

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, AND THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

The Reaction of Gold(III) with Some Bidentate Coördinating Groups¹

BY B. P. BLOCK² AND JOHN C. BAILAR, JR.

HAuCl_4 and KAuBr_4 react with 1,2-ethanediamine and 1,2-propanediamine to form complexes with one or two diamine molecules per atom of gold. These complexes may act as acids with the loss of a proton from a coördinated amine group under the proper conditions. The compounds $[\text{Au}(\text{en})_2]\text{Br}_3$ and $[\text{Au}(\text{en})(\text{en-H})]\text{Br}_2$ were isolated and studied. With 2,2'-bipyridine and 1,10-phenanthroline gold(III) forms a series of compounds, but in no case is more than one bidentate molecule coördinated to one gold atom.

In the course of their study of organogold compounds Gibson and co-workers reported the incidental preparation of $[\text{Au}(\text{en})_2]\text{Br}_3$ ³ and $[\text{Br}_2\text{Au}(\text{dipy})][\text{AuBr}_4]$.⁴ We have investigated the complexes formed by Au(III) and 1,2-ethanediamine (ethylenediamine, en), 1,2-propanediamine (propylenediamine, pn), 2,2'-bipyridine (α, α' -dipyridyl, dipy), and 1,10-phenanthroline (phen). In addition to the complexes prepared by Gibson, *et al.*, we have found evidence of the formation of other complexes between Au(III) and 1,2-ethanediamine and 2,2'-bipyridine, and have shown that similar complexes are formed with 1,2-propanediamine and 1,10-phenanthroline.

The addition of 1,2-ethanediamine to an aqueous solution of KAuBr_4 with subsequent precipitation by ethyl alcohol yields a yellow solid with two bromine atoms and two molecules of 1,2-ethanediamine per atom of gold, rather than the compound $[\text{Au}(\text{en})_2]\text{Br}_3$ as reported by Gibson and Colles.³ The solid is diamagnetic, however, and therefore is not a compound of Au(II), since Au(II) should contain an unpaired electron and consequently should be paramagnetic. Although the compound is reduced by mercury, it is still possible to measure a diffusion current polarographically. Comparison of the diffusion coefficient calculated from the Ilkovic equation⁵ for this gold compound with the corresponding quantity for $[\text{Au}(\text{en})_2]\text{Br}_3$ (prepared by another method) shows that the gold compound in question undergoes a three-electron reduction, or that the gold is tervalent. If three-electron reductions are assumed, the diffusion coefficients are 1.7×10^{-5} cm.²/sec. and 7.2×10^{-6} cm.²/sec. for the yellow compound and for $[\text{Au}(\text{en})_2]\text{Br}_3$, respectively. A further assumption that each cation contains one gold atom, and that they are about the same size, leads to the conclusion that the yellow compound must contain a cation with smaller charge than the cation in $[\text{Au}(\text{en})_2]\text{Br}_3$, because its diffusion coefficient is appreciably larger. It then seems probable that a proton has been lost from one molecule of 1,2-ethanediamine, so that the yellow compound is $[\text{Au}(\text{en})(\text{en-H})]\text{Br}_2$ (in which (en-H) represents the 1,2-ethanediamine molecule with one hydrogen lost from an amine group, *i.e.*, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}^-$). A sample of this compound titrated with dilute HClO_4 accepted one equivalent of acid per atom of gold, as would be ex-

pected for a structure of this kind (Fig. 1); at the same time the yellow solution became colorless.

