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A non-mass-dependent oxygen isotope effect in the production of ozone from molecular oxygen: The role of molecular symmetry in isotope chemistry

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It was previously reported that the reaction products from the synthesis of ozone in an electric discharge through molecular oxygen display a non-mass-dependent (NoMaDic) oxygen isotope effect. In this paper, we report a detailed characterization of the isotope effect, including the effect of molecular oxygen pressure, and the presence of a chemically inert third body (helium). The NoMaDic effect is due to an isotopically selective stabilization of the O₃ formation reaction intermediate, possibly resulting from the ability of the different isotopomers to exhibit different molecular symmetries.

INTRODUCTION

The chemical production of non-mass-dependent (NoMaDic) isotopic compositions is a subject of considerable relevance to cosmochemists. Additionally, the study of this particular class of isotope effects represents a unique approach to the observation of quantum effects such as selection rules in predissociation and inverse predissociation.

Mass-dependent isotope effects arise as a result of two general types of processes: (1) differences in isotopic translational partition functions (*viz.* velocity effects) or (2) differences in vibrational partition functions (bond strength effects) which arise primarily as a result of differences in zero point vibrational energy. Both processes lead to a similar result, which may be represented using the conventional delta notation for isotopic composition.¹

$$\delta^{17}\text{O}(\text{‰}) = \left\{ \left(\frac{{}^{17}R_{\text{Sample}}}{{}^{17}R_{\text{Std}}} \right) - 1 \right\} \times 1000, \quad (1)$$

$$\delta^{18}\text{O}(\text{‰}) = \left\{ \left(\frac{{}^{18}R_{\text{Sample}}}{{}^{18}R_{\text{Std}}} \right) - 1 \right\} \times 1000, \quad (2)$$

where δ represents the variation, in parts per thousand, of an isotopic ratio (${}^{17}R = {}^{17}\text{O}/{}^{16}\text{O}$ and ${}^{18}R = {}^{18}\text{O}/{}^{16}\text{O}$) of a sample relative to a standard material. Mass-dependent effects lead to isotopic abundance variations in oxygen which obey the relation

$$\delta^{17}\text{O} = 0.52 \delta^{18}\text{O}, \quad (3)$$

which illustrates why oxygen is so well suited for studying isotope effects; since it possesses three isotopes it is possible to unambiguously distinguish between mass-dependent and NoMaDic processes.

Mass-dependent oxygen isotope chemistry has been particularly important in cosmochemistry. NoMaDic isotopic distributions in meteorites have generally been presumed to reflect the intervention of nuclear processes² since chemical processes were thought to be incapable of producing NoMaDic fractionations.³ These observations have been attributed to processes such as spallation, radioactive decay, or the inclusion of material of exotic nucleosynthetic origin.⁴ The most striking NoMaDic oxygen compositions observed to date occur in high temperature mineral inclusions from carbonaceous chondrite meteorites, where a continuous set

of compositions have been reported,⁵ with $\delta^{17}\text{O}$ nearly equal to $\delta^{18}\text{O}$ over a range of approximately 40 ‰.

It has been shown that NoMaDic oxygen isotopic compositions are produced in the synthesis of ozone from molecular oxygen in an electric discharge.⁶ The ozone produced was enriched in the heavy isotopes with $\delta^{17}\text{O} = \delta^{18}\text{O}$. It was originally suggested that this fractionation might arise during the electron impact dissociation of molecular oxygen due to isotopic self-shielding. A similar process has been suggested to explain the large isotopic separation resulting from ozone production initiated by laser ultraviolet dissociation of O₂.⁷ There are two serious problems with this suggestion. First, self-shielding requires a reaction to be initiated by an absorption process⁸ (*i.e.*, O₂ + $h\nu$ → products or O₂ + e⁻ → O₂⁻, etc.), while the electron impact dissociation of O₂ (O₂ + e⁻ → O + O + e⁻) is more representative of a scattering process.⁹ Secondly, as discussed by Kaye and Strobel¹⁰ and Navon and Wasserburg,¹¹ any isotopic effect produced during O₂ dissociation should be obscured by isotopic exchange between oxygen atoms and O₂ molecules, which is significantly faster than ozone formation and distinctly mass dependent.¹²

The notion that isotopic exchange would eliminate NoMaDic effects produced in O₂ dissociation may not be valid under the present experimental conditions. While it is true at room temperature that atom-molecule isotopic exchange is faster than ozone formation, this is not the case at -196 °C, the temperature at which the experiments were performed. At lower temperatures the rate of ozone formation increases due to wall catalysis,¹³ hence experimental evidence is necessary to rule out O₂ dissociation as the source of the NoMaDic effect.

