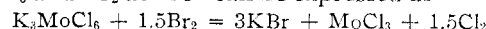


It was found that the  $\text{KBr-K}_2\text{MoCl}_6$  mixture decomposed at  $450^\circ$  in a current of nitrogen, and  $\text{MoCl}_3$  was deposited at the end of the reaction tube. Since excess bromine at  $450^\circ$  can change  $\text{KCl}$  to

$\text{KBr}$ , the equation for the over-all reaction of  $\text{K}_3\text{MoCl}_6$  and  $\text{Br}_2$  at  $450^\circ$  can be expressed as



CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

## The Chromium-Diphenylcarbazide Reaction<sup>1</sup>

BY RONALD T. PFLAUM AND LESTER C. HOWICK<sup>2</sup>

RECEIVED APRIL 6, 1956

A study of the nature of the chromium-diphenylcarbazide reaction was carried out. Absorptimetric data for the reactions of chromium(VI), chromium(III) and chromium(II) ions with diphenylcarbazide and diphenylcarbazone were compared. The stoichiometry of the various systems was determined together with the effects of  $\text{pH}$  and the extractability of the colored reaction product into non-aqueous media. The behavior of the colored complex under the influence of an electric field was observed. The nature of the highly absorbing complex formed in the reaction of chromium and the organic reagents was postulated.

### Introduction

The color reaction between diphenylcarbazide and chromium(VI) has long been used for the colorimetric determination of chromium.<sup>3</sup> Today it is one of the most widely used reactions for this particular analysis.<sup>4</sup> The colored system enjoys this popularity due to the sensitivity, selectivity, and simplicity inherent in the reaction. In addition, the organic reagent is readily available in a state of purity sufficient for analytical work.

In spite of the above situation, little is known of the actual nature of the red-violet species formed in the reaction. A survey of the literature reveals many inconsistent and contradictory statements, as well as many unexplained observations. The present investigation was undertaken in order to resolve certain of these factors and to gain a better insight into the nature of the color reaction.

Various formulations for the colored species formed in the reaction have been advanced in the 50-odd years since Cazeneuve first reported his observations.<sup>5,6</sup> He proposed that an organo-metallic compound was formed in the reaction of diphenylcarbazide and chromium. Babko and Paulii<sup>7</sup> and Feigl<sup>8</sup> have concluded, however, that the colored material is merely an oxidation product of the reagent. Moreover, the oxidation must be very selective since none of the other common oxidizing agents, *i.e.*, ceric salts, permanganate, persulfate, etc., give similar results. The most recent work was carried out by Bose<sup>9</sup> who postulated that it is highly unlikely that chromium(VI) should possess a unique oxidizing ability but that, however, some

type of oxidation-reduction with subsequent coordination must be involved in the reaction. He performed absorption, migration, extraction and magnetic susceptibility studies and concluded that the colored species was a neutral monodiphenylcarbazone-chromium(II) complex. This conclusion was based in part upon the observation that chromium(III) ion did not react with the reagent.

The present investigation became imperative when it was learned that the diphenylcarbazone used in the above study was in reality a 1:1 mixture of diphenylcarbazide and diphenylcarbazone<sup>10,11</sup> and when it was observed that chromium(III) did react with the reagents. The work described herein is intended to clarify some of the unresolved factors in the chromium-diphenylcarbazide reaction.

### Experimental Part

**Materials Used.**—Diphenylcarbazide was prepared by the condensation of urea and phenylhydrazine at  $155^\circ$ .<sup>12</sup> The pure white compound with a melting point of  $170^\circ$  (on repeated recrystallization from ethanol) was used as the pure reagent. Diphenylcarbazone was prepared by the oxidation of crude diphenylcarbazide with 3% hydrogen peroxide in alcoholic potassium hydroxide.<sup>10</sup> On neutralization and recrystallization, the red-orange mixture of the two reagents was obtained. Treatment of this product with sodium carbonate in hot ethanol, extraction of the diphenylcarbazide with ether and acidification of the aqueous solution with hydrochloric acid yielded a red powder melting at  $127^\circ$ . This material is pure diphenylcarbazone.<sup>11</sup>

Dimethylformamide was obtained from the Rohm and Haas Company. Purification was effected by treatment with barium oxide for a period of 24 hr. with subsequent rectification in an all glass system. The fraction boiling at  $151 \pm 1^\circ$  was used as the purified solvent. All other technical grade solvents were distilled before use.

