# NOTES

## SOME ISOTOPIC EXCHANGE REACTIONS OF IODINE CYANIDE

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Iodine cyanide is a well-defined molecular compound, but recent studies have pointed up its chemical peculiarities, both as regards some of its reactions in solution<sup>1-3</sup> and its ability to form mo-lecular complexes.<sup>4,5</sup> It was considered of interest to examine the nature of the various isotopic exchange reactions possible with this compound in an attempt to throw additional light on its chemistry. The reactions studied were

$$ICN + I^{131} \longrightarrow I^{131}CN + I^{-}$$
(1)

$$\frac{\text{ICN} + \text{C}^{14}\text{N}^{-}}{\text{ICN} + \text{I}^{131}\text{I}} \xrightarrow{\text{IC}^{14}\text{N} + \text{CN}^{-}} (2)$$

$$\frac{\text{ICN} + \text{I}^{131}\text{I}}{\text{ICN} + \text{I}_{2}} (3)$$

$$ICN + I^{131}I \swarrow I^{131}CN + I_2 \qquad (3)$$

#### Experimental

A. Preparation of Materials .--- Iodine cyanide was synthesized from iodine and sodium cyanide by the usual prothesized from iodine and sodium cyanide by the usual pro-cedure.<sup>6</sup> It was purified by recrystallization from chloro-form/heptane solvent followed by vacuum sublimation. Dioxane was purified by the method of Hess and Frahm,<sup>7</sup> omitting the freezing step. Acetone was purified by treat-ment with KMnO<sub>4</sub> and ignited  $K_2CO_3$ , followed by frac-tional distillation. Commercial *n*-heptane was purified by passage through a 30-inch silica-gel column. Other reagents were of analytical grade and were used without further treatment. Radiocyanide and radioiodide were obtained from commercial suppliers. Radioiodine was prepared by from commercial suppliers. Radioiodine was prepared by the exchange reaction between aqueous radioiodide and solid iodine.8

B. Procedure.—For reactions 1 and 2, accurately weighed portions of iodine cyanide (ca. 0.5 g.) were dissolved weighed portions of iodine cyanide (ca. 0.5 g.) were dissolved in 20 ml. of solvent and thermostated at the desired tem-perature (to within  $\pm 0.1^{\circ}$ ); 5 ml. of solution of radioactive potassium iodide or cyanide of accurately known concentra-tion (ca. 0.159 g. of KI or 0.100 g. of KCN per 5-ml. aliquot) were added rapidly with constant stirring. In most cases, satisfactory separations were achieved by direct precipita-tion of the iodide or cyanide in 1-ml. portions of the mixture with silver nitrate. In the pure organic solvents, however, silver iodide precipitation is incomplete, and in these in-stances the separations were made on Amberlite MB-1 stances the separations were made on Amberlite MB-1 resin. On shaking a 1-ml. aliquot of reaction mixture with 200 mg. of resin, all iodide ion was adsorbed within 30 sec. together with a small constant fraction of the iodine cyanide. The adsorbed iodide was eluted from the resin with concen-trated aqueous  $KNO_3$  and precipitated as before. The pre-cipitates were centrifuged down, washed and transferred to weighted atool along back in the form of check with the form weighed steel planchets in the form of alcohol slurry. After drying under an infrared lamp, the weighed samples were counted by conventional end-window G/M tube technique.

Reaction 3 was studied in *n*-heptane solution only. Weighed amounts of iodine cyanide (ca. 0.03 g.) were dis-solved in 25 ml. of heptane, brought to temperature and

(1) L. E. Bodnar and A. B. VanCleave, Can. J. Chem., 31, 923 (1953).

(2) F. Fairbrother, J. Chem. Soc., 180 (1950).

(3) A. A. Woolf, ibid., 4121 (1953); 252 (1954); G. Lord and A. A. Woolf, ibid., 2546 (1954).

(4) R. N. Haszeldine, ibid., 4145 (1954).