In a recent set of experiments involving the dissociation of carbon dioxide in an electrical discharge¹⁴ with subsequent production of carbon monoxide and molecular oxygen, the O₂ displayed a NoMaDic effect similar to that observed in the residual O₂ from the ozone production experiments. The effect was shown to be due to ozone formation, which is successfully competitive with other oxygen atom, sinks once a small O₂ reservoir has been produced, leaving the residual molecular oxygen depleted in ¹⁷O and ¹⁸O. This is another observation of the process operative during a discharge through O₂. The significant conclusion from

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these experiments was that electron impact dissociation was not responsible for the observed NoMaDic effect (refer to Fig. 1, which is a plot of the isotopic composition of the O_2 produced during the dissociation of CO_2). The observation that line segment BC, or its extension, does not pass through the origin implies there are two processes altering the isotopic composition in the O_2 - CO_2 system. The primary mass-dependent fractionation from points A to B in the figure may be attributed to isotopic exchange between oxygen atoms and CO_2 , similar to the process suggested in the O_2 - O_3 system.^{10,11} Since isotopic exchange would mask any isotope effect produced in the dissociation of CO_2 , it must be concluded that CO_2 dissociation is not responsible for the observed NoMaDic isotope effect. Likewise, since the same effect occurs when ozone formation is initiated by O_2 dissociation, the primary dissociation may be ruled out as the source of the NoMaDic effect.

The goal of the present work is to isolate the reaction step responsible for the NoMaDic effect using kinetic constraints, and identify the source. The approach involves a study of the effect of pressure in a static oxygen reservoir on the isotopic chemistry of ozone formation in an electric discharge. Experiments were performed using a system of sufficient volume to produce adequate ozone to permit precise isotopic composition determination, yet minimize changes in pressure.

EXPERIMENTAL

Materials

Two sets of experiments were performed, one using ultrahigh purity molecular oxygen (Matheson) and the second using a mixture of helium and O_2 (produced and analyzed by Matheson to contain 10.6% O_2).

Apparatus

All experiments were performed using the pyrex vacuum system shown in Fig. 2 (approximate ultimate vacuum

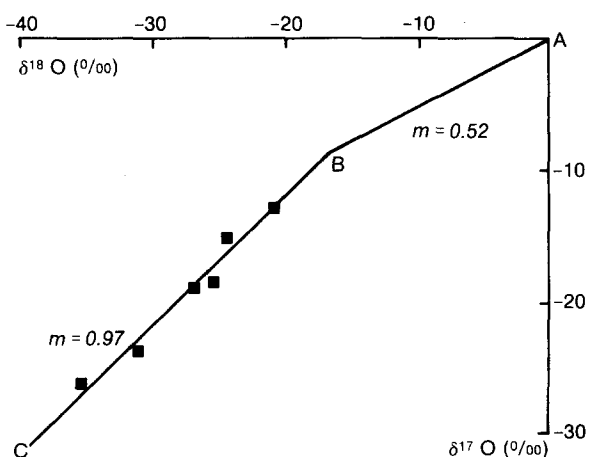


FIG. 1. Three isotope plot of the isotopic composition of O_2 produced during the dissociation of CO_2 in an electric discharge. The fractionation along line segment AB is due to $O + CO_2$ isotopic exchange and the fractionations of segments BC are due to the formation of ozone. The compositions are relative to the initial CO_2 isotopic composition.

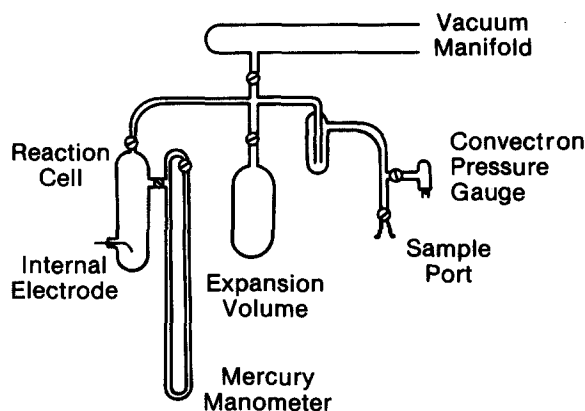


FIG. 2. Apparatus for the production of ozone.

of 10^{-5} Torr). The reaction cell (volume = 630 cm^3) had a sidearm fitting on the lower left side with a tungsten feed-through electrode attached, and the pressure in the cell was measured with the mercury manometer on the upper right side. The discharge was produced using a tesla coil high frequency generator (0.5 Mhz, model BD-50 from Electro Technic Products) attached to the external portion of the electrode.

