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27. To influence ET processes by pulsed IR excitation, both IR excitation and ET should occur on time scales shorter than or comparable to that of vibrational relaxation, i.e., typically a few picoseconds, while the minimum ~1.5-ps IR excitation pulse length is required to achieve the sub–12-cm^{-1} pulses necessary for selective vibrational excitation. The chemical system and the experimental setup used in this study fulfill these requirements.
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32. A broad transient signal appears as a baseline offset that decays with the lifetime of the initially formed DB^+A^- excited-state manifold. This signal is due to a broad electronic absorption profile of the initial charge-transfer state that extends into the mid-IR.
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35. Materials, methods, and additional information are available as supplementary materials on *Science* Online.
36. In diad **2**, the excited state populated as a result of 400-nm excitation is B^+A^-, an equivalent to the DB^+A^- branching state in **1**. However, in **2** no electron donor is present, and therefore no forward electron transfer is possible.
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43. Excitation of the high-frequency ν(C≡C) mode will affect other vibrations in its vicinity, which may in turn affect the nature and ordering of the excited states. Presently, exploring this multi-dimensional energy landscape is computationally intractable.

ACKNOWLEDGMENTS

We are grateful to M. Newton (Brookhaven National Laboratory), D. Phillips (Imperial College London), A. Orr-Ewing (Univ. of Bristol), D. Clary (Univ. of Oxford), and G. Worth (Univ. of Birmingham) for comments on the manuscript; to I. Rubtsov and R. Schmehl (Tulane University) for discussions; and to the Engineering and Physical Sciences Research Council, Univ. of Sheffield, and Science and Technology Facilities Council for support.

SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/346/6216/1492/suppl/DC1
Materials and Methods
Figs. S1 to S8
Table S1
References (*44*–*57*)

29 August 2013; accepted 14 November 2014
10.1126/science.1259995

PHOTOCHEMISTRY

One-pot room-temperature conversion of cyclohexane to adipic acid by ozone and UV light

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Nitric acid oxidation of cyclohexane accounts for ~95% of the worldwide adipic acid production and is also responsible for ~5 to 8% of the annual worldwide anthropogenic emission of the ozone-depleting greenhouse gas nitrous oxide (N_2O). Here we report a N_2O-free process for adipic acid synthesis. Treatment of neat cyclohexane, cyclohexanol, or cyclohexanone with ozone at room temperature and 1 atmosphere of pressure affords adipic acid as a solid precipitate. Addition of acidic water or exposure to ultraviolet (UV) light irradiation (or a combination of both) dramatically enhances the oxidative conversion of cyclohexane to adipic acid.

Adipic acid is a precursor for the synthesis of the nylon-6,6 polymer and, as such, is one of the most important industrial chemical intermediates. More than 3.5 million metric tons of adipic acid were produced in 2013, reflecting a ~5% growth rate per year over the past 5 years (*1*, *2*). Nearly 95% of the worldwide industrial production of adipic acid employed the nitric acid oxidation method (*3*). The first step is air oxidation of cyclohexane under high temperatures (125° to 165°C) and high pressure (8 to 15 atm) to produce KA oil (i.e., a mixture of cyclohexanone and cyclohexanol) with 4 to 11% conversion and ~85% selectivity (*4*, *5*). In the second step, nitric acid is applied as an oxidant: the conversion is ~100%, and the selectivity for adipic acid is 93 to 95% with some other short-chain acids as side products (see Fig. 1A). The process requires the nitric acid–to–KA oil ratio to be maintained at 40:1. Disadvantages of the current industrial process include low overall product yield; corrosion of reaction vessels by nitric acid; emission of the ozone-depleting greenhouse gas N_2O; and high energy consumption. It was estimated that ~0.3 kg of N_2O gas is formed per kilogram of adipic acid produced (*6*, *7*). After energy-consuming recovery and recycling, the amount of N_2O gas released to the atmosphere still accounts for ~5 to 8% of annual anthropogenic N_2O emission worldwide (*3*, *7*, *8*). Many efforts have been devoted to developing more efficient and environmentally friendly processes for industrial production of adipic acid that avoid the emission of N_2O. In 1998, Sato *et al.* reported a process using H_2O_2 as an oxidant to convert cyclohexene to adipic acid in the presence of a Na_2WO_4 catalyst and the phase-transfer reagent $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$. Although the overall adipic acid yield (93%) is very high (*9*), production of 1 mol of adipic acid requires consumption of 4 to 4.4 mol of H_2O_2. The price of H_2O_2 is ~55% of the price of adipic acid. The requirement of 4 to 4.4 mol of H_2O_2 for production of 1 mol of adipic acid is economically infeasible (*7*). In addition, other negative factors hinder commercialization of this process, including low availability