(5) D. L. Glusker and H. W. Thompson, ibid., 471 (1955).

(6) Org. Syntheses, 32, 29(1952).

(7) K. Hess and H. Frahm, Ber., 71B, 2627(1938).

(8) L. R. Darbee and G. M. Harris, THIS JOURNAL, 61, 111 (1957).

0.2-ml. portions of a heptane solution of radioiodine added with vigorous stirring. Two-ml. portions were withdrawn and shaken with an equal volume of water for 10 sec.; a 1-ml. aliquot from each layer was then assayed for radioactivity in a small erlenmeyer flask placed reproducibly over an in-verted end-window G/M tube. From a knowledge of the distribution coefficients of iodine cyanide and iodine between heptane and water,<sup>9</sup> the relative acitivity of the two reactants was readily obtainable.

Chemical concentrations of the reactants were determined in all needed cases by titration with dilute thiosulfate. Spectra were obtained as desired on a Beckmann DK-2 spectrophotometer.

## **Results and Discussion**

Even in non-aqueous media and at very low temperatures, all three reactions were found to have gone to completion within the few minutes required for separation. Table I summarizes the experimental conditions. There is the possibility that all

#### TABLE I

# IODINE CYANIDE EXCHANGE REACTIONS

Reaction	n Medium	Temp., °C.	Separation method
(1)	Water	0, 30.2	AgI pptn.
	Water-dioxane	0, 30.2	AgI pptn.
	(20, 40, 60 and 80%	% dioxane)	
	Acetone	-78, 30.2	Resin adsorption
	Ethanol	-78, 30.2	Resin adsorption
(2)	Water	30.2	AgCN pptn.
	Water-dioxane	30.2	AgCN pptn.
	(20, 40, 60 and 80%	% dioxane)	
(3)	Heptane	0, 30.2	Extraction with water

the exchanges are separation-induced; this possibility is greatest for the resin-adsorption separation. Since exchange was complete in every experiment, there is no way of investigating the roles of the various separation procedures. However, it seems reasonable to assume that a rapid homogeneous reaction is responsible for at least some of the exchange. Yost and Stone<sup>10</sup> have confirmed the existence of relatively stable complex ions of the types  $I_2CN^-$  and  $ICN_2^-$ . Logical mechanisms for reactions 1 and 2 are therefore offered by the equilibria

$$\frac{\text{ICN} + \text{I}^{*-}}{\text{ICN} + \text{C}^{*}\text{I}^{*-}} \xrightarrow{\text{I}^{*}\text{CN} - \xrightarrow{\text{CN}^{*-}}} \text{I}^{*}\text{CN} + \text{I}^{-} \xrightarrow{\text{IC}^{*}\text{N} + \text{CN}^{-}} \xrightarrow{\text{I}^{*}\text{C}^{*}\text{N} + \text{CN}^{-}} \xrightarrow{\text{I}^{*}\text{C}^{*}\text{N} + \text{CN}^{-}} \text{I}^{*}\text{C}^{*}\text{N} + \frac{\text{CN}^{*-}}{\text{C}^{*}\text{N} + \text{CN}^{-}} \xrightarrow{\text{CN}^{*-}\text{I}^{*}\text{C}^{*}\text{N} + \text{CN}^{-}} \xrightarrow{\text{CN}^{*-}\text{I}^{*}\text{C}^{*}\text{N} + \text{CN}^{-}} \xrightarrow{\text{CN}^{*-}\text{I}^{*}\text{C}^{*}\text{N} + \frac{\text{CN}^{*-}\text{I}^{*}\text{C}^{*}\text{N} + \frac{\text{CN}^{*}\text{I}^{*}\text{N} + \frac{\text{CN}^{*}\text{I}^{*}\text{C} + \frac{\text{CN}^{*}\text{I}^{*}\text{N} + \frac{\text{CN}^{*}\text{I}^{*}\text{C} + \frac{\text{CN}^{*}\text{I}^{*}\text{N} + \frac{\text{CN}^{*}\text{I}^{*}\text{C} + \frac{\text{CN}^{*}\text{I} + \frac{\text{CN}^{*}\text{I}^{*}\text{I} + \frac{\text{CN}^{*}\text{I} + \frac{\text{CN}^{*}\text{I} + \frac{\text{CN}^{*}\text{I} + \frac{CN}^{*}\text{I} + \frac{CN}^{*}\text{I} + \frac{CN}^{*}\text{I} + \frac{CN}^{*} + \frac$$