Solutions of chromium(II) ion were prepared according to the method of Hatfield<sup>13</sup> and stored under nitrogen. Standardization was carried out titrimetrically with standard ceric and ferrous sulfates. All other chemicals used were of reagent grade quality.

**Spectrophotometric Measurements.**—A Cary Model 11 recording spectrophotometer and a Beckman Model B spectrophotometer were used to obtain absorptimetric data. All measurements were made in matched  $1.00 \pm 0.01$  cm. cells at room temperature of approximately  $25^\circ$ .

(10) K. H. Slotta and K. R. Jacobi, *Z. Anal. Chem.*, **77**, 344 (1929).

(11) P. Krumholz and E. Krumholz, *Monatsh.*, **70**, 431 (1937).

(12) O. L. Barneby and S. R. Wilson, *THIS JOURNAL*, **35**, 157 (1913).

(13) M. R. Hatfield, "Inorganic Syntheses," Vol. III, 1st Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 148.

(1) Presented before the Division of Physical and Inorganic Chemistry at the 127th Meeting of the American Chemical Society, Cincinnati, Ohio.

(2) An Abstract of a thesis submitted by Lester C. Howick to the Graduate College of the State University of Iowa, 1955, in partial fulfillment of the requirements for the Degree of Master of Science.

(3) M. A. Moulin, *Bull. soc. chim.*, **31**, 296 (1904).

(4) F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," Vol. II, 3rd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 274.

(5) P. Cazeneuve, *Bull. soc. chim.*, **23**, 701 (1900).

(6) P. Cazeneuve, *ibid.*, **25**, 758 (1901).

(7) A. K. Babko and L. A. Paulii, *Zhur. Anal. Khim.*, **5**, 272 (1950).

(8) F. Feigl, "Spot Tests," Vol. I, 4th English Ed., Elsevier Publishing Co., New York, N. Y., 1954, p. 159.

(9) M. Bose, *Anal. Chim. Acta*, **10**, 201, 209 (1954).

**The Color Reaction.**—The reactions of diphenylcarbazide and diphenylcarbazone with chromium(VI), chromium(III) and chromium(II) ions in aqueous and in non-aqueous media were studied spectrophotometrically. Solutions of chromium(VI) were prepared by the dissolution of potassium dichromate in dilute solutions of sulfuric acid. Solutions of hydrated chromium(III) ion were prepared by the dissolution of chromium(III) perchlorate hexahydrate in dimethylformamide. Solutions of anhydrous chromium(III) ion were prepared by the dissolution of anhydrous chromium(III) chloride in dimethylformamide. Anhydrous chromium chloride dissolves in the solvent upon heating in the presence of traces of zinc dust. The anhydrous salt dissolves readily in organic solvents in the presence of catalytic amounts of reducing agents.<sup>14</sup> The solutions were cooled, filtered and allowed to stand in a dry-box to ensure anhydrous conditions with no possibility of the presence of chromium(II) ion. Chromium(II) solutions were prepared as described above.

**Determination of the Effect of pH.**—The effect of pH on the above systems and on solutions of the reagents was determined. Measurements of pH were made on a Beckman Model G pH meter. The effects of changes in pH were determined spectrophotometrically.

**Determination of Formulas.**—Formulas for the colored species in the various systems were determined by the method of continuous variations.<sup>15</sup> Stock solutions of  $8 \times 10^{-5} M$  chromium ion and the reagents were prepared and aliquots were mixed in the appropriate ratios. Absorption measurements were made at selected wave lengths. Corrected absorbance values were obtained by subtracting the absorbance for zero reaction from the observed readings. Formulas were determined from plots of absorbance against the mole fraction of chromium ion.

**Extraction Studies.**—A study on the extractability of the colored material formed in the reaction into non-aqueous solvents was carried out. Common solvents immiscible with water were added to aqueous solutions containing the colored material. The effects of the addition of soluble salts to the aqueous systems were studied. The colored extracts were evaporated and analyzed for chromium content.

**Migration Studies.**—A Hittorf type transference cell with platinum electrodes was used to study the migration of the colored species under the influence of an electric field. The colored reaction mixtures were introduced into the middle compartment of the apparatus while the electrode compartments were filled with 0.1 N sulfuric acid. An average current of 0.5 amp. was applied for 30 min. The tris-1,10-phenanthroline-iron(II) complex was studied under identical conditions as a reference system.