Procedure

Oxygen gas was purified by passage through a trap at liquid nitrogen temperature prior to admittance to the reaction cell. The cell was isolated by closing the stopcock at the top. A Dewar containing liquid nitrogen was placed around the bottom of the cell up to the level of the electrode sidearm and the system allowed to thermally equilibrate. Five minutes after the pressure stabilized, the starting pressure was recorded (approximately 0.58 times the pressure at room temperature) and the tesla coil was turned on for a predetermined time. One minute after the tesla coil was turned off the final pressure was recorded and the manometer was isolated to minimize interaction between mercury and ozone. A sample of the residual O_2 was collected by direct expansion into a sample tube or complete collection in a sample tube containing molecular sieve 13X pellets (Linde) refrigerated with liquid nitrogen (when direct expansion would not provide adequate sample size). The residual O_2 in the reaction cell was removed by stepwise expansion into the vacuum line. This expansion process was repeated until the pressure in the reaction cell, as monitored by a Convectron gauge (Granville-Phillips Company), was approximately 0.4 Torr. The liquid nitrogen Dewar was removed from the cell and the ozone, along with the O_2 "blank" were collected in a sample tube containing molecular sieve cooled by liquid nitrogen.

Collection on molecular sieve served two purposes. First, it allowed the ozone sample to be transferred to a vacuum system where the sample size could be measured by collection into a calibrated Toepler pump. Secondly, releasing the ozone from the molecular sieve at approximately 220°C results in reversion to O_2 , the requisite gas for isotopic ratio determination. As part of the ozone sample size mea-

surement, a correction was made to account for the O₂ blank (the unremoved residual gas). It was determined by variation of the unremoved residual O₂ pressure, without the discharge, that the O₂ blank is proportional to the final O₂ pressure (blank amount = 53.17 μmol/Torr). For example, if the O₂ is aliquoted to a pressure of 0.4 Torr, the O₃ sample contains 21 μmol of residual O₂.

For experiments using He–O₂ mixtures modification of this procedure was required. During sample collection, O₂ and ozone were separated from He by collecting the oxygen species on a cold molecular sieve (–196 °C), to which helium does not adhere. Pumping on the sieve removes the helium, but leaves the O₂ or O₃ adsorbed. The O₂ blank correction factor had to be modified to 24.50 μmol/Torr since most of the gas measured as the final pressure consisted of He.

Isotopic analysis

Isotopic compositions were determined using a Nier¹⁵-type isotope ratio mass spectrometer with a 6 in. radius of curvature flight tube and dual collectors as previously reported⁶ with one exception. Rather than measure both ozone (converted to O₂) and residual O₂ separately, relative to the starting O₂ composition, the ozone was measured relative to the residual O₂. Since it has previously been shown that isotopic mass balance is preserved using this experimental procedure,⁶ the initial O₂ isotopic composition must lie on a line, in a three isotope plot (δ¹⁷O vs δ¹⁸O), between the ozone and residual O₂ compositions, with its exact position determined by the relative size of each reservoir. In which case,

direct measurement of the O₃ relative to the residual O₂ increase the precision of the δ¹⁷O/δ¹⁸O ratio determination.

Precision

The uncertainty of the isotopic compositions (±0.5 ‰) was limited by the reproducibility of the experiments rather than the mass spectrometric precision (±0.2 ‰).

RESULTS

Data from experiments using pure O₂ with the initial pressure of the system ranging from 1.1 to 152 Torr, and reaction times between 20 and 120 s are listed in Table I. The table includes values for initial pressure (*P_i*), final pressure (*P_f*), extent of reaction *f* (the values in parentheses were calculated using the reservoir sizes and the others were calculated from the change in pressure), ozone formation rate (Rate), the isotopic composition of the ozone relative to the composition of the O₂ starting material (δ¹⁸O₃ and δ¹⁷O₃), and the ratio of δ¹⁷O to δ¹⁸O (*m*).

For experiments with *P_i* greater than 2 Torr the ratios of δ¹⁷O/δ¹⁸O have an average of ⟨*m*⟩ = 1.01 ± 0.02. For experiments with *P_i* greater than 2.5 Torr the heavy isotopes are enriched in the ozone produced (the δ's are positive) and the ratio is always very near unity. At the lowest pressures, the O₃ is depleted in ¹⁷O and ¹⁸O, with the δ¹⁷O/δ¹⁸O ratio decreasing as pressure decreases. Figure 3 shows the ozone isotopic fractionation (δ¹⁸O₃) as a function of *P_i*.

For experiments using a mixture of helium and O₂, the

TABLE I. Data for experiments using pure molecular oxygen mixtures as the starting material. The abbreviations are explained in the text.

