

TABLE I  
REDUCTION EMPLOYING CONSTANT CURRENT DENSITY  
Volume of cathode solution at start, 225 cc.  
Grams of Cr per cc., 0.11031  
Grams of Cr<sup>++</sup> per cc., 0.00128  
Total cathode surface, 1.24 sq. dm.

Time	Amperage	Hydrogen evolved Cc.	Total hydrogen Cc.	Efficiency %	Cr as Cr <sup>++</sup> %	K
9.47-11.05	1.6	0.0	...	100.0	17.4	....
11.05-11.35	1.6	0.4	334.1	99.9	23.6	....
11.35-12.05	1.6	0.7	334.1	99.8	29.9	....
12.05-12.35	1.6	0.9	334.1	99.7	36.1	....
12.35- 1.05	1.6	7.5	334.1	97.8	42.2	0.00335
1.05- 1.35	1.6	34.2	334.1	89.8	47.8	0.00338
1.35- 2.05	1.6	68.4	334.1	79.5	52.8	0.00336
2.05- 2.35	1.6	97.5	334.1	70.8	57.2	0.00334
2.35- 3.05	1.6	115.8	334.1	65.3	61.3	0.00334

Several experiments according to this method have shown that by reducing the amperage to correspond with the decrease in chromic chromium, an efficiency of 96% can be maintained over the period required to reduce 87% of the chromium; whereas, by holding the amperage constant only 53% efficiency could be obtained for the same amount of reduction.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]  
**COMPOUNDS OF TELLURIUM TETRABROMIDE WITH ORGANIC BASES<sup>1</sup>**

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This investigation was undertaken with a twofold purpose in view: (1) to prepare compounds of tellurium tetrabromide with organic bases which will be utilized in further research work, and (2) to prepare selenium and tellurium dyes analogous to the class of sulfur dyes by substituting the element selenium or tellurium in place of sulfur, as, for example, in the preparation of sulfur black, etc.

<sup>1</sup> Presented before the Division of Organic Chemistry of the American Chemical Society, New York, September 6-9, 1921.

<sup>2</sup> This report represents an abstract of a thesis presented by R. F. Dunbrook, in partial fulfilment of the requirements for the degree of Master of Science, September, 1921.

Rust<sup>3</sup> investigated the action of tellurium tetrachloride on phenols and phenol ethers and found that complexes of the type  $\text{TeCl}_2(\text{C}_6\text{H}_4\text{-OCH}_3)_2$  and  $\text{TeCl}_4(\text{C}_6\text{H}_5\text{.OH})_2$  were formed.

Lenher<sup>4</sup> has tried the action of tellurium tetrachloride and of tellurium tetrabromide on amines. When tellurium tetrachloride or tellurium tetrabromide, dissolved in the corresponding halogen acid, is added to an amine, also dissolved in the corresponding halogen acid, complexes of the type  $(\text{C}_6\text{H}_5\text{NH}_2\text{HBr})_2 \cdot \text{TeBr}_4$ , are formed in which two moles of the salt of the amine are combined with one mole of tellurium tetrabromide. The tellurium tetrabromide is prepared by dissolving tellurium dioxide in hydrobromic acid.

In the course of this investigation, it was found that when pure tellurium tetrabromide is dissolved in absolute ether or in glacial acetic acid, and a solution of a primary, secondary or tertiary aromatic amine, or a substituted amine is added to the solution, yellow or orange colored precipitates are formed which are the addition products of tellurium tetrabromide and the amines. It was further found that the number of moles of the amine that were combined with one mole of tellurium tetrabromide depended upon the number of amino groups in the molecule. If one amino group was present in the molecule, then two molecules of the amine combined with one mole of tellurium tetrabromide. When two amino groups were present in the molecule, then the ratio was one mole of the amine to one mole of tellurium tetrabromide. A list of compounds prepared is given under Experimental Part.

### Experimental Part

The pure tellurium tetrabromide was prepared as described by Hauer<sup>5</sup> and was recrystallized from acetic acid.

The data following contain the essential results obtained.

Name of product and formula	Color and form	Solvents	Ratio of amine to $\text{TeBr}_4$	Calc. %	Analysis Found %
Bis-aniline tellurium tetrabromide $(\text{C}_6\text{H}_5\text{NH}_2)_2 \cdot \text{TeBr}_4$	yellow amorphous	ether	2:1	Te, 20.13 Br, 50.47	20.09, 20.33 50.26, 50.53
Bis- <i>p</i> -bromo-aniline tellurium tetrabromide $(\text{BrC}_6\text{H}_4\text{NH}_2)_2 \cdot \text{TeBr}_4$	yellow amorphous	acetic acid	2:1	Te, 16.11 Br, 60.59	16.00, 15.99 60.63, 60.44
Bis-diphenylamine tellurium tetrabromide $[(\text{C}_6\text{H}_5)_2\text{NH}]_2 \cdot \text{TeBr}_4$	orange needles	acetic acid	2:1	Te, 16.23 Br, 40.69	16.25, 16.26 40.17, 40.94

<sup>3</sup> Rust, *Ber.*, **30**, 2828 (1897).

<sup>4</sup> Lenher, *THIS JOURNAL*, **22**, 136 (1900).

