her gratitude to Dr. Jones and Dr. Sörensen for reading the manuscript, and for making available their unpublished data.

THE NEW YORK BOTANICAL GARDEN
BRONX PARK
NEW YORK, N. Y.
RECEIVED OCTOBER 29, 1951

Non-exchange of Radiocyanide and Radiosulfide Ions with Aqueous Thiocyanate Ion[1]

BY ARTHUR W. ADAMSON AND PHILLIP S. MAGEE

The exchange reactions of $C^{14}N^-$ and $S^{35=}$ ions with thiocyanate ion have been investigated with essentially negative results.

Experimental

The $KC^{14}N$ solution was prepared from $BaC^{14}O_3$ by the method of Adamson,[2] and that of Na_2S^{35} by the addition of sulfate-free BaS^{35}.[3] The exchange experiments were carried out by mixing the appropriate solutions in small centrifuge tubes which were then sealed. Those containing sulfate were sealed in a nitrogen atmosphere.

After the elapse of the desired time, the separation of radiocyanide and thiocyanate ions was carried out by the precipitation of zinc cyanide. The zinc cyanide was purified by reprecipitation and then treated by the distillation and sample preparation method previously reported.[4] The separation of radiosulfide and thiocyanate ions was accomplished by precipitation of cadmium sulfide. The cadmium sulfide was subjected to a fairly elaborate purification before being counted, in order to remove coprecipitated thiocyanate ion. The samples of zinc cyanide or of cadmium sulfide were counted with a mica end window counter (2 mg./cm.^{2} window) and with an atmospheric pressure flow counter, respectively.

Approximate corrections for self absorption were made.

TABLE I

EXCHANGE OF RADIOCYANIDE WITH THIOCYANATE IN AQUEOUS SOLUTION

(KSCN) = 0.19 *f*; ($KC^{14}N$) = 0.59 *f*

*p*H	Temp., °C.	Exchange time, hr.	Exchange,[a] %
11.10	24	140	0.80
12.70	24	334	.61
12.70	60	170	.26
14.0	24	187	.65
14.0	60	163	.10
0.5	24	160	2.26

[a] Defined as in reference 5.

The data given in Table I are representative of the rather larger total amount of results obtained, and indicates no measurable exchange, with the possible exception of the system at *p*H 0.5. The results with radiosulfide agree with those reported in this issue by Heisig and Holt[5] in that no exchange was found in solutions 0.3 *f* in KSCN and 0.05 *f* in Na_2S at room temperature, after 204 hours at *p*H 12.6, and after 554 hours at *p*H 13.4.

These findings of negligible exchange are in accord with the difficulties of formulating potential mechanisms. Thus, the fact that the free energy for the primary dissociation of thiocyanate into sulfur and cyanide ion is positive by 16 kcal.[6] is in agreement with the fact that this path does not lead to exchange.

An alternative mechanism, in the case of the cyanide-thiocyanate system, might be considered to be an exchange of sulfur through the intermediate $NCSCN^{-2}$, but one is confronted with the impossibility of writing a structure for this species without exceeding the octet on carbon or invoking an improbable imide formulation for the cyanide group. It is noteworthy, however, that the analogous intermediate $O_3SSSO_3^{-4}$ has been proposed for the measurable exchange between sulfite and thiosulfate.[7] Here, however, structures of some *a priori* plausibility can be written since it is not unreasonable to exceed the octet on sulfur. Somewhat similar considerations serve to rationalize the lack of exchange of sulfide and thiocyanate, in contrast to the measurable exchange of sulfide with thiosulfate.[7]

---

[1] These investigations were carried out under contract N6onr23809 between the University of Southern California and the Office of Naval Research.

[2] A. W. Adamson, THIS JOURNAL, **69**, 2564 (1947).

[3] The tracers were obtained from the Atomic Energy Commission.

[4] A. W. Adamson, J. P. Walker and M. Volpe, THIS JOURNAL, **72**, 4030 (1950).

[5] G. E. Heisig and R. Holt, *ibid.*, **74**, 1597 (1952).

[6] W. M. Latimer, "The Oxidation States of the Elements," Prentice-Hall, Inc., New York, N. Y., 1938, p. 128.

[7] D. P. Ames and J. E. Willard, THIS JOURNAL, **73**, 164 (1951).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTHERN CALIFORNIA
LOS ANGELES, CALIFORNIA
RECEIVED JULY 31, 1951

The Kinetics of the Thermal Decomposition of Aluminum Borohydride[1]

BY RICHARD S. BROKAW AND ROBERT N. PEASE

Schlesinger, Sanderson and Burg[2] have observed that as the temperature is raised aluminum borohydride ($Al(BH_4)_3$) decomposes yielding hydrogen and solid products. This research was undertaken in order to obtain more detailed information as to the nature of the pyrolysis. Preliminary observations[3] of pressure–time curves at temperatures of 150° and higher showed the initial slopes of such curves to be proportional to the initial aluminum borohydride pressure, suggesting that the decomposition is essentially a first order process. Products were hydrogen and inhomogeneous solid products containing varying amounts of hydrogen.

Since both aluminum borohydride and the solid products yield hydrogen on heating it is not possible to calculate the aluminum borohydride pressure as a function of time from the total pressure. Instead, borohydride was run into a thermostated reaction bulb[4] to the desired pressure, and the clock started. After a predetermined time the thermostat was removed and the reaction bulb rapidly cooled to room temperature. A pressure reading was made, and then the hydrogen evolved was pumped off at liquid nitrogen temperature. On warming again to room temperature the pressure of undecomposed borohydride was measured, and from this the pressure at the reaction temperature was calculated. From a series of such runs for different time intervals the disappearance of aluminum borohydride as a function of time was determined. That the condensible residue was in fact undecomposed aluminum borohydride was established by observing (a) on exhaustive decomposition at 450–600° (by heating in the luminous flame of a torch) about 5.6–5.9 volumes of hydrogen are obtained both with the condensible gaseous residue and with aluminum borohydride and (b) if the residues from several runs are returned to the re-

---

[1] (a) Taken from a thesis submitted by Richard S. Brokaw in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University. (b) The work described in this paper was done in connection with Contract NOrd 7920 with the United States Naval Bureau of Ordnance, as coördinated by the Applied Physics Laboratory, The Johns Hopkins University, and Contract N6-ori-105 with the Office of Naval Research and Office of Air Research as coördinated by Project Squid, Princeton University. (c) We wish to acknowledge the assistance of Dean H. S. Taylor, who has general supervision of this project. (d) Reproduction in whole or in part permitted for any purpose of the United States Government.

[2] H. T. Schlesinger, R. T. Sanderson and A. B. Burg, THIS JOURNAL, **62**, 3421 (1940).

[3] E. J. Badin and P. C. Hunter, unpublished work.

[4] The apparatus was the one used in studying the reaction of aluminum borohydride with olefins: see Brokaw and Pease, THIS JOURNAL, **72**, 3237 (1950).