If an acid-base equilibrium is involved, it should be possible to prepare $[\text{Au}(\text{en})_2]\text{Br}_3$ in a more acid medium which would prevent the loss of the proton from 1,2-ethanediamine. The method of preparation employing this principle which was used is given by the equation $\text{HAuCl}_4 + 2\text{en} \rightarrow [\text{Au}(\text{en})_2]\text{Cl}_3 + \text{HCl}$ (in ethereal solution), followed by $[\text{Au}(\text{en})_2]\text{Cl}_3 + 3\text{KBr} \rightarrow [\text{Au}(\text{en})_2]\text{Br}_3 + 3\text{KCl}$ (at 5°). The compound $[\text{Au}(\text{en})_2]\text{Br}_3$ is almost colorless, not bright yellow as reported by Gibson and Colles.³ In the titration of $[\text{Au}(\text{en})_2]\text{Br}_3$ with dilute sodium hydroxide, one equivalent of sodium hydroxide reacts per gold atom and the solution goes from colorless to yellow (Fig. 2). Thus the product of the reaction of Au(III) with 1,2-ethanediamine will depend on the acidity or basicity of the solution, for the equilibrium $[\text{Au}(\text{en})_2]^{3+} \rightleftharpoons [\text{Au}(\text{en})(\text{en-H})]^{2+} + \text{H}^+$ is involved. It is likely that Gibson and Colles carried out their preparation in a solution acidic enough to yield mainly $[\text{Au}(\text{en})_2]\text{Br}_3$, but that enough $[\text{Au}(\text{en})(\text{en-H})]\text{Br}_2$ was present to impart a yellow color to the product.

The reaction product of 1,2-propanediamine and HAuCl_4 or KAuBr_4 was too soluble to be isolated. In all trials there was formed an oil which partially decomposed to yield gold before solidifying. Consequently, the system was studied by measuring the pH of aqueous solutions of KAuBr_4 to which varying amounts of 1,2-propanediamine were added. A similar study was made with 1,2-ethanediamine for comparative purposes. In Fig. 3 the pH is plotted as a function of volume of diamine. The two curves are similar, but the breaks are sharper for the addition of 1,2-propanediamine. The main features of these curves are the initial decrease in pH and the decreasingly sharp breaks at one, two and three equivalents of diamine per gold atom.

Bjerrum⁶ has reported that the hydrolysis of AuCl_4^- decreases the pH of the medium by the formation of $\text{AuCl}_3(\text{OH})^-$, H^+ and Cl^- . To determine whether or not the decrease was caused by a measurably slow hydrolysis of KAuBr_4 , the pH of a 0.03 M KAuBr_4 solution was followed for 12 days, and instead of a decrease there was a slight increase in pH. The observed decrease during the addition of the diamines must then be the result of a reaction between the diamine and AuBr_4^- , probably to form $[\text{AuBr}_2(\text{diamine-H})] + \text{H}^+ + 2\text{Br}^-$, in which (diamine-H) signifies a diamine molecule which has lost a proton from one amine group. This postulated compound is a non-electrolyte and should be insoluble. During the measurements a

(1) Taken in part from the Doctoral Thesis of B. P. Block, University of Illinois, 1949.

(2) Department of Chemistry, University of Chicago.

(3) C. S. Gibson and W. M. Colles, *J. Chem. Soc.*, 2415 (1931).

(4) M. E. Foss and C. S. Gibson, *ibid.*, 3074 (1949).

(5) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946, p. 55.

(6) N. Bjerrum, *Bull. soc. chim. Belg.*, **57**, 432 (1948).

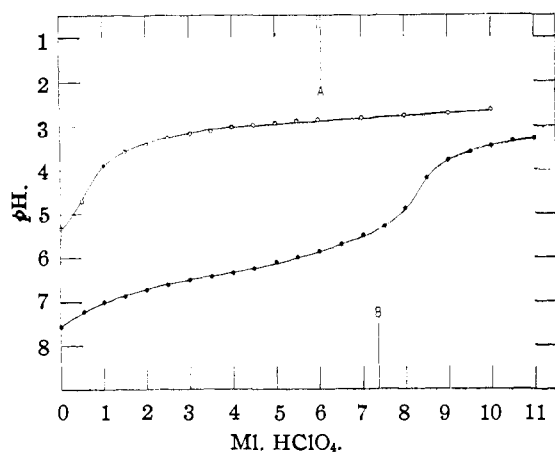


Fig. 1.—The titration of 0.216 mmole. of $[\text{Au}(\text{en})_2]\text{Cl}_2$ (open circles) and 0.261 mmole. of $[\text{Au}(\text{en})(\text{en}-\text{H})]\text{Br}_2$ (filled circles) with 0.0355 M HClO_4 . Point A indicates 0.216 mmole. of HClO_4 , B 0.261 mmole. of HClO_4 .