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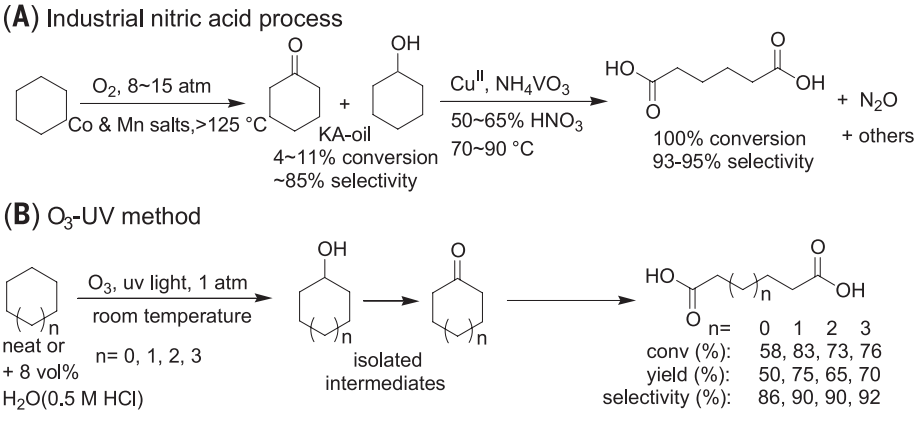


Fig. 1. Comparison of the industrial process and the method presented herein for production of adipic acid. (**A**) Industrial nitric acid process. (**B**) O_3-UV method.

of the cyclohexene substrate, poor solubility in water, and challenging recyclability of the catalysts (*10*–*13*). Adipic acid can also be produced via a multistep enzymatic conversion of D-glucose via an o-hydroxy phenol intermediate (*14*). Despite a very high overall yield of 97%, this process requires a large quantity of enzymes and is too costly for commercial production.

Inspired by literature reports that ozone and ultraviolet (UV) irradiation are primarily responsible for oxidative degradation of most hydrocarbons in the atmosphere, we sought to investigate whether both treatments in combination could oxidize cyclohexane, which exclusively contains unactivated sp^3 C-H bonds. In a simple experiment, ozone gas was bubbled through neat cyclohexane with concurrent UV irradiation at room temperature. No metal catalyst or solvent was used. After 2 to 8 hours, a solid product gradually precipitated to the bottom of the reaction vessel (see Fig. 1B and fig. S1 for reaction scheme and pictures, respectively). A portion of the liquid cyclohexane evaporated due to the O_3 gas bubbling. The solid oxidation product of cyclohexane was subjected to ^1H nuclear magnetic resonance (NMR) and ^{13}C NMR analysis (in deuterated chloroform) for structure characterization and proven to be adipic acid. We further grew single crystals and adopted x-ray crystallography to confirm that the solid precipitate is adipic acid (see fig. S2); our spectroscopic data are consistent with recently reported data (*15*). The isolated yield of solid adipic acid was ~53 (± 2) mol % at room temperature (an average of three runs, relative to the starting quantity of cyclohexane; the number in parentheses represents the stardard error). The mass balance (i.e., all products plus recovered starting materials) was ~63 (± 2) mol %, with the rest of ~37 (± 2) mol % cyclohexane being evaporated as vapor. A stronger UV light fluence and a longer irradiation time generally lead to higher adipic acid yields. When in the presence of 8 volume % aqueous 0.5 M HCl and exposure to ozone-UV irradiation, both the final adipic acid yield and the mass balance could be further improved to ~75 (± 2) mol % and ~84 (± 3) mol %, respectively. The use of a chilled water-methanol condenser (–5° to –10°C) reduced the loss of the starting substrate and intermediates via evaporation and thus improved the mass balance substantially. All experiments were repeated at least three times (see tables S1 to S5). Experimental details can be found in the materials and methods section in the supplementary materials.

