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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]

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[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).

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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-

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[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).

action bulb they decompose at the same rate as aluminum borohydride.

The initial decomposition rate for 1000 seconds at 159° was found to be unaffected by the nature of the flask surface (either clean or coated with solid products in various stages of decomposition). Furthermore, this rate was the same in the presence of added hydrogen. Half-lives were about 6500 seconds at 159° and 450 seconds at 189°.

The borohydride pressure as a function of time may be expressed by the equation

$$P_{\mathrm{Al(BH_4)_3}} = P_{0\mathrm{Al(BH_4)_3}}\left[ae^{-k_{\mathrm{i}}t} + (1 - a)e^{-k_{\mathrm{f}}t}\right] \quad (1)$$

where

$P_{\mathrm{Al(BH_4)_3}}$ = pressure of aluminum borohydride at time t
$P_{0\mathrm{Al(BH_4)_3}}$ = initial pressure of aluminum borohydride
a = constant $1 > a > 0$
k_{i}, k_{f} are constants

In Table I the experimental results are summarized in terms of the constants of equation (1). The runs at 159° and 85 mm. initial pressure were performed in a reaction vessel packed with glass beads so that the area–volume ratio was increased by a factor of about twelve, and it is seen that the rate is unaffected.

TABLE I

Temp., °C.	Initial $Al(BH_4)_3$ pressure (mm.)	a	k_1(sec.$^{-1}$)	k_f(sec.$^{-1}$)
159	110.0	0.127	1.68×10^{-3}	8.51×10^{-5}
	85.0	.146	....	8.25×10^{-5}
	57.5	.125	1.4×10^{-3}	7.88×10^{-5}
189	85.0	.406	4.48×10^{-3}	6.33×10^{-4}

In the hope of determining the number of hydrogen atoms split off in the initial stage of the reaction plots of pressure of hydrogen evolved divided by pressure of borohydride decomposed *versus* time at 159 and 189° were made. These plots were very steep near the origin and it was only possible to conclude that not more than three hydrogen atoms are lost in the initial process.

The differential equations for successive first order reactions with reversible steps have been solved by Rakowski.[5] For such systems expressions similar in form to equation (1) are obtained. However, one would expect that the reverse of the reactions in which hydrogen is split off should be second order and should show a dependence on the hydrogen pressure, yet such an effect is not observed.

It is to be concluded, therefore, that while equation (1) adequately describes the aluminum borohydride concentration as a function of time, the mechanism of the reaction may be determined only when the nature and concentrations of the intermediate species become known.

[5] Rakowski, *Z. physik. Chem.*, **57**, 321 (1907).

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Condensation of Lactones with Benzene

BY ROBERT V. CHRISTIAN, JR.

Eijkman[1] studied the reaction of benzene and its homologs with a few aliphatic lactones in the presence of aluminum chloride. For example, γ-valerolactone with benzene gave γ-phenylvaleric acid in unspecified yield.[1a] The ready availability of several simple, aliphatic lactones suggested an examination of this reaction as a means for the synthesis of certain aryl-aliphatic acids.

It was found that the $AlCl_3$ catalyzed condensation of benzene with the appropriate lactone yielded γ-phenylbutyric acid, γ-phenylvaleric acid and δ-phenylvaleric acid in yields of 44, 61 and 51%, respectively. Significantly, no isomerization of the side chain took place and the phenyl radical was attached at the position of the alcohol function in the parent hydroxy acid. A competing reaction was the further alkylation of the initially formed product to yield polyfunctional acids. This could probably be minimized by a suitable choice of reaction conditions.

Lactide did not condense with benzene in the presence of aluminum chloride even upon heating at 70–80°. In the case of β-propiolactone the principal reaction seemed to be destruction of the lactone by the aluminum chloride and the expected β-phenylpropionic acid was not isolated in quantities sufficient to permit conclusive identification.

Experimental

The condensations were carried out in flasks equipped for reflux and mechanical stirring. The temperature during the early stages of the reaction was held below 45° by varying the rate of addition of the last component and by external cooling with water when necessary.

γ-**Phenylbutyric Acid**.—To a stirred solution of 43 g. (0.5 mole) of γ-butyrolactone (Cliffs Dow Chemical Co., Marquette, Michigan) in 100 g. of benzene, 93 g. (0.7 mole) of powdered aluminum chloride was added in small portions. After 4 hours 100 ml. of benzene was added and the mixture was allowed to stand overnight at room temperature. Subsequent to heating in a water-bath for an hour, the mixture was hydrolyzed with ice and hydrochloric acid. Distillation of the benzene layer gave 36 g. (44%) of white crystals of b.p. 120–125° (1 mm.). Crystallization from methanol and water yielded material whose melting point, 48–49°, was undepressed when mixed with authentic γ-phenylbutyric acid. Approximately 30 g. of higher boiling material was not examined further.

γ-**Phenylvaleric Acid**.—To a stirred suspension of 50 g. (0.38 mole) of aluminum chloride in 60 g. of benzene, there was added dropwise 30 g. (0.3 mole) of γ-valerolactone (Monsanto Chemical Co., St. Louis, Missouri). After being heated in a water-bath for 30 minutes, the mixture was hydrolyzed as before. Distillation of the benzene layer gave 32.5 g. (61%) of colorless liquid boiling at 123–126° (0.5 mm.).

That the substance was γ-phenylvaleric acid was confirmed by conversion to 4-methyl-1-tetralone[2] from which the known solid semicarbazone[2,3] was obtained in the usual manner. The heretofore undescribed *p*-bromophenacyl ester was also prepared. It crystallized from dilute methanol as white leaflets melting at 76°. *Anal.* Calcd. for $C_{19}H_{19}O_3Br$: Br, 21.3. Found: Br, 21.1.

In other experiments, the residue remaining after distillation of γ-phenylvaleric acid was esterified with ethanol. The resulting material had boiling point 165–169° (0.5 mm.), d^{25}_{4} 1.0212, n^{25}_{D} 1.4914. Analysis indicated that it was probably diethyl γ,γ′-phenylenedivalerate. *Anal.* Calcd. for $C_{20}H_{30}O_4$: MR_{D}, 94.62; sapn. equiv., 167; C, 71.9; H, 9.04 Found: MR_{D}, 94.84; sapn. equiv., 169, 171; C, 72.2; H, 9.37.

δ-**Phenylvaleric Acid**.—Aluminum chloride (33.4 g., 0.25 mole) was added in portions to a stirred solution of 20 g. (0.20 mole) of δ-valerolactone (prepared in quantitative yield from δ-hydroxyvaleraldehyde[4] by oxidation with per-

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[1] (a) J. F. Eijkman, *Chem. Weekblad*, **1**, 421 (1904); (b) J. F. Eijkman, *ibid.*, **2**, 229 (1905); **4**, 191, 727 (1907).

[2] M. C. Kloetzel, THIS JOURNAL, **62**, 1708 (1940).

[3] F. Mayer and G. Stamm, *Ber.*, **56**, 1424 (1923); J. von Braun and A. Stuckenschmidt, *ibid.*, **56**, 1724 (1923).

[4] G. F. Woods, Jr., *Org. Syntheses*, **27**, 43 (1947).