J. Am. Chem. Soc. **1998,** *120,* 8711−8714

Chemical Synthesis of Ozone, Isotopic Labeling, and Redistribution

Anton Dimitrov,[1a] Konrad Seppelt,*[,1a] Dieter Scheffler,[1b] and Helge Willner[†,1b]

Contribution from the Institut für Anorganische und Analytische Chemie der Freie Universität, D-14195 Berlin, Germany, and Institut für Anorganische Chemie der Universität, D-30167 Hannover, Germany

Received March 16, 1998

Abstract: Ozone is formed in good yield by reacting O_2^+ salts with water in HF at −78 °C. With isotopically labeled water $^{17}O-^{16}O-^{16}O$ and $^{18}O-^{16}O-^{16}O$ can be prepared, and other isotopomers could be made by starting with $^{17}O_2^+$ and $^{18}O_2^+$ precursors. ^{17}O NMR spectroscopy and IR matrix spectroscopy are used for detection and decay of the isotopomers. The ^{17}O or ^{18}O label at the terminal position remains at −78 °C, but at higher temperatures scrambling of the atoms is observed. Under strict monomolecular conditions no scrambling is observed till 450 °C, however. Irradiation of ozone in a 15K argon matrix with $\lambda = 254$ nm affords scrambling of the label and formation of oxygen. Irradiation with $\lambda > 420$ nm initiates only scrambling with little decay. The possible mechanisms of the atomic scrambling are discussed.

Introduction

Ozone is a fascinating molecule for science ever since it was isolated for the first time in 1840.[2] It took about 10 years to establish ozone as an allotrope of oxygen. Its importance is based on many properties, of which only a few are named here: the occurrence as an allotrope of oxygen under natural conditions in the upper atmosphere, its molecular structure, its reactivity toward carbon−carbon double bonds, and lately, its possible depletion in the atmosphere by man-made gases.

Ozone soon became available in preparative amounts with the simple process of generating atomic oxygen by the electric discharge method in the Siemens ozonizator. This method can be used for preparation of gaseous ozone diluted by oxygen or for pure ozone as well, and works so simply and effectively that no other preparation has been needed ever since. Ozone, however, has been observed in many chemical reactions under high oxidative conditions, but in no case has a preparative method been derived from such a reaction.

In the course of our study on heterogeneous reactions between H_2O_2/H_2SO_4 and atmospheric trace gases, we also rediscovered formation of ozone by fast heating of a $H_2O_2/H_2O/H_2SO_4$ mixture (mass ration 4/3/93) with a heat gun up to 250 °C under dynamic vacuum. Yields are better than 30%. This chemical formation of ozone by thermal decomposition of peroxomonosulfuric acid was first observed in 1902.[3]

Lately the surprising reaction

$$\mathrm{Fe^{III}(porphyrin)NO_2 + O_2 \rightarrow Fe^{II}(porphyrin)NO + O_3} \quad (1)$$

allows a chemical preparation in solution and for immediate further reaction.[4] In principle this reaction could be used for the preparation of isotopically labeled ozone also.

Isotopically labeled ozone requires a preparation from two different oxygen precursors. One might conceive a preparation by reacting electrically generated atomic oxygen from one source reacting with molecular oxygen from another source. To our knowledge this has never been tried, and the outcome is questionable in the light of the atomic scrambling mechanisms, which we will discuss below.

In our investigations of high oxidative materials in liquid HF[5] we have found a simple and high yield chemical synthesis of ozone that can also be used for generation of specifically isotopically labeled ozone.

Experimental Section

Reagents. $O_2^+AsF_6^-$ and $O_2^+SbF_6^-$ are prepared by UV irradiation of $O_2/F_2/AsF_5$ or $O_2/F_2/SbF_5$ gaseous mixtures in large glass containers, following literature procedures.[6] HF is purified by 2-fold distillation in a stainless steel vacuum line and poly-perfluoroethylene-perfluorovinyl ether (PFA) container. No requirement for extreme drying of the HF is needed, since water will take part in the reaction anyway. But natural water in traces will influence the isotopic yield if $H_2{}^{17}O$ and $H_2{}^{18}O$ are used as reactants.