<i>P_i</i> (Torr)	<i>P_f</i> (Torr)	<i>f</i>	Rate (×10 ¹⁷ s ⁻¹)	δ ¹⁸ O ₃ (‰)	δ ¹⁷ O ₃ (‰)	<i>m</i>
1.1	...	(0.17)	0.38	-24.7	-17.8	0.720
1.7	...	(0.21)	1.15	-10.5	-9.1	0.862
2.0	...	(0.26)	1.76	-5.7	-5.5	0.952
2.2	...	(0.24)	2.06	-3.3	-3.3	0.991
2.4	...	(0.26)	2.50	-1.5	-1.6	1.040
3.0	1.7	(0.17)	2.46	4.3	4.2	0.979
5.2	3.7	(0.15)	4.66	14.8	14.7	0.991
7.4	6.0	0.19(0.10)	5.74	17.8	17.8	0.999
10.2	9.2	0.10(0.10)	7.90	19.8	19.9	1.004
15.1	13.0	0.14(0.09)	10.7	26.2	26.2	0.998
20.0	18.0	0.10(0.06)	13.3	32.4	32.4	0.999
25.8	24.3	0.058(0.05)	16.0	35.8	35.1	0.982
30.5	28.5	0.066	16.3	34.5	34.3	0.995
37.3	35.3	0.054	15.9	35.0	34.9	0.997
43.9	41.7	0.050	15.5	33.8	33.8	1.001
53.2	50.9	0.043	13.1	31.7	31.5	1.008
60.2	55.3	0.081	14.1	28.5	29.4	1.032
64.7	63.9	0.012	10.8	27.2	27.8	1.020
74.3	72.1	0.030	9.81	27.8	28.8	1.037
86.0	84.4	0.019	7.66	23.3	23.6	1.013
92.2	90.0	0.024	6.25	23.3	24.0	1.032
106.5	105.0	0.014	5.40	25.4	25.5	1.006
120.2	118.0	0.018	3.98	21.0	21.3	1.016
136.6	134.6	0.015	3.20	21.2	21.5	1.015
151.8	149.5	0.015	2.99	15.7	16.3	1.043
151.2	148.2	0.020	2.75	12.5	12.3	0.988

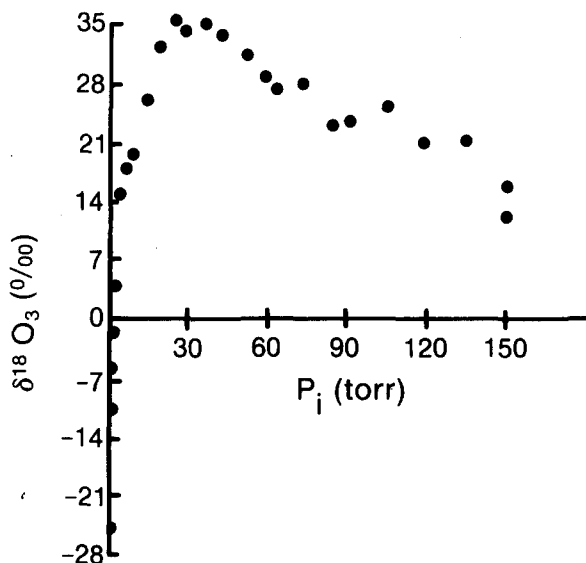


FIG. 3. The ^{18}O composition of ozone ($^{18}\text{O}_3$) as a function of initial pressure (P_i) for experiments using pure O_2 as the starting material.

range of initial total pressures was from 19 to 423 Torr, with reaction times between 20 and 40 s. The data are listed in Table II with the column headings defined as above. All ozone samples show enrichment in the heavy isotopes, and with the exception of the experiment with $P_i = 236$ Torr, the $\delta^{17}\text{O}$'s are essentially equal to the $\delta^{18}\text{O}$'s ($m = 0.99 \pm 0.01$). Figure 4 shows the ^{18}O composition of the ozone ($\delta^{18}\text{O}_3$) as a function of P_i .

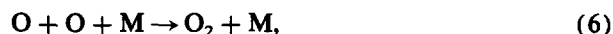
DISCUSSION

The ozone formation mechanism

The first question to be addressed is the isolation of the NoMaDic effect to a specific step of the O_3 formation mechanism. The classic Chapman¹⁶ mechanism for ozone formation has been thoroughly studied but may not be relevant at the low temperature employed in the present experiments. The rate constant for three body O_3 formation ($\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$) has a negative activation energy,¹⁷ which is characteristic of reactions which proceed by different mechanisms as a function of temperature,¹⁸ usually implying wall catalysis at low temperatures and homogeneous gas phase reactions at higher temperatures. Additional evidence which favors ozone formation via wall catalysis at low tem-

peratures is the work of Wojtowicz *et al.*,¹³ who observed that at -196°C and an oxygen pressure of approximately 1 Torr, the conversion of oxygen atoms to O_3 was completely quantitative, implying no $\text{O} + \text{O}$ or $\text{O} + \text{O}_3$ side reactions, and an ozone formation rate which would only be consistent with heterogeneous O_3 formation. It remains to be demonstrated whether this result is applicable throughout the pressure range in which the NoMaDic effect has been observed.

