chromic than ⊥-absorption for the second band of tetrahalogeno-complex ions, since halogens stand very low in the series. Thus two kinds of dichroism for the second band, which might seem quite different from each other, can be united by taking the spectrochemical series into consideration.

From discussion above, the general regularities of dichroism for planar complex ions can be deduced as follows: (1) The second band in ||-absorption of planar complex ions are more hypsochromic or more bathochromic than that of ⊥-absorption, according as ligands stand higher or lower in the spectrochemical series. (2) In palladous complex ions, the second bands of ||-absorption have larger intensities than those of ⊥-absorption. In platinous complex ions, the second bands of ||- and ⊥-absorptions have almost equal intensities. (3) The first absorption bands lie at about the same wave length in both ||- and ⊥-absorption.

The author wishes to express his sincere thanks to Professor R. Tsuchida for his kind suggestions and encouragement throughout this work.

Summary

Dichroism of microscopic crystals of compounds with planar complex ions were measured in the region from visible to near-ultraviolet by the microscopic method. It was found that dichroism of planar complexes can be classified into two types, the tetrahalogeno-type and the tetracyano-type. Discussion was made on these two types of dichroism from standpoints of the theory of absorption spectra for metallic compounds and the new coördination theory of valency, which had been proposed by Tsuchida. From comparative consideration about results of the measurements, general regularities were deduced on dichroism of planar complexes.

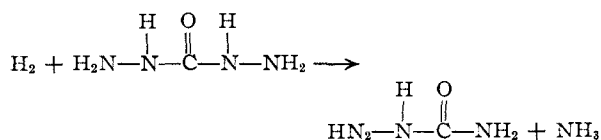NAKANOSHIMA, KITA, OSAKA, JAPAN

The Reduction of Carbohydrazide. The Acidity of Carbohydrazide, Semicarbazide and Urea[1]

BY ALSOPH H. CORWIN AND JOHN D. REINHEIMER

In a previous paper, Corwin and Jackson[2] found that 1,5-diphenylthiocarbazide could be reduced to 1-phenylthiosemicarbazide, and no further. Since the 1,5-diphenylthiocarbazide is symmetrical, the hydrogenolysis of one N–N bond but not the other is surprising. The reduction of the parent compound, carbohydrazide, was therefore indicated in order to ascertain whether this compound showed the same resistance toward hydrogenation.

Another method of showing that a fundamental difference between the ease of reduction of the carbohydrazide and the semicarbazide should exist is a determination of the relative acidity of these compounds. If one assumes that reduction is essentially an addition of electrons, the more acidic of these two compounds should be more easily reduced.

The carbohydrazide was reduced catalytically with Raney nickel in a low pressure hydrogenation apparatus. The theoretical amount of hydrogen was absorbed after 8 hours and no further change in pressure noted after 24 hours. The course of the reaction is given by the equation

$$H_2 + H_2N\overset{\overset{\displaystyle H}{|}}{N}\overset{\overset{\displaystyle O}{||}}{C}\overset{\overset{\displaystyle H}{|}}{N}NH_2 \longrightarrow$$
$$HN_2\overset{\overset{\displaystyle H}{|}}{N}\overset{\overset{\displaystyle O}{||}}{C}NH_2 + NH_3$$

The presence of ammonia was shown by its odor and no further test was run. Semicarbazide was identified by two derivatives, the white benzal-

dehyde derivative, d.p. 208–210° and a decomposition product of d.p. 243–245°. The literature values for these derivatives are 214° and 245–246°.[3] Chemical reduction was attempted but with no success. The reaction had to be run in the cold, for the carbohydrazide is unstable in the presence of acids or base when heated.

The acidity of very weak acids in ether and benzene has been determined by Conant and Wheland[4] and McEwen.[5] Since the solubility of urea in ether is very small,[6] liquid ammonia was used as the solvent for the acidity determination. The indicators developed by Conant were used. The results are recorded in Table I.

TABLE I

Sample	Indene $pK\ 21$	Fluorene $pK\ 25$	$(C_6H_5)_3CH$ $pK\ 33$	pK_a
Urea		Yellow	Colorless	25–33
Semicarbazide		Yellow	Colorless	25–33
Carbohydrazide	Yellow	Colorless	Colorless	21–25

Experimental

I. **Reduction of Carbohydrazide.**—Four grams of carbohydrazide[7] was dissolved in 100 ml. of commercial absolute alcohol and 2 ml. of Raney nickel was added. (Activity of catalyst was checked by reducing p-nitroaniline just prior to its use.) The calculated pressure drop for 1 mole of hydrogen was 3.7 pounds gage, and the observed drop after 24 hours shaking was 3.8 pounds gage. A strong odor of ammonia was observed when the bottle was opened. The solution was filtered, hydrochloric acid added, and the sol-

(1) This paper is from the Doctoral Dissertation of John D. Reinheimer, The Johns Hopkins University, 1948.

