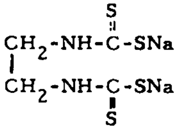
NOTES

SYNTHESIS OF ^{14}C-LABELLED DISODIUM ETHYLENEBISDITHIOCARBAMATE

Received on April 24, 1974

Disodium ethylenebisdithiocarbamate (nabam, I) is the parent compound of an

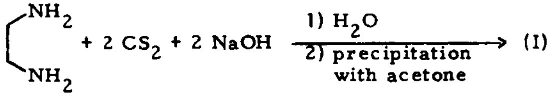


$$\begin{matrix} CH_2\text{-}NH\text{-}\overset{\overset{S}{\|}}{C}\text{-}SNa \\ | \\ CH_2\text{-}NH\text{-}\underset{\underset{S}{\|}}{C}\text{-}SNa \end{matrix}$$

(I)

important group of agricultural fungicides. Several studies on the fate of the compound in plants have appeared in recent years (1, 2, 5). The use of 1, 2-^{14}C-labelled nabam was found to be indispensable for a quantitative analysis of the fate of nabam.

The conventional synthesis of nabam (3) utilizes a reaction in a predominantly aqueous solvent according to the scheme



$$\left(\begin{matrix} NH_2 \\ NH_2 \end{matrix}\right. + 2\,CS_2 + 2\,NaOH \xrightarrow[\text{2) precipitation with acetone}]{\text{1) } H_2O} (I)$$

The yield of this reaction, however, is rather poor, and so it is unsuitable as a radiochemical synthesis. Since aqueous solutions of nabam tend to decompose within a day (1, 4), a more promising approach seemed to be to perform the reaction in a non-aqueous medium. To this end we screened several solvents capable of accommodating the water liberated during the reaction. A significant improvement in yield was achieved by the use of dioxane as a solvent.

The above-mentioned instability of the product made it impossible to determine its radiochemical purity by means of thin-layer chromatography. We therefore had to resort to direct determination of its specific activity. The radiochemical purity of the product was further checked by the inverse isotope dilution method.

Experimental

1,2-^{14}C-Ethylenediamine-diHCl[*] (specific activity 4.84 mCi/mmol, overall activity 150 µCi) was diluted with unlabelled ethylenediamine-diHCl to a total weight of 25.3 mg. For determination of its specific activity, 0.1 mg samples of the compound were weighed and directly transferred to scintillation bottles. Scintillation liquid consisting of a solution of 0.5% PPO and 0.05% POPOP in a mixture of 3 ml of ethanol (96%) and 12 ml of toluene was poured into each of the bottles, and the samples were counted in a Packard Tricarb model 3380 liquid scintillation spectrometer. The specific activity of the starting material was found to be 761 µCi/mmol (S.D. ± 7; n = 3).

25.0 mg of the 1,2-^{14}C-ethylenediamine-diHCl thus obtained was transferred to one bulb of the reaction vessel depicted in Fig. 1.

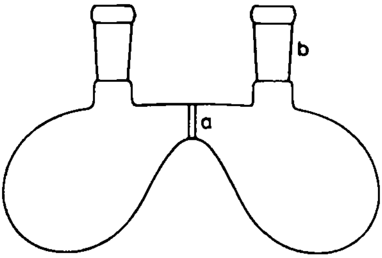


Fig. 1. Reaction vessel for the synthesis of ^{14}C-labelled nabam.
The volume of each bulb is about 10 ml
a. glass filter plate
b. B10 ground glass joint

Freshly distilled peroxide-free dioxane (2.5 ml), aqueous 9.95 N NaOH (75 µl), and CS_2 (0.5 ml) were added successively. The mixture was then stirred magnetically for 2 hours at room temperature.

During this period a semi-crystalline mass had formed which adhered to

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[*] purchased from the Radiochemical Centre, Amersham, England

the wall. Subsequently 1 ml of anhydrous acetone was added, and stirring was continued for an additional 1.5 hr. More crystals had now appeared, and the liquid was filtered off through the filter plate by nitrogen pressure. The sticky precipitate was stirred for 0.5 hr with a mixture of 2 ml of dry acetone and 1 ml of dry ether. On repetition of this procedure the washings were colourless.

The pale yellow crystals were dried in a stream of nitrogen, and extracted (3x) with 1 ml portions of absolute ethanol, NaCl remaining behind. The extracts were pooled and the solvent was removed at reduced pressure. The yield of dry product was 35.6 mg, or 52% (based on nabam.6aq). The specific activity of the product was determined according to the method described above, and was found to be 758 μCi/mmol (S.D. ± 9; n = 3).

Within the limits of experimental error, this result is consistent with the specific activity of the starting material. In the inverse isotope dilution method, the product (0.36 μCi) was diluted with inactive nabam.6aq (1 g) and recrystallized three times from ethanol-water (50:6, v/v).

The results are shown in Table 1.

recrystallization no.	specific activity
0	0.132 μCi/mmol
1	0.126
2	0.112
3	0.121

Table 1. Specific activity of ^{14}C-nabam after recrystallization

The relatively large spread in the specific activities of the three crystallizates may be due to variations in the crystal water stoichiometry.

The radiochemical yield, based on the specific activity, was 52%, which is equal to the chemical yield.

Acknowledgements

The authors wish to thank Mr. J. W. Vonk, who performed the dilution analysis. Financial support from the International Atomic Energy Agency at Vienna is gratefully acknowledged.

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