Spectrophotometric Study of the Complex of Hg(II)-X-Diphenylcarbazone [X: I, Br]*[1]

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(Received November 13, 1967)

Mercury(II) forms a reddish-violet complex with diphenylcarbazone which may be easily extracted by benzene.[1] Ions such as cyanide which react with mercury(II) decrease the color intensity.[2] However, in the presence of iodide or bromide ions, the color intensity increases slightly with an increase in the ions in the first step, while the color intensity decreases greatly above an equimolor concentration of mercury(II)[3] (see Fig. 1).

From these results, it is considered that a mercury-(II)-diphenylcarbazone complex containing iodide or bromide will be formed, although the composition of this complex has not yet been reported.

We have previously reported a spectrophotometric method for the determination of minute quantities of such anions as chloride,[4] thiosulfate,[5] sulfide,[6] cyanide,[7] sulfite,[8] iodide,[9] and bromide[9] ions by using a complex formed of mercury(II), iodide (or bromide), and diphenylcarbazone.

This paper will report the results of more detailed studies of the reaction of mercury(II), iodide (or bromide), and diphenylcarbazone, and of the composition of the complex.

Experimental Results and Discussion

Reagents and Apparatus. *So-Called Diphenylcarbazone (DC).* The reagent is a molecular compound of diphenylcarbazone and diphenylcarbazide, and its color is orange.[10]

$C_6H_5NHNHCONHNHC_6H_5 \cdot C_6H_5N{=}NCONHNHC_6H_5$ (mp 153°C).

Diphenylcarbazone (H_2DCN). Pure orange-yellow diphenylcarbazone was prepared by the removal of diphenylcarbazide from the so-called diphenylcarbazone using the method of Gerlach.[11]

$C_6H_5N{=}NCONHNHC_6H_5$ (mp 118—120°C).

Diphenylcarbazide (H_4DCD). White crystals were used.

$C_6H_5NHNHCONHNHC_6H_5$ (mp 170°C).

These solutions of various concentrations were prepared by dissolving the reagent in ethanol, and a 1 m*l* portions of the solution were used in all the experiments.

Mercuric Nitrate Solution. A mercuric nitrate solution was prepared by dissolving 8.5 g of mercuric nitrate in water containing 2 ml of concentrated nitric acid, and by then diluting it to 500 m*l* (about 0.05 mol/*l*). This solution was standardized by Volhards method, and then stored in a brown glass bottle. The working solutions were prepared by diluting the stock solution properly.

The other materials and apparatus used in this investigation were the same as those described in previous papers.[4-9]

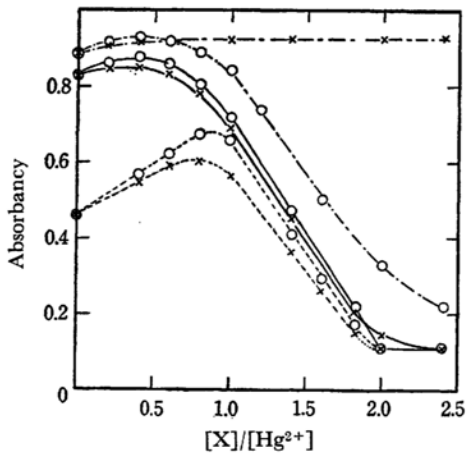

Fig. 1. The reactions between Hg(II)-diphenylcarbazone and iodide (or bromide) ion

Hg^{2+}; 1.5×10^{-5} mol/*l*
H_2DCN; 1.5×10^{-4} mol/*l*
Wavelength ; 562 mμ, at 25°C
X^-; ○ I^-, × Br^-,
pH; -·-· 7.0, —— 2.5, ---- 1.4

*1 Presented at the 16th Annual Meeting of the Japan Society for Analytical Chemistry, Chiba, October, 1967.

