METHOD TO PRODUCE A CALIBRATION, REAGENT OR THERAPEUTIC GAS BY EXPOSING A PRECURSOR GAS TO ULTRAVIOLET LIGHT

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Provisional application No. 60/914,087, filed on Apr. 26, 2007.

Publication Classification
Int. Cl. C01B 21/24 (2006.01)
U.S. Cl. ................................................. 204/157.46

ABSTRACT

The present invention provides a means of producing nitric oxide (NO) by photolysis of nitrous oxide (N₂O) at ultraviolet wavelengths. One application is the production of a known concentration of NO in a diluent gas for calibration of analytical instruments that measure nitric oxide in gases such as exhaled breath, ambient air and automobile exhaust. A potentially important medical application is the production of NO for inhalation therapy, an advantage being that very little toxic NO₂ gas is produced. The method is useful for producing NO for industrial applications as well. Advantages of this method of NO production include the use of a single, inexpensive, readily available reagent gas of very low toxicity. Furthermore, the concentration of NO produced can be easily controlled by varying the ultraviolet (UV) lamp intensity and relative gas flow rates. The method may also be applied to the production of controlled concentrations of other gases as well such as CO and F₂ by using reagent gases other than N₂O.
Figure 2
METHOD TO PRODUCE A CALIBRATION, REAGENT OR THERAPEUTIC GAS BY EXPOSING A PRECURSOR GAS TO ULTRAVIOLET LIGHT

BACKGROUND

Nitrile oxide (NO) is used in numerous commercial and industrial applications. As a raw material it is used in the semiconductor industry for surface oxidation processes. As a synthesis gas, NO is used in the preparation of nitric acid, hydroxylamine, nitrosyl chloride, metal nitrosyls, and caprolactam, which is used in the synthesis of nylon. Nitrile oxide is also used commercially as a polymerization inhibitor during the preparation of olefins and to modify the properties of various polymers.

Several processes have been developed for the preparation of nitrile oxide. Commercially, NO is produced by the Ostwald process in which ammonia is oxidized at temperatures near 800°C in the presence of a platinum group catalyst. Nitrile oxide can also be produced from the reaction of nitric acid and copper or the reaction of sodium nitrate and sulfuric acid. These methods are not convenient for small scale NO production due to the power requirements for heating the reaction mixtures to several hundred degrees Celsius and the hazards inherent in handling strong acids. Several processes have been proposed for bench-scale production of nitric oxide for on-site use in laboratories, production facilities and medical facilities. Attention is directed to U.S. Pat. Nos. 3,853,790; 3,948,610; 4,272,336; 4,774,069; 4,812,500; 5,396,882; 5,478,549; 5,670,127; 5,683,668; 5,692,495; 5,827,420; 6,103,275; 6,534,029; 6,743,404; 6,758,214; 7,025,869; 7,040,313 and 7,048,951. Each of these methods has disadvantages relative to the photolysis of nitrous oxide (N₂O). For example, some require toxic starting materials or produce toxic byproducts such as nitrogen dioxide (NO₂), while others require high temperatures, high voltages or use of strong acids.

In the analysis of air and other gases for nitrile oxide, it is necessary to calibrate the analytical instrument using a gas standard having a known concentration of NO. The most common method used for NO detection is based on chemiluminescence in the reaction of NO with an excess of ozone. The method, which is widely used for air pollution monitoring, for measurements of NO in automobile exhaust and for measurements of NO in exhaled breath, requires frequent calibration with a standard gas mixture. Nitrile oxide measurements based on electrochemical techniques, chemiluminescence with luminol and other methods require calibration using a gas standard as well.

A well known problem with NO gas standards is that NO is unstable in gas cylinders at low concentrations; when NO standards are prepared at part-per-billion by volume (ppbv) levels there is a strong tendency for the concentration of NO in the cylinder to decline with time even though the NO is diluted into an unreactive gas such as nitrogen. One reason for this is that NO is thermodynamically unstable with respect to disproportionation to form N₂O and NO₂ according to the equilibrium:

\[ 2NO \rightleftharpoons N₂O + NO₂ \]  

Although extremely slow in the gas phase, this reaction may be catalyzed on the interior walls of compressed gas cylinders. The walls may be treated in various ways to slow the reaction, but the treatment is not always effective, and one cannot be certain that the concentration of NO in a gas cylinder is what it was when the cylinder was first filled. Furthermore, even trace amounts of oxygen (O₂) in the diluent gas can react to oxidize NO to NO₂ according to the well known reaction:

\[ 2NO + O₂ \rightarrow 2NO₂ \]  

Also, because of reaction 4, NO compressed gas standards cannot be made with air as the diluent. This is a disadvantage since it is desirable to calibrate an NO instrument using the same diluent gas as the gas being analyzed, which is most commonly air.