Even though the Chapman mechanism is not completely valid under the low temperature conditions where the NoMaDic has been observed, it is a valuable starting point in developing an appropriate model. Consider the following mechanism;



where M may be any gas phase molecule. Since this mechanism was devised to explain ozone formation in the atmosphere it must be modified in accordance with the conditions relevant in an electric discharge. The agent responsible for the initiation of the reaction is electron impact rather than absorption of photons.¹⁹ Also, the condensation of ozone on the cold walls must be considered.



The primary limiting factor in determining which of the reactions [Eqs. (5)–(7)] are important is the negative activation energy of three body ozone formation, thus the rate constant for the reaction increases as temperature decreases. To give an example of the importance of this fact consider the competition between ozone formation and oxygen atom recombination [reactions (5) and (6)]. The ratio of the reaction rates is given by

$$\frac{\text{Rate}[\text{O}_3]}{\text{Rate}[\text{O}_2]} = \frac{k_5[\text{O}][\text{O}_2][\text{M}]}{k_6[\text{O}]^2[\text{M}]}, \quad (9)$$

where $\text{Rate}[\text{O}_3]$ is the rate of ozone formation via reaction (5), $\text{Rate}[\text{O}_2]$ is the rate of O_2 formation by reaction (6), k_5 and k_6 are the rate constants for the respective reactions, and the bracketed quantities are the concentrations of the enclosed species. Note that in this case, the expression simplifies to the following:

TABLE II. Data for experiments using helium–molecular oxygen mixtures as the starting material. The abbreviations are explained in the text.

P_i (Torr)	P_f (Torr)	f	Rate ($\times 10^{17} \text{ s}^{-1}$)	$\delta^{18}\text{O}_2$ (‰)	$\delta^{17}\text{O}_3$ (‰)	m
18.6	17.8	(0.20)	2.52	22.0	21.7	0.985
31.4	29.9	(0.17)	4.95	23.7	23.2	0.980
60.7	59.0	(0.12)	8.27	25.1	24.9	0.991
89.0	88.3	(0.092)	9.83	28.9	28.0	0.972
116.5	115.8	(0.076)	10.4	28.0	27.9	0.997
147.6	146.4	(0.060)	10.5	27.4	27.0	0.985
176.1	174.2	(0.040)	8.30	25.8	25.2	0.978
235.6	233.6	(0.024)	6.77	19.9	16.2	0.814
295.8	291.9	(0.019)	4.34	19.8	19.3	0.974
423.2	418.8	(0.009)	2.27	8.8	8.9	1.007

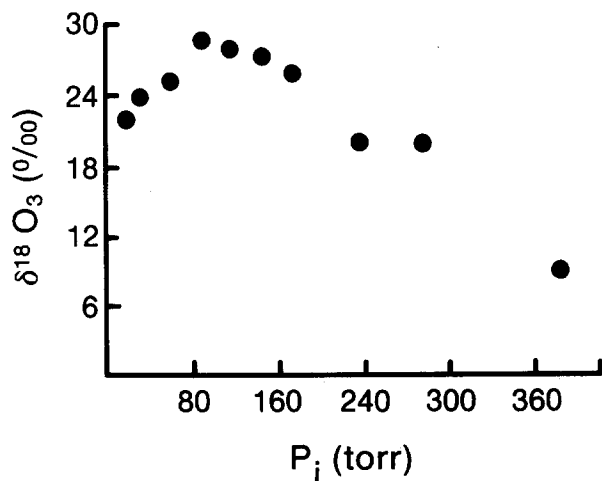


FIG. 4. The ^{18}O composition of ozone ($^{18}\text{O}_3$) as a function of initial pressure (P_i) for experiments using a mixture of helium and O_2 as the starting material.

$$\frac{\text{Rate}[\text{O}_3]}{\text{Rate}[\text{O}_2]} = \frac{k_5[\text{O}_2]}{k_6[\text{O}]} \quad (10)$$

If Anderson's values for the rate constants¹⁷ are used [$k_5 = 1.0 \times 10^{-34} \exp(500/T)$ and $k_6 = 3.8 \times 10^{-30} T^{-1} \exp(-170/T)$] one reaches the conclusion that at 300 K the reactions proceed at equal rates when the oxygen atom concentration is approximately 7% of the O_2 concentration, but at 75 K the O atom concentration must be 15 times that of O_2 for the same situation to prevail. Thus, while at room temperature the two reactions should both be important in the ozone formation process, at liquid nitrogen temperature the O_2 recombination reaction should be on the order of 100 times (or more) slower than O_3 formation.