## Results and Discussion

**The Color Reaction.**—Spectrophotometric examinations of solutions of diphenylcarbazide and diphenylcarbazone with chromium in its three oxidation states reveals some very interesting relationships. For clarity, systems of the two reagents will be treated separately. Absorption curves for the two systems are shown in Figs. 1 and 2.

Diphenylcarbazide reacts with chromium(VI) in acidic solution to produce an intense red-violet coloration. The absorption curve for the aqueous system is shown in Fig. 1, curve 4. The absorption maximum occurs at  $540 m\mu$ . In solutions of pH 1.3, the molar absorptivity of the colored species (based upon the concentration of chromium) is 26,000. This value is somewhat lower than the value of 31,000 reported by Ege and Silverman.<sup>16</sup>

The addition of diphenylcarbazide to green solutions of anhydrous chromium(III) chloride or to chromium(III) perchlorate hexahydrate in dimethylformamide does not cause an immediate forma-

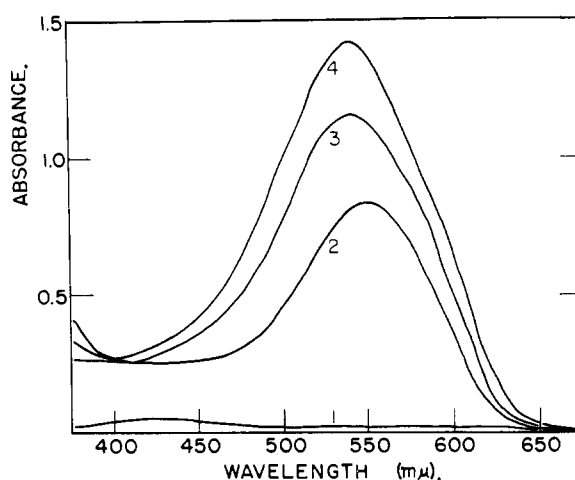


Fig. 1.—Absorption spectra for diphenylcarbazide systems: 1,  $1.0 \times 10^{-3} M$  reagent in  $H_2O$  at pH 1.5; 2,  $8.0 \times 10^{-5} M$  Cr(III) and reagent in dimethylformamide; 3,  $4.0 \times 10^{-6} M$  Cr(VI) and reagent in  $H_2O$  at pH 2.09; 4,  $4.0 \times 10^{-6} M$  Cr(VI) and reagent in  $H_2O$  at pH 1.30.

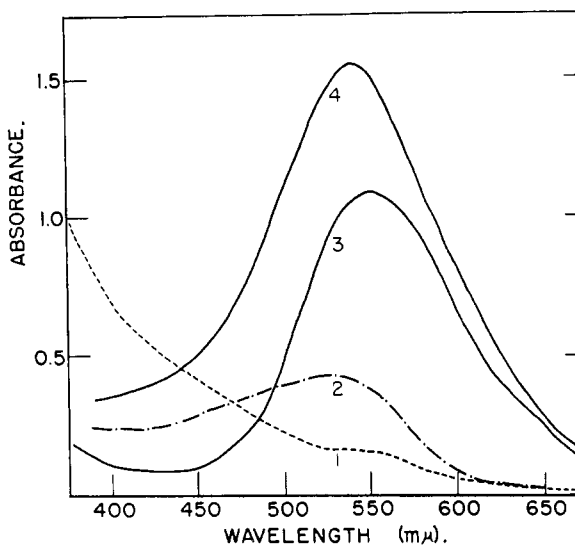


Fig. 2.—Absorption spectra for diphenylcarbazone systems: 1,  $1.0 \times 10^{-3} M$  reagent in  $H_2O$  at pH 1.5; 2,  $1.0 \times 10^{-3} M$  reagent in dimethylformamide; 3,  $8.0 \times 10^{-5} M$  Cr(III) and reagent in dimethylformamide; 4,  $4.0 \times 10^{-5} M$  Cr(II) and reagent in  $H_2O$ .

tion of a purple coloration. Color does develop, however slowly, and the degree of color is dependent upon several factors. The addition of small amounts of water or acid interferes in the color development. An increase in temperature from 25 to  $50^\circ$  causes approximately a fivefold increase in the rate of the reaction. Traces of base, added in the form of solid anhydrous lithium hydroxide, greatly increase the rate of color formation. Treatment with oxygen at elevated temperatures, in the presence of traces of base, causes immediate color formation. It was found also that diphenylcarbazide readily could be oxidized to diphenylcarbazone under these latter conditions.