Extremely rapid reaction is possible, since exchange may occur at almost every encounter of iodine cyanide molecule with iodide or cyanide ion. Evidence for this is offered for the first case by the almost instantaneous development of the well-known  $I_3^-$  spectrum when solutions of ICN and  $I^-$  are mixed; this must result from the rapid occurrence of the series of equilibria ICN +  $I^- \rightleftharpoons I_2 CN^- \rightleftharpoons$  $I_2 + CN^-$  and  $I_2 + I^- \rightleftharpoons I_s^-$ .

(9) Values for  $K_D = C_{heptane}/C_{water}$  at 25° are 53 and 0.075 for Is and ICN, respectively.

(10) Don M. Yost and W. E. Stone, J. Am. Chem. Soc., 55, 1889 (1983).

Mixtures of ICN and CN<sup>-</sup> solutions show a very rapid development of faint yellowish color; the spectrum of such a solution is very similar to that of a dilute cyanogen solution in which partial polymerization has occurred. Apparently the reac-tions  $\text{CNI} + \text{CN}^- \rightleftharpoons \text{I}(\text{CN})_2 \stackrel{-}{\rightleftharpoons} \text{I}^- + (\text{CN})_2$  are also very fast. The mechanism for reaction 3 is similarly most likely one of molecular association, though the spectroscopic evidence is inconclusive: the spectrum of an  $I_2/ICN$  mixture in heptane is almost exactly the sum of the spectra of the separate constituents, showing only a very slight increase in absorption in the near ultraviolet.

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# THERMODYNAMICS OF THE FORMATION OF THE SILVER DITHIOSULFATE COM-PLEX ION

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The equilibrium  $Ag^+ + 2S_2O_3^{--} \rightleftharpoons Ag(S_2O_3)_2^{3(-)}$ was studied by potentiometry between 25 and 70°.1 To obtain these measurements, it was necessary to determine first the normal potential of the silver electrode<sup>2</sup> and the potential of the reference calomel electrodes<sup>3,4</sup> in that interval of temperature.

As a function of the temperature, the dissociation constant of the silver dithiosulfate complex varies according to the equation

$$\log K = -\frac{4166}{T} + 0.510$$

T being the absolute temperature.

From this result we obtained, at 25°, for the heat of formation of the complex from the ions, the free energy and the molal entropy, the values

$$\Delta H^{\circ} = -19.05 \pm 0.5 \text{ kcal./mole}$$
  
$$\Delta G^{\circ} = -18.35 \pm 0.5 \text{ kcal./mole}$$
  
$$\Delta S^{\circ} = -2.3 \pm 2 \text{ cal./mole degree}$$

Heat of Formation.-Only a few investigations of the heat of formation of the complex  $Ag(S_2O_3)_2^{3(-)}$ have been reported. Fogh<sup>5</sup> made the first measurements in 1890. He used the calorimetric method and found that the heat of formation of sodium silver thiosulfate from solutions of sodium thiosulfate and silver nitrate is 20 kcal. This comparatively old value is slightly higher than the one we obtained. Fogh's experiments cannot give an exact result, for the sodium thiosulfate concentrations he studied were too high, so that, apart from the complex  $Ag(S_2O_3)_2 \overset{\delta(-)}{\longrightarrow}$ , a substantial amount of the complex  $Ag(S_2O_3)_3 \overset{\delta(-)}{\longrightarrow}$  was formed.<sup>6</sup> It is un-

(1) H. Chateau, B. Hervier and J. Pouradier, J. chim. phys., to be published.