Nitrile oxide standards are much more stable at high concentrations of NO; thus, it is common to prepare gas standards at the high ppmv level in an unreactive gas such as N₂ to make a compressed gas standard and then dynamically dilute that standard with N₂ or air prior to entering the analytical instrument being calibrated. Although the dynamic dilution method works well for calibration, flow rates are required, and the flow meters must be accurately calibrated, thus adding to the complexity, expense and uncertainty of the calibration procedure.

Nitrile oxide has several medical applications. Blood vessels use nitric oxide to signal the surrounding smooth muscle to relax, thus dilating the artery and increasing blood flow. This underlies the action of nitroglycerin, amyl nitrate and other nitrate derivatives in the treatment of heart disease; the compounds undergo reactions that release nitric oxide, which in turn dilates the blood vessels around the heart, thereby increasing its blood supply.

Some disorders or physiological conditions can be mediated by inhalation of nitric oxide. Dilation of pulmonary vessels in the lungs due to inhaled NO causes pulmonary gas exchange to be improved and pulmonary blood flow to be increased. The administration of low concentrations of inhaled nitric oxide can prevent, reverse, or limit the progression of disorders such as acute pulmonary vasconstriction, adult respiratory distress syndrome, acute pulmonary edema, acute mountain sickness, post cardiac surgery acute pulmonary hypertension, persistent pulmonary hypertension in a newborn, perinatal asphyxia syndrome, and asthma. For inhalation therapy, it is important that the NO gas mixture be free of the toxic gas NO₂, which can form inside compressed gas cylinders.

The present invention provides a simple method for the production of nitric oxide from a non-hazardous, gas-phase precursor. Without the need for high temperatures, strong acids, and aqueous solution, the invention allows NO to be produced from a small apparatus for portable, on-site use. The concentration of NO produced can be accurately controlled, thereby making the NO source highly useful as a calibration device for analytical instruments that measure nitric oxide in gases.

The foregoing example of the related art and limitations related therewith are intended to be illustrative and not exclusive. Other limitations of the related art will become apparent to those of skill in the art upon a reading of the specification and a study of the drawings.

SUMMARY

One aspect of this invention is a means to produce NO by exposing N₂O to ultraviolet light.

Another aspect of the invention is to dilute NO produced by exposure of N₂O to UV light into air, oxygen or a
gas mixture for the purpose of inhalation therapy. For example, the NO/gas mixture could be administered to new- born babies, especially those born prematurely.

Another aspect of the invention is to dilute NO produced by exposure of \( \text{N}_2\text{O} \) to UV light with air, nitrogen or another gas for calibration of analytical instruments that measure NO such as nitric oxide monitors used to measure NO in ambient air, automotive exhaust and analyzers that measure NO in exhaled breath.

Another aspect of this invention is to control the concentration or mixing ratio of NO produced by controlling the UV light intensity, pressure, temperature, \( \text{N}_2\text{O} \) flow rate and/or diluent gas flow rate, with particular attention given to control of the UV light intensity.

Another aspect of this invention is to produce concentrations of gases other than NO at controlled levels by using different reagent gas sources.

Disclosed herein is a method for producing nitric oxide by exposing nitrous oxide (\( \text{N}_2\text{O} \)) to ultraviolet light in a controlled environment. This method has advantages over other methods of producing NO. For example, only one chemical reagent (\( \text{N}_2\text{O} \)) is required, and this reagent is relatively non-toxic (used at mixing ratios of up to 50% in air as an anesthetic) and commercially available in small cartridges as a consumer product for making whipped cream. The only significant byproducts produced are nitrogen and oxygen, the major components of air. For applications where it is desirable or necessary to remove the unreacted \( \text{N}_2\text{O} \), methods for the catalytic decomposition of \( \text{N}_2\text{O} \) into \( \text{N}_2 \) and \( \text{O}_2 \) have been developed. In this regard, reference is made to U.S. Pat. Nos. 5,314,673; 5,347,627; 6,429,168 and 6,743,404. The simplicity of the method described herein provides for a compact, low power, portable NO source in which the concentration of NO produced is easily controllable.