(2) Corwin and Jackson, THIS JOURNAL, **71**, 3698 (1949).

(3) Curtius and Heidenreich, J. prakt. Chem., **52**, 466 (1895).

(4) Conant and Wheland, THIS JOURNAL, **54**, 1212 (1932).

(5) McEwen, ibid., **58**, 1124 (1936).

(6) Seidell, "Solubilities of Organic Compounds," 3rd Ed., D. Van Nostrand and Co., New York, N. Y., Vol. II, p. 61.

(7) Prepared by method of Cazeneuve and Moreau, Comp. rend., **129**, 1255 (1899).

vent was removed by aspirator. The solid obtained was recrystallized from alcohol. The sticky crystals obtained could not be dried and had no definite melting point. These crystals were washed with water. A part dissolved, leaving a white residue of d.p. 243–245°. The water solution was shaken with benzaldehyde to obtain a white compound of d.p. 208–210° after recrystallization from alcohol–water. Carbohydrazide and benzaldehyde gives a pale yellow benzaldehyde derivative of d.p. 198°.[8]

Acidity Studies.—The sodium triphenylmethyl solution was prepared and handled by the method of Corwin and Ellingson.[9] The nitrogen purification train used was described by Corwin and Erdman[10] (see Fig. 1). Organophobic stopcock[11] grease was used on the buret.

Procedure for Titration.—This method is a modification of that of McEwen.[5] The entire apparatus (Fig. 1) is alternately evacuated and filled with nitrogen through D. After the last flush with nitrogen, C is closed by a pinch clamp and liquid ammonia is introduced into the storage flask from A. When the storage flask is about half full, the flow of liquid ammonia is shut off, C is opened and B is closed. The liquid ammonia siphons over into the reaction flask, and is stopped by opening B and closing C. A slow stream of N₂ is maintained throughout to prevent back diffusion of air. The weighed sample is introduced from the bent side arm or placed in the flask at the start of the flushing operation. The suspension (or solution) is stirred with a magnetic stirrer as the sodium triphenylmethyl solution is dropped in from the buret.

Two types of reaction were carried out. (A) The sodium salt of the acid was prepared by titrating with an insufficient amount of sodium triphenylmethyl and then adding the indicator. The indicator changed from colorless to the colored sodium salt if it were a stronger acid than the sample. (B) The sample and indicator were placed in the reaction vessel together and competed for the sodium of the sodium triphenylmethyl. The stronger acid acquired the sodium.

Miscellaneous Experiments.—(1) Dryness of the liquid ammonia: When 0.088 M sodium triphenylmethyl was added to the liquid ammonia, about 2 or 3 ml. was used before a permanent color was obtained. This was first attributed to the presence of water. However, when fluorene was added to the liquid ammonia, one drop of sodium triphenylmethyl changed the color to a pale yellow. Since water is a stronger acid than fluorene, the solution should have remained colorless until the usual 2–3 ml. of solution was used, then changed to yellow. The decolorization was therefore attributed to the equilibrium

$$NH_3 + C(C_6H_5)_3^- \longrightarrow HC(C_6H_5)_3 + NH_2^-$$

The pK_a of ammonia is 33[12] and that of triphenylmethane is also 33.[4]

(2) Suitability of fluorene, and indene and xanthane as indicators: Fluorene plus liquid ammonia gives a colorless solution which changes to pale yellow when 1 drop of sodium triphenylmethyl is added. If benzoic acid and fluorene are placed in the reaction flask and titrated with sodium triphenylmethyl, no change to yellow is noted. If sodium fluoryl is made and some alcohol then added, the yellow color fades to very pale or almost colorless and a white precipitate appears within 1 minute.

Indene changes to yellow slowly when it is treated with sodium triphenylmethyl in the reaction flask. When benzoic acid is added this color fades.

Xanthane was not a suitable indicator, for its sodium salt either did not form or the xanthane was too insoluble. The experiment performed was to use ether as a solvent, add sodium triphenylmethyl to a permanent color and then double the volume with ammonia. The solution immediately became colorless.

