

MASTER

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Chemical Effects of the Nuclear Reaction $N^{14}(n,p)C^{14}$
In Various Nitrogenous Compounds

by

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I. Hot Atom Chemistry of C^{14} in Alkali Azides

A. Potassium Azide

At the time of the previous report (COO-1620-4), the work on irradiated KN_3 had advanced to such a point that we were planning to publish after a limited number of additional experiments. These additional experiments were designed to provide information on the origin of oxygen in the hydrolyzable or carbonate fraction; ie. the carbon dioxide evolute from acidified solutions of target compound. The hydrolyzable activity accounted for 25-30% of the activity of unannealed target dissolved in water, from 40% to 100% in thermal annealed target dissolved in water, and up to 100% in target specimens thermally decomposed in the absence of carriers. Prior to beginning the additional experiments, we hypothesized that the hydrolyzable activity arose from cyanate ion, presumed to be an hydrolysis product of cyanamide when the target was dissolved. New experimental results, together with a re-examination of old ones, strongly suggested that the target compound of Spring, 1970 was altered from that of December, 1968, and that further experimentation on it obscured rather than clarified the chemistry of C^{14} in KN_3 . A summary of the evidence follows: (1) The methylamine activity decreased from 12% in December, 1968 to 3% in 1970. The hydrolyzable yield increased from 2% to 26% in the same interval, while cyanamide* decreased from 13% to 4%. (2) Up to 100% yield of carbonate activity was obtained in thermally decomposed target samples, dissolved in water after decomposition. Neither cyanamide nor cyanide hydrolyze to either cyanate or to carbonate at room temperature in water. Indeed, urea is the hydrolysis product of cyanamide. Target samples decomposed in the presence of KCN and K_2CN_2 added as carriers yielded 32% $C^{14}N^-$ and 28% $C^{14}N_2^-$, indicating that these carriers served as protectors of $C^{14}N^-$ and $C^{14}N_2^-$ in the melt as KN_3 decomposition

* An error in the standardization of an aqueous cyanamide solution could account for part of the change in cyanamide activity.

proceeded. (3) The physical appearance of the target changed from brown to almost white from December 1968 to Spring 1970, attributable to possible loss of metallic potassium (a reactor radiation product) as well as to dissipation of color centers.

The above evidence suggested that the changes from less to more oxygen-containing labeled products was a consequence of oxygen impurity rather than hydrolytic reactions. The target was protected from moisture but not from atmospheric oxygen nor carbon dioxide. Moreover, the target was a fine powder, with a corresponding large surface area. Metallic potassium could serve as a getter initially, but constant air exposure could cause its depletion. It is possible that oxygen could have been occluded in the crystal during recrystallization, or perhaps diffused within from the surface. Irrespective of the origin of the oxygen, we resolved to prepare a new KN_3 specimen for irradiation, rigorously excluding air and water, before, during, and after irradiation. We report the investigation of the newly irradiated target in detail in the enclosed manuscript pre-print entitled "Chemical Effects of the Nuclear Reaction $\text{N}^{14}(\text{n},\text{p})\text{C}^{14}$ in Potassium Azide," which has been submitted to the Journal of Physical Chemistry.

B. Sodium Azide

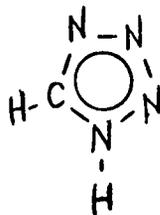
Sodium azide was recrystallized three times from water, dried at 110°C , then $7\frac{1}{2}$ g. in a necked quartz ampoule was heated to 220°C for one hour under vacuum. The ampoule was sealed off under helium, and irradiated in the thermal column of the Omega West Reactor at Los Alamos for 113 hours at 5×10^{11} n/cm²sec. The target is now ready for investigation.

C. Ammonium Azide

Ammonium azide (NH_4N_3) was purified by sublimation under reduced pressure. A sample of the purified solid was dried under vacuum in a quartz ampoule, sealed off under helium, then irradiated for 113 hours at 5×10^{11} n/cm²sec. Unfortunately, the sample exploded during irradiation, stopping our investigation on it, but doing no damage to the reactor.

II. Nitrogen Heterocycles

Tetrazole (I) recrystallized three times from ethylacetate



(I)

was oven dried and vacuum dried prior to being sealed off in a quartz ampoule. The sample was irradiated in the thermal column in the Los Alamos reactor for 13 3/4 hours at 3×10^{12} n/cm²sec. The sample ampoule has not been opened at this time, while gas chromatographic procedures for separating and identifying possible products are being investigated. The following columns have been tested for the indicated products: (1) Molecular sieve 5A for CH₄ and CO. (2) Silica gel for CH₄, C₂H₅, C₂H₄, C₂H₂, and CO₂. (3) 20% Di(2-ethylhexyl)-sebacate on acid-washed Chromasorb W for separation of tetrazole, methyltetrazoles, and tetrazines. (5) 20% Hexadecanol on base-washed firebrick for CH₃NH₂, C₂H₅NH₂, and CH₃NHCH₃. A flow proportional counter* has been constructed to determine the C¹⁴ radioactivity of the chromatograph effluent. Dissolution of the target in solvent and also solid injection of it into the chromatograph are planned.

* Wolfgang and Rowland, Anal. Chem., 30, 905 (1958).