Spectroscopy. ^{17}O NMR spectra were taken of a JEOL JNM-LA 400 instrument at 54.10 MHz with H_2O as external standard. The reactions are performed in PFA tubes equipped with stainless steel valves that are connected to a stainless steel vacuum line. Matrix isolation studies are performed on an equipment described previously.[7]

Synthesis of Ozone. *Caution: Pure ozone can detonate.* A 2180 mg (9.58 mmol) sample of $O_2^+AsF_6^-$ was weighed into a 20 mL PFA tube, and 10 mL of HF was condensed into it. A 450−500 mg (∼25 mmol) sample of $H_2{}^{16}O$, $H_2{}^{17}O$, or $H_2{}^{18}O$ was added by syringe at −78 °C. Under stirring the dioxygenyl salts dissolve, the solution turns deep blue, and another colorless precipitate is found, which is identified by its Raman spectrum as $H_3O^+AsF_6^-$.[8] In cases when H_2O excess is used, which is advisable for completing the reaction, the remaining nonvolatile material is partly liquid at room temperature, possibly due to formation of $H_5O_2^+AsF_6^-$. Its ^{19}F NMR spectrum in CH_3CN clearly shows the quartet fine structure of AsF_6^-, because of the coupling of the ^{19}F nuclei with the spin $^3/_2$ ^{75}As atom. The ozone dissolved in HF

---

[1] (a) Freie Universität Berlin. (b) Universität Hannover.

[2] Schönbein, C. F. *Pogg. Am.* **1840**, *50*, 616.

[3] W. Steadel, *Z. Anorg. Chem.* **1902**, *14*, 642.

[4] Castro, E. *J. Am. Chem. Soc.* **1996**, *118*, 3984.

[5] Drews, T.; Seppelt, K. *J. Angew. Chem.* **1997**, *109*, 264; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 273.

[6] McKee, D. E.; Bartlett, N. *Inorg. Chem.* **1973**, *12*, 2738.

[7] Jacobs, J.; Kronberg, M.; Müller, H. S. P.; Willner, H. *J. Am. Chem. Soc.* **1994**, *116*, 1106.

[8] Christe, K. O.; Schack, C. J.; Wilson, R. D. *Inorg. Chem.* **1975**, *14*, 2224. Christe, K. O.; Charpin, P.; Soulie, E.; Bougon, R.; Fawcett, J.; Russel, D. R. *Inorg. Chem.* **1984**, *23*, 3756.

S0002-7863(98)00887-7 CCC: $15.00

is pumped from −78 °C via PFA tubing into a −196 °C cold trap, containing a few 100 mg of powdered, dry NaF for absorbance of residual HF. Oxygen is pumped away under these conditions. The yield was determined by oxidation of a KI solution and back-titration of the liberated iodine with a standardized solution of thiosulfate.[9] The yield turned out to be 83%, based on $O_2^+AsF_6$. It is desired not to keep the ozone for prolonged times in the HF solution since under these conditions decomposition is observed. $O_2^+SbF_6^-$ or $O_2^+Sb_2F_{11}^-$ can be used similarly. Ozone was also prepared by the discharge method in a closed system,[10] both with natural oxygen, with oxygen enriched to 35% ^{17}O and with oxygen enriched to 50% ^{18}O.

Results

Ozone is chemically generated by the reaction

$$2O_2^+AsF_6^+ + 3H_2O \rightarrow O_3 + O_2 + 2H_3O^+AsF_6^- \quad (2)$$

The ozone can be easily identified by the known characteristics such as color, smell, vapor pressure, and, occasionally and involuntarily, its explosiveness. For the latter reason the preparation of only small amounts of undiluted ozone is strongly recommended. Ozone can be safely dissolved in inert solvents at low temperature like $CFCl_3$ and CH_2Cl_2, or it can safely be absorbed on silica gel at −78 °C for further chemical use.[11]

The major advance of the chemical preparation presented here over the electric discharge method is of course the possibility of generating certain specifically labeled ozone. Here we present $^{16}O-^{16}O-^{17}O$ and $^{16}O-^{16}O-^{18}O$ by reaction of $^{16}O_2^+$ with ^{17}O and ^{18}O enriched water. With ^{17}O and ^{18}O enriched O_2^+ the isotopomers $^{17}O-^{17}O-^{16}O$ and $^{18}O-^{18}O-^{16}O$ could be made, and if both components are enriched four more isotopomers are within preparative reach. Isotopomers not accessible by this route are those which contain a central oxygen isotope different from both terminal oxygen isotopes, such as $^{16}O-^{17}O-^{16}O$.