The absorption curve for a dimethylformamide solution of hydrated chromium(III) ion and di-

(14) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, Oxford University Press, London, 1950, p. 1012.

(15) P. Job, *Compt. rend.*, **180**, 928 (1925).

(16) J. Ege and L. Silverman, *Anal. Chem.*, **19**, 693 (1947).

phenylcarbazide is represented by curve 2 in Fig. 1. The absorption maximum of the red-violet solution occurs at 550 m $\mu$ . Addition of water after color formation shifts the maximum to 545 m $\mu$ . The absorption of the reagent itself in the solvent is similar to that shown for the reagent in water as represented by curve 1.

Chromium(II) ion does not react with diphenylcarbazide. This same observation has been made previously.<sup>9</sup> Color does not develop even under every variation in the reaction conditions.

It was found that pure diphenylcarbazone does not react with chromium(VI) ion. This observation clarifies much of the difficulty reported with this reagent.<sup>9</sup> Solutions of the reagent and chromium(VI) did not show any color change even after a period of standing. Little oxidation of the red-orange colored diphenylcarbazone to the colorless diphenylcarbadiazone takes place.

Red-violet solutions (curve 3, Fig. 2) are obtained on reaction of diphenylcarbazone with chromium(III) ion in dimethylformamide. (The absorption spectrum of the reagent itself in the solvent is represented by curve 2.) The effects of added water or acid are similar to those described above for the diphenylcarbazide system. Oxygen appears to have little effect on the system. Color development is rapid on the addition of traces of base to an anhydrous system of chromium(III) ion. The rate of reaction is immeasurably fast on heating an anhydrous solution with base.

Diphenylcarbazone, contrary to diphenylcarbazide, does react with chromium(II) ion. Reaction is immediate and the absorption of aqueous solutions (curve 4) is identical in all respects to that for the chromium(VI) diphenylcarbazide system. The solutions show a great stability after reaction and after the addition of acid to pH of 1.5.

The results of the above study show that the same absorbing species can be obtained by the reaction of three oxidation states of chromium. These data are summarized in Table I. It can be seen that the color formed in the reactions is not due to either reagent alone. Likewise, color is not due to a higher oxidation product, diphenylcarbadiazone, which is known to be colorless and non-reactive toward metal ions.<sup>17</sup> A complex between the reagent or reagents and a species of chromium ion must be responsible for the intense coloration observed.

TABLE I  
SUMMARY OF ABSORPTIMETRIC DATA

System	$\lambda_{\max}$ abs, m $\mu$	$a_m$
Diphenylcarbazide (pH 1.5)	285	2490
Diphenylcarbazide (pH 12)	490	4280
Diphenylcarbazone (pH 1.5)	303	11,600
Diphenylcarbazone (pH 9)	487	1,800
Cr(VI)-Diphenylcarbazide (H <sub>2</sub> O)	540	26,000
Cr(III)-Diphenylcarbazide (DMF)	550	<sup>a</sup>
Cr(III)-Diphenylcarbazone (DMF)	550	<sup>a</sup>
Cr(II)-Diphenylcarbazone (H <sub>2</sub> O)	540	25,000

<sup>a</sup> Time dependent.

It is postulated that the reaction of chromium(VI) in acidic solution with diphenylcarbazide in-

volves an oxidation of the reagent to diphenylcarbazone by the dichromate with simultaneous reduction of chromium(VI) to chromium(III). Complexation between the newly formed products accounts for the intense color in the reaction. In dimethylformamide solutions of chromium(III) ion, diphenylcarbazide is air oxidized to diphenylcarbazone in the basic solvent. Subsequent complexation of chromium(III) and diphenylcarbazone gives the same species as observed for the chromium(VI) reaction. Reaction in the presence of oxygen, as described earlier, precludes the formation of a chromium(II) complex. In the reaction of chromium(II) ion with diphenylcarbazone, a portion of the reagent may be reduced to form diphenylcarbazide and chromium(III) ion. Reaction of chromium(III) and the remaining diphenylcarbazone again results in the formation of the colored complex.