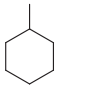
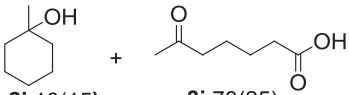
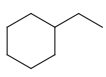
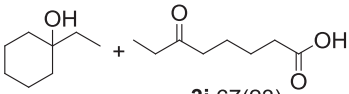
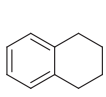
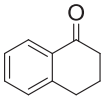
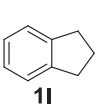
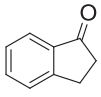
Control experiments show that ozonolysis of neat cyclohexane in the dark can also generate 12 mol % yield of adipic acid, and ozonolysis of cyclohexane–8 volume % aqueous 0.5 M HCl in the dark can also result in the formation of 45 mol % yield of adipic acid (see Table 1). Previously, Barletta *et al.* carried out ozonolysis of neat cyclohexane for 1 hour at 10°C in the dark, and derivatization of the final products with "MTBSTFA" (where "MTBSTFA" was not defined). Based on gas-liquid chromatography–mass spectrometry analysis of their ozonolysis products, they claimed detection of formation of cyclohexanol and cyclohexanone (*16*). No adipic acid formation was observed, no ozonolysis of cyclohexane-acidic water result was reported, and no light irradiation was applied in their experiments. Similar dicarboxylic acid products can also be obtained from other cycloalkanes (C_nH_{2n}, where n = 5, 6, 7, and 8). For large-ring cycloalkanes, less evaporation occurs, and thus, good yields (65 to 70%) of the dicarboxylic acid products were obtained at room temperature. Upon short-time (0.5 hours) irradiation, a mixture of KA oil (cyclohexanol and cyclohexanone) instead of adipic acid was obtained (see Table 1). To investigate the reaction mechanism, neat cyclohexanol was used as a substrate for reaction with ozone under UV irradiation. Upon short-time (0.5 hours) ozone treatment under UV irradiation, a mixture of cyclohexanone (major product) and adipic acid (minor product) was obtained. Prolonged UV irradiation led to the formation of a large amount of adipic acid as a solid precipitate (84 mol % isolated yield) along with a small amount of cyclohexanone (10 mol %), suggesting that cyclohexanone was further converted to adipic acid (see Table 1). Indeed, direct ozone treatment and

Table 1. Substrate scope for oxidative C-H functionalization of cycloalkanes. Neat liquid substrate was used unless otherwise stated. The reactions were carried out either under irradiation by a 100-W Hg lamp (200 mW/cm^2 at 310 nm), reported first below, or in the dark (reported below in parentheses) at room temperature. The ozone flow rate was 0.45 ml/min. The reactor was connected to a chilled water-methanol circulator condenser (–5° to –10°C) to trap evaporating reactants and intermediates. For substrates with higher freezing points (**1c**, **1g**, and **1h**), the temperature of the condenser was set between 5° and 10°C.

Substrates	Products %Yield	Time (h)	%Conversion	%Selectivity for **2**	%Mass balance
1a	**1a'** 8(12) + **2a** 50(10)	10	58(22)	86(45)	58(25)
1b	**1d** 11(15) + **2b** 53(13)	15	64(28)	84(46)	64(53)
1b + 8 vol% aqueous 0.5 M HCl	**1d** 8(10) + **2b** 75(45)	15	83(55)	90(82)	83(55)
1b	**1b** 68 + **1c** 15 + **1d** 10 + **2b** (trace)	0.5	25	—	93
1c	**1c** 49 + **1d** 40 + **2b** 10	0.5	50	20	99
1d	**1d** 10(15) + **2b** 84(25)	8	94(40)	90(63)	98(96)
1d	**1d** 6(65) + **2b** 90(30)*	8	90(30)	99(99)	96(95)
1e 2.3 M in CCl_4	**2b** 99(99)	0.3	99(99)	99(99)	99(99)
1f 1.0 M in CCl_4-1% H_2O	**2a** 97(97)	1.0	97(97)	99(99)	99(99)
1g	**1g'** 8(12) + **2g** 65(15)	15	73(27)	90(56)	76(60)
1h	**1h'** 6(12) + **2h** 70(20)	15	76(32)	92(63)	85(78)

*Addition of 8 vol% aqueous 0.5 M HCl to neat cyclohexanone promotes the adipic acid yield from 30 mol% to 45 mol% at room temperature in the dark.