The same apparatus designed for producing calibrated concentrations of NO in a diluent gas by photolysis of \( \text{N}_2\text{O} \) may, with either no or only minor modifications, be used to produce calibrated concentrations of other gases as well. For example, if \( \text{N}_2\text{O} \) is replaced with carbon dioxide (\( \text{CO}_2 \)), the same apparatus may be used to produce controlled concentrations of carbon monoxide (\( \text{CO} \)). If \( \text{N}_2\text{O} \) is replaced with \( \text{SF}_6 \), calibrated concentrations of molecular fluorine (\( \text{F}_2 \)) in a diluent gas can be produced. In fact, concentrations of many different gases may be produced by proper choice of the reagent gas.

These and other features and advantages of the disclosed method with the chosen components and the combination thereof, the mode and operation and use, as well become apparent from the following description, reference being made to the accompanying drawings that form a part of this specification wherein like reference characters designate corresponding parts in several views. The embodiments and features thereof are described and illustrated in conjunction with systems, tools and methods which are meant to exemplify and to illustrate, not being limited in scope.

The following embodiments and aspects thereof are described and illustrated in conjunction with systems, tools and methods which are meant to be exemplary and illustrative, not limiting in scope. In various embodiments, one or more of the above described problems have been reduced or eliminated, while other embodiments are directed to other improvements.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a schematic diagram of an apparatus used to produce NO by photolyzing \( \text{N}_2\text{O} \). FIG. 2 is a schematic diagram of an apparatus used to produce a variable concentration of NO in a flowing gas stream.

FIG. 3 is a chart of data showing the measured concentrations of NO produced using the apparatus of FIG. 1.

Before explaining the disclosed embodiment of the present invention in detail, it is to be understood that the invention is not limited in its application to the details of the particular arrangement shown, since the invention is capable of other embodiments. Exemplary embodiments are illustrated in referenced figures of the drawings. It is intended that the embodiments and figures disclosed herein are to be considered illustrative rather than limiting. Also, the terminology used herein is for the purpose of description and not of limitation.

**DETAILED DESCRIPTION**

In this method \( \text{N}_2\text{O} \) is photolyzed in the absence of ambient air to produce electronically excited oxygen atoms, which then react with \( \text{N}_2\text{O} \) to produce NO as follows:

\[
\begin{align*}
\text{N}_2\text{O} + h\nu &\rightarrow \text{N}_2 + \text{O}^*(D_2) \\
\text{O}^*(D_2) + \text{N}_2\text{O} &\rightarrow \text{N}_2 + \text{O}_2 \\
\text{Net: } 2\text{N}_2\text{O} &\rightarrow 2\text{N}_2 + \text{O}_2 \\
\text{and} & \\
\text{N}_2\text{O} + h\nu &\rightarrow \text{N}_2 + \text{O}^*(D_2) \\
\text{O}^*(D_2) + \text{N}_2\text{O} &\rightarrow 2\text{NO} \\
\text{Net: } 2\text{N}_2\text{O} &\rightarrow 2\text{NO} + \text{N}_2
\end{align*}
\]

Here, \( \text{O}^*(D_2) \) is an electronically excited state of the oxygen atom. \( \text{N}_2\text{O} \) has a broad absorption band in the wavelength region 160-260 nm, and the quantum yield for reaction 1 is unity at wavelengths shorter than the thermodynamic limit of 230 nm (NASA, 2006). It is believed that the most efficient wavelengths for the conversion are between 170 to 190 nm, inclusive. In pure \( \text{N}_2\text{O} \), \( \text{O}^*(D_2) \) reacts with \( \text{N}_2\text{O} \) to form two sets of products, either \( \text{N}_2 + \text{O}_2 \) (reaction 3) or 2NO (reaction 5). The two sets of products are produced with yields of 41% and 59%, at 298 K, respectively based on the measured rate coefficients for reactions 3 and 5 (NASA, 2006).