In the case of ^{17}O labeling the corresponding NMR spetroscopy is the analytical tool of choice. In Figure 1 are shown the ^{17}O NMR spectra of normal ozone, such as ^{17}O enriched ozone generated by the electric discharge method, and of the $^{17}O-^{16}O-^{16}O$ isotopomer generated by the chemical method. Our measurement shows a two-line spectrum, as has been measured once before, and the chemical shift data agree quite well.[12] The assignment of the two lines with quite extreme chemical shifts to the two different oxygen environments was done correctly in the original paper but was reversed later for unknown reasons. The correct assignment is obvious from the intensity ratio and the fine structure of the two signals (see below). Thus the terminal oxygen atoms have an even more extreme shift than the central oxygen atom.

In the $^{17}O/^{18}O$ enriched but statistically labeled ozone, isotopic shifts as well as some $^{17}O-^{17}O$ coupling is partially resolved (Figure 1b). Figure 1c shows the $^{16}O-^{16}O-^{17}O$ spectra, made from $H_2{}^{17}O$ (10% enrichment). The intensity ratio of the terminal versus the central oxygen labeling is found to be 60:1. The theoretical expectation would be 270:1. The difference can be caused by traces of normal water in the HF and/or some scrambling of the label during the reaction.

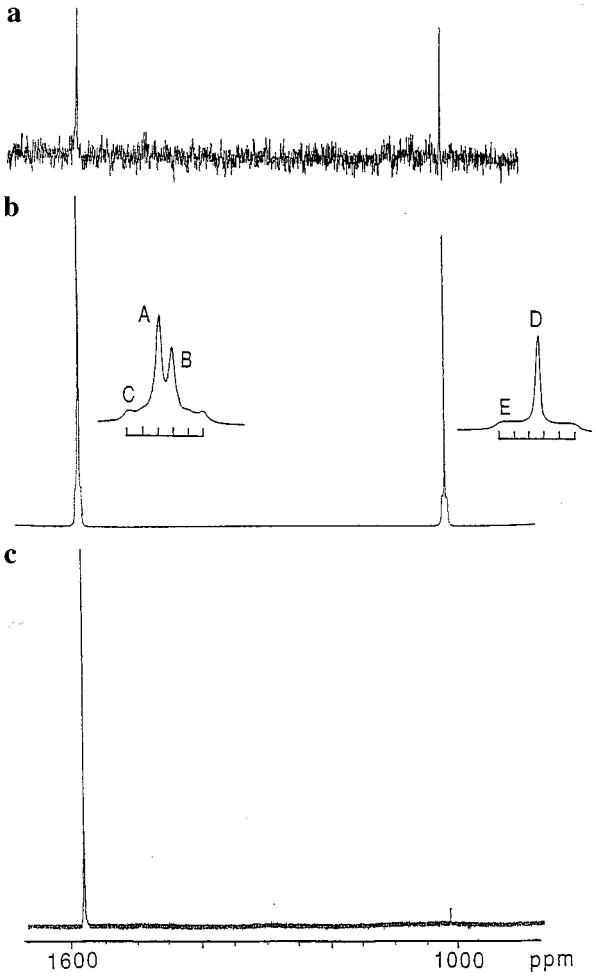

Figure 1. (a) ^{17}O NMR spectrum of ozone with natural abundance of ^{16}O, ^{17}O, and ^{18}O, relative to $H_2{}^{17}O$. $\delta = 1586.1, 1021.9$ ppm. Solution in $CFCl_3$, −78 °C. (b) ^{17}O NMR spectrum of ozone, made by the discharge method from oxygen containing 40% ^{16}O, 35% ^{17}O, and 25% ^{18}O. Inserts show isotopic splitting and $^{17}O-^{17}O$ coupling: A, $^{17}O\text{-}^{16}O\text{-}^{x}O$, $\delta = 1587.1$ ppm; B, $^{17}O-^{18}O-^{x}O$, $\delta = 1585.5$ ppm; C, $^{17}O-^{17}O-^{x}O$, $\delta = 1586.3$ ppm, partially resolved six equidistant lines due to $I = {}^5/_2$, $J = 101.5$ Hz; D, $^{16/18}O-^{17}O-^{16/18}O$, $\delta = 1021.9$ ppm; E, $^{17}O-^{17}O-^{16/18}O$, $\delta = 1021.9$ ppm, partially resolved six equidistant lines. (c) ^{17}O NMR spectrum of $^{17}O-^{16}O-^{16}O$ prepared by the chemical method from O_2^+ and $H_2{}^{17}O$.

