CHEMICAL EFFECT OF $^{13}$N FORMED IN BUTYRIC-$d_7$ ACID IRRADIATED IN A PILE

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A distinct phase effect was observed on the formation of $^{13}$NH$_3$, H$^{13}$NO$_x$ and [${}^{13}$N]-amide in pile-irradiated butyric-$d_7$ acid, although the magnitude of the effect was rather smaller than that in deuterated trifluoroacetic, acetic and propionic acids previously reported. In frozen butyric-$d_7$ acid, most of $^{13}$N was found in the forms such as $^{13}$NH$_3$ (54.8±0.7%), H$^{13}$NO$_x$ (26.8±0.6%), and [${}^{13}$N]-amide (15.9±1.8%). The yields of HC$^{13}$N and [${}^{13}$N]amino-butyric acid were only 0.6±0.3 and 1.2±0.3% even in the liquid, respectively. The scavenger effect of acetic anhydride-$d_6$ on the formation of $^{13}$NH$_3$, H$^{13}$NO$_x$ and [${}^{13}$N]-amide was examined. In liquid and frozen carboxylic acids, the yields of $^{13}$NH$_3$ and H$^{13}$NO$_x$ were proportional and inversely proportional to the number of hydrogen atoms in a target molecule in the region of the number of hydrogen from unity to eight.

Introduction

There have been many successful works on the chemical effect of $^{13}$N atoms generated mainly by reactions such as $^{12}$C(d, n)$^{13}$N, $^{13}$C(p, n)$^{13}$N, $^{14}$N(n, 2n)$^{13}$N and $^{16}$O(p, $\alpha$)$^{13}$N in various organic compounds. Several studies have been reported on the reaction of $^{13}$N and $^{16}$N with water such as reactor coolant, pointing out the importance of the chemical effect on the formation of NH$_3$ and NO$_x$. The authors have found a remarkable phase effect, in connection with radical reactions, on the formation of $^{13}$N-compounds in pile-irradiated hydrocarbons and carboxylic acid, together with a parallel relation between the formation of $^{13}$NH$_3$ and the viscosity of the substrates in acetone and ethyl ether. On the other hand, KLIMENT and SENSUI have found neither a phase nor a temperature effect on $^{13}$N-compounds formed in nitrobenzene and methanol, respectively.

Recently, the authors have revealed a correlation between the yields of $^{13}$NH$_3$ and H$^{13}$NO$_x$ and the number of hydrogen atoms in a target molecule in pile-irradiated trifluoroacetic acid-$d$, acetic acid-$d_4$ and propionic acid-$d_6$ within the number of hydrogen in a molecule from 1 to 6.
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In this paper, temperature effect on the formation of $^{13}$NH$_3$, H$^{13}$NO$_x$ and [13N]butyramide was studied in pile-irradiated butyric-d$_7$ acid, together with the scavenging effect of acetic anhydride-d$_6$ on the formation of the $^{13}$N-compounds, and the correlation between the yields of $^{13}$NH$_3$ and H$^{13}$NO$_x$ and the number of hydrogen in a target molecule was verified in the range of the number of hydrogen from 1 to 8.

**Experimental**

Deuterated reagents: butyric-d$_7$ acid (C$_3$D$_7$COOH, MD-171) and acetic anhydride-d$_6$ (MD-43) are supplied by the Division of Merck Frosst, Canada, Inc. Acetic anhydride-d$_6$ was refined by distillation in a nitrogen gas atmosphere prior to pile irradiation.

Pile irradiation and chemical separation were done in a similar way to previous works. Counting was carried out by pure germanium detector (well-type) supplied by EG&G Ortec Co. which has a counting efficiency 13.1±0.5% at 511 keV for the geometry in the present experiments.

**Results and discussion**

*Phase and scavenger effects on the yield of $^{13}$N-compounds*

The yield of $^{13}$NH$_3$ in butyric-d$_7$ acid was larger than that in the other deuterated carboxylic acids such as trifluoroacetic, acetic and propionic acids in all temperature range examined. A distinct increase in the yield of $^{13}$NH$_3$ was observed also when the phase of butyric-d$_7$ acid changed from solid to liquid as is shown in Fig. 1a. The magnitude of increase in the yield of $^{13}$NH$_3$ with the phase change was 6.1±1.6% in the medium, being smaller than 7.9±3.5% in trifluoroacetic acid-d, 13.9±3.9% in acetic acid-d$_4$ and 8.2±3.1% in propionic acid-d$_6$ previously reported.

With the phase change of the medium, only a little decrease, -(2±2)%, was observed in the yield of H$^{13}$NO$_x$ as shown in Fig. 1b. The magnitude of the decrease in the yield of H$^{13}$NO$_x$ is too small to compensate that of the increase in $^{13}$NH$_3$ in Fig. 1a. This is at variance with the fact that the magnitude of decrease in H$^{13}$NO$_x$ is well balanced with that of the increase in $^{13}$NH$_3$ in the previous carboxylic acids.

On the contrary, [13N]butyramide showed a steep decrease amounting to -(4.1±2.1)% in the yield with the phase change of the medium. That differs from the results on [13N]acetamide in acetic acid-d$_4$ and [13N]propionamide in propionic acid-d$_6$ which showed just a bit of increase in their yields with the phase change of the media. The sum of the decrease in the yields of H$^{13}$NO$_x$ (Fig. 1b) and [13N]butyramide (Fig. 1c) was balanced with the increase in the yield of $^{13}$NH$_3$ (Fig. 1a).