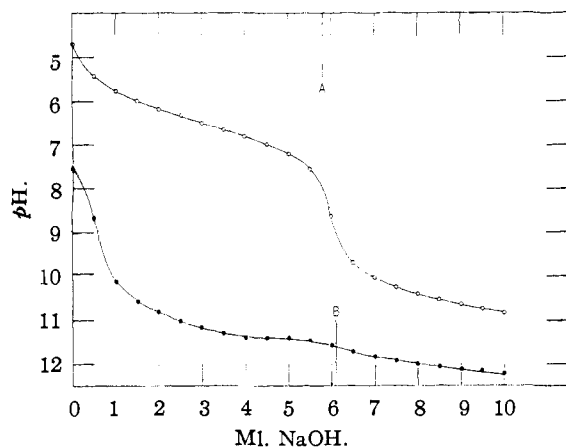


Fig. 2.—The titration of 0.237 mmole. of $[\text{Au}(\text{en})_2]\text{Cl}_2$ (open circles) and 0.249 mmole. of $[\text{Au}(\text{en})(\text{en}-\text{H})]\text{Br}_2$ (filled circles) with 0.0408 M NaOH . Point A indicates 0.237 mmole. of NaOH , B 0.249 mmole. of NaOH .

slight precipitate was noted in the mixtures of lower pH , but it had disappeared by the time the first break was reached. The disappearance of this precipitate indicates that at the first break the predominant species is in solution and is therefore probably the ion $[\text{AuBr}_2(\text{diamine})]^+$. The second break, at two equivalents of diamine per gold atom, corresponds to the formation of $[\text{Au}(\text{diamine})_2]^{3+}$. At the third break there is a color change which, in the light of the previous findings in the 1,2-ethanediamine system, suggests that this break is associated with the formation of $[\text{Au}(\text{diamine})(\text{diamine}-\text{H})]^{++}$. An alternative explanation might be that $[\text{Au}(\text{diamine})_3]^{3+}$ is formed; but this does not seem probable, since Au(III) generally is tetravalent,⁷ although it may have a coordination number of six in the crystalline lattice of some of its compounds.⁸

If a proton is lost, the reaction involved is $[\text{Au}(\text{diamine})_2]^{3+} + \text{diamine} \rightleftharpoons [\text{Au}(\text{diamine})-$

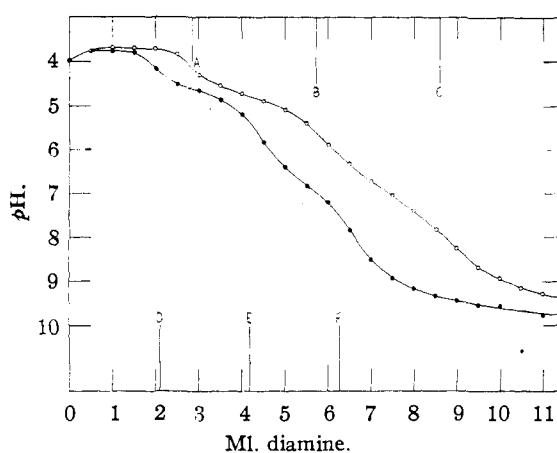


Fig. 3.—The reaction of 0.328 M en with 0.0940 mmole. of KAuBr_4 (open circles) and of 0.0313 M pn with 0.0654 mmole. of KAuBr_4 (filled circles). Points A, B, and C indicate one, two, and three moles of en per mole of KAuBr_4 , respectively, and points D, E, and F indicate one, two, and three moles of pn per mole of KAuBr_4 , respectively.

