Relative Quenching Cross Sections in the Reaction of \( \text{Hg}(6^3P_1) \) Atoms with Isotopic \( \text{N}_2\text{O} \) Molecules

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The \( N^1/N^16 \) and \( O^9/O^{18} \) isotope effects in the \( \text{Hg}(6^3P_1) \)-photosensitized decomposition of nitrous oxide have been measured. Observed isotopic fractionation factors, \( S_0^9 \) (interpreted in terms of ratios of rate constants for quenching by \( N^1/N^16 \text{N}^16\text{O}^{18}, N^1\text{N}^16\text{O}^9, \) and \( N^1\text{N}^16\text{O}^9 \)), are related to the ratio of isotopic quenching cross sections by the equation \( Q/Q^* = S_0^9(\mu/\mu^*)^t \), where \( \mu \) and \( \mu^* \) are the collisional reduced masses for \( \text{Hg} \) and the light and heavy isotopic molecules, respectively. The quenching cross section ratio for \( N^1\text{N}^16\text{O}^{18}/N^1\text{N}^16\text{O}^9 \) was unity within the experimental uncertainty (±0.1%). The ratios for \( N^1\text{N}^16\text{O}^{18}/N^1\text{N}^16\text{O}^9 \) and \( N^1\text{N}^16\text{O}^{18}/N^1\text{N}^16\text{O}^9 \) differed from unity by +0.98% and +0.44%, respectively. The order of the quenching cross sections for the isotopic nitrous oxide molecules is thus: \( N^1\text{N}^16\text{O}^{18}<N^1\text{N}^16\text{O}^9<N^1\text{N}^16\text{O}^9 \leq N^1\text{N}^16\text{O}^9 \). The implications of the present observations are briefly discussed.

INTRODUCTION

When \( \text{Hg}(6^3P_1) \) atoms interact with molecules of a foreign gas, a transfer of energy may occur with the return of the \( \text{Hg} \) atoms to the ground state \( (6^3S_0) \) by means of a nonradiative transition. The \( (6^3P_1) \rightarrow (6^3S_0) \) fluorescence is thus quenched. The theory of the optical method of measuring effective quenching cross sections is well known. Absolute values of quenching cross sections have been reported but their accuracy is limited, perhaps because of the variations in the optical systems used.

Attempts to correlate quenching cross sections in terms of a mechanism of energy transfer have been rather unsuccessful. Furthermore, the values obtained by the optical method represent effectively the sum of the cross sections for the \( (6^3P_1) \rightarrow (6^3S_0) \) and \( (6^3P_1) \rightarrow (6^3P_0) \) transitions. If dissociation of the quenching molecule occurs, then the quenching cross section may be deduced by chemical means, thus yielding a value which refers to the \( (6^3P_1) \rightarrow (6^3S_0) \) transition alone. Such chemical determinations are difficult, requiring a knowledge of the kinetics of the reaction, evaluation of the rate constant of the quenching step, and from this the effective quenching cross section.

However, the determination of relative quenching cross sections may be accomplished more readily.

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5 Footnote reference 2(c), p. 97.
Cline and Forbes measured the rates of reaction of \( \text{Hg}(6^3P_1) \) with \( \text{O}_3, \text{H}_2\text{S}, \) and \( \text{N}_2\text{O} \) and determined their relative quenching efficiencies; unfortunately, the reaction mechanisms were not considered in detail. Cvetanovic measured the quantum yield of \( \text{N}_2 \) and \( \text{H}_2 \) production for binary mixtures of \( \text{N}_2\text{O} \) and hydrocarbons and obtained quenching cross sections relative to \( \pi_\text{C}_3\text{H}_6 \). He also determined the relative efficiencies of quenching the \( \text{Hg}(6^3P_1) \) to the ground state and the \( (6^3P_0) \) state. Relative quenching cross sections of ethylene oxide, acetaldehyde, and butylene oxide were also measured.