Another possible fate of the \( \text{O}^*(D_2) \) atom produced in reaction 1 is deactivation to the ground state according to the following reaction:

\[
\text{O}^*(D_2) + \text{M} \rightarrow \text{O} + \text{M}
\]

Here, \( \text{M} \) is any molecule or atom, principally \( \text{N}_2\text{O} \). In reaction 7, a ground state oxygen atom is formed. It has been reported that less than 4% of \( \text{O}^*(D_2) \) produced in the presence of \( \text{N}_2\text{O} \) is collisionally deactivated to ground state atoms (Wine and Ravishankara, 1982). To the extent that it is formed, the primary fate of this O atom is recombination to form molecular oxygen:

\[
\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}
\]

Again, \( \text{M} \) is any molecule or atom, principally \( \text{N}_2\text{O} \).

The only byproducts produced in reactions 1-8 are \( \text{N}_2 \) and \( \text{O}_2 \), the principal components of air. Significantly, the
reaction system does not directly produce the toxic gas nitrogen oxide (NO$_2$). Potentially, nitrogen dioxide could be produced in the secondary reaction

$$2NO + O_3 \rightarrow NO_2$$

(9)

where the O$_3$ is derived from reaction 2 and to a much smaller extent from reaction 8. However, reaction 9 has a small rate coefficient and is second order in NO concentration, with the result that reaction conditions can be chosen where the concentration of NO$_2$ produced is insignificant. As an example, in inhalation therapy the concentration of NO administered is typically in the range 20-100 parts per million (ppm). In order to produce 100 ppm NO in air with a 1% dilution of the N$_2$/NO source gas into air, the concentration of NO in the N$_2$ source gas would need to be 10,000 ppmv. The corresponding amount of oxygen produced in reaction 2 would be 3,500 ppmv. Using the rate coefficient of 1.9 e$^{-38}$ cm$^6$ molec$^{-2}$ S$^{-2}$ at 298 K for reaction 9 (NBS, 1977), the half-life for reaction of 10,000 ppmv NO in the presence of 3,500 ppmv O$_3$ is calculated to be 0.7 hours, and for a 10 second residence time in the photolytic chamber the NO$_2$ concentration produced is 40 ppmv, which after diluted into air is 0.4 ppmv. By comparison, the U.S. Occupational Safety and Health Administration permissible exposure limit (PEL) to NO$_2$ is 5 ppmv and 8 hour time weighted average (TWA) is 3 ppmv.

[0026] Referring first to FIG. 1, a reaction chamber 1 contains N$_2$/O gas or liquid. The reaction chamber 1 has been purged of substantially all of the ambient air by the N$_2$/O flowing into the chamber prior to the start of the reaction. Light from a UV lamp 3 passes through a window 2 into the test chamber. Reaction chamber 1 optionally has an inlet 4 for admitting the N$_2$/O gas or liquid and an exit 5 for removing reaction products and unreacted N$_2$/O gas or liquid. When the lamp is turned on, the NO concentration begins to increase inside the reaction chamber. The rate at which NO is produced increases with the density of N$_2$/O in the chamber and the UV light intensity. Optionally, lamp 3 may be placed inside reaction chamber 1, in which case window 2 is not required. It is understood that the reaction chamber itself is not required to produce NO provided that the lamp is surrounded by N$_2$/O gas or liquid.

[0027] Referring next to FIG. 2, a schematic diagram is provided of an actual apparatus used to produce and control the concentration of NO in a flowing stream of air. Nitrous oxide gas contained in N$_2$/O cartridge 6 passes through pressure regulator 7, through connecting tube 8, through flow controller 9, through connecting tube 10, through flow meter 11, through connecting tube 12, and into reaction chamber 13. Ultraviolet light from UV lamp 14 causes NO to be formed inside chamber 13. UV light from lamp 14 is monitored by photodiode 15. In the depicted embodiment, a low pressure mercury lamp, which has a weak emission near 185 nm in addition to its principal emission at 254 nm, is used. The radiation at 185 nm, where the N$_2$/O absorption cross section is high, is responsible for the production of NO. Other types of UV emitting lamps could be used as well, including a high pressure mercury lamp, xenon arc lamp, hydrogen lamp, deuterium lamp and other known or later developed UV emitting sources. A feedback loop in which the voltage to the UV lamp is pulse width modulated is used to maintain a constant signal at photodiode 15 so that NO is produced at a constant rate.