$(\text{diamine}-\text{H})]^{++} + \text{diamine}\cdot\text{H}^+$. The equilibrium constant for this reaction is $K_E = C_1C_2/C_3C_4$, in which C_1 is M of $[\text{Au}(\text{diamine})(\text{diamine}-\text{H})]^{++}$, C_2 is M of $\text{diamine}\cdot\text{H}^+$, C_3 M of $[\text{Au}(\text{diamine})_2]^{3+}$, and C_4 M of diamine. However, $C_4C_{\text{H}^+}/C_2$ is equal to K' , the acidity constant for $\text{diamine}\cdot\text{H}^+$, and when the value obtained from this expression is substituted for C_2/C_4 in the K_E expression, the equation $C_1C_{\text{H}^+}/C_3 = K_EK'$ results. In Table I the quantity $C_1C_{\text{H}^+}/C_3$ is evaluated for the curves in Fig. 3 between 2 and 3 equivalents of diamine for the two systems, and is seen to be approximately constant over the major part of the range in both cases. The complexes formed between Au(III) and 1,2-ethanediamine or 1,2-propanediamine are of the same kind, and their nature depends on the relative amounts of the reactants and the pH of the medium.

TABLE I

K_EK' FOR THE Au(III)-1,2-ETHANEDIAMINE AND Au(III)-1,2-PROPANEDIAMINE SYSTEMS

Ml. 0.0313 M pn	135 C_1	135 C_3	pH	$C_1C_{\text{H}^+}/C_3 \times 10^2$
4.50	0.0100	0.0554	5.82	2.7
4.75	.0178	.0476	6.10	3.0
5.00	.0257	.0397	6.39	2.6
5.25	.0335	.0319	6.61	2.6
5.50	.0413	.0241	6.82	2.6
5.75	.0491	.0163	7.01	2.9
6.00	.0570	.0084	7.20	4.3
Ml. 0.0328 M en	135 C_1	135 C_2	pH	$C_1C_{\text{H}^+}/C_3 \times 10^2$
6.00	0.0085	0.0855	5.88	1.3
6.50	.0249	.0691	6.32	1.7
7.00	.0413	.0527	6.71	1.5
7.50	.0577	.0363	7.03	1.5
8.00	.0741	.0199	7.40	1.5
8.50	.0905	.0035	7.81	4.0

At the time we carried out these investigations, Gibson and co-workers had formulated a large number of organogold compounds containing 1,2-

(7) C. S. Gibson, *Nature*, **140**, 583 (1937); A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, Oxford, 1946, p. 508.

(8) A. Ferrari, *Gazz. chim. Ital.*, **67**, 94 (1937); see also N. Elliott and L. Pauling, *THIS JOURNAL*, **60**, 1846 (1938).

ethanediamine and 2,2'-bipyridine as molecules in which these bidentate groups served as bridges between two gold atoms.⁹ This did not seem the most probable structure for these compounds, and, as a result of our studies with 1,2-bipyridine and 1,10-phenanthroline, we concluded that it was more probable that both ends of the bidentate group were bonded to the same gold atom. After we had completed our studies, but before publication, Foss and Gibson⁴ reached substantially the same conclusions, and revised the formulation of a large group of compounds previously reported. We studied the coordination compounds involving Au(III) and 2,2'-bipyridine or 1,10-phenanthroline more completely than Foss and Gibson, and will briefly report our results.

The treatment of HAuCl_4 with 2,2'-bipyridine in ethyl alcohol yields first a yellow precipitate of $[\text{AuCl}_2(\text{dipy})][\text{AuCl}_4]$. Further addition of 2,2'-bipyridine is slow, but by more vigorous treatment with excess 2,2'-bipyridine an orange compound with composition approaching $[\text{AuCl}_2(\text{dipy})]\text{Cl}$ is formed. It is easily converted to the yellow $[\text{AuCl}_2(\text{dipy})][\text{AuCl}_4]$ by treatment with water or by gentle heating. KAuBr_4 reacts with 2,2'-bipyridine in ethyl alcohol to give $[\text{AuBr}_2(\text{dipy})][\text{AuBr}_4]$, which was prepared by Foss and Gibson⁴ by a slightly different method. When 1,10-phenanthroline is substituted for 2,2'-bipyridine in the reaction with HAuCl_4 , a yellow precipitate is again formed; it starts to turn orange almost immediately, however, and the orange substance can be isolated as pure $[\text{AuCl}_2(\text{phen})]\text{Cl}$. This compound gives a relatively stable aqueous solution in which one Cl^- is more labile than the others and can be replaced by a NO_3^- ion. Treatment of the aqueous solution with HAuCl_4 gives the yellow compound $[\text{AuCl}_2(\text{phen})][\text{AuCl}_4]$. $[\text{AuBr}_2(\text{phen})]\text{Br}$ is precipitated by treating $[\text{AuCl}_2(\text{phen})]\text{Cl}$ with potassium bromide in water. We did not succeed in obtaining compounds with more than one 2,2'-bipyridine or 1,10-phenanthroline molecule per gold atom.