As yet there is no quantitative theoretical interpretation which accounts for these relative values of quenching cross sections. It has been stated "there is no simple way of predicting the efficiency of a physical quenching process, but that a potential-energy surface must be constructed for each case under consideration." This statement, of course, could be extended to "chemical quenching" wherein the quenching molecule dissociates.

In order to aid in the understanding of the energy transfer mechanism, one may consider the relative quenching cross sections of isotopic molecules, whose potential energy curves are essentially identical. Such measurements have been reported for \( \text{H}_2\text{D}_2, \text{N}_2\text{D}_2, \text{H}_2\text{O}-\text{D}_2\text{O}, \) and \( \text{PH}_3\text{PD}_3 \) using the optical technique. The precision of the optical method is insufficient for use with isotopes other than deuterium.

In the present work, the relative quenching cross sections of isotopic \( \text{N}_2\text{O} \) have been measured by chemical means. The isotopic fractionation in the photosensitized decomposition has been measured, from

Footnote references 2(c), p. 166.


which ratios of quenching cross sections for the various isotopic (N\(^{15}\) and O\(^{18}\)) species of N\(_2\)O have been evaluated.

**EXPERIMENTAL**

Nitrous oxide, containing natural-abundance nitrogen and oxygen isotopes, (Matheson Company, stated purity: >98.0\%) was purified by repeated distillations from -160° to -196°C; the middle fractions were collected and stored over mercury at room temperature. The vapor pressure at the triple point and the infrared spectrum agreed well with the literature.\(^{14,15}\)

For certain experiments dealing with the N\(^{15}/\)N\(^{14}\) isotope effect, isotopically labeled nitrous oxides were used. They were prepared from the appropriately labeled NH\(_2\)NO\(_3\) by thermal decomposition.\(^{16}\) The N\(^{15}\)-labeled ammonium nitrates had been prepared by the reaction of ammonia and nitric acid with subsequent evaporation to dryness and recrystallization from hot water. By using N\(^{15}\)-labeled HNO\(_3\), NH\(_4\)N\(^{15}\)O\(_3\) was produced and from it NN\(^{15}\)O (sample A). By using N\(^{15}\)-enriched (NH\(_4\))\(_2\)SO\(_4\) (liberating the ammonia with NaOH), NH\(_4\)N\(^{15}\)H\(_2\)O\(_3\) was produced and from it NN\(^{15}\)NO (sample B). The atom fractions of N\(^{15}\) in samples A and B (as determined mass spectrometrically\(^{17}\)) were nearly the same (4.3±0.1\%).

A conventional vacuum apparatus was used. The reactants were continuously circulated through the illuminated zone (the "reactor") at a rate of 100 to 200 cc/min by a glass circulating pump\(^{18}\) with a Teflon-covered magnetic bar and by convection using an auxiliary heater. The reactor was constructed of Vycor (type 7910), 30 mm o.d. and 26 mm i.d. Concentric with this tubing was an inner wall (24 mm o.d.). The reaction zone thus consisted of an annulus, 13 cm long with a width of 2 mm. This Vycor is transparent only for λ~2000 A and served as a filter to remove the 1849-A Hg line. Liquid mercury was present in the closed loop through which the gases circulated.

The 2537-A radiation was supplied by a Hanovia Company low-pressure Hg arc (helix). An aluminum reflector was used. The lamp and reaction zone were cooled by a stream of air at 25±3°C. The lamp surrounded the reaction zone with a clearance of 1–2 mm.