**The Effect of pH.**—The two reagents, together with the various chromium systems, were studied over a range of pH values to determine the effect of changes in acidity. The effects were determined spectrophotometrically as shown in Figs. 1 and 2.

Considering diphenylcarbazide firstly, an increase in pH greatly increases the absorption of the reagent. At low pH, 1.5 (curve 1, Fig. 1), the reagent shows a molar absorptivity of 200 at 540 m $\mu$ . In basic solution, pH 9.4, a molar absorptivity of 1525 m $\mu$  is observed at the same wave length. It is evident that the absorbance due to the reagent at low pH is negligible.

Diphenylcarbazone likewise shows a molar absorptivity of about 200 at 540 m $\mu$  at pH 1.5 (curve 1, Fig. 2). Again at pH 9.0, the value is about 1500. Neither reagent shows the higher molar absorptivity observed for the chromium complex.

A study of the effects of changes in pH shows that maximum color formation for the chromium(VI) diphenylcarbazide reaction occurs in a pH range of 1.0–1.4. Color fades very rapidly in solutions of higher pH. No color is observed on addition of the reagent to a neutral or basic solution of chromium(VI) ion. The addition of a small amount of acid results in the immediate formation of color.

It is known that the reagents react with a number of metal ions to form inner complex salts of the metal ion and diphenylcarbazone.<sup>18</sup> Metal ions, such as copper, mercury, nickel, react to produce purple colored species. These compounds exhibit very little stability in solutions of low pH and are, in fact, dissociated at approximately pH 4. Chromium compounds show a behavior dissimilar to that for these inner complex salts. This indicates that the chromium complex is probably not an inner complex salt.

An inner complex salt of chromium(II)-diphenylcarbazone has been postulated<sup>9</sup> for chromium on the basis of extraction, migration and magnetic observations. The postulate necessitates the reaction of diphenylcarbazone in its enolic form in order to lose two protons and thus preserve the electroneutrality of the complex. The occurrence of such a

(17) F. Feigl and F. Lederer, *Monatsh.*, **45**, 115 (1924).

(18) H. Fischer, *Mikrochem.*, **30**, 38 (1942).

reaction in strong acid solution is a distinct improbability.

**Determination of Formulas.**—The chromium-diphenylcarbazide and -diphenylcarbazone systems were examined by the method of continuous variations. Plots of the data obtained are shown in Fig. 3.

The data for the chromium(VI)-diphenylcarbazide reaction at 540 and 600  $m\mu$  are shown as plots 4 and 1, respectively. Maxima are found at 0.4 mole fraction of chromium. Values for absorbance at several selected wave lengths indicate that only one primary absorbing species is present in solution and that it is formed by the reaction of 3 moles of reagent with 2 moles of chromium ion. This ratio was also found by Bose<sup>9</sup> and is in agreement with the reduction of two moles of chromium(VI) to chromium(III) and the oxidation of three moles of diphenylcarbazide to diphenylcarbazone.

Continuous variations data were obtained for the chromium(III)-diphenylcarbazide and -diphenylcarbazone reactions in dimethylformamide. Absorbance measurements at 550  $m\mu$  were made for solutions after reaction times of 4.5, 10.0 and 20.0 hr. Data for the diphenylcarbazide reaction after 10.0 hr. are represented by curve 2 in Fig. 3. Curve 3 results from a plot of the data from the diphenylcarbazone reaction after 20.0 hr. In both cases, the 3:2 ratio of reagent to metal ion is evident.

A continuous variations study of the chromium(II)-diphenylcarbazone system showed a maximum at 0.3 mole fraction of chromium. A value of 0.33 would be expected on the oxidation of 2 moles of chromium(II) to chromium(III) and the reduction of one mole of diphenylcarbazone to diphenylcarbazide with subsequent reaction of the two moles of chromium(III) and 3 additional moles of diphenylcarbazone. This result is at variance with the 1:1 ratio obtained by Bose.<sup>9</sup> However, in view of the reagent he used as diphenylcarbazone (a 1:1 mixture of carbazide and carbazone), a continuous variations study with equimolar solutions was not carried out and the results obtained do not necessarily indicate the stoichiometry of the reaction.<sup>15</sup>

All of the data obtained prove conclusively that a complex species is responsible for the absorption observed. The formula of this species may be something different from the ratio found. However, the conformity of all systems to essentially one pattern indicates a singular species. The analysis on this isolated entity might prove useful in assigning a formula. All attempts toward the isolation of a solid colored product from the various systems were unsuccessful.