Acidity of Carbohydrazide.—(1) Thirty milligrams (0.33 millimole) of carbohydrazide and 10 mg. of fluorene were placed in the reaction flask and liquid ammonia added. As the mixture was stirred, sodium triphenylmethyl (0.088 M) was added. The solution was colorless until 4 ml. (0.35 millimole) was added, then it turned yellow. Therefore

(8) Curtius and Heidenreich, *J. prakt. Chem.*, **52**, 471 (1895).
(9) Corwin and Ellingson, THIS JOURNAL, **64**, 2098 (1942).
(10) Corwin and Erdman, *ibid.*, **68**, 2477 (1946).
(11) Meloche and Frederick, *ibid.*, **54**, 3264 (1932).
(12) Pleskov and Monoszon, *Acta Physico-Chim. U. S. S. R.*, **1**, 725 (1935).
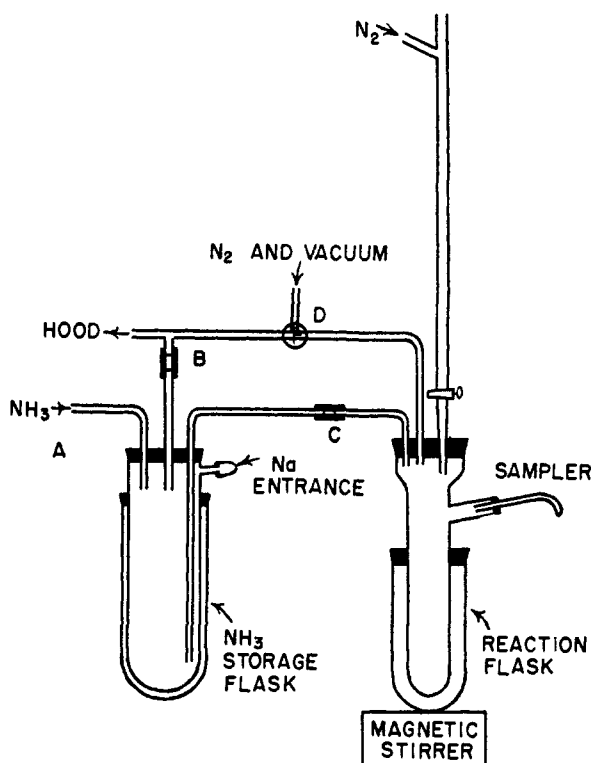
Fig. 1.

carbohydrazide is a stronger acid than fluorene and reacts with sodium triphenylmethyl as a mono-basic acid. (2) Twenty milligrams of carbohydrazide and 0.5 ml. of indene were added to the reaction flask and sodium triphenylmethyl was added. The solution turned yellow slowly. Therefore carbohydrazide is a weaker acid than indene. (3) Three-tenths milliliter of indene was placed in the reaction flask and ammonia added; 1.5 ml. of sodium triphenylmethyl was added and the color slowly changed to a pale yellow. The yellow color continued to deepen after the addition of 20 mg. of carbohydrazide. Addition of benzoic acid caused decolorization.

Acidity of Semicarbazide.—(1) Thirty-five and five-tenths milligrams of semicarbazide hydrochloride (0.317 millimole was placed in a reaction flask and liquid ammonia added; 5.0 of 0.088 M sodium triphenylmethyl was added and the solution remained colorless. When fluorene was added the color changed to yellow within 30 seconds. (2) Forty-one and five-tenths milligrams of semicarbazide hydrochloride (0.375 millimole) and a small amount of fluorene were placed in a reaction flask and liquid ammonia added; 5.0 ml. of 0.088 M (0.44 millimole) sodium triphenylmethyl was added and the color changed slowly to light yellow. The color became deeper as more sodium triphenylmethyl was added.

Acidity of Urea.—(1) Fluorene and urea were placed in the reaction flask and liquid ammonia added. Addition of a few drops of sodium triphenylmethyl solution gave a yellow color immediately. (2) Sodium triphenylmethyl solution was added to liquid ammonia until a permanent color was obtained (3.15 ml.). Urea (30 mg.) was then added and this color was immediately discharged. Additional sodium triphenylmethyl solution was decolorized immediately. (3) Thirty milligrams of urea was placed in the reaction vessel and a solution of sodium in liquid ammonia was siphoned into it. The blue color disappeared instantly. On addition of fluorene the color changed to yellow. This color changed to pale yellow when alcohol was added.

Discussion

The ease of reduction of the carbohydrazide to the semicarbazide parallels that of 1,4-diphenylcarbohydrazide to 1-phenylthiosemicarbazide. Since there can be no doubt that the structure of
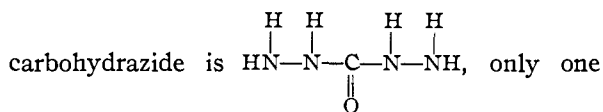
H   H   H   H
| | | |
carbohydrazide is HN—N—C—N—NH, only one
‖
O

N–N bond has undergone hydrogenolysis. Thus it appears that a property of the carbohydrazide structure is this resistance to complete hydrogenolysis.

