Relative Quenching Cross Sections in the Reaction of Hg(6³P₁) Atoms with Isotopic N₂O Molecules*

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The N^{14}/N^{15} and O^{16}/O^{18} isotope effects in the $Hg(6^3P_1)$-photosensitized decomposition of nitrous oxide have been measured. Observed isotopic fractionation factors, S^0 (interpreted in terms of ratios of rate constants for quenching by $N^{14}N^{14}O^{16}$ vs $N^{15}N^{14}O^{16}$, $N^{14}N^{15}O^{16}$, and $N^{14}N^{14}O^{18}$), are related to the ratio of isotopic quenching cross sections by the equation $Q/Q^* = S^0(\mu/\mu^*)^{\frac{1}{2}}$, where μ and μ^* are the collisional reduced masses for Hg and the light and heavy isotopic molecules, respectively. The quenching cross section ratio for $N^{14}{}_2O^{16}/N^{14}{}_2O^{18}$ was unity within the experimental uncertainty ($\pm 0.1\%$). The ratios for $N^{14}N^{14}O^{16}/N^{15}N^{14}O^{16}$ and $N^{14}N^{14}O^{16}/N^{14}N^{15}O^{16}$ 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: $N^{15}N^{14}O^{16} < N^{14}N^{15}O^{16} < N^{14}N^{14}O^{18} \cong N^{14}N^{14}O^{16}$. The implications of the present observations are briefly discussed.

INTRODUCTION

WHEN Hg(6³P₁) atoms interact with molecules of a foreign gas, a transfer of energy may occur with the return of the Hg atoms to the ground state (6^1S_0) by means of a nonradiative transition. The $(6^3P_1) \rightarrow (6^1S_0)$ fluorescence is thus quenched. The theory[1] of the optical method of measuring effective quenching cross sections is well known.[2] Absolute values of quenching cross sections have been reported[2] but their accuracy is limited, perhaps[3] 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 $(6^3P_1) \rightarrow (6^1S_0)$ and $(6^3P_1) \rightarrow (6^3P_0)$ transitions.[4] 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 $(6^3P_1) \rightarrow (6^1S_0)$ 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.[5]

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

Cline and Forbes[6] measured the rates of reaction of Hg(6³P₁) with O₂, H₂S, and N₂O and determined their relative quenching efficiencies; unfortunately, the reaction mechanisms were not considered in detail. Cvetanović[7] measured the quantum yield of N₂ and H₂ production for binary mixtures of N₂O and hydrocarbons and obtained quenching cross sections relative to n-C₄H₁₀. He also determined the relative efficiencies of quenching the Hg(6³P₁) to the ground state and the (6^3P_0) state. Relative quenching cross sections of ethylene oxide,[8] acetaldehyde,[9] and butylene oxide[10] 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[11] "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 H₂-D₂,[12] NH₃-ND₃,[12] H₂O-D₂O,[12] and PH₃-PD₃[13] 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 N₂O have been measured by chemical means. The isotopic fractionation in the photosensitized decomposition has been measured, from

¹ M. W. Zemansky, Phys. Rev. **36**, 919 (1930).
² For a review of the quenching of Hg-resonance radiation, see (a) A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, Cambridge, England, 1934); (b) W. A. Noyes, Jr., and P. A. Leighton, *The Photochemistry of Gases* (Reinhold Publishing Corporation, New York, 1941); (c) K. J. Laidler, *The Chemical Kinetics of Excited States* (Clarendon Press, Oxford, England, 1955).
³ W. A. Noyes, Jr., J. Am. Chem. Soc. **53**, 514 (1931).
⁴ B. de B. Darwent and F. G. Hurtubise, J. Chem. Phys. **20**, 1684 (1952).
⁵ Footnote reference 2(c), p. 97.

⁶ J. E. Cline and G. S. Forbes, J. Am. Chem. Soc. **63**, 2152 (1941).
⁷ R. J. Cvetanović, J. Chem. Phys. **23**, 1208 (1955).
⁸ R. J. Cvetanović, Can. J. Chem. **33**, 1684 (1955).
⁹ R. J. Cvetanović, Can. J. Chem. **34**, 775 (1956).
¹⁰ R. J. Cvetanović and L. C. Doyle, Can. J. Chem. **35**, 605 (1957).
¹¹ Footnote reference 2(c), p. 106.
¹² M. G. Evans, J. Chem. Phys. **2**, 445 (1934).
¹³ H. W. Melville, J. L. Bolland, and H. L. Roxburgh, Proc. Roy. Soc. (London) **A160**, 406 (1937).