A similar comparison between reactions (5) and (7) (using $k_7 = 1.9 \times 10^{-11} \exp(-2300/T)$ and calculating the M concentration by applying the ideal gas law at a total pressure of 30 Torr) gives an even more striking result. For the two reactions to have a similar rate at room temperature, the gas phase ozone concentration must be approximately 6% of the O_2 concentration, and if the O_3 composition is lower the rate of reaction (5) will be greater than reaction (7). On the other hand, at 75 K the two reactions only proceed at equal rates when the O_3 concentration exceeds the O_2 concentration by 10 orders of magnitude. Given these arguments, it seems warranted to ignore reactions (6) and (7) as important parts of the chemical mechanism under the experimental conditions where the NoMaDic effect has been observed.

These arguments lead to the conclusion that under low temperature conditions ozone formation is a relatively simple process, consisting of O_2 dissociation by electron impact, three body O_3 formation, and ozone condensation on the walls of the system. It has been pointed out earlier that the isotope effect could not be produced during O_2 dissociation, and condensation is a process which depends on the masses of the species involved,²⁰ leaving only one alternative. Three body ozone formation must, in some way be responsible for the NoMaDic effect.

Three body ozone formation

It is instructive to view ozone formation as a set of separate processes. The reaction is initiated by an oxygen atom- O_2 molecule collision leading to the formation of a reaction intermediate (O_3^*). If a stable O_3 molecule is to be formed the intermediate must undergo a second collision (to allow O_3^* to release its excess internal energy) within its lifetime τ . Without the second collision the intermediate is unable to survive its own instability. This leads to a slightly different view of the chemical mechanism:



Atomic oxygen is produced in the discharge and diffuses toward the cold walls driven by the temperature gradient. During this process it undergoes a series of collisions with O_2 molecules which results in the formation of O_3^* . If the O_3^* does not undergo a collision during its lifetime τ it will redissociate. On the other hand, if the O_3^* is involved in a collision it will lose its excess internal energy and the ozone molecule formed will condense on the cold walls.

Isotopic chemistry

One mechanism for producing the observed isotope effect is to assume that the isotopomers of O_3^* containing the heavy isotopes ($^{49}\text{O}_3^*$ and $^{50}\text{O}_3^*$) have a longer lifetime than the species containing only ^{16}O . This assumption is made on the premise that: (a) the probability of a metastable O_3^* molecule undergoes a collision and quenching within its lifetime is equal to the collision rate times the O_3^* lifetime (τ), (b) the collision rate is dependent on the mass of the species involved and hence would lead to mass-dependent isotopic fractionation, therefore differences in isotopomeric lifetimes must be much larger than differences in collision rates, and (c) if the lifetime for the ^{17}O species ($^{17}\tau$) is equal to the lifetime of the ^{18}O species ($^{18}\tau$) and both are longer than the phenomenological τ , the probability of forming the heavy isotopomers of ozone would be equal and greater than the probability of forming O_3 containing only ^{16}O .

Concerning a mechanism to explain the differences in τ for the isotopically substituted reaction intermediates, a possibility exists involving inverse predissociation. A thorough description of this process has been given by Herzberg.²¹ An atom-atom collision is theoretically straightforward. The participants interact with one another subject to the relevant diatomic potential, with a lifetime consistent with a single molecular vibration (on the order of 10^{-13} s). In the case of an atom-molecule collision the situation is more complex. It is not a valid approximation to hold the molecule fixed in space and assume that the collision consists of a decrease of the atom-molecule distance along the reaction coordinate. An actual collision consists of an intricate combination of vibrational and rotational motions which increase the life-

time of the intermediate above 10^{-13} s. An additional aspect which increases the intermediate lifetime is the possibility of inverse predissociation. This may occur when the collision partners have the correct energy to match one of the diffuse energy levels near the dissociation limit of the polyatomic molecule being formed. There is a finite probability that once the predissociative state is reached, the intermediate will emit a photon and remain bound within the polyatomic potential well, however this process is highly unlikely. Another consequence of predissociative states which has a more direct bearing on the present discussion, is that their existence increases the lifetime of the reaction intermediate. The actual lifetime is an intricate function of the reaction dynamics which is strongly influenced by the number of available predissociative levels. As the number of levels increases, τ increases as well. It is left to propose a reason for a difference in the number of predissociative states for different isotopomers.

One explanation for a difference in the number of available predissociative states involves molecular symmetry. Ozone containing only ^{16}O has C_{2v} symmetry and possesses only one-half of its complement of possible rotational lines²² for rotations about the twofold axis. On the other hand, ozone containing one of the heavy isotopes may have two different symmetries, C_{2v} for X-Y-X molecules and C_s for Y-X-X molecules. The C_{2v} isotopomers, as above, possess only one-half their complement of possible rotational states, however, the C_s isotopomers have their full complement. Isotopomers with one of the heavy isotopes on the terminus of the molecules should have longer τ 's, with the net result that $^{18}\tau = ^{17}\tau > \tau$.