[0028] Unreacted N$_2$/O, NO and other reaction products flow out of reaction chamber 13, into connecting tube 16, and are mixed with a flow of NO-scrubbed air in tube 25. The NO/air mixture, having a substantially constant NO concentration, exits tube 25 and may be sampled by a NO measurement device for the purpose of calibration. The NO-scrubbed air is produced by drawing in ambient air by air pump 18 through inlet 17. The air then passes through connecting tube 19, through NO scrubber 20, through connecting tube 21, through flow controller 22, through connecting tube 23, through flow meter 24 and into tube 25. For a fixed lamp intensity, the mixing ratio of NO exiting tube 25 may be varied by varying the diluent air flow rate using flow controller 22. Because the absorption of UV light is nearly optically thick (nearly every photon of sufficient energy to cause photolysis is absorbed by N$_2$/O), the output mixing ratio of NO is nearly insensitive to the flow rate of N$_2$/O.

[0029] The apparatus of FIG. 2 may be used to produce controlled mixing ratios of other gases in a dilute gas as well. For example, if the N$_2$/O cartridge of FIG. 2 is replaced by a CO$_2$ cartridge or other source of CO$_2$, carbon monoxide and molecular oxygen may be produced by the following mechanism:

$$2x(CO_2 + h\nu \rightarrow CO + O)$$

(10)

$$O + O_3 \rightarrow 2O_2 + M$$

(11)

Net: 2CO$_2$ + 2h$\nu \rightarrow 2CO + O_2$

Thus, the photolysis reaction can be used to produce a controlled concentration of CO and O$_2$. Again, the CO$_2$ flowing into the reaction chamber 1 purges the reaction chamber of substantially all of the ambient air. Although a low pressure mercury lamp can be used to produce low concentrations of CO according to this mechanism, a preferred lamp would be a hydrogen or deuterium lamp, because the lamp emission spectrum better overlaps that of the CO$_2$ absorption spectrum.

[0030] Similarly, if the N$_2$/O source is replaced with a source of sulfur hexafluoride (SF$_6$), then a controlled concentration of SF$_4$ and F$_2$ could be produced according to the sequence of reactions:

$$SF_6 + h\nu \rightarrow SF_4 + F$$

(12)

$$SF_4 + F \rightarrow SF_2 + F_2$$

(13)

Net: 2SF$_6$ $\rightarrow$ 2SF$_4$ + F$_2$

Many other reagents can be photolyzed with ultraviolet light. In many of these, the presence of ambient air will cause the photolysis to produce a gas product or products such as ozone. However, if the photolysis is done in the absence of ambient air, a different, and possibly more desirable gas product will be formed. As would be known by the practitioner of the art, a number of gases could be used to produce either the gas products discussed above, or other reaction products, the key being that the concentration of the gas product is controlled by a combination of lamp intensity, flow rate of gas through the photolysis chamber and flow rate of diluent gas. The apparatus of FIG. 2 can thus be used to produce controlled concentrations of specific gases for many applications including calibration of analytical instruments.

Example 1

[0031] Referring next to FIG. 3, experimental results are shown for production of NO at different mixing ratios using an apparatus described by the schematic diagram of FIG. 2. The vertical axis is the mixing ratio of NO in parts-per-billion
by volume (ppbv) measured using a 2B Technologies Model 400 Nitric Oxide Monitor™. The horizontal axis is time in minutes. The N₂O volumetric flow rate is 18 cc/min, the air volumetric flow rate is 940 cc/min, the temperature of the reaction chamber is thermostated at 37°C, and the pressure in the reaction chamber is 848 mbar. The UV lamp used was a low pressure mercury lamp with greater than 95% of the surface of the lamp painted to be opaque. The average intensity of the lamp was varied by pulse width modulation to produce NO concentrations in the range 0-270 ppbv as summarized in Table 1.