The nitrous oxide was metered into the reaction loop and the decomposition followed manometrically for a time (ca 1 hr) corresponding to a small (<0.15) fraction of reaction. The reaction mixture, containing unreacted N\(_2\)O, N\(_2\), O\(_2\), and traces of higher oxides of nitrogen,\(^{19}\) was separated by passage through a trap at -78°C into a trap at -196°C. The volatile gases were cycled through Cu(435°C) and the N\(_2\) remaining was measured and collected for subsequent N\(^{15}\) assay. The product O\(_2\), retained as CuO, was quantitatively removed by cycling hydrogen (previously purified by passage through a Deoxo unit, a trap at -196°C, and a Pd thimble) over the CuO and collecting the resulting H\(_2\)O at -196°C for O\(^{18}\) isotopic assay.\(^{20}\)

By means of the photosensitized reduction of N\(_2\)O in excess H\(_2\) (time required: ca 1 hr),\(^{21}\) the nitrogen in each batch of N\(_2\)O was converted quantitatively (±1%) to N\(_2\) and the oxygen to H\(_2\)O, yielding "reference samples" for isotopic analysis.

The mass spectrometer was a Nier-type double-beam isotope-ratio instrument. N\(^{15}\) analyses were performed by alternating samples with tank N\(_2\) and recording the ratio of the 29/28 peaks for tank vs sample. During every series a "reference sample" was measured. The isotopic fractionation factor S is defined

\[
S = \frac{[\text{sample}]}{[\text{reference}]} = \frac{[\text{(N15N14)}]/[\text{(N14N14)}]}{[\text{(N15N14)}]/[\text{(N14N14)}]} = \frac{\text{sample}}{\text{reference}}.
\]

The usual small correction of S to zero extent of reaction was made using the standard logarithmic formula\(^{22}\)

\[
S_0 = \ln(1-f)/\ln(1-f/S),
\]

where f = fraction of substrate reacted. For f ≤ 0.1 (the usual case), the simplified form\(^{22}\) was used: \(S_0 = 1 - (S - 1)(1 + f/2)\).

The H\(_2\)O samples were equilibrated\(^{23}\) with CO\(_2\) for 3–5 days at 25°C. The CO\(_2\) was freed of H\(_2\)O by distillation and collected for O\(^{18}\) assay; the mass-spectrometric procedure was similar to that described for N\(^{15}\). The ratio of the 46/44 peaks was measured for the "reference samples," all compared with tank CO\(_2\). From the ratio of (46/44) \(_{\text{sample}}/(46/44) \(_{\text{tank}}\) for the CO\(_2\) samples, the atom fraction of O\(^{18}\) in the "unknown" water was calculated using the simplified form\(^{24}\) of the Dostrovsky-Klein formula.\(^{25}\)

The O\(^{18}\) isotopic fractionation factor, S, is defined \(S_0 = (Z_0)/\text{sample} = (Z_0)/\text{sample}\) where Z\(_0\) is the atom fraction of O\(^{18}\) in the water before equilibration. The usual small correction to zero extent of reaction was applied to this value of S.

**RESULTS**

The qualitative aspects of the reaction reported by Cvetanović\(^{19}\) have been confirmed. The ratio of N\(_2\) to O\(_2\) produced was in the range 2.00–2.08 (i.e., a slight deficiency in O\(_2\)). Small amounts of HgO, which deposited on the wall of the reactor, were removed before each experiment by flaming. The rate of N\(_2\) production was not consistent, varying over a threefold range;\(^{26}\)

\(^{21}\) In the case of NN\(^{15}\)O\(_3\), for example, the 4.3 at. % N\(^{15}\) would be distributed as follows, in terms of all the molecules: N\(^{15}\)NO\(_2\) = 0.4\%, NN\(^{15}\)O\(_3\) = 3.9\%, and NNO\(_3\) = 95.7\%.
\(^{24}\) Typical quantities of H\(_2\)O obtained were in the range of 6.5–15 mg.
\(^{27}\) M. Cohn and H. C. Urey, J. Am. Chem. Soc. 60, 679 (1938).
TABLE I. Observed isotope effects in the Hg-photosensitized decomposition of N₂O.

