Production of Active Molecular Nitrogen by the Reaction of Recoil Nitrogen-13

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DESPITE the interest in the chemistry of active nitrogen,[1] studies with nitrogen-13 ($t_{\frac{1}{2}}$ 9·96 min.) have been limited to reactions with oxides of nitrogen and simple organic molecules.[2,3]

We produced atomic nitrogen-13 ($\simeq 10^8$ atoms) by the ${}^{12}C({}^{2}_{1}H,n){}^{13}N$ reaction, using a 7 Mev deuteron beam (from the Washington University Medical Cyclotron). The nitrogen was produced from the carbon in carbon dioxide and allowed to react with various carbon dioxide–nitrogen mixtures at 760 mm. pressure. The radiation dose of the sample was always less than 0·3 ev/molecule and the products were analyzed by conventional radio-g.l.c.[4]

Under all irradiation conditions only three products were detected, and the product identifications were performed as follows:

${}^{13}NN$ by its retention time on three chromatographic columns;

${}^{13}NO$ by its chromatographic behaviour, and by quantitative measurement by trapping ${}^{13}NO_2$, produced by air oxidation of ${}^{13}NO$, in caustic soda,[5] counting the solution, and comparing the activity with the original gas activity; and

${}^{13}N_2O$ by its retention time on three chromatographic columns; verified by the fact that the compound would not dissolve in caustic soda, but could be decomposed to ${}^{13}NN$ by passage through a stainless steel tube heated to 675°.[6]

Assuming that the total amount of the three products was 100%, the percentage compositions of the product spectra were determined from the activity in each of the three product peaks. The amounts of the products, thus calculated, were

TABLE

Radiation dose ev/mol.	8×10^{-3}	8×10^{-1}	2×10^{-1}	5×10^{-2}	5×10^{-2}	5×10^{-2}	5×10^{-2}
Dose rate ev/mol./sec.	4×10^{-3}	4×10^{-3}	2×10^{-2}	1×10^{-2}	1×10^{-2}	1×10^{-2}	1×10^{-2}
% N_2 in sample	$\simeq$0·2	$\simeq$0·2	$\simeq$0·2	2·5	5·0	7·5	10·0
% CO_2 in sample	99·8	99·8	99·8	97·5	95·0	92·5	90·0
% ${}^{13}NN$ formed	46·7 ± 3·0	45·0 ± 2·5	48·2 ± 3·0	49·2 ± 3·0	50·5 ± 3·0	50·8 ± 3·0	51·5 ± 3·0
% ${}^{13}NNO$ formed	52·5 ± 3·5	53·3 ± 3·0	50·5 ± 3·0	50·8 ± 3·0	49·5 ± 3·0	49·5 ± 3·0	48·5 ± 3·0
% ${}^{13}NO$ formed	1·2 ± 0·4	1·2 ± 0·4	1·3 ± 0·5	Trace	Trace	0·0	0·0

found to be independent of radiation dose and dose rate over the ranges studied (Table). If, however, the dose was increased by another order of magnitude, the nitrous oxide peak decreased in size owing to the high *G* value (12·0 ± 0·4) for N_2O decomposition.[7]

It is seen from the Table that the product spectrum is, to a first approximation, independent of nitrogen concentration, over the ranges studied. Concentrations of higher than 10% nitrogen were not used due to the production of ^{15}O ($t_{\frac{1}{2}}$ 2 min.) by the $^{13}N(^2_1H,n)^{15}O$ reaction which interfered with the product analysis. The product spectrum can be explained by the following reaction Scheme:

$$\begin{aligned} {}^{13}N^* + CO_2 &\xrightarrow{k_1} {}^{13}NO + CO \\ {}^{13}N^* + N_2 &\xrightarrow{k_2} {}^{13}NN^* + N \\ {}^{13}NN^* + CO_2 &\longrightarrow {}^{13}NNO + CO \\ {}^{13}NN^* + M &\longrightarrow {}^{13}NN + M^* \end{aligned}$$

if $k_2 \gg k_1$.

This Scheme involving active molecular nitrogen is more likely than the possible alternative involving long-lived $^{13}NO^*$; $^{13}NO^*$ is not a likely intermediate as ^{13}NO produced by the reaction of nitrogen with nitric oxide does not abstract nitrogen to form nitrous oxide.[3] The production of compounds containing two nitrogen atoms cannot be explained by the recombination of two ^{13}N atoms as the nitrogen atom concentration is so small. It appears therefore that by the reaction of recoil nitrogen with nitrogen, active molecular nitrogen can be formed and the reaction of this species with other molecules in the system can be studied. When active molecular nitrogen reacts with carbon dioxide at 760 mm. pressure, nitrous oxide is the only product observed. Nitric oxide is only observed at very low nitrogen concentrations and is presumably formed by the reaction of nitrogen atoms with carbon dioxide.

The excitation given to the molecule with which the active nitrogen reacts is low compared to other methods of studying active molecular nitrogen[1,8] which involve microwave excitation to produce the species, and this, combined with the fact that the pressure used in this work (760 mm.) is much higher than the pressure (< 10 mm.) used in the microwave work, means that stable products not previously isolated can be observed by the recoil technique.

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