedures based upon definite or indefinite integration of equation 4 and subsequent rearrangement of the integrated equations it also has been emphasized[7] that such procedures are applicable only when the reaction in question has been allowed to proceed to an extent compatible with the eventual evaluation of K_P. Since the attainment of this goal will in part be determined not only by the absolute magnitude of K_P but also by the relative magnitudes of K_P and K_S, it will be appreciated that experiments conducted in the absence of prior knowledge of the values of K_P and K_S may frequently yield data that are incapable of precise evaluation by any one of the above graphical procedures. However, since such data can be used in conjunction with any one of the above graphical procedures to determine approximate values of K_P and K_S we believe it worth while to describe an evaluation procedure that can be used to determine initial velocities in cases of this kind as well as in those in which an added competitive inhibitor is also present.

An enzyme-catalyzed reaction that is competitively inhibited by its reaction products and by an added competitive inhibitor may be represented by equations 1, 2, 3 and 5 and under certain circumstances such a reaction may be described

$$\text{E}_f + \text{I}_f \underset{k_9}{\overset{k_8}{\rightleftarrows}} \text{EI} \quad (5)$$

throughout its course by equation 6 where $K_I = k_9/k_8$.

$$k_3[\text{E}]t = K_\text{S}(1 + [\text{S}]_0/K_\text{P} + [\text{I}]/K_\text{I}) \ln([\text{S}]_0/[\text{S}]_t) + (1 - K_\text{S}/K_\text{P})([\text{S}]_0 - [\text{S}]_t) \quad (6)$$

When $[\text{I}] = 0$ and $K_\text{P} >> K_\text{S}$, equation 6 is approximated by equation 7. It has been shown

$$k_3[\text{E}]t = K_\text{S} \ln([\text{S}]_0/[\text{S}]_t) + ([\text{S}]_0 - [\text{S}]_t) \quad (7)$$

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[1] Supported in part by a grant from Eli Lilly and Co.

[2] National Science Foundation Postdoctoral Fellow.

[3] To whom inquiries regarding this article should be sent.

[4] R. J. Foster and C. Niemann, *Proc. Natl. Acad. Sci.*, **39**, 999 (1953).

[5] T. M. Applewhite and C. Niemann, This Journal, **77**, 4923 (1955).

[6] R. R. Jennings and C. Niemann, *ibid.*, **77**, 5432 (1955).

[7] K. A. Booman and C. Niemann, *ibid.*, **77**, 5733 (1955).