Experimental

$[\text{Au}(\text{en})(\text{en-H})]\text{Br}_2$.—The addition of 4 ml. of 1,2-ethanediamine monohydrate to a solution of 2.0 g. of KAuBr_4 in 6 ml. of water caused the solution to become yellow. Seventy ml. of ethyl alcohol was added to the solution, and the next day 1.36 g. of a yellow solid was isolated from the mixture, washed with ethyl alcohol, and dried. *Anal.* Found: Au, 41.8, 41.69; Br, 33.35; C, 10.11; H, 3.43. Calcd. for $\text{Au}_2\text{C}_4\text{H}_{16}\text{N}_4\text{Br}_2$: Au, 41.41; Br, 33.56; C, 10.09; H, 3.18. The compound deflected a modified Curie-Cheveneau balance in the diamagnetic direction.

$[\text{Au}(\text{en})_2]\text{Cl}_3$ and $[\text{Au}(\text{en})_2]\text{Br}_3$.—A gummy yellow precipitate was formed by the addition of a solution of 1 ml. of 1,2-ethanediamine monohydrate in 5 ml. of diethyl ether to a solution of 1.0 g. of HAuCl_4 in 10 ml. of ether. A white precipitate resulted when 20 ml. of ethyl alcohol was added to the orange solution of the preceding product in 2.8 ml. of water. This precipitate, which weighed 0.95 g., was dissolved in 2.3 ml. of water and reprecipitated with 15 ml. of ethyl alcohol to give 0.90 g. of a white solid. *Anal.* Found: Au, 46.3, 46.5, 46.69; Cl, 25.05; N, 13.42; C, 11.57; H, 3.92. Calcd. for $\text{Au}_2\text{C}_4\text{H}_{16}\text{N}_4\text{Cl}_3$: Au, 46.53; Cl, 25.11; N, 13.22; C, 11.34; H, 3.81. A solution of 0.4 g. of $[\text{Au}(\text{en})_2]\text{Cl}_3$ in 3 ml. of water was added to 4 ml. of water containing 2.0 g. of KBr, and the mixture was cooled to 5°.

After the crystals had been removed, 1 ml. of water containing 0.5 g. of KBr was mixed with the filtrate and the mixture again cooled. The combined yield of light yellow crystals was 0.35 g. *Anal.* Found: Au, 35.4, 36.00; Br, 43.18; C, 8.55; H, 2.87. Calcd. for $\text{Au}_2\text{C}_4\text{H}_{16}\text{N}_4\text{Br}_2$: Au, 35.38; Br, 43.03; C, 8.62; H, 2.89.

Polarographic Analysis.—Polarograms of $5.04 \times 10^{-4} M$ $[\text{Au}(\text{en})(\text{en-H})]\text{Br}_2$ and $5.01 \times 10^{-4} M$ $[\text{Au}(\text{en})_2]\text{Cl}_3$ with 0.1 M KCl as a supporting electrolyte were made using a Sargent Model XXI recording polarograph with a dropping mercury electrode. The gold compounds both reacted with mercury, for the reduction waves were continuations of the anodic oxidation wave of mercury. However, the diffusion currents determined from the wave heights for the reductions were found to be 4.0 and 3.9 microamp., respectively. The diffusion coefficients calculated from the Ilkovic equation,⁵ assuming 3-electron reductions in each case, are $1.7 \times 10^{-6} \text{ cm.}^2/\text{sec.}$ and $7.2 \times 10^{-6} \text{ cm.}^2/\text{sec.}$, respectively.

