complicating factor in the observations. Since the yield falls off only at DPPH concentrations of the order of 10^{-4} M in air-saturated solutions it would appear that DPPH is a more efficient scavenger than iodine and that its presence in solution in any appreciable concentration would effectively eliminate reaction 1. It would seem, therefore, that the drop in yield observed at low DPPH concentrations is not due to radical-radical combination.

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Isotopic Fractionation in the System Iodine Cyanide/Cyanide by a Combined Equilibration–Precipitation Process[1]

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The equilibrium constant for the reaction $CNI + C^{14}N^- \rightleftarrows C^{14}NI + CN^-$ as predicted by statistical thermodynamics is $K = 1.05$ at 30°. The experimental values obtained by examination of the activity of precipitated silver cyanide are always larger than the predicted value, and vary with the composition of the dioxane–water solvent used. The results can be interpreted quantitatively in terms of a combination of isotope effects in the equilibration and precipitation reactions.

A recent study has shown that the exchange reaction $CNI + C^{14}N^- \rightleftarrows C^{14}NI + CN^-$ takes place very rapidly in a variety of media.[2] The predicted thermodynamic equilibrium constant for the reaction, K, is 1.05 at 30°,[3] and the present study began as an attempt to confirm this value experimentally. It was planned to determine K by comparison of the specific activities of cyanide ion before and after exchange equilibration, A_0 and A_e, respectively. Then

$$K_{exp} = a/b\,(A_0 - A_e)/A_e \qquad (1)$$

where a and b are the molar concentrations of cyanide and iodine cyanide, respectively. This relation assumes that no isotopic fractionation results from the reactant separation process. Much larger K_{exp} values than expected were obtained, and can be explained quantitatively in terms of a combination of isotope effects in the equilibration and precipitation reactions involved.

Experimental

The reagents were prepared and purified as described elsewhere.[2] Iodine cyanide and carbon-14-labeled sodium cyanide were equilibrated in solutions containing various proportions of water and dioxane. Inorganic cyanide was completely precipitated from suitable aliquots with silver nitrate dissolved in the same water/dioxane solvent; the silver cyanide was transferred by alcohol slurry technique to a metal planchet and dried. The badly rimmed samples so prepared were dissolved in pyridine added to the planchet; when the pyridine was evaporated slowly under an infrared lamp, smoothly uniform microcrystalline deposits remained which gave activity counts with a gross reproducibility of better than 0.7% by standard end-window G/M tube assay technique.[4]

Results and Discussion

The values of K_{exp} obtained for a number of solvent compositions and a/b ratios are summarized in Table I. The reactions involved are

$$CNI + C^{14}N^- \rightleftarrows C^{14}NI + CN^- \qquad R_1,\ R_1^*$$
$$Ag^+ + C^{14}N^- \longrightarrow \underline{AgC^{14}N} \qquad R_2^*$$
$$Ag^+ + CN^- \longrightarrow \underline{AgCN} \qquad R_2$$

where the R's are the various reaction rates. The differential equations describing the system are

$$\frac{d(C^{14}NI)}{dt} = R_1\frac{(C^{14}N^-)}{(CN^-)} - R_1^*\frac{(C^{14}NI)}{(CNI)}$$

and

$$\frac{d(AgC^{14}N)}{d(AgCN)} = \frac{R_2^*}{R_2}\,\frac{(C^{14}N^-)}{(CN^-)}$$

Explicit solution of the problem is possible for two limiting cases:

(1) If equilibrium is established in the CNI/CN^- system prior to separation, and R_2 (and R_2^*) $>>$ R_1 (and R_1^*), the $(C^{14}N^-)/(CN^-)$ ratio is the same in the precipitate as in the original equilibrated aliquot of solution. Then K_{exp} as determined by eq. 1 is in fact the true equilibrium constant $K = R_1/R_1^*$.