We have established the fact that carbohydrazide is a stronger acid than fluorene, while semicarbazide is weaker. That it is not much weaker follows from an observation of Conant and Wheland.[4] These investigators observed cases of several extremely weak acids in which salts of acids only slightly weaker reacted with them slowly while in cases in which the difference in acidity was great, the reaction was instantaneous. Since the appearance of the color of sodium fluoryl is delayed after an equivalent of sodium triphenylmethyl has been added to the hydrochloride of semicarbazide, it is concluded that semicarbazide is only slightly weaker as an acid than fluorene. By the same argument, urea is a much weaker acid than fluorene, since the yellow color of sodium fluoryl appears instantly when one drop of sodium triphenylmethyl is added to a solution of urea and fluorene. We may conclude that the relative acidity of these three compounds in liquid ammonia is: carbohydrazide > semicarbazide > urea. The NH_2

group is an electron attracting group, causing the semicarbazide nitrogen to become more acidic than that of urea through the inductive effect. The additional inductive effect of the second NH_2 group would cause carbohydrazide to be a slightly stronger acid than semicarbazide. We believe that the magnitude of the effect observed is much too great to be explained in this manner, however.

The difference in reducibility of the two substances parallels the acidity. The compound with the more positive N, carbohydrazide, should be the one which would add electrons more easily. Thus the stronger acid should be more readily reduced. This is the order actually observed.

One of the authors (J.D.R.) wishes to express his appreciation of a grant-in-aid from the Hynson, Westcott and Dunning Research Fund.

Summary

1. Carbohydrazide has been reduced to semicarbazide.
2. The relative acidity of carbohydrazide, semicarbazide and urea has been determined in liquid NH_3.
3. Fluorene and indene are suitable acid indicators in liquid NH_3.
4. Resistance to hydrogenolysis is a characteristic of semicarbazide structure.

Copolymerization. VIII. Reactivity of Fumaronitrile in Vinyl Copolymerization

BY REID G. FORDYCE AND GEORGE E. HAM

In the course of an exploratory study of styrene copolymerization, mass copolymers of styrene and fumaronitrile were prepared. These copolymers, which were without exception incompatible, nevertheless showed a remarkable improvement over mass polystyrene with regard to heat distortion characteristics. It was realized that the incompatibility of these copolymers was probably the result of heterogeneity with respect to fumaronitrile content. Accordingly, an investigation of fumaronitrile reactivity in copolymerization with styrene was undertaken.

Results and Discussion

Various monomer mixtures of styrene and fumaronitrile dissolved in dioxane were allowed to polymerize to low conversions. Copolymerization was interrupted by precipitation of the slightly viscous copolymer solutions in ethanol, followed by thorough washing of the fibrous copolymer with more ethanol. The samples after drying were analyzed for nitrogen by the Kjeldahl method and the fumaronitrile content of the copolymers was calculated. As determined from the slope of the copolymerization curve (Fig. 1) at 0% fumaronitrile, the reactivity of fumaronitrile monomer for a styrene free radical is approximately 11.0 times as great as the reactivity of styrene for a styrene free radical. Since the completion of this

research, Lewis and Mayo[1] have reported reactivity ratios for styrene and fumaronitrile. However, their calculated values ($r_1 = 0.19 \pm 0.03$, $r_2 = 0.0$) differ from those reported here. Monomer reactivity ratios for the system styrene–fumaronitrile were calculated by the Mayo and Lewis intersection method[2] and by curve fitting of experimental points, but no consistent values could be obtained. The reactivity of fumaronitrile unexpectedly diminishes at higher concentrations, causing deviation from the theoretical copolymerization curve. Accordingly, the initial slope was taken as the best indication of fumaronitrile reactivity, and yielded an r_1 value of 0.09 $\pm$ 0.005 and an r_2 value of 0.0. The anomalous behavior characteristic of the system styrene–fumaronitrile has also been observed with styrene–maleic anhydride.[3] In the case of styrene–fumaronitrile an azeotrope point of 38 mole % was obtained instead of the ~50 mole % obtained with styrene–maleic anhydride. No completely satisfactory explanation of the copolymerization behavior of styrene and fumaronitrile has been found. However, at higher fumaronitrile concentrations the opportunity for electrostatic repulsion between fumaronitrile monomer and polymer chains rich

(1) F. M. Lewis and F. R. Mayo, THIS JOURNAL, **70**, 1533 (1948).
(2) F. R. Mayo and F. M. Lewis, ibid., **66**, 1594 (1944).
(3) T. Alfrey, Jr., and E. Lavin, ibid., **67**, 2044 (1945).