Table 2. Substrate scope for oxidative C-H functionalization of substituted cycloalkanes. Neat liquid substrate was used unless otherwise stated. The reactions were carried out either under irradiation by a 100-W Hg lamp (200 mW/cm^2 at 310 nm) or in the dark at room temperature (reported in parentheses). The ozone flow rate was 0.45 ml/min. The reactor for substrates **1i** and **1j** was connected to a chilled water-methanol circulator condenser (−5° to −10°C), but no condenser was used for the **1k** and **1l** substrates due to their high boiling points.

Substrates	Products %Yield	Time (h)	%Conversion	%Selectivity for **3**	%Mass balance
 **1i**	 **2i** 10(15) + **3i** 70(25)	5	80(40)	88(63)	85(60)
 **1j**	 **2j** 10(12) + **3j** 67(23)	5	77(35)	87(66)	93(72)
 **1k**	 **2k** 72(35)	8	72(35)	94	99(99)
 **1l**	 **2l** 76(38)	8	76(38)	95	99(99)

UV irradiation of neat cyclohexanone led to the formation of a solid adipic acid precipitate in ~90 mol % yield. The results clearly show that ozone treatment and UV irradiation of neat cyclohexane leads to the formation of cyclohexanol, then cyclohexanone, and finally adipic acid. Measurements of intermediate and product concentrations (by ^{1}H NMR) during the reaction time course also support the above reaction scheme for the neat cyclohexane-ozone-UV irradiation system (see fig. S3 and discussion therein). The selectivity for adipic acid is nearly quantitative because the intermediates (including cyclohexanol and cyclohexanone) will eventually be converted to adipic acid upon prolonged UV irradiation, and the solid precipitate contains only one product (adipic acid). No short-chain dicarboxylic acids or other products were observed or detected by ^{1}H NMR measurements.

When substituted cyclohexanes were used as substrates, a similar trend was observed (see Table 2). For example, 1-methylcyclohexanol was obtained as the major product after short-time (2 hours) ozone treatment and UV irradiation of methylcyclohexane, whereas open-chain keto-carboxylic acid emerged as the major product upon prolonged (5 hours) irradiation, with a trace amount of 1-methylcyclohexanol as a minor product (see Table 2). For substrates that have two types of C-H bonds, selective oxidation occurs at methine C-H over methylene C-H bonds and at benzylic C-H over methylene C-H bonds (see Table 2).

It is well established that upon UV (306 to 328 nm) irradiation, ozone decomposes to generate singlet $^1O_2$ and a singlet O(^{1}D) atom with a quantum yield of 0.79 (*17*, *18*). The singlet O(^{1}D) atom is highly reactive and can insert into C-H bonds of hydrocarbons to form C-O-H bonds in the gas phase with the conservation of total spin angular momentum (*19*, *20*). Our control experiments show that exposure of cyclohexane to singlet $^1O_2$ (by photoirradiation of cyclohexane in the presence of photosensitizers) does not generate adipic acid, suggesting that the formation of adipic acid is mainly due to chemical reactions between atomic O(^{1}D) with cyclohexane, cyclohexanol, and cyclohexanone. A possible reaction pathway for the neat cyclohexane-ozone-UV system is proposed in fig. S4(i) to account for formation of adipic acid via selective C-H bond oxidation of cyclohexane by O(^{1}D). First, direct C-H bond insertion of O(^{1}D) into cyclohexane would lead to the formation of cyclohexanol (*21*), which is further oxidized by O(^{1}D) at the weakest methine C-H bond to form a geminal diol, 1,1′-dihydroxycyclohexane. Geminal diols are known to be very unstable and will rapidly undergo dehydration to form stable ketones (*22*). The bonding energies of methine C-H, methylene C-H, and O-H bonds are ~96, ~99, and ~105 kcal/mol, respectively (*23*). Insertion of O(^{1}D) into a C-H bond in cyclohexane requires cleavage of one C-H bond and formation of two bonds (i.e., C-O and O-H), which are exothermic and thermodynamically favored. Subsequent insertion of O(^{1}D) into the methine C-H bond of cyclohexanol is also thermodynamically favored. Both cyclohexanol and cyclohexanone were isolated as stable intermediates upon short-time UV irradiation of cyclohexane in the presence of ozone. The conversion of cyclohexanone to adipic acid by reaction with a singlet O(^{1}D) atom probably proceeds via dihydroxylation at the α-C-H bond adjacent to the ketone functionality, because the α-C-H bond is weaker than other remote methylene C-H bonds.