which ratios of quenching cross sections for the various isotopic (N^{15} and O^{18}) species of N_2O 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^{14}/N^{15} isotope effect, isotopically labeled nitrous oxides were used. They were prepared from the appropriately labeled NH_4NO_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, $NH_4N^{15}O_3$ was produced and from it $NN^{15}O$ (sample A). By using N^{15}-enriched $(NH_4)_2SO_4$ (liberating the ammonia with NaOH), $N^{15}H_4NO_3$ was produced and from it $N^{15}NO$ (sample B). The atom fractions of N^{15} in samples A and B (as determined mass spectrometrically[17]) were nearly the same $(4.3\pm0.1\%)$.

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 $\lambda>2100$ 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 $25\pm3°C$. 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_2O, 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_2O at $-196°C$ for O^{18} isotopic assay.[20]

By means of the photosensitized reduction of N_2O in excess H_2 (time required: ca 1 hr),[21] the nitrogen in each batch of N_2O was converted quantitatively ($\pm1\%$) to N_2 and the oxygen to H_2O, 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

$$S=\frac{[(N^{15}N^{14})/(N^{14}N^{14})]_{ref}}{[(N^{15}N^{14})/(N^{14}N^{14})]_{sample}}.$$

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 $f\leq0.1$ (the usual case), the simplified form[22] was used: $S^0-1=(S-1)(1+f/2)$.

The H_2O samples were equilibrated[23] with CO_2 for 3–5 days at $25°C$. The CO_2 was freed of H_2O 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 CO_2 from the equilibration with H_2O from the decomposition reaction and from the "reference samples," all compared with tank CO_2. From the ratio of $(46/44)_{sample}/(46/44)_{tank}$ 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 $S=(Z_0)_{ref}/(Z_0)_{sample}$ 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;

[14] H. Hoge, J. Research Natl. Bur. Standards **34**, 281 (1945).

[15] G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1951), p. 277.

[16] L. Friedman and J. Bigeleisen, J. Chem. Phys. **18**, 1325 (1950).

[17] In the case of $NN^{15}O$, for example, the 4.3 at. % N^{15} would be distributed as follows, in terms of all the molecules: $N^{15}NO=0.4\%$, $NN^{15}O=3.9\%$, and $NNO=95.7\%$.

[18] Adapted from the design of M. M. Benarie, I. Amariglio, and M. Mokady, J. Sci. Instr. **35**, 70 (1958).

[19] R. J. Cvetanović, J. Chem. Phys. **23**, 1203 (1955).

[20] Typical quantities of H_2O obtained were in the range of 6.5–15 mg.

[21] H. A. Taylor and N. Zwiebel, J. Chem. Phys. **14**, 539 (1946).

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TABLE I. Observed isotope effects in the Hg-photosensitized decomposition of N_2O.

| | | | Isotope fractionation | |
Set Experiment	P_0 (mm Hg)	S° (N^{14}/N^{15})	S° (O^{16}/O^{18})
A. NN*O (4.3 at. % N^{15})	503	1.0134	
	503	1.0153	
	506	1.0133	
		Av 1.0140±0.0009[a]	
B. N*NO (4.3 at. % N^{15})	299	1.0188	
	304	1.0184	
	322	1.0185	
		Av 1.0186±0.0001[a]	
C. NNO (natural isotopic abundance: 0.4 at. % N^{15})	224	1.0164	
	230	1.0172	
	243	1.0169	
	310	1.0171	
	312	1.0172	
	325	1.0173	
	595	1.0170	
		Av 1.0170±0.0002[a]	
D. NNO (natural isotopic abundance: 0.2 at. % O^{18})	237		1.0196
	237		1.0195
	322		1.0187
	322		1.0220
	502		1.0182
	530		1.0192
			Av 1.0195±0.0008[a]

[a] Average deviation from the mean.

this difficulty had been previously noted[19] and had been attributed to a variable decrease in the Hg-vapor concentration (and thus the light absorbed) during the early stages of reaction.

Table I summarizes the isotopic fractionation data at various initial pressures P_0.

DISCUSSION

Cvetanović[19] concluded that the primary step in the quenching of $Hg(6^3P_1)$ atoms (Hg') to the ground state by N_2O produced N_2+O and that all the product nitrogen was formed in that step. The fate of the O atom was not certain but there was strong indication that atom recombination occurred. The fact that nearly stoichiometric amounts of O_2 are produced and that N_2O is not attacked by O atoms[26] lends strength to this supposition.

