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Kinetics of the Reaction of Hydrocyanic Acid with Triiodide Ion

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In the course of a study of the aqueous chemistry of cyanogen chloride, it became necessary to learn some aspects of the chemistry of cyanogen iodide. The kinetics of formation by the reaction

$$I_3^- + HCN \rightarrow 2I^- + ICN + H^+$$

was of particular importance. For other reasons, the study had to be truncated at the point that the rate law for the process was known. Our results are presented here in brief form.

The reaction is said to reach a point of equilibrium;[1] however our data indicate that under our conditions (excess HCN) all of the triiodide is converted to product. The reaction rate study turned up one unique feature—cyanide ion apparently can attack triiodide ion directly.

Results

Kinetics. The rate of reaction was followed by loss of the triiodide ion band at 350 nm. Since this component was always at limiting concentration, the reaction was in each case carried out under pseudo-first-order conditions.

The reaction followed a first-order dependence (log $[I_3^-]$ against time plots were always linear) when all other components were held constant.

HCN Dependence. Over an eightfold variation in [HCN], from 0.625×10^{-3} to 5×10^{-3} M, the reaction showed a first-order dependence. The data are presented in Table I. The small increase in the values of $k_{obsd}/[HCN]$ may be real but it is not large enough to warrant consideration of any alternative kinetic order in [HCN].

pH Dependence. Over the pH range 4.20–4.95, the reaction rate is inversely proportional to $[H^+]$. The data are given in Table II. The reactions were carried out at constant acetic acid concentration; changes in sodium acetate concentrations brought forth the changes in pH. Ionic strength was maintained constant with sodium chloride.

Other data at 18 °C in the $[H^+]$ range 1.1×10^{-5} to 5×10^{-4} M gave a good linear plot for k_{obsd} against $1/[H^+]$. Thus over a wide pH range (4.96 down to 3.30), no evidence for any other pH dependence was found.

Iodide Ion Dependence. Over an eightfold increase of $[I^-]$, the reaction showed a decreasing rate. It was not, however, the simple inverse relationship expected if the rate was proportional to the concentration of free iodine. Also unexpected was the fact that the value of k_{obsd} became almost independent of $[I^-]$ at high $[I^-]$. Some of the relevant data are presented in Table III.

The plot of k_{obsd} against reciprocal iodide ion concentration was a straight line (see Figure 1) with a definite intercept at $k_{obsd} \simeq 21$ under the conditions of the set of experiments. A derivation of this type of plot is given in the Appendix.

Rate Law. Combination of the four rate dependences leads to the rate law

$$\frac{-d[I_3^-]}{dt} = k_1\left\{\frac{[HCN][I_3^-]}{[H^+][I^-]}\right\} + k_2\left\{\frac{[HCN][I_3^-]}{[H^+]}\right\}$$

Least-squares analysis of the data presented in Table III yields the following values: $k_1 = (2.55 \pm 0.10) \times 10^{-3}$ M s^{-1} and $k_2 = (2.740 \pm 0.004) \times 10^{-1}$ s^{-1}. A short derivation of this law is given in the Appendix.

Table I. Dependence of Rate on Hydrocyanic Acid Concentration[a]

10^3 [HCN], M	k_{obsd}, s^{-1}	10^{-4} k_{obsd}/[HCN], s^{-1} M^{-1}	10^3 [HCN], M	k_{obsd}, s^{-1}	10^{-4} k_{obsd}/[HCN], s^{-1} M^{-1}
0.625	6.71	1.08	3.75	48.9	1.30
1.24	12.5	0.99	4.00	52.5	1.31
2.50	31.0	1.24	4.50	57.9	1.29
2.50	29.7	1.13	5.00	72.0	1.44

[a] At 10 °C, $\mu = 0.013$, and pH 4.8 with $[CH_3CO_2^-] = [CH_3CO_2H] = 5 \times 10^{-4}$ M, $[I^-] = 1.25 \times 10^{-2}$ M, and $[I_2]_T = 1.25 \times 10^{-5}$ M.

Table II. Dependence of Rate on pH[a]

pH	$10^5[H^+]$, M	k_{obsd}, s^{-1}	10^4 $k_{obsd}[H^+]$, s^{-1} M
4.95	1.12	51.6	5.8
4.85	1.41	40.6	5.7
4.75	1.78	34.4	6.1
4.55	2.82	26.3	7.4
4.35	4.47	14.7	6.6
4.20	6.31	10.6	6.7

[a] At 10 °C, $\mu = 0.0135$, $[I_2]_T = 1.25 \times 10^{-5}$ M, and $[HCN] = 2.5 \times 10^{-3}$ M.