(2) If R_1 (and R_1^*) $>>$ R_2 (and R_2^*), equilibrium is continuously maintained during precipi-

TABLE I

EXPERIMENTAL AND CALCULATED APPARENT EQUILIBRIUM CONSTANTS FOR THE REACTION $CNI + C^{14}N^- \rightleftarrows C^{14}NI + CN^-$ AT 30.6°

Vol. % dioxane in solvent	Reactant ratio $f = a/b$	No. of determinations	K_{exp} (av. ± std. dev.)	$K_{calcd.}$	Reac. rate ratio $s = R_1^*/R_2$
0	0.9	12	1.08 ± 0.02	1.08[b]	0.15[b]
20	.9	22	1.15 ± .02	1.15[b]	0.75[b]
28	.9	22	1.18 ± .03	1.18[b]	1.25[b]
40	.1	8	1.15 ± .10[a]	1.23[c]	Large
40	.9	40	1.28 ± .02	1.29[c]	Large
40	12.2	12	1.63 ± .14[a]	1.58[c]	Large
60	0.9	22	1.29 ± .03	1.29[c]	Large

[a] Errors greater in these instances since determination is much less precise for f values far from unity. [b] From Fig. 1, curve E. [c] Calculated by eq. 2.

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[1] A preliminary report was made of this work in THIS JOURNAL, **77**, 4439 (1955).

[2] F. E. Jenkins and G. M. Harris, to be published.

[3] D. R. Stranks and G. M. Harris, THIS JOURNAL, **75**, 2015 (1953).

[4] It was found impossible to achieve this high a degree of reproducibility by means of the zinc cyanide precipitation procedure used by Adamson and co-workers (*ibid.*, **73**, 4786 (1951); **74**, 1590 (1952)).

tation. In this case, it readily can be deduced that

$$K_{\text{calcd}} = f\left(\frac{K}{K+f}\right)^r \Big/ 1 - \left(\frac{K}{K+f}\right)^r \qquad (2)$$

where $f = a/b$ and $r = R_2^*/R_2$.[5]

The intermediate cases where the R's have a similar order of magnitude cannot be solved algebraically, but solutions for a large number of such possibilities have been obtained by electronic computation.[6] Selected examples of these results are presented in Fig. 1, where curves A, B and C were calculated directly and D and E were obtained by inter- and extrapolation of calculated data. The short lines at the right-hand side of the figure are the limiting values of K_{exp} attained for $s = R_1^*/R_2 = \infty$, as calculated by eq. 2.

The interpretation of the data of Table I is now clear. The true thermodynamic equilibrium constant K is undoubtedly close to the predicted value of 1.05 irrespective of the medium.[7] On the other hand, the ratio of the rates of equilibration to precipitation reactions (given by s) is expected to be greatly dependent on solvent properties. The first reaction, a result of homogeneous ion–molecule association,[2] should be dependent on solvent composition to a rather small extent.[8] The precipitation reaction is a complex coagulation process for which there is no solvent effect theory as yet. It was qualitatively observed,[9] however, that the reaction is much slower in solutions of high dioxane content than in pure water, and indeed in these cases must be quite slow relative to the equilibration.[10] The variation of K_{exp} values with dioxane content is thus attributable to variation of s; as seen in Fig. 1, K_{exp} rapidly approaches the maximum predicted by eq. 2 as s exceeds a few units.

A value for r cannot be obtained experimentally for this system, since it is impossible to precipitate cyanide fractionally with silver ion. Downes' method[11] for determination of isotope effect in precipitation reactions is, therefore, inapplicable. However, an estimated value of $r = 0.86$ is not unreasonable for a C^{14}/C^{12} intermolecular isotope effect.[12] Using this value and $K = 1.05$, $f = 0.9$, curve E of Fig. 1 was constructed. This accurately duplicates the corresponding experimental data of Table I, assuming the s values given in the last column. It is seen that s needs to change by a factor of less than 100 to account for the observed facts.