We can only speculate on the mechanism of the ozone formation, since no intermediates in the overall reactions have been observed. One possibility is the electrophilic attack of O_2^+ on H_2O, resulting in $O-O-OH_2^+$, which can be oxidized further by another O_2^+ to protonated ozone (reaction 3). This mechanism is less likely than the following one, since H_2O is present in anhydrous HF solely as H_3O^+, which has very little nucleophilicity. We therefore assume that at first a redox reaction occurs between O_2^+ and H_2O, giving H_2O^+. After loss of H^+, the OH radical combines with a second O_2^+ to protonated ozone (reaction 4).

$$O_2^+ + H_2O \rightarrow {}^{\bullet+}OOOH_2 \xrightarrow{-H^+} {}^{\bullet}O-O-OH \xrightarrow[-O_2^+]{+O_2^+} OOOH^+ \xrightarrow{-H^+} O_3 \quad (3)$$

$$O_2^+ + H_2O \rightarrow O_2 + H_2O^{+\bullet} \xrightarrow{-H^+} OH \xrightarrow{+O_2^+} OOOH^+ \xrightarrow{-H^+} O_3 \quad (4)$$

IR spectroscopy of matrix isolated ozone is the second method we have used for analysis. Here we have chosen the ^{18}O isotope

---

(9) Boelter, E. D.; Putnam, G. L., Lash, E. J. *Anal. Chem.* **1950**, *22*, 1533.

(10) Griggs, M.; Kaye, S. *Rev. Sci. Instrum.* **1968**, *39*, 1685.

(11) Hesse, G.; Bayer, E. *Z. Naturforsch. B* **1964**, *19*, 875.

(12) McFarlane, W.; McFarlane, H. C. E. Oxygen. In *Multinuclear NMR*; Mason, Joan Ed.; Plenum Press: New York, 1987; Chapter 14, p 406.

Table 1. Vibrational Wavenumbers (cm^{-1}) for IR Band Positions (main matrix side) of ^{16}O, ^{18}O Isotopomers of Ozone Isolated in Neon and Argon (in parentheses) Matrix and Their Assignments

$^{16}O_3$	I^a	$^{18}O^{16}O^{16}O$	I^a	$^{18}O^{16}O^{18}O$	$^{16}O^{18}O^{16}O$	$^{18}O^{18}O^{16}O$	$^{18}O_3$	assign acc C_{2v}, C_s sym
3041.0	1.4	2994.7	1.0	2975.4	2947.5	2899.0	2878.9	$3\nu_3$, $3\nu_2$
2782.8	0.2	2746.1	0.3	2715.6	2701.0	2677.8	2631.9	$2\nu_3 + \nu_2$
2109.7	14	2089.1	15	2059.0	2048.2	2026.1	1994.9	$3\nu_3$, $2\nu_2$
(2108.4	13)	(2087.6	14)	(2057.5)	(2047.4)	(2024.7)	(1993.5)	
1796.0	0.2	1767.0	0.3	1733.1	1759.8	1730.4	1697.0	$\nu_1 + \nu_2$
1722.8	0.7	1693.4	0.9	1668.1	1683.0	1653.3	1628^c	$\nu_2 + \nu_3$
1104.3	1.6	1091.4	9	1073.5^c	1075.5^c	1061.4	1042.7	$\nu_1(a_1)$, $\nu_1(a)$
(1104.5	0.7)	(1090^b	6)	–	–	(1060.4)	(1042.7)	
1039.6	100	1025.6	100	1016.7	1006.0	991.6	982.2	$\nu_3(b_1)$, $\nu_2(a)$
(1039.8	100)	(1025.8	100)	(1016.7)	(1006.3)	(991.6)	(982.5)	
699.8	7	683.4	9	667.0^c	692.2	676.3	660.3	$\nu_2(a_1)$, $\nu_3(a)$
(703.6	7)	(687.2	11)	(670.9)	(696.2)	(680.2)	(664.0)	