Table III. Dependence of Rate on Iodide Ion Concentration[a]

$10^2[I^-]$, M	k_{obsd}, s^{-1}	$1/[I^-]$, M^{-1}	$10^2[I^-]$, M	k_{obsd}, s^{-1}	$1/[I^-]$, M^{-1}
1.25	37.9	80.0	7.5	24.2	13.3
2.5	29.4	40.0	10.0	23.5	10.0
5.0	26.4	20.0			

[a] At 10 °C, $\mu = 0.10$, NaCl used to maintain constant μ, pH 4.5, $[I_2] = 1.25 \times 10^{-5}$ M, $[HCN] = 2.5 \times 10^{-3}$ M, $[CH_3CO_2H] = [CH_3CO_2Na] = 5 \times 10^{-4}$ M.

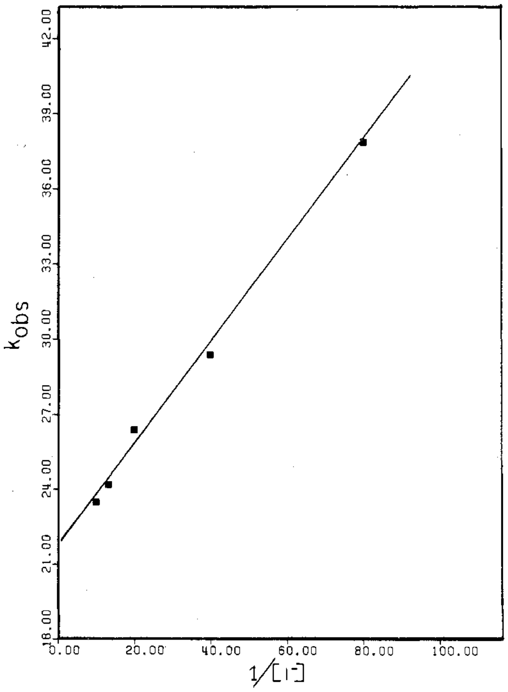

Figure 1. Dependence of observed rate on reciprocal iodide ion concentration. Conditions are given in Table III.

Discussion

The reaction of triiodide ion with hydrocyanic acid was expected to be straightforward and the first term of the rate law

$$\text{rate} = k_1 \frac{[\mathrm{HCN}][\mathrm{I_3^-}]}{[\mathrm{H^+}][\mathrm{I^-}]}$$

was not unexpected. The related mechanism is

$$\begin{array}{ll} \mathrm{HCN} \rightleftarrows \mathrm{H^+} + \mathrm{CN^-} & \text{(fast)} \\ \mathrm{I_3^-} \rightleftarrows \mathrm{I^-} + \mathrm{I_2} & \text{(fast)} \\ \mathrm{I_2} + \mathrm{CN^-} \rightarrow \mathrm{I_2CN^-} & \text{(slow)} \\ \mathrm{I_2CN^-} \rightleftarrows \mathrm{ICN} + \mathrm{I^-} & \text{(fast)} \end{array}$$

with the intermediate I_2CN^- being postulated in analogy to I_2Cl^-, etc.

The second term is surprising, since the intermediate I_2X^- generally arises from the mechanistic step

$$\mathrm{I_2} + \mathrm{X^-} \rightleftarrows \mathrm{I_2X^-}$$

as in the third step above. In the k_2 term, however, the formation of I_2CN^- must come about by direct displacement

$$\mathrm{I_3^-} + \mathrm{CN^-} \rightarrow \mathrm{I_2CN^-} + \mathrm{I^-}$$

Using the values $k_1 = 2.55 \times 10^{-3}$ M s^{-1}, $K_{\mathrm{I_3^-}} = 870$ M^{-1}, and $K_{\mathrm{HCN}} = 4.8 \times 10^{-10}$ M, it is possible to estimate the rate constant for the step

$$\mathrm{I_2} + \mathrm{CN^-} \rightarrow \mathrm{I_2CN^-}$$

The value so obtained is 3×10^9 M^{-1} s^{-1}. Similarly, the constant for the step

$$\mathrm{I_3^-} + \mathrm{CN^-} \rightarrow \mathrm{I_2CN^-} + \mathrm{I^-}$$

can be estimated from k_2 (0.740 s^{-1}) and K_{HCN}; this gives the value 4×10^8 M^{-1} s^{-1}. Neither step indicates reaction at every collision, but they are very rapid steps indeed.