We also experimentally observed that the addition of acidic water could promote both light and dark conversion of cyclohexane to adipic acid by ozone, as well as improve the mass balance substantially. Both ozone and O(^{1}D) (generated by UV irradiation of ozone) are reported to react with water to form a hydroxyl radical (·OH) [see eqs. 3 and 4 in fig. S4(ii)] (*24*, *25*). The reaction mechanism is likely to involve hydroxyl radical–mediated selective hydrogen atom abstraction and a peroxidation chain reaction [see proposed mechanism in fig. S4(ii) and discussion therein]. A more detailed discussion of reaction mechanisms can be found in the supplementary text and fig. S4.

Oxidation of cyclohexane by singlet O(^{1}D) and a hydroxyl radical can occur at any of the 12 equivalent C-H bonds. In the case of later intermediates (i.e., cyclohexanol and cyclohexanone), oxidative C-H bond functionalization seemed to occur exclusively at the weakest α-C-H bond adjacent to the electron-withdrawing hydroxyl or carbonyl site. Note that benzylic C-H (~90 kcal/mol) and methine C-H (~96 kcal/mol) bond strengths are, in general, weaker than that of methylene C-H bonds (~99 kcal/mol) (*23*). Such site selectivity is unusual because oxidative C-H bond functionalization by electron-deficient oxidants, such as a combination of an organometallic catalyst and H_2O_2, usually occurs at the most remote (or the most electron-rich) C-H bond away from electron-withdrawing groups or directing groups (*14*, *26*–*29*). The site selectivity here is most likely governed by the singlet spin nature of the O(^{1}D) atom rather than by its electrophilicity. A similar type of spin-electronic effect governing C-H bond oxidation was also observed in the direct rhodium carbenoid insertion into C-H bonds in tetrahydrofuran and alkanes (*29*).

Varkony *et al.* previously reported (without discussion of reaction mechanism) that the tertiary C-H site in methylcyclohexane and analogs can be oxidatively converted to 1-methylcyclohexanol by ozone on silica gel at −78°C in the dark with 99.5% conversion and 65% yield (*30*). A tricopper cluster in tandem with H_2O_2 can oxidatively convert cyclohexane to cyclohexanol and cyclohexanone (*31*). These processes do not generate dicarboxylic acid as the final product, and their experimental conditions are not suitable for industrial applications. Overall, the process we report here opens up opportunities to oxidatively convert many other inexpensive hydrocarbons to value-added chemicals by using singlet O(^{1}D) or hydroxyl radical–mediated selective C-H bond functionalization.

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ACKNOWLEDGMENTS

We are grateful for financial support from the Ministry of Science and Technology, Taiwan. K.C.H. conceived the idea, designed the experiments, and wrote the manuscript. A.S. conducted the experiments. Metrical parameters for the x-ray structures of **2b** and **2g** are available free of charge from the Cambridge Crystallographic Data Centre under accession numbers CCDC 1025098 and CCDC 1025099, respectively. A patent application is pending.

SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/346/6216/1495/suppl/DC1
Materials and Methods
Supplementary Text
Figs. S1 to S6
Tables S1 to S15
References (*32*–*44*)
^{1}H and ^{13}C NMR Data
^{1}H and ^{13}C NMR Spectra

6 August 2014; accepted 11 November 2014
10.1126/science.1259684

CATALYSIS

Catalytically active Au-O(OH)$_x$-species stabilized by alkali ions on zeolites and mesoporous oxides

Ming Yang,[1] Sha Li,[2] Yuan Wang,[1] Jeffrey A. Herron,[2] Ye Xu,[3] Lawrence F. Allard,[4] Sungsik Lee,[5] Jun Huang,[6] Manos Mavrikakis,[2] Maria Flytzani-Stephanopoulos[1]*