[a] Integrated relative intensities $I_{(\nu 3)} = 100$. [b] Broad band. [c] ± 0.5 cm^{-1}.

Table 2. Vibrational Wavenumbers (cm^{-1}) of Isotopomers of O_2 Isolated in an Argon Matrix

	$^{16}O_2$	$^{16}O^{18}O$	$^{18}O_2$
monomer	1550.0	1506.2	1461.5
dimer	1544.9	1501.6	1457.2

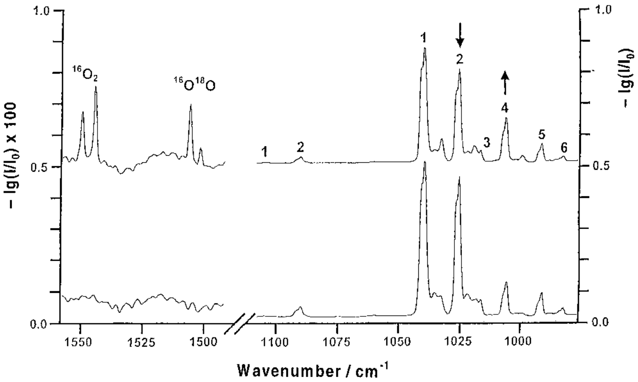

Figure 2. IR spectra of ozone enriched in ^{18}O isolated in an argon matrix. Main matrix sites are of $^{16}O_3$ (1) and $^{16}O^{16}O^{18}O$ (2), besides $^{18}O^{16}O^{18}O$ (3), $^{16}O^{18}O^{16}O$ (4), $^{16}O^{18}O^{18}O$ (5), and $^{18}O_3$ (6). Lower trace without and upper trace with UV photolysis $\lambda = 254$ nm. Arrows in the upper trace indicate increase of $^{16}O-^{18}O-^{16}O$ and decrease of $^{16}O-^{16}O-^{18}O$ during photolysis, along with formation of O_2.

for a larger band separation than would be achieved with ^{17}O. Also ^{18}O is much less expensive than ^{17}O. For matters of unambiguous assignments vibrational data are collected on all $^{16}O-^{18}O$ ozone isotopomers, see Table 1. These data complete (and in some part correct) previous measurements.[13,14]

The lower traces of Figures 2 and 3 show matrix IR spectra of isotopic mixtures of ozone consisting mainly of $^{16}O_3$ and $^{16}O^{16}O^{18}O$. It is interesting to note that the intensity of the ν_1 band of $^{16}O^{16}O^{18}O$ strongly increases in comparison to that of $^{16}O_3$ due to the break of symmetry.

Labeled ozone should be of use for mechanistic studies, e.g., for the investigation of the reaction mechanism of the ozonization of olefines (Crigée reaction.[15]). Here we will only deal with the mechanism of scrambling of the atoms within the molecule. For an intramolecular exchange of the atoms within one ozone molecule two mechanisms are conceivable: (1) closing of the molecule to a three-membered-ring species and opening at any of the three bonds of the regular triangle; and (2) elimination of one terminal oxygen atom that would remain in the environment of the residual O_2 species, and recombination of these two entities in a statistical manner.