**Extraction Studies.**—The colored material formed in the reaction of diphenylcarbazide or diphenylcarbazone with chromium in its three oxidation states is not readily extractable out of aqueous solutions into non-aqueous media. Only a fraction of the color is extracted into benzene, isoamyl alcohol, chloroform or carbon tetrachloride. Extraction was forthcoming when an excess of acetate, chloride or perchlorate ion was added. These observations are in agreement with Bose<sup>9</sup> who found that the colored material was extracted into ben-

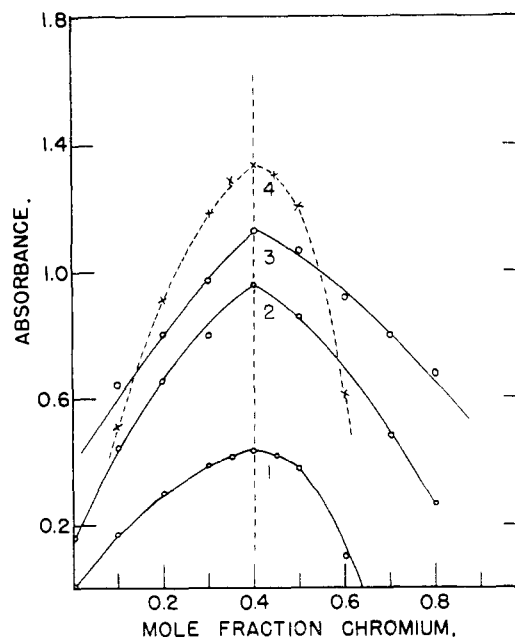


Fig. 3.—Continuous variations study of the chromium systems: 1, Cr(VI)-diphenylcarbazide at 600  $m\mu$ ; 2, Cr(III)-diphenylcarbazide at 550  $m\mu$  (DMF); 3, Cr(III)-diphenylcarbazone at 550  $m\mu$  (DMF); 4, Cr(VI)-diphenylcarbazide at 540  $m\mu$ .

zene, chloroform and cyclohexanol in the presence of acetate ion.

It was found on analysis of an isoamyl alcoholic extract of the colored material from aqueous chloride solution that chloride ion and chromium were present. These two ions were not extracted under identical conditions in the absence of the organic reagent. The results of this study show that the colored material is a complexed chromium species. Furthermore, the species is not an inner complex salt such as the copper salt which is readily extracted into benzene. Rather, the species is a charged cation which is extracted together with an anion as a neutral molecule.

**Migration Studies.**—Experiments designed to determine the charge on the complexed chromium ion were carried out using a Hittorf transference cell. It was found that the colored complex migrated to the cathode under the influence of an electric current. Migration was reversible on reversal of the polarity of the platinum electrodes. The tris-1,10-phenanthroline-iron(II) complex showed identical behavior.

The results of this study indicate that the colored complex is in reality a charged cation and not a neutral species as reported by one worker.<sup>9</sup> The migration supports the view that the chromium complex is not an inner complex salt.

### Conclusions

Several factors pertaining to the chromium-diphenylcarbazide-diphenylcarbazone reaction can be concluded from the study. These can be formulated in the following manner. 1. Diphenylcarbazide reacts with Cr(VI) and Cr(III) ions to form a singular red-violet complex. No reaction is forth-

coming with Cr(II) ion. 2. Diphenylcarbazone reacts with Cr(III) and Cr(II) ions to form the same complex as observed above. No reaction occurs with chromium(VI) ion. 3. The stoichiometry of the reaction of chromium and the reagents is in a ratio of three moles of reagent to two moles of the metallic ion. 4. The highly absorbing chromium complex exists as a cationic species in aqueous solution. 5. The chromium complex is extracted, together with an anion, into non-aque-

ous media as a neutral molecule. 6. A chromium-(III)-diphenylcarbazone complex is postulated as the colored species in the reactions.