We report that the addition of alkali ions (sodium or potassium) to gold on KLTL-zeolite and mesoporous MCM-41 silica stabilizes mononuclear gold in Au-O(OH)$_x$-(Na or K) ensembles. This single-site gold species is active for the low-temperature (<200°C) water-gas shift (WGS) reaction. Unexpectedly, gold is thus similar to platinum in creating –O linkages with more than eight alkali ions and establishing an active site on various supports. The intrinsic activity of the single-site gold species is the same on irreducible supports as on reducible ceria, iron oxide, and titania supports, apparently all sharing a common, similarly structured gold active site. This finding paves the way for using earth-abundant supports to disperse and stabilize precious metal atoms with alkali additives for the WGS and potentially other fuel-processing reactions.

The water-gas shift (WGS) reaction ($CO + H_2O \rightarrow CO_2 + H_2$) is an important reaction for hydrogen upgrading during fuel gas processing. Emerging applications in fuel cells require active, nonpyrophoric, and cost-effective catalysts. Along with a new group of platinum catalysts with atomically dispersed Pt sites to maximize activity and catalytic efficiency (*1*–*3*), the lower apparent activation energy E_a for the WGS reaction (~45 kJ/mol) for gold (Au) versus ~75 kJ/mol for platinum (*3*–*5*) can be exploited for low-temperature WGS and other reactions (*6*, *7*). Low-temperature activity is important to avoid multiple-treatment units in practical low-temperature proton-exchange membrane (PEM) fuel cell systems, whereby the deleterious CO should be totally removed for stable, long-term operation. The active Au species in the WGS catalysts are atomic species anchored through –O ligands to different supports such as ceria (*3*, *8*, *9*), iron oxide (*10*–*12*), lanthana (*13*), and titania (*4*), and the number of the active Au sites can be increased through a variety of catalyst preparation protocols. Gold nanoparticles (Au NPs) that can form during catalyst preparation are spectator species in these chemistries (*3*, *4*, *10*), in that most of the Au atoms are not activated by the support. Thus, the approach of "cage encapsulation" of Au NPs in mesoporous supports is not advantageous for the stability of the active (atomically dispersed) Au sites.

Other approaches—for example, $AuCl_3$ vapor produced by sublimation and introduced into various zeolites (*14*, *15*)—may be used to produce active Au(I)-Cl species for ambient-temperature NO reduction to N_2O by CO. Mohamed and Ichikawa (*16*) have shown that the Au(I) species are the main active sites for the WGS reaction at temperatures as low as 50°C. Because these sites are not chloride-free (Au-Cl bonds exist) and have weak chemical binding to the zeolites, the Au(I) sites are easily reduced to inactive Au(0) and form Au NPs upon increasing the temperature to only 100°C (*16*). Similarly, low stability of gold on zeolites was found by Gates and coworkers (*17*, *18*). Careful anchoring of mononuclear Au(III) complexes from organometallic precursors produced chloride-free single-atom Au(III)-O-NaY catalytic centers that were active for CO oxidation but unstable at 25°C and 760 torr, losing ~75% of their initial activity after 15 min on stream (*17*). Finally, attempts to ion exchange gold in zeolites have been unsuccessful. Thus, gold ions in zeolites tend to be unstable toward aggregation in realistic reaction gas environments at temperatures above the ambient, an issue already understood for other inert supports such as silica or alumina, minimally interacting with gold (*19*). Hence, it is difficult to determine if the gold catalysts operate through similarly structured Au-O(OH)$_x$- species on inert supports as in the Au-CeO_x, Au-FeO_x, and Au-TiO_x systems (*20*).

To study the nature of the active gold sites on inert supports, it is important to maximize the number of the atomically dispersed gold sites and fully eliminate the formation of Au NPs. Titania is inferior to ceria and iron oxide in that Au NP growth occurs rapidly on its surfaces (*21*), but with special ultraviolet (UV)–assisted preparation methods, mononuclear Au-O(OH)$_x$- species

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One-pot room-temperature conversion of cyclohexane to adipic acid by ozone and UV light

Kuo Chu Hwang and Arunachalam Sagadevan

Science **346**, 1495 (2014);
DOI: 10.1126/science.1259684

Science (print ISSN 0036-8075; online ISSN 1095-9203) is published weekly, except the last week in December, by the American Association for the Advancement of Science, 1200 New York Avenue NW, Washington, DC 20005.