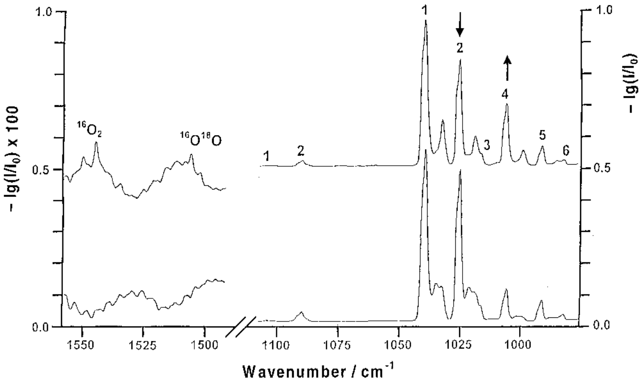

Figure 3. IR spectra of ozone enriched in ^{18}O isolated in an argon matrix. Main matrix sites are of $^{16}O_3$(1) and $^{16}O^{16}O^{18}O$ (2), besides $^{18}O^{16}O^{18}O$ (3), $^{16}O^{18}O^{16}O$ (4), $^{16}O^{18}O^{18}O$ (5), and $^{18}O_3$ (6). Lower trace without and upper trace with UV photolysis $\lambda > 420$ nm. Arrows in the upper trace indicate increase of $^{16}O-^{18}O-^{16}O$ and decrease of $^{16}O-^{16}O-^{18}O$ during photolysis, with little formation of O_2.

In this connection it is noteworthy that the existence of a regular, triangular ozone has been predicted by ab initio calculations many times as being the second minimum on the potential hyperface, with an energy ≅30 kcal/mol higher than normal ozone.[16−22] A barrier of 55 kcal is calculated between the normal and triangular ozone. This transition state with C_{2v} symmetry and a bond angle of $\alpha \cong 83°$ is extremely close in energy and geometry to the minimum of an excited state. Historically the D_{3h} ring structure of ozone as the ground state has already been rejected by L. Pauling following guesses on the heats of formation.[23] But it took the measurement of the

---

(13) Green, D. W.; Ervin, K. M. *J. Mol. Spectrosc.* **1981**, *88*, 51.

(14) Anmin, T.; Ruifeng, L.; Zemin, S.; Xuefeng, Z.; Guosen, Y. *Int. J. Quantum Chem.* **1989**, *36*, 765. Flaud, J.-M.; Camy-Peyret, C.; Malathy Davy, V.; Rinsland, C. P.; Smith, M. A. H. *J. Mol. Spectrosc.* **1987**, *122*, 221−228. Perkin, A.; Vasserot, A.-M.; Flaud, J.-M.; Camy-Peyret, C.; Rinsland, C. P.; Smith, M. A. H.; Malathy Davy, V. *J. Mol. Spectrosc.* **1990**, *143*, 311−317. Flaud, J. M.; Bourgeois, M. T.; Barbe, A.; Plateaux, J. J.; Camy-Peyret, C. *J. Mol. Spectrosc.* **1994**, *165*, 464−469. Bourgeois, M. T.; Flaud, J. M.; Barbe, A.; Regalia, L.; Camy-Peyret, C.; Plateaux, J. J. *J. Mol. Spectrosc.* **1995**, *172*, 552−558.

(15) Kuczkowski, R. L. *Acc. Chem. Res.* **1983**, *16*, 42.

(16) Wright, J. S. *Can. J. Chem.* **1973**, *51*, 139.

(17) Hay, P. J.; Dumming, T. H.; Goddard, W. A., III *J. Chem. Phys.* **1975**, *62*, 3912; *Chem. Phys. Lett.* **1973**, *23*, 457.

(18) Shih, S.; Buonker, R. J.; Peyerimhoff, S. D. *Chem. Phys. Lett.* **1974**, *28*, 463.

(19) Burton, P. G.; Harcey, M. Dawn, *Nature* **1977**, *266*, 826.

(20) Hay, P. J.; Dumming, T. H. *J. Chem. Phys.* **1977**, *67*, 2290.

(21) Jones, R. O. *J. Chem. Phys.* **1985**, *82*, 325.

(22) Xantheas, S. S.; Atakity, G. J.; Ellert, S. T.; Ruedenberg, K. *J. Chem. Phys.* **1991**, *94*, 8054.

(23) Pauling, L. *J. Am. Chem. Soc.* **1932**, *54*, 3570.

electron diffraction[24] and the microwave spectrum[25] to establish the ground-state structure as it is known until today.