To summarize, this proposed mechanism for the NoMaDic effects includes: (a) the isotopomers of ozone containing the heavy isotopes the possibility of forming with C_s symmetry, in which case this reservoir has an extra probability of forming O_3^* in a predissociative state, (b) inverse predissociative states increase the lifetime of the reaction intermediate (the collisions become "sticky"), (c) the extra stability of the C_s O_3^* 's implies that $^{17}\tau = ^{18}\tau > ^{16}\tau$, (d) the probability of a two body collision also being a three body collision is greater for the isotopomers of O_3^* containing ^{17}O or ^{18}O , and hence (e) the O_3 produced would be enriched in the heavy isotopes, with $\delta^{17}\text{O} = \delta^{18}\text{O}$.

Model Implications

To describe the effect of pressure on isotopic fractionation it is necessary to define a parameter which is a function of pressure. This parameter (R_c) is a critical radius surrounding the internal electrode, within which the probability of an O_3^* being dissociated by electron impact in a time shorter than τ is nearly one. As the pressure of the system increases, R_c decreases due to contraction of the electron density to the vicinity of the electrode. Consider the system as a cylindrical cold wall of radius R_w with an electrode in the center and a critical cylindrical volume of radius R_c surrounding the electrode. Shown in Fig. 5 is a qualitative description of the O_3^* dissociation probability (P_d) as a function of distance from the electrode (R). Notice that the R

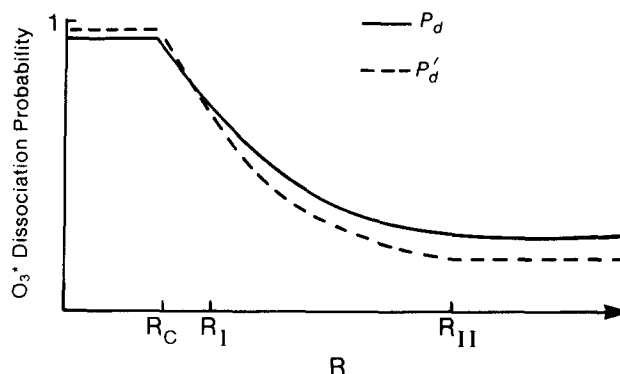


FIG. 5. The dissociation probability of the O_3^* reaction intermediate as function of radial distance from the electrode (R). The solid curve represents the probability for the O_3^* species containing only ^{16}O , and the dashed curve represents the probability for the isotopomers containing one of the heavy isotopes.

less than R_c , P_d is very nearly equal to one, implying that virtually all of the O_3^* which forms will be dissociated by electron impact, but the probability will always be slightly larger for the heavy isotopomers (P_d') due to their longer lifetime. For R 's greater than R_c the dissociation probability drops to an asymptotic value consistent with the natural metastability of O_3^* . Of course, the asymptote for the heavy isotopomers has a lower value, implying that there must be a crossover point between the two curves (with R labeled as R_l). The point at which the difference between P_d and P_d' reach the asymptotic limit has a value of R defined as R_{II} .

Figure 5 may be used to predict isotope effects as a function of pressure by assuming that the scale of the abscissa varies inversely with pressure. At very low pressures the unit of R is large and R_c is greater than the distance to the wall, while at higher pressures the unit of R is sufficiently small the R_w is much greater than R_{II} . When the pressure is such that R_w is equal to R_l (corresponding to a pressure between 2.4 and 3.0 Torr for the present experimental arrangement), the dissociation probabilities are equal for all isotopomers and no isotopic fractionation occurs. At lower pressures, corresponding to R_w less than R_l , the fact that P_d is always less than P_d' manifests itself as a NoMaDic isotopic fractionation, with the heavy isotopes depleted in the product ozone, as is experimentally observed at pressures below 2.4 Torr. For pressures above 3 Torr, where R_w is greater than R_l but less than R_{II} , notice that P_d is greater than P_d' with the difference increasing as pressure increases. This results in a NoMaDic fractionation with the heavy isotopes enriched in ozone, and the magnitude of the fractionation increasing as pressure increases.

To explain the behavior at the extremes of pressure a slightly more sophisticated approach is necessary which is based on the premise that the number of $\text{O} + \text{O}_2$ collisions leading to the formation of stable ozone molecules [$N(\text{O}_3)$] is equal to the total number of $\text{O} + \text{O}_2$ collisions (N) times the probability of a particular two body collision also being a three body collision (already shown to be equal to the collision rate Z times the intermediate lifetime τ):

$$N(\text{O}_3) = NZ\tau. \quad (16)$$

This equation may be used to determine the relative isotopic

composition of the ozone produced by calculating the ratio of amounts:

$$\frac{N(\text{O}_3)'}{N(\text{O}_3)} = \frac{(N'Z'\tau')}{(NZ\tau)}, \quad (17)$$

where the primed terms represent values for the species containing one of the heavy isotopes. Each of the terms in the ratio may be treated independently, in which case the isotope effects at the pressure extremes are quite different.