<table>
<thead>
<tr>
<th>Region of FIG. 3</th>
<th>Time Interval</th>
<th>% Pulse Modulation</th>
<th>Average Measured NO Mixing Ratio = Standard Error of the Mean, ppbv</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>0.0-11.2</td>
<td>0.0</td>
<td>0.2 ± 0.9</td>
</tr>
<tr>
<td>27</td>
<td>11.8-25.0</td>
<td>3.2</td>
<td>50.7 ± 0.7</td>
</tr>
<tr>
<td>28</td>
<td>25.7-39.9</td>
<td>6.4</td>
<td>102.3 ± 0.6</td>
</tr>
<tr>
<td>29</td>
<td>41.3-54.7</td>
<td>9.6</td>
<td>156.3 ± 0.8</td>
</tr>
<tr>
<td>30</td>
<td>55.8-69.8</td>
<td>12.8</td>
<td>209.1 ± 0.5</td>
</tr>
<tr>
<td>31</td>
<td>71.2-85.0</td>
<td>16.0</td>
<td>269.1 ± 0.7</td>
</tr>
<tr>
<td>32</td>
<td>86.2-99.8</td>
<td>12.8</td>
<td>295.5 ± 0.6</td>
</tr>
<tr>
<td>33</td>
<td>101.0-115.0</td>
<td>9.6</td>
<td>156.7 ± 0.6</td>
</tr>
<tr>
<td>34</td>
<td>116.2-129.5</td>
<td>6.4</td>
<td>103.6 ± 0.5</td>
</tr>
<tr>
<td>35</td>
<td>131.3-151.5</td>
<td>0.0</td>
<td>-0.1 ± 0.4</td>
</tr>
</tbody>
</table>

Example 2

In a second example, the apparatus of FIG. 2 was used to generate different concentrations of CO in air by using CO₂ as the reactant gas and varying the UV lamp intensity. In this example, the N₂O cartridge 6 of FIG. 2 was replaced with a CO₂ cartridge, and the NO scrubber was replaced with a hopcalite scrubber to remove CO. The low-pressure mercury lamp was replaced with an unpainted mercury lamp because the extinction coefficient for absorption of the 185 nm emission line of mercury is approximately 400 times less for CO₂ as compared to N₂O. Also, the volume of the reaction chamber was increased from 4.1 cm³ to 118.4 cm³. A flow of 72-83 cm³/min of CO₂ passed through the reaction chamber 13 and mixed with a flow rate of approximately 1 liter/minute of air. The output of the apparatus was analyzed for CO by use of a Thermo Electron Corporation Model 48i CO Gas Analyzer. The results are given in Table 2, which shows that CO is produced in the apparatus and that the concentration produced can be varied by varying the lamp intensity.

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CITED LITERATURE

[0033] While a number of exemplary aspects and embodiments have been discussed above, those of skill in the art will recognize certain modifications, permutations, additions and sub-combinations therefore. It is therefore intended that the following appended claims hereby introduced are interpreted to include all such modifications, permutations, additions and sub-combinations are within their true spirit and scope. Each apparatus embodiment described herein has numerous equivalents.


1. A method of synthesizing nitric oxide (NO) which comprises exposing nitrous oxide (N₂O) to ultraviolet light in an atmosphere substantially free of ambient air at wavelengths shorter than 230 nm for an amount of time sufficient to allow a desired concentration of nitric oxide (NO) to be formed.

2. The method of claim 1 wherein a mercury lamp is a source of ultraviolet light.

3. The method of claim 1 wherein the N₂O is contained in a reaction chamber.

4. The method of claim 3 further comprising the steps of flowing N₂O into the reaction chamber and flowing NO, unreacted N₂O and other reaction products out of the reaction chamber after a chosen time.

5. The method of claim 3 wherein a source of ultraviolet light is a mercury lamp.

6. The method of claim 5 wherein the mercury lamp is inside the reaction chamber.

7. The method of claim 4 further comprising the step of varying an intensity or duty cycle of the ultraviolet light thereby varying a concentration of NO produced.

8. A method to produce NO in a diluent gas comprising the steps of:

   1. passing a flow of N₂O gas through a photoysis chamber;
   2. irradiating the N₂O gas within the photoysis chamber with a UV light source emitting light of wavelengths less than 230 nm for a chosen amount of time until photoysis products form; and
   3. mixing the photoysis products with a flow of diluent gas at a desired ratio.

9. The method of claim 8 wherein the UV light source is a mercury lamp.

10. The method of claim 8 wherein the amount of NO produced is controlled by varying the intensity or duty cycle of light at wavelengths less than 230 nm.