(2) J. Pouradier, A. M. Venet and H. Chateau, ibid., 51, 375 (1954).

(3) J. Pouradier and H. Chateau, Compt. rend., 237, 711 (1953).

(4) H. Chateau, J. chim. phys., 51, 590 (1954).

(5) J. Fogh, Ann. chim. phys., 21, 43 (1890).

(6) H. Chateau and J. Pouradier, Sci. et inds. phot., [2] 24, 129 (1953).

In their studies on silver bromochloride mixed crystals, Eastman and Milner<sup>7</sup> have determined the heat of solution of silver bromide and silver chloride in a solution of 0.73 M sodium thiosulfate containing little silver. Under these conditions, according to our study,<sup>6</sup> there is as much  $Ag(S_2O_3)_3^{5(-)}$  com-plex as  $Ag(S_2O_3)_2^{3(-)}$  complex. Therefore, the value of the heat of formation of the complex deduced from the Eastman and Milner measurements must be slightly high. Actually, 20 kcal. was obtained, which confirms our estimate.

The heat of formation in solution of the complex  $Ag(S_2O_3)_2^{3(-)}$  calculated from the values published by the National Bureau of Standards<sup>8</sup> is -19.3kcal. This value, which was also cited by Williams,<sup>9</sup> is in good agreement with the  $-19.05 \pm$ 0.5 kcal. value obtained from our own results.

Entropy.-To explain the stability of the complex ions, Williams<sup>9</sup> considered the entropy. According to him, the change in entropy in the course of the reaction  $Ag^+ + 2S_2O_3 - \rightarrow Ag(S_2O_3)_2^{3(-)}$ would be -26 cal./deg. This high negative value disagrees with our own results.

Moreover, the value of -26 cal./deg. for the change of molal entropy of the reaction of formation of the complex leads to an abnormally high value of the dissociation constant of the complex

$$\log_{10} K = \frac{\Delta G^{\circ}}{4.572T} = \frac{\Delta H^{\circ} - T\Delta S^{\circ}}{4.572T}$$

The calculations made with  $\Delta S^{\circ} = -26$  cal./deg. and  $\Delta H^{\circ} = -19.3$  kcal. give  $\log_{10} K = -8.51$ , or  $K = 3.1 \times 10^{-9}$ . Such a value does not agree with the results published by the various authors who have studied this complex<sup>10</sup> (see results and bibliography, ref. 6).

Nevertheless, in a recent study, Bent<sup>11</sup> used the value published by Williams to calculate the "unitary entropy" of the complex. This has been defined as being the difference between the molal entropy and the configurational entropy. The latter entropy is equal to 8 times the change in the number of ions in the course of the reaction. The unitary entropy of the complex  $Ag(S_2O_3)_2^{3(-)}$  would be -26+ (8 × 2) = -10 cal./deg. Bent tried to explain this extremely rare example of negative "unitary entropy" by a spatial configuration quite peculiar to that complex ion.

The value of the molal entropy used by Bent being too small, it is interesting to calculate the "unitary entropy" of the complex from the exact value.

(7) E. D. Eastman and R. T. Milner, J. chim. phys., 1, 444 (1933). (8) "Selected Values of Chemical Thermodynamic Properties,"

Natl. Bur. of Standards, Circular 500, Washington, D. C., 1952.

(9) R. J. P. Williams, THIS JOURNAL, 58, 121 (1954). (10) The value  $K = 3.1 \times 10^{-9}$  is comparatively close to the value  $K = 1.5 \times 10^{-9}$  corresponding to the dissociation constant of the complex  $AgS_2O_3^{-,6,12}$  One might think that the constant of this last complex has been wrongly attributed to the complex  $Ag(S_2O_3)_2^{3(-)}$ . (11) H. A. Bent, THIS JOURNAL, 60, 123 (1956).

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