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The reaction of N-atoms with NO_2 using $^{15}NO_2$

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Chimica. — *The reaction of* N*-atoms with* NO_2 *using* $^{15}NO_2$ (*).

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RIASSUNTO. — La reazione tra azoto atomico e ipoazotide è uno dei più importanti processi che avvengono nel corso dell'irraggiamento con radiazioni ionizzanti di miscele azoto-ossigeno. Allo scopo di poter valutare quantitativamente l'effetto di tale reazione nel sistema accennato, la sua costante di velocità è stata misurata direttamente in un sistema in flusso, usando uno spettrometro di massa a tempo di volo per la rivelazione dei reagenti e dei prodotti. È stata usata ipoazotide marcata con azoto 15 per discriminare le varie reazioni che avvengono nel sistema. I risultati confermano i valori stimati in precedenza e mostrano che la produzione di protossido d'azoto predomina sugli altri processi possibili.

INTRODUCTION.

A number of years ago, Harteck and Dondes [1] postulated the following series of reactions to explain the presence of nitrous oxide in the radiolysis of pure NO, pure NO_2 and in nitrogenoxygen mixtures and estimated the ratios of these reactions:

$$\text{(1)} \qquad \rightarrow N_2O + O$$
$$\text{(2)} \qquad N + NO_2 \rightarrow 2\,NO$$
$$\text{(3)} \qquad \rightarrow N_2 + 2\,O$$

or

$$N_2 + O_2 .$$

It is possible to investigate directly this reaction in a flow system using a mass spectrometer to detect the species involved and thus measure the kinetics. This technique, which has been used by Kistiakowski and Volpi [2] and by Phillips and Schiff [3], is particularly useful because the presence of any ions or excited states which occur during radiolysis is avoided. Due to the overall complexity of this system, especially in determining the ratios of reactions (1), (2) and (3), and the role of these reactions in the radiolysis of pure NO, of pure NO_2 and in nitrogen-oxygen mixtures, this system was reinvestigated. To avoid complications in measuring N_2O, which appears at *m/e* 44 and therefore may be masked by CO_2, which is always present in the ion source of a mass spectrometer, $^{15}NO_2$ was used. The remainder of the technique was similar to that used by the previous investigators.

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RESULTS AND DISCUSSION.

The apparatus used in this work has been previously described [4]. Nitrogen atoms were prepared by the use of a condensed discharge in a Woods-Bonhoeffer tube. The concentration of the nitrogen atoms was determined by titration with NO and monitored with a Time-of-Flight Mass Spectrometer. The partial pressure of the nitrogen atoms was 0.025 torr.

TABLE I.

Reaction of Excess ^{14}N*-atoms with* $^{14}NO_2$ *at Room Temperature.*

A

Conditions: Pressure = 0.5 torr.; Ionizing Energy of Electrons in Mass Spectrometer = 20 ev
Concentration of ^{14}N atoms = 6.5×10^{13} atoms/cc
Concentration of $^{14}NO_2$ = 5×10^{12} molecules/cc

Signal Strength at M/*e* 46 (Arbitrary Scale)	Reaction Time ($t \times 10^3$ sec)	Overall Reaction rate(*), *k* (cc/part. sec) $\times 10^{11}$
23.5	1.98	2.10
44	1.55	2.04
74	1.13	2.13
140	0.62	2.29
350	0	

B

Conditions: Pressure = 0.3 torr.
Concentration of ^{14}N atoms = 5×10^{13} atoms/cc
Concentration of $^{14}NO_2$ = 5×10^{12} molecules/cc

Signal Strength at M/*e* 46 (Arbitrary Scale)	Reaction Time ($t \times 10^3$ sec)	Overall Reaction rate(*), *k* (cc/part. sec) $\times 10^{11}$
12	2.40	1.99
23.5	1.70	2.00
43.5	1.08	2.04
75	0.53	2.35
130	0	
		Average $k = 2.12 \pm$ $\pm 0.20 \times 10^{-11}$ cc/part. sec.

(*) Overall Reaction Rate, $k = k_1 + k_2 + k_3$.

The experiments were conducted at an overall pressure of 0.5 and 0.3 torr and at a flow rate of about 13 meters per second. Where $^{15}NO_2$ was used, it was diluted with argon to a concentration of 1 %. Normal NO_2 was prepared by the oxidation of tank NO (obtained from the Matheson Company) and fractionally distilled at cryogenic temperatures. Only the middle fraction was used. The $^{15}NO_2$ was obtained from the Isomet Corporation, Palisades Park, New Jersey with a ^{15}N concentration of 99.4 %. All the measurements were performed at room temperature.

