

3 Isotopic Enrichment of Nitrogen in the Photolysis of NO 6

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Abstract

Photolysis of NO in the vacuum ultraviolet yielded N₂, O₂, NO₂, and N₂O. When the photolysis was carried out using the 1633 Å line of bromine, the N₂ initially formed was found to be enriched in nitrogen-15. The dependence of the enrichment on several parameters was studied, including temperature, pressure, the initial isotope ratio, and inert gases. The enrichment of the N₂ in N¹⁵N¹⁴ over N₂¹⁴ produced in the photolysis was due to relatively more N¹⁵O being excited, and reacting before isotope scrambling occurred by energy transfer.

Introduction

The enrichment of isotopes can be expected by photochemical methods due to the difference in absorption coefficients for any two isotopes at a specific wavelength. Prediction in advance for such enrichment is extremely difficult. Carbon monoxide has been shown to be selectively excited by the 2062 Å iodine line⁽¹⁾. The excited CO reacts with CO to give CO₂ and a carbon atom⁽²⁾, which also reacts with an additional CO to produce carbon suboxide (C₂O₃); which has

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been shown to be isotopically enriched in C^{13} ⁽³⁾. The 2062 Å iodine line is absorbed by the CO in the Cameron band ($X^1\Sigma^+ v = 0 \rightarrow a^3\Pi v = 0$). When a similar irradiation of nitric oxide was carried out using the 2062 Å line and the 1633 Å bromine line, an isotopic enrichment of the nitrogen initially formed was observed.

Experimental

The bromine lamp used for these experiments has been described in detail⁽⁴⁾. Purified NO was mixed with a rare gas, usually argon, so that (a) calculation of the percentage of NO reacted could be made by a material balance with the inert Ar, and (b) the effect of an unreactive third body on the reaction could be studied. The mixture was put into the lamp and irradiated for several hours. Samples were removed periodically and analysed on a CEC 21-130 mass spectrometer. Due to the presence of overlapping m/e peaks, the numerical analysis of the various components of the photolysis was carried out using standard mass spectrometric correction methods. Pressures of the various reaction mixtures between 100 and 400 mm were used. At such pressures, 90% of the original NO can be photolyzed within a few hours. The irradiation was carried out at three different temperatures: -78°C , 0°C and 79°C .

Results and Discussion

The results of several typical runs are shown in figure 1. The x-co-ordinate is the percentage of NO converted to N_2 . The y-co-ordinate is the N_2^{29}/N_2^{28} ratio divided by the normal ratio of .0074.

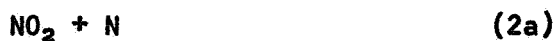


As can be seen from this graph, the maximum enrichment obtained is about a factor of four greater than the normal ratio. This is a large enrichment ratio, compared to the separation factors for most isotopic separation processes.

In the ultraviolet, the absorption spectrum of NO starts near 2300 A, and down to about 1500 A consists mostly of sharp bands⁽⁵⁾. It is this sharp band structure that allows the possibility of separating isotopes photochemically, due to frequency shifts in the absorption spectrum of N¹⁵O. Excitation could possibly be to any one of several electronic states which have vibrational bands in this region, and a specific assignment of the transition was not possible. To get an idea of the spectral situation three things must be considered: (1) the shift of the absorption spectrum as a function of wavelength as determined by the specific level which is excited, and is usually in the order of .1-1.0 A; (2) the width of the individual rotational absorption lines are less than .01 A wide and closely spaced; (3) the bromine emission, being an atomic electronic transition, will be a single line with a width, of somewhat less than .1A. From this we can conclude that, in general, the bromine emission line may cover one or more rotational absorption lines of both N¹⁴O and N¹⁵O. Therefore, the relative absorption coefficients of the N¹⁴O and the N¹⁵O at 1633 A could differ considerably, accounting for an enhancement of the excitation of an NO isotope.

The excited NO reacts, producing N₂, N₂O, NO₂ (N₂O₃), and O₂.

The following series of reactions may be assumed to take place and account for the products observed:

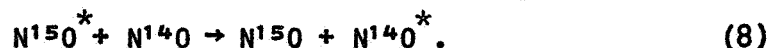


As can be seen from this sequence, the excited NO produced in (1) may then react with an unexcited NO (2a, 2b, or 2c), exchange energy (3) or dissociate (4a or 4b). The atoms produced by the dissociation may then produce additional reactions (5, 6 or 7).*

^a This reaction represents oxidation of NO to NO₂ which may occur by several paths.

* Except for the initial period of irradiation, the products will also absorb the 1633 Å line and react.

If the electronic energy exchange by reaction (3) was fast relative to the other reactions, any isotopic selectivity in the initial photochemical excitation would be lost by:



Since substantial enrichment is observed, this can't be a dominant reaction; that is, the NO^* must react before significant exchange has occurred. If some exchange does occur, however, then the addition of a rare inert gas, such as Ar, would lower the number of $\text{NO}^* - \text{NO}$ collisions, thereby decreasing the probability of isotope scrambling, and increasing the enrichment. This effect is shown in figure 1. In both the high and low pressure runs, approximately the same amount of Ar was added (50 mm Hg), so that the Ar/NO ratio is much higher in the low pressure runs, where greater enrichment was observed. Addition of Xenon yielded similar results to those obtained with argon. Further experiments were also made where the N^{150} was increased to about 3% or eight times the normal isotope abundance in NO. Approximately the same results were obtained with perhaps a little less relative enrichment.

Since the N^{150} appeared to be selectively excited when the 1633 A line was used, it could be expected that the N^{140} could also be selectively excited using another emission line producing N_2 depleted in N^{15} . Such a depletion was observed when NO was irradiated with the 2062 A iodine line although to a lesser extent than the enrichment at 1633 A. The $\text{N}_2^{29}/\text{N}_2^{28}$ ratio was approximately 75% of the normal ratio.

It should be noted that the energy of the 2062 Å line, 6.00 eV, is not enough to dissociate the NO molecule (6.49 eV).

Experiments were conducted with the bromine lamp in which 95% of the NO was N¹⁵O, and 7.67% of the mixture was Ar. On the basis of selective excitation of N¹⁵O, it was expected that the N₂ formed would be enriched in N₂³⁰ relative to N₂²⁹; however, the reverse effect occurred. The N₂ formed was enriched in N¹⁴, as if N¹⁴O were selectively excited. Therefore the overall results shows an enhancement of the excitation of the NO isotope present in relatively minor concentration.

Such a concentration dependence does seem reasonable, since the discrete absorption spectrum of the $\overset{\vee}{\underset{\wedge}{\text{NO}}}$ isotope is not expected to be uniform over the effective line width of the 1633 Å line. It can be assumed that the resulting absorption would not be proportional, under these conditions, to the concentration of an isotope. The isotope at the lower concentration, usually N¹⁵O, must from the results observed, absorb a relatively greater amount of the radiation; therefore, high percentage of excited molecules will be produced leading to the subsequent product enrichment.

These two effects, selective absorption and isotope concentration, are obviously not mutually exclusive. Both probably occur. The maximum observed enrichment for 95% N¹⁵O was not as great as that for the 97-99%

$N^{14}O$, so that the selective absorption must also have enhanced the enrichment. A run was made at 42% $N^{15}O$ and 58% $N^{14}O$. Since the concentrations were close, the enrichment was found to be minor.

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FIGURE 1
 Isotopic Ratios in N₂ Formed
 by Photolysis of NO at 1633 Å