chemistryworld

Chemistry from the skies promises low-emission nylon raw material

22 December 2014 **Andy Extance**

After bubbling ozone through cyclohexane illuminated with a UV lamp for a few hours adipic acid began to precipitate out © Science/AAAS

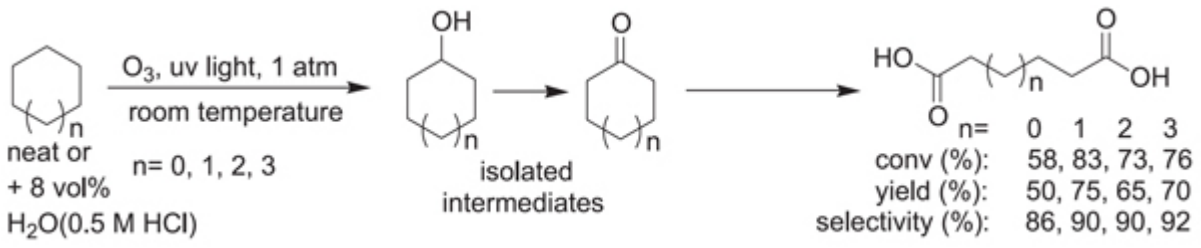
Mimicking the breakdown of atmospheric organic compounds has led to **a cleaner way to make a key nylon raw material**.

Today, **adipic acid** is produced by opening cyclohexane using large volumes of nitric acid, a process that emits the ozone-depleting greenhouse gas **nitrous oxide**. But **Kuo Chu Hwang** and Arunachalam Sagadevan from the National Tsing Hua University in Taiwan have discovered that ozone and UV light provide an effective alternative. 'Our process is far greener, milder and more environmentally friendly,' Hwang tells *Chemistry World.*

Industrial adipic acid production first oxidises cyclohexane to cyclohexanol and cyclohexanone at high temperatures and pressures. This step's yield can be less than 10%, a significant limitation. Secondly, nitric acid oxidation opens up these ring structures, completely converting them into straight-chain adipic acid.

Nitrous oxide released from this process accounts for 5–8% of all annual human-related emissions of the gas. As well as being the dominant human-emitted ozone depleter, nitrous oxide is the third most important greenhouse gas. Cleaning up adipic acid production could therefore have clear environmental benefits – but so far all efforts have been too costly.

Hwang and Sagadevan came upon their route by chance, in exploring how ozone and UV light oxidise and break down organic compounds in the atmosphere. 'It occurred to me to oxidise cyclohexane, which contains only unactivated C–H bonds, this way,' Hwang says. 'In organic chemistry C–H bond functionalisation of hydrocarbons is extremely difficult, and considered a Holy Grail.'



UV and ozone are effective at activating C–H bonds and initiating ring-opening in a variety of carbocycles © Science/AAAS

The physical chemists bubbled ozone through neat cyclohexane while shining UV light on it at room temperature and pressure. After a few hours, adipic acid precipitated. They optimised the cyclohexane to adipic acid conversion yield to 75% by getting a brighter lamp,

letting the reaction run longer and adding weak acid. The method also worked well on a variety of other ring structures.

Yale University's **Nilay Hazari** calls the C–H bond oxidation method 'elegant', and asserts that it could result in improved industrial adipic acid synthesis methods. While Hwang is yet to work out a cost comparison for the new route, he notes ozone can be made cheaply from oxygen in the air. His next step will be increasing the scale from 6.5ml currently, including bringing in chemical engineers to design and optimise larger scale reactors. Though Hwang says 'many things have to be overcome and optimised' he is 'optimistic' about the prospects.

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K C Hwang and A Sagadevan, *Science,* 2014 DOI: 10.1126/science.1259684

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'Sky Chemistry' Leads To Greener Way To Make Plastic

Nylon production creates a greenhouse gas but combining ozone and UV light eliminates it

chemistryworld

December 24, 2014 | By Andy Extance and ChemistryWorld |

Mimicking the breakdown of atmospheric organic compounds has led to a cleaner way to make a key nylon raw material.