<table>
<thead>
<tr>
<th>Set</th>
<th>Experiment</th>
<th>( P_o ) (mm Hg)</th>
<th>( S_0 ) (N₁₄/N₁₆)</th>
<th>( S_0 ) (O₁₈/O₁₆)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. N*NO</td>
<td>(4.3 at. % N₁₄)</td>
<td>503</td>
<td>1.0134</td>
<td>1.0140±0.0009</td>
</tr>
<tr>
<td></td>
<td></td>
<td>503</td>
<td>1.0153</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>506</td>
<td>1.0133</td>
<td></td>
</tr>
<tr>
<td>B. N*NO</td>
<td>(4.3 at. % N₁₆)</td>
<td>299</td>
<td>1.0188</td>
<td>1.0186±0.0001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>304</td>
<td>1.0184</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>322</td>
<td>1.0185</td>
<td></td>
</tr>
<tr>
<td>C. NNO</td>
<td>(natural isotopic abundance: 0.4 at. % N₁₅)</td>
<td>224</td>
<td>1.0164</td>
<td>1.0170±0.0002*</td>
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<tr>
<td></td>
<td></td>
<td>230</td>
<td>1.0172</td>
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</tr>
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</tr>
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<td>310</td>
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<td>312</td>
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<td>325</td>
<td>1.0173</td>
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<td></td>
<td></td>
<td>595</td>
<td>1.0170</td>
<td></td>
</tr>
<tr>
<td>D. NNO</td>
<td>(natural isotopic abundance: 0.2 at. % O₁₈)</td>
<td>237</td>
<td>1.0196</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>237</td>
<td>1.0195</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>322</td>
<td>1.0187</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>502</td>
<td>1.0182</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>530</td>
<td>1.0192</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Av 1.0195±0.0008*</td>
<td></td>
</tr>
</tbody>
</table>

* Average deviation from the mean.

Assuming negligible extent of reaction and tracer isotopic level, the fractionation factors may be related to appropriate ratios of rate constants 1–4, as follows.

The atom fraction of O₁₈ in the oxygen atoms produced in steps 1 and 4 is directly measured by the O₁₈ atom fraction in the product O₂ (and thus in the H₂O assayed) so that

\[
\frac{k_1}{k_4} = S_{140} \quad (for \ O_18/O_16).
\]

Thus from the data of set D in Table I, \( k_1/k_4 = 1.0195 ± 0.0008 \).

From the kinetic equations (1–3), the over-all \( N_14/N_15 \) isotope effect (corrected to zero extent of reaction), \( S^0 \), may be approximated by

\[
(S^0 - 1) = Y (S_{12} - 1) + (1 - Y) (S_{13} - 1),
\]

where \( Y = (N^*NO)/(N^*NO + NNO^*) \); \( S_{12} = k_1/k_2 \); \( S_{13} = k_1/k_2 \). \( S_{12}^0 \) and \( S_{13}^0 \) represent so-called "intermolecular isotope effects" which refer to the relative probability for rupture of the NN—O bond in a molecule of \( N^14N^14O \) vs a molecule containing an \( N^16 \) atom.

For the \( N^15 \)-labeled nitrous oxides (4.3 at. % \( N^15 \)), using the data of sets A and B (Table I), the simultaneous solution of Eq. (2) yields \( S_{12}^0 = 1.0191 \) and \( S_{13}^0 = 1.0136 \).

Using these values in Eq. (2) for \( N_2O \) of natural \( N^15 \) abundance (where \( Y = 0.5 \)), a calculated value of \( S^0 = \) 1.039.

\( * \) The value of \( Y \) for sample A is: \( Y = (0.004)/(0.004+0.039) = 0.093 \); for sample B, \( Y = (0.039)/(0.039+0.004) = 0.907 \).
REACTION OF Hg(64P1) ATOMS WITH N2O

1.0163 is obtained, which agrees well with the observed value of 1.0170 (set C, Table I).