The above conclusions are the result of all of the experimental data obtained. This situation is unique in studies of the systems under consideration. Such a situation serves to clarify much of the unsatisfactory nature of the existing literature on the subject.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY]

## The Molecular Structure of Perfluorotrimethylamine by Electron Diffraction<sup>1</sup>

By R. L. LIVINGSTON AND G. VAUGHAN

RECEIVED MARCH 15, 1956

The molecular structure of perfluorotrimethylamine has been investigated by electron diffraction using the visual correlation procedure. The structural parameters, as determined by this investigation, are as follows: C-F =  $1.32 \pm 0.02$  Å., C-N =  $1.43 \pm 0.03$  Å.,  $\angle$ FCF =  $108.5 \pm 2.0^\circ$ , and  $\angle$ CNC =  $114 \pm 3^\circ$ .

### Introduction

Previous investigations of the structures of hexafluoropropene<sup>2</sup> and octafluorocyclobutane<sup>3,4</sup> in this Laboratory indicated, for these molecules, that the closest approach of fluorine atoms which are bonded to different carbon atoms is about 2.70 Å. or twice the van der Waals radius of fluorine. Preliminary calculations on perfluorotrimethylamine indicated that if a similar F··F distance prevailed in this compound, then rather unusual structural parameters would be encountered; hence an investigation of the molecular parameters of this compound was undertaken.

### Experimental

The sample of perfluorotrimethylamine was supplied by Dr. W. H. Pearson of the Minnesota Mining and Manufacturing Company. In the absence of any comparative data, their estimate of a purity greater than 98 mol per cent. was based on the constancy of the boiling point and the molecular weight over successive distillations. No known compounds were observed as impurities in the infrared spectrum.

The diffraction photographs were obtained in the usual way<sup>5</sup> using a camera designed and constructed by Professor H. J. Yearian of the Purdue Physics Department. The camera distance was about 107.1 mm., and the electron wave length, as determined from a transmission pattern of ZnO, was about 0.0588 Å. The recorded diffraction pattern of perfluorotrimethylamine extended to a  $q$  value of about 95.

**Interpretation of the Diffraction Pattern.**—The visual correlation method<sup>5,6</sup> and the radial distribution method<sup>7,8</sup> were used in interpretation of the diffraction pattern. The measurements of the

diffraction features on three of the best plates are summarized in Table I. These values are based on measurements of each feature by two observers. The visual curve shown in Fig. 1 was based on independent interpretations of the patterns by three observers. The interpretations were in close agreement on all features except as noted below in the case of the eighth maximum and the ninth minimum. The portion of the curve in the interval  $q = 0$  to  $q = 20$  was copied directly from the most acceptable model as is customary.

Due to the diffuse nature of the eighth maximum and the ninth minimum, there was some doubt as to the exact shape of these features. However, it was the opinion of all observers that the maximum was asymmetric to the outside and that the indicated shapes of these features are approximately correct. Due consideration was given to this uncertainty in selecting acceptable models.

The radial distribution curve appearing in Fig. 1 was calculated using the equation<sup>8</sup>

$$rD(r) = \sum_{q=1}^{q_{\max}} I(q)_0 \exp(-bq^2) \sin \frac{\pi q}{10} r \quad (1)$$

The values  $I(q)_0$  were read from the visual curve, Fig. 1, and the radial distribution curve was calculated on I.B.M. tabulators.<sup>8</sup> The peak at 1.37 Å. corresponds to the C-F and C-N distances and at 2.23 Å. corresponds to the N··F distance and the F··F distance in the CF<sub>3</sub> group. If preliminary calculations of models showed quantitative incompatibility with the curve with respect to these two peaks, further investigations of these models were abandoned. It was later demonstrated that none of these models was within the range of acceptability. In view of the complex nature of the vibrational problem for this molecule, as indicated later, a complete quantitative interpretation of the radial distribution was not attempted.

The structural determination of perfluorotrimethylamine involves the evaluation of four param-

(1) Contains material from the Ph.D. thesis of G. Vaughan, Purdue Research Foundation Fellow in Chemistry, 1951-1953.

(2) F. A. M. Buck and R. L. Livingston, *J. Chem. Phys.*, **18**, 570 (1950).

(3) H. P. Lemaire and R. L. Livingston, *ibid.*, **18**, 569 (1950).

(4) H. P. Lemaire and R. L. Livingston, *THIS JOURNAL*, **74**, 5732 (1952).

(5) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

(6) L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

(7) L. Pauling and L. O. Brockway, *THIS JOURNAL*, **57**, 2684 (1935).

(8) P. A. Shaffer, V. Schomaker and L. Pauling, *J. Chem. Phys.*, **14**, 659 (1946).