1) A. Tomonari, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **82**, 864 (1961).
2) A. Tomonari, *ibid.*, **83**, 455 (1962).
3) A. Tomonari, *ibid.*, **83**, 459 (1962).
4) S. Utsumi and T. Okutani, *ibid.*, **85**, 543 (1964).
5) T. Okutani, S. Utsumi, K. Shibata and I. Iwasaki, *ibid.*, **86**, 831 (1965).
6) T. Okutani and S. Utsumi, *ibid.*, **86**, 1149 (1965).
7) T. Okutani and S. Utsumi, *ibid.*, **87**, 444 (1966).
8) T. Okutani and S. Utsumi, This Bulletin, **40**, 1386 (1967).
9) T. Okutani, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)* **88**, 737 (1967).
10) M. Uchida and M. Nakada, *Bulletin of the Faculty of Education, Chiba University*, **15**, 138 (1966).
11) J. L. Gerlach and R. G. Frazier, *Anal. Chem.*, **30**, 1142 (1958).

Formation of a Mercury(II)-Diphenylcarbazone Complex Containing Iodide or Bromide. Ten milliliters of a aqueous solution containing mercury(II), H_2DCN, and X^-(X^-; iodide or bromide ions) in which the pH was kept at 7, 2.5, or 1.4, and 10 m*l* of benzene were placed in a brown separatory funnel. Then the separatory funnel was shaken for about 1 min. The absorbance of benzene phase was measured at 562 mμ against pure water as a reference. The experimental results are plotted in Fig. 1. From Fig. 1 it may be considered that a complex of mercury(II)-diphenylcarbazone containing X^- is formed in the first step, and that then the color of all such complexes except one containing bromide at pH 7 fade as a result of the formation of HgX_2.

Therefore, mole ratio method was applied in order to clarify the relations of mercury(II) and X^- in the presence of H_2DCN (the molar concentration of H_2DCN was adjusted so as to be equal to that of X^-).

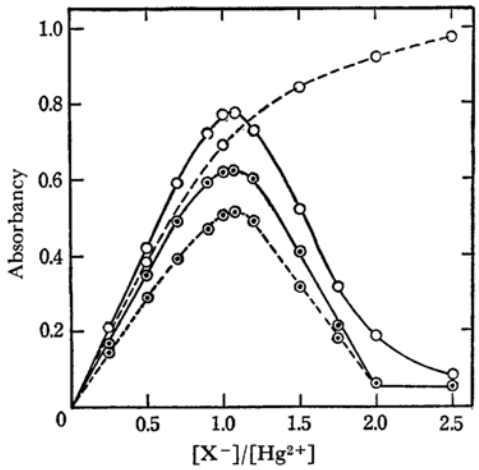

Fig. 2. Mole ratio method
Hg^{2+} ; 2.0×10^{-5} mol/*l* $[H_2DCN]=[X^-]$
Wavelength ; 562 mμ, at 25°C
—— I^-, - - - Br^-, ○ pH 7.0, ⊙ pH 2.5

As is shown in Fig. 2, all the curves except that of a complex containing bromide at pH 7 have a maximum absorbance in about an equimolar concentration of X^- and Hg^{2+}.

Similar experiments were carried out in which the molar concentration of H_2DCN was adjusted so as to be twice that of X^-. The maximum absorbance was also obtained in about an equimolar concentration of X^- and Hg^{2+}.

It may be considered that the diphenylcarbazone forms a complex with HgX^+ which is in a state of equilibrium as follows:

$$Hg^{2+}+X^- \rightleftharpoons HgX^+$$

These experiments (Figs. 1 and 2) were carried out using DC, and the experimental results were in agreement with the above results.