Titration of $[\text{Au}(\text{en})(\text{en-H})]\text{Br}_2$ and $[\text{Au}(\text{en})_2]\text{Cl}_3$.—A few tenths of a millimole of the complex was dissolved in 100 ml. of water and the standard HClO_4 or NaOH solution was added in 0.25-ml. portions. After each addition and while the solution was stirred continuously, the pH of the solution was measured with a Beckman Model H-2 pH Meter at 10-minute intervals until the pH remained constant. The results for the titration of $[\text{Au}(\text{en})_2]\text{Cl}_3$ and $[\text{Au}(\text{en})(\text{en-H})]\text{Br}_2$ with 0.0355 M HClO_4 and 0.0408 M NaOH are plotted in Figs. 1 and 2.

The Reactions of 1,2-Ethanediamine and 1,2-Propanediamine with KAuBr_4 .—A series of solutions was made by mixing 3 or 4 ml. of a standard KAuBr_4 solution, a standard 1,2-ethanediamine or 1,2-propanediamine solution (0 to 12 ml. in 0.5-ml. increments), and sufficient water to give a total volume of 135 ml. These solutions were kept in the dark, and the pH was measured several times over a period of four or five days with a Beckman Model G pH Meter to show that equilibrium was reached. The equilibrium pH values are plotted against volume of diamine solution in Fig. 3. The values of $C_1C_H + C_2$ in Table I were calculated from these pH values, the number of millimoles of KAuBr_4 , and the number of millimoles of diamine, by assuming that $135C_1 = (\text{mmoles diamine}) - (2 \text{ mmoles } \text{KAuBr}_4)$, and $135C_2 = (\text{mmoles } \text{KAuBr}_4) - (135C_1)$.

Hydrolysis of KAuBr_4 .—The pH of a 0.03071 M solution of KAuBr_4 was measured with a Beckman Model G pH Meter as soon as possible after preparation. The solution was then kept in the dark at room temperature, and the pH was measured intermittently for 12 days. During this time it increased from 3.54 to 3.58.

$[\text{AuCl}_2(\text{dipy})][\text{AuCl}_4]$.—A solution of 1.0 g. of HAuCl_4 in 25 ml. of ethyl alcohol was added with stirring to a solution of 1.0 g. of 2,2'-bipyridine in 25 ml. of ethyl alcohol. After two hours the yellow precipitate was removed, washed with ethyl alcohol, and dried; 0.75 g. was obtained. *Anal.* Found: Au, 51.9, 51.5; C, 16.02; H, 1.12; N, 3.68; Cl, 27.89. Calcd. for $\text{Au}_2\text{C}_8\text{Cl}_{10}\text{H}_8\text{N}_2$: Au, 51.67; C, 15.73; H, 1.06; N, 3.67; Cl, 27.88.

$[\text{AuCl}_2(\text{dipy})]\text{Cl}$ (?).—The addition of a solution of 1.0 g. of HAuCl_4 in 10 ml. of ethyl alcohol to a solution of 1.5 g. of 2,2'-bipyridine in 10 ml. of ethyl alcohol gave the preceding yellow precipitate. After the mixture was heated several hours on a steam-cone, 0.98 g. of an orange solid was obtained. *Anal.* Found: Au, 43.9. Calcd. for $\text{Au}_2\text{C}_8\text{Cl}_8\text{H}_8\text{N}_2$: Au, 42.9. Careful heating of 0.60 g. of this orange solid gave 0.51 g. of a yellow solid containing Au, 51 (51.7 calcd. for $[\text{AuCl}_2(\text{dipy})][\text{AuCl}_4]$), and dense white fumes with the odor of 2,2'-bipyridine. The calculated weight of $[\text{AuCl}_2(\text{dipy})][\text{AuCl}_4]$ which would be formed from 0.60 g. of $[\text{AuCl}_2(\text{dipy})]\text{Cl}$ by the loss of 2,2'-bipyridine is 0.50 g.