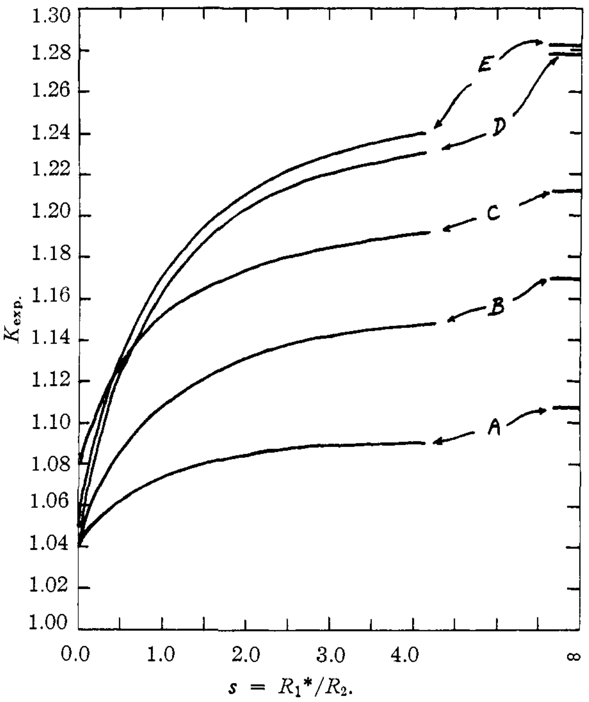

Fig. 1.—Variation of K_{exp} with reaction rate ratio $s = R_1^*/R_2$: Curve A, $K = 1.04$, $f = 1.0$, $r = 0.96$; curve B, $K = 1.04$, $f = 1.0$, $r = 0.92$; curve C, $K = 1.08$, $f = 1.0$; $r = 0.92$; curve D, $K = 1.04$; $f = 1.0$; $r = 0.86$; curve E, $K = 1.05$, $f = 0.9$, $r = 0.86$.

Further confirmation of the ideas here presented is provided by the three sets of data at 40% dioxane content, where f was varied as shown. The K_{calcd} values obtained by means of eq. 2, which is applicable at 40% dioxane, are in good agreement with the observed data.

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(5) The solution proceeds as follows. Let $(CN^-)_0 = a$, $(CNI)_0 = b$, $(AgCN) = x$, $(C^{14}N^-)_0 = d$, $(C^{14}NI) = y$, $(AgC^{14}N) = z$. Then, since equilibrium is continuously maintained and there is only tracer labeling with carbon-14, $K = y(a - x)/b(d - y - z)$. The differential equation: $dz/dx = R_2^*/R_1 \times (d - y - z)/(a - x)$ can now be solved for the ratio z/x. The value of $K_{\text{calcd}} = (C^{14}NI)(AgCN)/(CNI)(AgC^{14}N) = xy/bz$ can then be determined.

(6) Computations done on ORNL "Oracle" Computer.

(7) The predicted value applies, of course, only to ideal gaseous species. The nature of the medium does modify the molecular properties, but these effects should largely cancel out in the partition function ratios involved in the K calculation.

(8) K. J. Laidler and P. A. Landskroener, *Trans. Faraday Soc.*, **52**, 200 (1956).

(9) As indicated by the rate at which visible precipitate particles develop on addition of the silver nitrate solution.

(10) A few experiments were done in which pure aqueous or 40% dioxane–water solution of labeled sodium cyanide was added directly to one containing both iodine cyanide and silver nitrate. In each case it was found that the K_{exp} values agreed within experimental error with those tabulated above. Clearly the exchange is an extremely rapid process, and the K_{exp} values are not influenced by the order of the separation operations.

(11) A. M. Downes, *Aust. J. Sci. Research*, **A5**, 521 (1952).

(12) J. Bigeleisen, *J. Phys. Chem.*, **56**, 823 (1952).