<sup>5</sup> Hauer, *J. prakt. Chem.*, **73**, 98 (1858).

Name of product and formula	Color and form	Solvents	Ratio of amine to TeBr <sub>4</sub>	Analysis	
				Calc. %	Found %
Bis-dimethylaniline tel- lurium tetrabromide [C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> .TeBr <sub>4</sub>	orange needles	acetic acid	2:1	Te, 18.49 Br, 46.36	18.51, 18.79 46.32, 46.56
Bis-β-naphthylamine tel- lurium tetrabromide (C <sub>10</sub> H <sub>7</sub> NH <sub>2</sub> ) <sub>2</sub> .TeBr <sub>4</sub>	orange needles	acetic acid	2:1	Te, 17.38 Br, 43.58	17.58, 17.21 43.63, 43.71
p-phenylenediamine tel- lurium tetrabromide C <sub>6</sub> H <sub>4</sub> (NH <sub>2</sub> ) <sub>2</sub> .TeBr <sub>4</sub>	yellow amorphous	acetic acid	1:1	Te, 22.96 Br, 57.57	22.60, 22.57 57.70, 57.54
m-tolylenediamine tel- lurium tetrabromide C <sub>7</sub> H <sub>6</sub> (NH <sub>2</sub> ) <sub>2</sub> .TeBr <sub>4</sub>	yellow amorphous	acetic acid	1:1	Te, 22.40 Br, 56.15	22.70, 22.44 56.12, 56.71
Benzidine tellurium tetra- bromide H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> .C <sub>6</sub> - H <sub>4</sub> NH <sub>2</sub> .TeBr <sub>4</sub>	yellow amorphous	acetic acid	1:1	Te, 20.19 Br, 50.63	20.46, 20.24 50.88, 50.59
Tetramethyl-diamino-di- phenylmethane tellurium tetrabromide (CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> .CH <sub>2</sub> .C <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub> .- TeBr <sub>4</sub>	yellow amorphous	acetic acid	1:1	Te, 18.18 Br, 45.57	18.21, 18.51 45.76, 45.73

The compounds described in the table were prepared by mixing solutions of the amines and of tellurium tetrabromide in the ratios given, in ether or in glacial acetic acid. The yield in all cases was practically quantitative.

The bases are all yellow amorphous powders, but those that can also be prepared crystalline have an orange color. They are stable in the air, but water and alcohol readily decompose them with the formation of tellurous acid. They have no melting points and decompose when heated above 100°. The bases described are insoluble in absolute ether, chloroform, carbon tetrachloride, carbon disulfide, benzene, toluene, petroleum ether, acetone and in glacial acetic acid. Dilute acids readily dissolve them.

When bis-aniline tellurium tetrabromide is dissolved in dil. hydrobromic acid and recrystallized twice from the same solvent, the base forms a new complex, consisting of four moles of aniline hydrobromide combined with one mole of tellurium tetrabromide.

Subs., 0.2110, 0.3850. Calc. for (C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>HBr)<sub>4</sub>.TeBr<sub>4</sub>: Te, 11.15. Found: 11.13, 10.91.

Subs., 0.1844, 0.2600. Calc. for (C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>HBr)<sub>4</sub>.TeBr<sub>4</sub>: Br, 55.92. Found: 55.62, 55.75.

The other bases form analogous products with hydrobromic acid.

Alkaloids such as brucine and quinine also give yellow amorphous precipitates with tellurium tetrabromide.

Experiments were conducted to prepare selenium and tellurium dyes analogous to the sulfur dyes obtained in processes which employ the element sulfur. The conclusions from our experiments seem to be that, in the preparation of selenium and tellurium dyes, compounds of selenium and tellurium would have to be used instead of the elements themselves. It seems that under conditions similar to those which hold for sulfur, selenium and tellurium do not form dyes.

When selenium or tellurium was suspended in concentrated solutions of sodium hydroxide, together with various organic compounds, such as dinitrophenol, diphenylamine, and *p*-phenylenediamine, and the mixtures were refluxed, no color formation seemed to take place, although in some experiments, the mixtures were refluxed for 100 hours. The temperatures ranged from 100–120°.

It seemed probable that if selenium or tellurium were fused with sodium hydroxide or sodium carbonate,  $\text{Na}_2\text{Se}_n$  or  $\text{Na}_2\text{Te}_n$  would be formed and that in the presence of suitable organic compounds,  $\text{Na}_2\text{Se}_n$  or  $\text{Na}_2\text{Te}_n$  would react as fast as formed, and that the reaction would proceed until dyes would be formed. Many experiments were conducted at atmospheric pressure and in an autoclave, in which selenium or tellurium and sodium hydroxide or sodium carbonate were mixed with dinitrophenol, diphenylamine or *p*-phenylenediamine, and fused in a molten metal bath at temperatures ranging from 200° to 360°. The time of fusion varied from 6 to 48 hours, but no color was observed.

### Summary

1. Tellurium tetrabromide reacts with primary, secondary and tertiary organic bases to produce complexes.
2. Nine products were prepared and analyzed.
3. No selenium and tellurium dyes were prepared, analogous to the sulfur dyes, by substituting the element selenium or tellurium in place of sulfur.

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