11. The method of claim 8 wherein the desired ratio of NO to diluent gas is controlled by varying one or both of flow rate of N₂O gas and the flow rate of diluent gas.

12. A method of synthesizing carbon monoxide (CO) which comprises exposing carbon dioxide (CO₂) to ultraviolet light in an atmosphere substantially free of ambient air at wavelengths shorter than 200 nm for an amount of time sufficient to allow a desired concentration of carbon monoxide (CO) to be formed.
13. The method of claim 12 wherein a mercury lamp is a source of ultraviolet light.
14. The method of claim 12 wherein the ultraviolet light source is either a hydrogen lamp or deuterium lamp.
15. The method of claim 12 wherein the CO₂ is contained in a reaction chamber.
16. The method of claim 15 further comprising the steps of flowing CO₂ into the reaction chamber and flowing CO, unreacted CO₂ and other reaction products out of the reaction chamber after a chosen time.
17. The method of claim 15 wherein the source of ultraviolet light selected from the group of a mercury lamp, hydrogen lamp or deuterium lamp.
18. The method of claim 17 wherein the lamp is inside the reaction chamber.
19. The method of claim 12 wherein the concentration of CO produced is controlled by varying the intensity of the ultraviolet light.
20. A method to produce CO in a diluent gas consisting of the steps of:
   passing a flow of CO₂ gas through a photolysis chamber having an inlet and an outlet;
   irradiating the CO₂ gas within the photolysis chamber with a UV light source emitting light of wavelengths less than 200 nm; and
   mixing the photolysis products from the exit of the reaction chamber with a flow of diluent gas at a desired ratio.
21. The method of claim 20 in which the UV light source is a mercury lamp, hydrogen lamp or deuterium lamp.
22. The method of claim 20 in which an amount of CO produced is varied by varying the intensity of light at wavelengths less than 200 nm.
23. The method of claim 20 wherein the desired ratio of CO to the diluent gas is controlled by varying one or both of a flow rate of CO₂ gas and a flow rate of diluent gas.
24. A method to produce a desired gas A in a diluent gas comprising the steps of:
   passing a flow of a reagent gas R known to photolyze to produce gas A through a photolysis chamber which is substantially free of contaminating reagents having an inlet and an outlet;
   irradiating the gas R within the photolysis chamber with a light source emitting photons having sufficient energy to photolyze R;
   and mixing the photolysis products exiting the reaction chamber with a flow of diluent gas at a desired ratio.
25. The method of claim 24 wherein a mixing ratio of A is varied by varying the intensity of light.
26. The method of claim 24 wherein the desired ratio of gas A to the diluent gas is controlled by varying one or both of a flow rate of gas R and a flow rate of diluent gas.
27. A method of synthesizing a gas X selected from the group consisting of NO, CO and F₂, which comprises the steps of:
   exposing an appropriate precursor gas Y selected from the group consisting of N₂O, CO₂ and SF₆ respectively, to light source emitting photons having sufficient energy to photolyze gas Y to a gas X in an atmosphere substantially free of ambient air for an amount of time sufficient to allow a desired concentration of a desired gas to be formed.
28. A device to produce a desired gas A in a diluent gas consisting of:
   a reaction chamber having an inlet and an outlet;
   an attachment point on the inlet for a container of a reagent gas R known to photolyze to produce gas A allowing reagent gas R to flow into the reaction chamber;
   an ultraviolet light source positioned to provide ultraviolet light to the reaction chamber, thereby irradiating the gas R within the reaction chamber with a wavelength of light having sufficient energy to photolyze R;
   a source of the diluent gas having an outlet attached to the outlet of the reaction chamber;
   the outlet of the diluent gas having a means of flow control located upstream of the connection to the reaction chamber outlet functioning to mix the diluent gas with the flow of gas A out of the reaction chamber at a desired ratio.
29. The device of claim 28 further comprising a means to scrub gas A from the diluent gas located upstream of the flow control means, functioning to ensure that the amount of gas A in the gas mix is determined by the amount of gas A produced by photolysis.
30. The device of claim 28 wherein the source of ultraviolet light is a mercury lamp.
31. The device of claim 30 wherein the mercury lamp is inside the reaction chamber.
32. The device of claim 28 further comprising a means of varying an intensity or duty cycle of the ultraviolet light thereby varying a concentration of gas A produced.

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