The isotopic rate-constant ratios thus determined may be related to ratios of isotopic quenching cross sections by the equation

\[ q = \frac{Q}{Q^*} = S^0(\mu/\mu^*)^4, \]  

(3)

where \( Q \) and \( Q^* \) are the isotopic quenching cross sections and \( S^0 \) is the appropriate ratio of rate constants; \( \mu \) and \( \mu^* \) are the collisional reduced masses for Hg and the light and heavy isotopic molecules, respectively. Table II expresses the results as relative quenching cross sections (q) for the isotopic nitrous oxides.

These results should aid in elucidating the nature of the quenching process. The potential energy diagram of nitrous oxide, formulated30 on the basis of the uv absorption spectrum, has led to the postulate39 that the quenching step involves the transfer of 4.86 ev to ground-state N2O (\( ^1\Sigma \)) to form an electronically excited repulsive state (which could be \( ^3\Pi, ^1\Pi \), \( ^1\Delta \), or \( ^3\Pi \)) immediately leading to dissociation. The over-all process is thus39 \( \text{Hg}(64P) + \text{N}_2\text{O}(^1\Sigma) \rightarrow \text{N}_2(1^1\Sigma) + O(3P), \) or \( \text{Hg}(6^1S_0) \). In addition, the infrared spectra of the N14-labeled nitrous oxides have been measured (and vibrational analyses carried out),30-32 so that the electronic ground-state vibrational levels for all isotopic modifications are reasonably well known.

An attempt to interpret the order of the isotopic quenching cross sections by analogy with the theory of the isotope effect in photolysis33 was unsuccessful. Here it was assumed that the transfer of the quantum of energy from the Hg' to the N2O results in a vertical electronic transition from the ground-state zero-point level to the upper repulsive state. The observed order of the isotopic cross sections (\( \text{N}^{14}\text{N}_2\text{O}^{16} > \text{N}^{14}\text{N}_2\text{O}^{18} > \text{N}^{15}\text{N}_2\text{O}^{16} > \text{N}^{16}\text{N}_2\text{O}^{16} \)) would thus imply that the zero-point levels were in the same order. This is not in agreement with the order obtained from the calculated31 zero-order frequencies, \( \text{N}^{14}\text{N}_2\text{O}^{16} > \text{N}^{14}\text{N}_2\text{O}^{18} > \text{N}^{15}\text{N}_2\text{O}^{16} > \text{N}^{16}\text{N}_2\text{O}^{16} \), nor with that from the contribution to the zero-point energy of the presumably important antisymmetric stretching mode (\( \omega_3 \)):

\( \text{N}^{14}\text{N}_2\text{O}^{16} > \text{N}^{14}\text{N}_2\text{O}^{18} > \text{N}^{15}\text{N}_2\text{O}^{16} > \text{N}^{16}\text{N}_2\text{O}^{16} \).

It is, however, believed that observations on isotope effects in quenching cross sections should serve as valuable constraints in connection with any future theoretical treatment of intermolecular energy transfer in the quenching process.

ACKNOWLEDGMENT

The authors thank J. N. Doshi for his assistance with the mass spectrometric analyses.

<table>
<thead>
<tr>
<th>Isotope effect considered</th>
<th>Isotopic molecules compared</th>
<th>q</th>
<th>Percent isotope effect*</th>
</tr>
</thead>
<tbody>
<tr>
<td>O16/O18</td>
<td>N14N14O16</td>
<td>1.0011</td>
<td>0.11±0.10</td>
</tr>
<tr>
<td></td>
<td>N14N14O18</td>
<td>1.0098</td>
<td>0.98±0.10</td>
</tr>
<tr>
<td>N15/N14</td>
<td>N14N14O16</td>
<td>1.0044</td>
<td>0.44±0.10</td>
</tr>
<tr>
<td></td>
<td>N14N15O16</td>
<td>1.0054</td>
<td>0.54±0.10</td>
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</tbody>
</table>

* The uncertainties listed refer to the over-all estimated probable errors.

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