We found that the terminal oxygen label scrambles to the central position under various conditions, e.g., if gaseous ozone is kept in an inert vessel (Kel-F) at room temperature and approximately 1 bar of pressure for 1 day. Simultaneously strong decomposition into oxygen is observed. We can show that there is an intermolecular atomic exchange taking place by mixing ${}^{17}O_2$ and ${}^{16}O_3$ under similar conditions and keeping the mixture at room temperature for several days. In the ozone remaining after 1 day we could qualitatively observe ${}^{17}O$ enrichment in all atomic positions (reaction 5). Alternatively we have observed IR spectra of ${}^{18}O_3$ and ${}^{16}O_2$ (1:1, 200 mbar) and find no scrambling within 2 h at room temperature. This, however, changes when the mixture is heated to 100 °C for a few minutes. It is noteworthy that intermolecular exchange is not observed between different isotopomers of ozone under similar conditions (6).

$$ {}^{16}O_3 + {}^{17(18)}O_2 \xrightarrow[\text{hours, 70 °C}]{\text{days, r.t.}} {}^{17(18)}O_3 + {}^{16}O_2 \qquad (5) $$

$$ {}^{16}O_3 + {}^{18}O_3 \overset{\text{days, r.t.}}{\nrightarrow} {}^{16,16,18}O_3 \text{ etc.} \qquad (6) $$

Labeled ozone pumped through quartz tubes of 30 cm length at 1 and 10^{-2} mbar results, beginning at 350 °C, in scrambling of the label along with strong decomposition, as evidenced by ${}^{17}O$ NMR spectroscopy.

To arrive at clearly monomolecular conditions ozone consisting mainly of ${}^{16}O_3$ and ${}^{16}O-{}^{16}O-{}^{18}O$ mixed with a large excess of argon (1:500) is pumped through a quartz tube at 10^{-4} mbar of partial pressure. Not until 450 °C (the maximum temperature possible) have we observed any scrambling of the label, as evidenced by IR matrix spectroscopy. Therefore we conclude that a monomolecular atomic exchange does not take place thermally, leaving no room for speculation of a transient triangular ozone species under these conditions.

Irradiation of ozone in the matrix at 14 K has been done by light of $\lambda = 254$ and > 420 nm. The high-energy light produces decomposition into oxygen and scrambling of the terminal ${}^{18}O$ label in the remaining ozone, see Figure 2. The low-energy light produces very little oxygen, but nevertheless scrambling of the label occurs, see Figure 3.

Upon irradiation with $\lambda = 254$ nm generation of O(${}^{1}D$) and $O_2({}^{1}\Delta_g)$ occurs.[26] Because under matrix condition ${}^{1}O_2$ is more long living than ${}^{1}O$ atoms, the latter changes into ${}^{3}O$, which is prohibited from recombining back to ozone, and therefor has time to escape from the matrix cage. Reaction of diffusing O atoms with isolated ozone molecules will finally form two O_2 in one matrix cage. As evidence of this we observe the splitting of the vibrational bands of ${}^{16/18}O_2$ oxygen isotopomers into two lines, which we assign to a single oxygen molecule in a matrix cage, and to two such molecules, see Table 2.

Ozone absorbs also in the visible region (Chappius band), and in our matrix experiment with less energetic irradiation of $\lambda > 420$ nm only ${}^{3}O_2$ and ${}^{3}O$ are formed, so that (almost) quantitative recombination can occur.

While this discussion is based on the assumption that the transient intermediate of the ozone decomposition is a van der Waals molecule $O_2 \cdots O$, which is also supported by ab initio calculations,[22] the possibility of a triangular regular ozone as the transient cannot be excluded totally. Short-time spectroscopy is needed to address this important question.

Acknowledgment. We thank the Fonds der Chemischen Industrie and the European Union (EU contract LAMOCS ENV4-CT 95-0046) for financial support of this study.

JA980887N

---

[24] Shand, W.; Spurr, R. A. *J. Am. Chem. Soc.* **1943**, *65*, 179.

[25] Trambarulo, R.; Guosh, S. N.; Burrns, C. A.; Gordy, W. *J. Chem. Phys.* **1995**, *21*, 851; *Phys. Rev.* **1993**, *91*, 222.

[26] International geophysics series: Warneck, P. *Chemistry of the natural atmosphere*; Academic Press: London, 1987; Vol. 41.