TABLE II.

Reaction of Excess ^{14}N-atoms with $^{15}NO_2$ at Room Temperature.

A

Conditions: Overall pressure = 0.5 torr., Ionizing Energy of Electrons in Mass Spectrometer = 20 ev

Concentration of ^{14}N-atoms = 1.3×10^{14} atoms/cc

Concentration of $^{15}NO_2$ = 10^{13} molecules/cc

$^{14}N\,^{15}N$ Pressure (torr $\times 10^4$)	$^{14}N\,^{15}NO$ Pressure (torr $\times 10^4$)	Reaction Time ($t \times 10^3$ sec)	Ratio of Reaction Rates, $\frac{k_2+k_3}{k_1}$
1.5	1.35	1.4	1.11
1.6	1.40	3.2	1.14
1.6	1.50	5.3	1.06
1.7	1.45	7.8	1.17

B

Conditions: Overall Pressure = 0.3 torr.

Concentration of ^{14}N-atoms = 1.0×10^{14} atoms/cc

Concentration of $^{15}NO_2$ = 10^{13} molecules/cc

1.50	1.30	1.2	1.15
1.50	1.40	2.5	1.07
1.55	1.40	4.1	1.11
1.50	1.35	8.2	1.11
			Average $\frac{k_2+k_3}{k_1} = 1.11 \pm 0.03$

The results obtained in the reaction of an excess of N atoms with normal NO_2 at pressures of 0.5 and 0.3 torr and at room temperature are shown in Table I. The overall reaction rate, k, (which equals $k_1 + k_2 + k_3$) from this work is $2.12 \pm 20 \times 10^{-11}$ cc/particles sec., which is in good agreement with that of Kistiakowski and Volpi of 0.8×10^{-11} and Phillips and Schiff of 1.8×10^{-11}. In our experiments the concentration of the N atoms was in considerable excess over the concentration of the NO_2, so that all the NO_2 would interact with the N–atoms rather than O atoms produced in reactions (1) and (3). Thus, reaction:

$$(4) \qquad NO_2 + O \rightarrow NO + O_2$$

does not occur to an appreciable extent. Also, since the N atom concentration is practically constant, no determination of the mass spectrometric sensitivity for NO_2 is necessary. The overall rate constant can be calculated using the integrated first order rate equation, as follows:

$$(I) \qquad -0.434\, k[N]\, t = \log \frac{[NO_2]_t}{[NO_2]_0}\,.$$

This equation involves only the ratio of the mass spectrometric signal of NO_2 for various reaction times to the signal at zero time, that is in the signal obtained in absence of N atoms. Table II shows the production of $^{14}N\,^{15}N$ and $^{14}N\,^{15}NO$ using $^{15}NO_2$ under the same conditions, i.e. excess N atoms. Here the ratio of $^{14}N\,^{15}N$ to $^{14}N\,^{15}NO$ provides the relationship between $k_2 + k_3$ and k_1 since the NO produced in reaction (2) reacts rapidly with the excess N atoms to produce N_2, as:

$$(5) \qquad N + NO \rightarrow N_2 + O\,.$$

Also, of the two NO molecules produced in reaction (2) only one enters into the formation of $^{14}N\,^{15}N$. In this work, the $^{14}N\,^{15}N$ could be accurately measured by using a 5 % N_2—95 % argon mixture which minimizes the signal from the $^{14}N\,^{15}N$ in natural N_2. The ratio of k_2+k_3 to k_1 is in good agreement with the measurements of Phillips and Schiff; this work being 1.11, that of Phillips and Schiff being 1.30 (calculated). Owing to the difficulty of measuring $^{14}N\,^{15}N$ from reaction (3) and that formed by the $^{14}N\,^{15}N$ produced by reaction (5), resolution as to the formation of $^{14}N\,^{15}N$ from reactions (2) and (3) is not possible in these experiments.

In conclusion, this technique allows for accurate determination of rates of reactions occurring in relatively complex systems. Using the labeling technique, contribution of reaction (1) can be accurately determined in the system. The other two reactions (2) and (3) in the system are difficult to separate due to interference of reaction (5), therefore only their sum is known. Reaction (1) is of special importance as a means of measuring the amount of nitrogen atoms formed in the radiolysis of nitrogen-oxygen mixtures.

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