$[\text{AuBr}_2(\text{dipy})][\text{AuBr}_4]$.—The addition of a solution of 0.35 g. of 2,2'-bipyridine in 10 ml. of ethyl alcohol to a solution of 0.50 g. of KAuBr_4 in 10 ml. of ethyl alcohol gave a red solution from which a red-brown precipitate slowly separated. This precipitate was removed by filtration and washed sparingly, first with ethyl alcohol and then with water, to remove KBr. The dried product weighed 0.33 g. *Anal.* Found: Au, 38.2; C, 11.73; H, 0.85; Br, 46.74. Calcd. for $\text{Au}_2\text{Br}_6\text{C}_{10}\text{H}_8\text{N}_2$: Au, 38.3; C, 11.66; H, 0.78; Br, 46.56.

$[\text{AuCl}_2(\text{phen})]\text{Cl}$, $[\text{AuCl}_2(\text{phen})]\text{NO}_3$, and $[\text{AuBr}_2(\text{phen})]\text{Br}$.—A solution of 1.0 g. of 1,10-phenanthroline in 10 ml. of ethyl alcohol added to a solution of 1.0 g. of HAuCl_4 in 10

(9) C. S. Gibson *et al.*, *J. Chem. Soc.*, 219, 1024 (1935); 762 (1939); 102 (1941).

ml. of ethyl alcohol gave a yellow precipitate which started to turn orange rapidly. This transformation was completed by heating the mixture four hours on a steam-bath. The washed and dried product weighed 1.2 g. *Anal.* Found: Au, 40.7; C, 40.75; H, 1.76; N, 5.65; Cl, 22.18. Calcd. for $\text{AuCl}_2\text{C}_6\text{H}_5\text{N}_4$: Au, 40.77; C, 29.79; H, 1.67; N, 5.79; Cl, 22.00. The addition of ten drops of concentrated HNO_3 to a solution of 0.20 g. of $[\text{AuCl}_2(\text{phen})]\text{Cl}$ in 35 ml. of water gave 0.19 g. of a yellow precipitate. *Anal.* Found: Au, 38.7; C, 28.64; H, 2.19; Cl, 13.64. Calcd. for $\text{AuCl}_2\text{C}_{12}\text{H}_8\text{N}_4\text{O}_3$: Au, 38.64; C, 28.25; H, 1.58; Cl, 13.89. The addition of 0.12 g. of KBr in 0.4 ml. of water to 0.15 g. of $[\text{AuCl}_2(\text{phen})]\text{Cl}$ in 25 ml. of water gave 0.13 g. of a tan solid. *Anal.* Found: Au, 32.5. Calcd. for $\text{AuBr}_2\text{C}_{12}\text{H}_8\text{N}_4$: Au, 32.0.

$[\text{AuCl}_2(\text{phen})][\text{AuCl}_4]$.—The addition of a solution of 0.42 g. of HAuCl_4 in 1 ml. of water to a solution of 0.4 g. of $[\text{AuCl}_2(\text{phen})]\text{Cl}$ in 30 ml. of water gave 0.70 g. of a yellow precipitate. *Anal.* Found: Au, 50.3; C, 18.57; H, 1.17; Cl, 27.17. Calcd. for $\text{Au}_2\text{Cl}_6\text{C}_{12}\text{H}_8\text{N}_4$: Au, 50.09; C, 18.31; H, 1.02; Cl, 27.01.

Acknowledgment.—We are indebted to Drs. H. A. Laitinen and C. E. Shoemaker for their generous assistance with the polarographic studies. The analyses were in large part made by the University of Illinois microanalysts and the Clark Microanalytical Laboratory.

CHICAGO, ILL.