Consider the high pressure situation, which is representative of the conditions under which the lifetime constraints were derived. Earlier, it was pointed out that the differences in collision rates could not be responsible for the isotope effect since a mass-dependent fractionation would result. The mathematical statement of this idea is that the variation of τ'/τ from 1 must be much larger than the variation of Z'/Z . A measure of the resulting ratio ($Z'\tau'/Z\tau$) is given by the high R asymptotic values of P_d/P'_d in Fig. 5. As for the ratio of collision numbers, a first approximation is given by the ratio of the relative isotopic abundances. However, this is unsatisfactory for large values of N indicative of the high pressure regime. The longer lifetimes of the O_3^* isotopomers containing the heavy isotopes must result in fewer $\text{O} + \text{O}_2$ collisions involving ^{17}O or ^{18}O , with the disparity increasing as the pressure increases. Mathematically, the ratio N'/N has a limiting value equal to the ratio of the isotopic abundances, and decreases as N increases. This implies that as the pressure in the system increases, the magnitude of the isotopic fractionation decreases, just as is observed when the initial pressure of the system exceeds 30 Torr.

When the pressure in the system is very low, the formation of ozone may result from a single $\text{O} + \text{O}_2$ collision (quenched on the cold walls). In this case the ratio of N'/N may be set equal to the ratio of the isotopic abundances and has no effect on the resulting isotopic fractionation. In the limit of extremely low pressure the differences in the lifetimes of the isotopomers of O_3^* is insignificant (when the average time between the first $\text{O} + \text{O}_2$ collision and the quenching-trapping of O_3 is less than τ , the species containing a heavy isotope gains no advantage by having a lifetime longer than τ) and the important factor in determining the isotopic fractionation is the ratio of collision rates. This ratio depends on the masses of the participants, resulting in mass-dependent fractionations with the heavy isotopes depleted in ozone, as observed for the experiments at the lowest pressures.

This model is equally consistent with the results from experiments using helium- O_2 mixtures, which show the same features as the experiments using pure O_2 with the exception of the low pressure phenomena, where the necessary experiments could not be performed. Changing the composition of the "buffer" gas in the system appears to have no effect in the static system, as would be expected given the proposed mechanism.

Predictions

This model allows a number of verifiable predictions to be made. Since the effect arises in the formation of ozone, rather than initial dissociation, it should be observable, inde-

pendent of the method of O_2 dissociation. It should be possible to produce the same effect in ozone production initiated by either optical radiation or electric discharge, which opens interesting possibilities for the use of isotopic composition to determine the conditions under which a particular sample of ozone formed, once the effects of the relevant parameters have been investigated.

Having a different number of rotational states as a function of isotopic substitution is a fairly common property, implying that NoMaDic effects might be observable for a number of other chemical reactions. These effects should occur whenever the following conditions are satisfied; (a) the reaction of interest occurs in the gas phase, (b) the reaction intermediate is subject to symmetry constraints as discussed, (c) the products may be separated to decrease the possibility of secondary mass-dependent isotope effects, and (d) the element of interest has three or more isotopes (it may be possible to use radioactive isotopes and adjust the product compositions to account for decay effects) so the effect may be observed. Specifically, the formation of CO_2 from oxygen atoms and carbon monoxide is a possible candidate.

The proposed model has the property that the anomalous isotopic component of the ozone reservoir should be present in the isotopomers with C_s symmetry. If adequate sensitivity could be achieved, it may be possible to observe this excess abundance spectroscopically.

SUMMARY

Isotopic data and results on the chemistry and kinetics of the formation of ozone in an electric discharge through molecular oxygen have been presented. The chemical mechanism of the reaction was shown to be greatly simplified relative to the classical Chapman mechanism, by the low temperature at which the experiments were performed. This situation, when coupled with additional experimental results, particularly, for CO_2 dissociation, allows restriction of the mechanistic step responsible for the NoMaDic oxygen isotope effect. The effect is due to the lifetime of the transition state produced during ozone formation (O_3^*). The isotopomers of this species with C_s symmetry (those which have one of the heavy isotopes on the end of the molecule) may be responsible for this longer lifetime since they have a greater probability of being the product of a collision involving an inverse predissociative state. If this explanation is correct, this type of isotope effect should be present in a large number of reactions and may be responsible for the NoMaDic oxygen isotopic distributions observed in many meteorites.

This suggests a number of areas which require further study. The oxygen isotope chemistry of many reactions of importance in the natural environment need to be reevaluated. Since the concept of all chemical isotope effects being mass dependent is no longer valid, these studies must not overlook ^{17}O . The present experiments are an example of the way in which isotopic chemistry may offer a unique method of probing properties such as the effect of symmetry on chemical reactions.

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