Experimental Section

All chemicals used were of reagent grade and the laboratory-distilled water was further purified by passage through a mixed-bed ion-exchange column. Potassium iodide was kept at least 50 times in excess of iodine, solutions being prepared immediately prior to the kinetic studies. Hydrogen ion concentrations were measured on a Leeds and Northrup pH meter.

The kinetics of the reaction were followed at a single wavelength, 350 nm, using a Durrum D-110 stopped-flow spectrophotometer, all temperatures being maintained to within ±0.2 °C. The output of the photomultiplier of the stopped-flow served as input to the A/D converter of a PDP-8/e computer and as input to a storage-type oscillosope. The computer, through locally designed software and hardware, was used to convert the voltage output of the photomultiplier to absorbance vs. time data. One hundred data points were collected in each kinetic run. The rate at which the photomultiplier was sampled was a function of the rate of the reaction of interest. The rate of sampling was chosen such that the reaction was followed to 90% completion. The absorbance vs. time data were then processed on line, using a linear least-squares technique, to yield pseudo-first-order rate constants. All reported rate constants are averages of at least ten kinetic runs.

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Appendix A

The iodide ion dependence indicates a two term-rate law of the form

$$k_{\mathrm{obsd}} = \frac{k_1'}{[\mathrm{I^-}]} + k_2'$$

where the primes indicate pseudo constants. This form can be obtained from the rate law

$$-\frac{\mathrm{d}[\mathrm{I_3^-}]}{\mathrm{d}t} = k_1 \frac{[\mathrm{HCN}][\mathrm{I_3^-}]}{[\mathrm{H^+}][\mathrm{I^-}]} + k_2 \frac{[\mathrm{HCN}][\mathrm{I_3^-}]}{[\mathrm{H^+}]}$$

With all other concentrations much larger than $[I_3^-]$ the latter equation can be rewritten as

$$-\frac{\mathrm{d}\ln[\mathrm{I_3^-}]}{\mathrm{d}t} = \left\{ \frac{k_1}{[\mathrm{I^-}]} + k_2 \right\} \frac{[\mathrm{HCN}]}{[\mathrm{H^+}]}$$

so that

$$k_{\mathrm{obsd}} = \left\{ \frac{k_1}{[\mathrm{I^-}]} + k_2 \right\} \frac{[\mathrm{HCN}]}{[\mathrm{H^+}]}$$

which has the requisite form.

Registry No. I_3^-, 14900-04-0; HCN, 74-90-8; I^-, 20461-54-5.

References and Notes

(1) H. E. Williams, "The Chemistry of Cyanogen Compounds", J. & A. Churchill, London, 1915.

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Studies Involving Nitrogen–Oxygen Donor Macrocyclic Ligands. 2. Copper(II), Zinc(II), and Cadmium(II) Complexes of Cyclic Tetradentate Ligands Derived from Salicylaldehyde[1]

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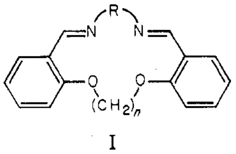
A large number of metal complex studies involving polyether macrocycles of the "crown" type have now been reported.[2] Such ligands incorporate a number of oxygen donors (typically five or more) in a large-ring system and often exhibit novel coordination behavior particularly toward certain non transition metal ions such as the alkali and alkaline earths.[2]

A second category of macrocyclic ligands[3] consists of those ligands which contain nitrogen, sulfur, or (more recently[4]) phosphorus donor atoms. Of these, tetradentate ligands containing four nitrogen donor atoms have been studied in most detail and such ligands often resemble the natural macrocycles (for example, the porphyrins or corrins) in their coordination behavior.[5]

Only a few cyclic ligands of intermediate structure between the "crown" ethers and the second category of macrocycles mentioned above have been reported and the coordination behavior of these intermediate ligands toward a range of metal ions has received much less attention up to the present.[2,3] In view of the often special properties associated with each of the above main ligand categories, it is of considerable intrinsic interest to investigate both the transition and non transition metal chemistry of ligands which fall between these main categories. The work now reported forms part of an overall study in this general area.

The macrocycles used for the present study are of structure I. The syntheses, properties, and some reactions of the nickel complexes of ligands of type I have been discussed in part 1



I

R	Abbreviations when $n = 2$	Abbreviations when $n = 3$
$-(CH_2)_2-$	*O*-en-*N*-en	*O*-tn-*N*-en
$-(CH_2)_3-$	*O*-en-*N*-tn	*O*-tn-*N*-tn
$-CH_2CH(CH_3)-$	*O*-en-*N*-pn	