RECEIVED MARCH 15, 1951

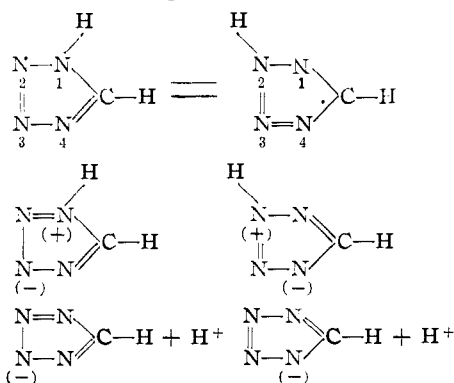
[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE U. S. NAVAL ORDNANCE TEST STATION]

The Heats of Combustion of Compounds Containing the Tetrazole Ring¹

BY W. S. McEWAN¹ AND M. W. RIGG²

The heats of combustion for some twenty-eight compounds related to tetrazole have been determined in order to provide fundamental knowledge of the average bond strength and resonance energy of this type of compound. By use of reported bond energies the resonance energy of the tetrazole ring is found to be between 55 and 70 kcal./ring depending upon substituent groups. Elimination of the tautomeric shift appears to increase rather than decrease the resonance energy of the tetrazole ring.

Tetrazole (CH_2N_4) is an interesting molecule since the combination of four atoms of nitrogen and one of carbon in a stable compound is seldom found. The stability of tetrazole is indicated by the relatively high melting point, 155° , without decomposition, and the relative stability of the compound in chemical reactions involving side groups, *i.e.*, the diazotization of 5-aminotetrazole and the oxidation of the phenyl group in phenyltetrazole. The apparent stability of the tetrazole ring indicates that a considerable resonance or stabilizing energy must be present in the system. This stability is undoubtedly due to the following factors: It is possible to have two tautomeric isomers, an ionized form (tetrazole is a weak acid, $K_a = 1.28 \times 10^{-5}$) which would have resonance stability, and the possibility of an electron shift within the molecule, with a resultant charge separation, which would also have resonance stability. The electron shift could be considered the first step in the ionization.



It should be pointed out, in this case, that substitution in the 1- or 2-position on the tetrazole ring removes the contribution of the tautomeric shift, and of the ionized form to the stabilization energy.

(1) Article not copyrighted.

(2) Temple University, Philadelphia 22, Pennsylvania.

Thus, the work presented here contains data on compounds from the following important groups: 5-substitutions, 1- or 2-substitutions, 1,5- and 2,5-disubstitutions. The 1-substituted compounds contain the conjugated system $-\text{N}=\text{N}-\text{N}=\text{C}-$ whereas the 2-substituted compounds contain the conjugated system $-\text{N}=\text{N}-\text{C}=\text{N}-$ and the two systems may not have identical stabilities.

A value of 30 kcal./mole for the resonance energy has been assumed in a number of calculations, although a recent reference (Elpern, *THIS JOURNAL*, 72, 3379 (1950)) claims that tetrazole has little or no resonance energy. This statement is based upon the fact that tetrazole shows no absorption in the ultraviolet region. In order to obtain some additional information which might be used to estimate the resonance energy, the heats of combustion of tetrazole and a number of tetrazole derivatives were measured and the data combined with values for the heats of formation of water³ and carbon dioxide⁴ to obtain a value for the heat of formation of the various compounds. The calculations are based upon the formation of molecular nitrogen from the nitrogen in the sample.

Experimental

The calorimeter was similar to standard units which have been described by the Bureau of Standards. The unit was placed in a constant temperature water-bath, controlled to $\pm 0.002^\circ$, as measured by a platinum resistance thermometer. The calorimeter was filled with the same quantity, ± 0.1 g., of distilled water before each run. The cover to the calorimeter was designed in such a way that the thermostat stirrer forced a flow of water through the cover, thus completely enclosing the calorimeter in a constant temperature water jacket.

The standard Parr double valve bomb was used in all of these experiments. The samples, in the shape of a pellet (1.5 cm. dia., 0.5 cm. thick), and placed on a piece of fuse paper, were burnt in a small platinum crucible supported by one of the firing electrodes in an atmosphere of oxygen

(3) D. D. Wagman, J. W. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. of Standards*, 34, 143 (1945).(4) E. J. Prosen, R. S. Jessup and F. D. Rossini, *ibid.*, 33, 447 (1944).