The relevant isotopic reactions[27] can be written

1. $Hg'+NNO\rightarrow N_2+O+Hg$

2. $Hg'+N*NO\rightarrow N*N+O+Hg$

3. $Hg'+NN*O\rightarrow NN*+O+Hg$

4. $Hg'+NNO*\rightarrow N_2+O*+Hg$

5. $O+O+M\rightarrow O_2+M$

6. $O*+O+M\rightarrow O*O+M$.

[26] G. B. Kistiakowsky and G. G. Volpi, J. Chem. Phys. 27, 1141 (1957).

[27] The symbols N and N* represent N^{14} and N^{15}, respectively, while O and O* refer, respectively, to O^{16} and O^{18}.

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 O^{18} in the oxygen atoms produced in steps 1 and 4 is directly measured by the O^{18}-atom fraction in the product O_2 (and thus in the H_2O assayed) so that

$$k_1/k_4 = S_{14}^0 \text{ (for } O^{16}/O^{18}).   (1)$$

Thus from the data of set D in Table I, $k_1/k_4 = 1.0195 \pm 0.0008$.

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

$$(S^0-1) = Y(S_{12}^0-1)+(1-Y)(S_{13}^0-1),   (2)$$

where $Y=(N*NO)/(N*NO+NN*O)$; $S_{12}^0=k_1/k_2$; $S_{13}^0=k_1/k_3$.

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 $N^{14}N^{14}O$ vs a molecule containing an N^{15} atom.

For the N^{15}-labeled nitrous oxides (4.3 at. % N^{15}),[28] 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 $S^0 =$

[28] The value of Y for sample A is: $Y=(0.004)/(0.004+0.039) = 0.093$; for sample B, $Y=(0.039)/(0.039+0.004)=0.907$.

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[7]

$$q \equiv Q/Q^* = S^0(\mu/\mu^*)^{\frac{1}{2}}, \qquad (3)$$

where Q and Q^* are the isotopic quenching cross sections and S^0 is the appropriate ratio of rate constants; μ and μ^* 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, formulated[29] on the basis of the uv absorption spectrum, has led to the postulate[19] that the quenching step involves the transfer of 4.86 ev to ground-state N_2O ($^1\Sigma$) to form an electronically excited repulsive state (which could be $^1\Sigma$, $^3\Sigma$, $^1\Pi$, $^1\Delta$, or $^3\Pi$) immediately leading to dissociation. The *over-all* process is thus[19] $Hg(6^3P_1) + N_2O(^1\Sigma) \rightarrow N_2(^1\Sigma) + O(^3P$, or $^1D) + Hg(6^1S_0)$. In addition, the infrared spectra of the N^{15}-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 photolysis[33] was unsuccessful. Here it was assumed that the transfer of the quantum of energy from the Hg$'$ to the N_2O results in a vertical electronic transition from the ground-state zero-point

TABLE II. Relative quenching cross sections (q) for isotopic N_2O molecules.

Isotope effect considered	Isotopic molecules compared	q	Percent isotope effect[a] $100(q-1)$
O^{16}/O^{18}	$\dfrac{N^{14}N^{14}O^{16}}{N^{14}N^{14}O^{18}}$	1.0011	0.11±0.10
N^{14}/N^{15}	$\dfrac{N^{14}N^{14}O^{16}}{N^{15}N^{14}O^{16}}$	1.0098	0.98±0.10
	$\dfrac{N^{14}N^{14}O^{16}}{N^{14}N^{15}O^{16}}$	1.0044	0.44±0.10
	$\dfrac{N^{14}N^{15}O^{16}}{N^{15}N^{14}O^{16}}$	1.0054	0.54±0.10

[a] The uncertainties listed refer to the over-all estimated probable errors.

level to the upper repulsive state. The observed order of the isotopic cross sections ($N^{14}N^{14}O^{16} \gtrsim N^{14}N^{14}O^{18} > N^{14}N^{15}O^{16} > N^{15}N^{14}O^{16}$) would thus imply that the zero-point levels were in the same order. This is not in agreement with the order obtained from the calculated[31] zero-order frequencies, $N^{14}N^{14}O^{16} > N^{15}N^{14}O^{16} > N^{14}N^{14}O^{18} > N^{14}N^{15}O^{16}$, nor with that from the contribution to the zero-point energy of the presumably important antisymmetric stretching mode (ω_3): $N^{14}N^{14}O^{16} > N^{14}N^{14}O^{18} > N^{15}N^{14}O^{16} > N^{14}N^{15}O^{16}$.

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

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