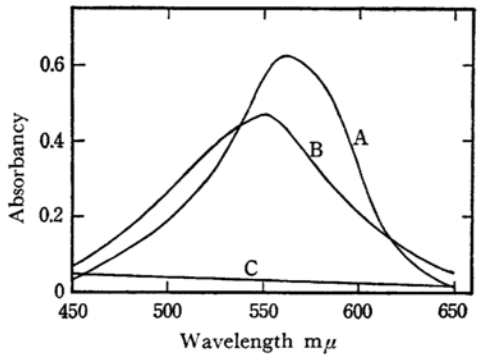

Fig. 3. Absorption spectra of Hg^{2+}-H_2DCN and HgI^+-H_2DCN complexes
Hg^{2+}(or HgI^+); 1.3×10^{-5} mol/*l*
H_2DCN; 2.6×10^{-5} mol/*l*
pH 7.0, at 25°C
A : HgI^+, B : Hg^{2+}, C : H_2DCN alone

Absorption Spectra. The absorption spectra of the benzene solution of the complex are shown in Fig. 3. The Hg^{2+}-H_2DCN complex has a maximum absorbance at 552 mμ, while the HgX^+-H_2CDN complex has its at 562 mμ, indicating that they are different.

Composition of the Complex. The compositions of the Hg^{2+}-H_2DCN and HgX^+-H_2DCN complexes were determined by the continuous-variation method. Mixed solutions of the Hg^{2+} (or HgX^+) and H_2DCN in various ratios were prepared, and the pH values of the solutions thus prepared were adjusted to 7.0, then the absorbances of the extracted benzene phase were measured at 562 mμ.

The results are shown in Fig. 4. The figure shows that either the Hg^{2+} or HgX^+ complex forms a 1-to-1 complex with H_2CDN. Moreover, the continuous-variation method was carried out using DC and H_4DCD. The mole ratio of DC and

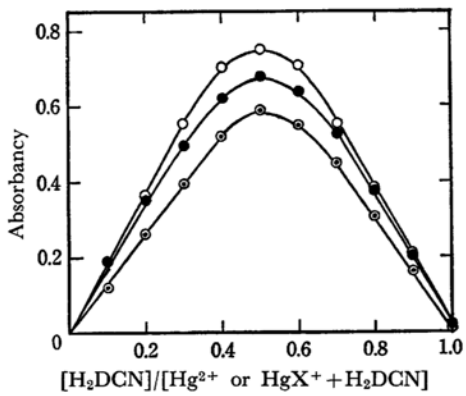

Fig. 4. Continious variation method
$[Hg^{2+}$ or $HgX^+] + [H_2DCN] = 4\times15^{-5}$ mol/*l*
Wavelength ; 562 mμ, at 25°C, pH 7.0
-○- HgI^+, -●- $HgBr^+$, -⊙- Hg^{2+}.

Hg^{2+}(or HgX^+) was also 1-to-1; on the other hand, H_4DCD did not form a complex at the concentration of 4×10^{-5} mol/*l*. The experimental results indicate that Hg^{2+} or HgX^+ forms a 1-to-1 complex with the H_2DCN which is present in the DC. These results were also conformed by further experiments using the mole-ratio method.

Gerlach *et al.*[11] have also reported a mole ratio of 1-to-1 between mercury(II) and diphenylcarbazone; on the other hand, a 1-to-2 complex has been reported by Feigl *et al.*[12]

If the so-called diphenylcarbazone(DC) is assumed to be a true diphenylcarbazone(H_2DCN), the mole ratio between mercury(II) and DC may become the 1-to-2 shown by Feigl *et al.*[12]

12) F. Feigl and F. L. Lendere, *Monatsh*, **45**, 115 (1924).

The reactions between mercury(II) or HgX^+ and H_2DCN may be expressed by the following equations;

$$Hg^{2+} + H_2DCN \rightleftharpoons HgDCN + 2H^+$$

$$HgX^+ + H_2DCN \rightleftharpoons HgXHDCN + H^+$$

As may be seen in Figs. 1 and 2, all the complexes are more stable at pH 7 than at pH 2.5. With regard to the effect of light, it has previously been reported[4] that the complex of HgXHDCN is more stable than that of HgDCN. The formation of the HgClHDCN complex is difficult under these conditions.[1]

The author wishes to express his gratitude to Professor Satori Utsumi of Nihon University for his kind guidance throughout this study.