Today, adipic acid is produced by opening cyclohexane using large volumes of nitric acid, a process that emits the ozone-depleting greenhouse gas nitrous oxide. But Kuo Chu Hwang and Arunachalam Sagadevan from the National Tsing Hua University in Taiwan have discovered that ozone and UV light provide an effective alternative. 'Our process is far greener, milder and more environmentally friendly,' Hwang tells *Chemistry World*.

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Credit: USEPA

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Volume 92 Issue 51 | p. 6 | News of The Week
Issue Date: December 22, 2014 | Web Date: December 18, 2014

New Route To Adipic Acid Avoids Nitrous Oxide Production

Synthesis: Process provides another option for making nylon precursor without production of potent greenhouse gas

By Stephen K. Ritter

Department: Science & Technology
Keywords: adipic acid, nitrous oxide, oxidation, ozone, green chemistry

A new route to adipic acid that uses ozone and ultraviolet light to eliminate the problematic nitrous oxide by-product has researchers intrigued. But once again, issues of scale-up and safety with a greener route to this chemical intermediate—used to make nylon, polyurethane, and plasticizers—temper the good news.

Right now, 95% of the world's adipic acid production uses nitric acid as an oxidant, which releases N_2O as a by-product. The gas eats away at Earth's protective ozone layer and ranks behind only carbon dioxide and methane when it comes to greenhouse gas emissions. Some producers trap and destroy N_2O, and emissions have been cut in half since 1990. But significant emissions remain.

Chemists have been exploring N_2O-free routes to adipic acid for years by using O_2 or H_2O_2 or employing enzymes. These methods tend to be more energy efficient, have better yields, and avoid corrosion problems from using nitric acid, but none has yet proven to be economical on a large scale.

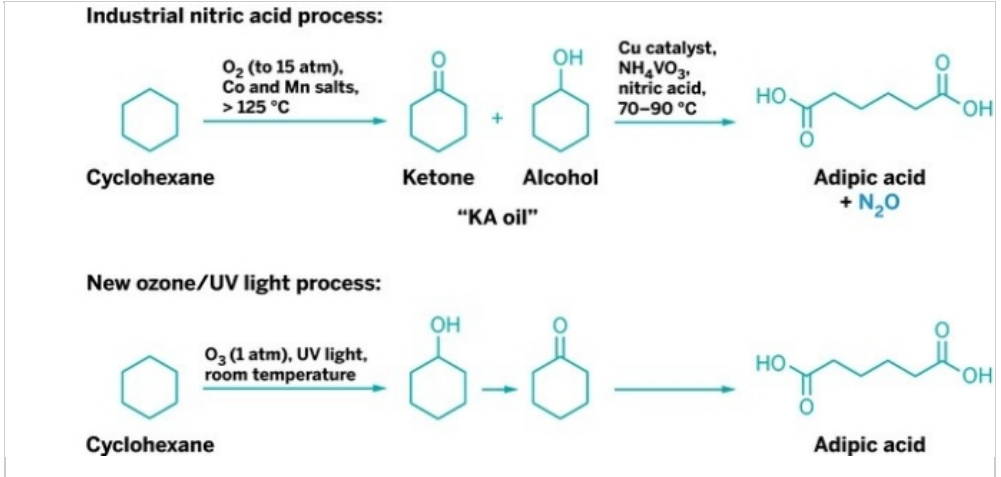
Kuo Chu Hwang and Arunachalam Sagadevan of Taiwan's National Tsing Hua University have developed an approach that uses ozone and UV light at room temperature and pressure (*Science* 2014, DOI: 10.1126/science.1259684).

Ozone and UV light may be more economical than other routes. But using them as "reagents" is potentially problematic from a commodity-scale perspective, says Thomas Boussie, cofounder of Rennovia. His company is developing a commercial process to make N_2O-free adipic acid from glucose using an O_2 (air) oxidation process coupled with a hydrogenation step.

Using ozone in organic oxidations can potentially form explosive organic peroxides, Boussie notes. Technical issues of efficient light penetration into large reactors also raise a red flag, he adds. "This paper reports an intriguing laboratory synthetic method," Boussie says, "but it is one that would encounter significant hurdles scaling to an industrial process."

Hwang doesn't view those challenges as insurmountable. Any organic peroxides formed are short-lived, he says, and the engineering of photochemical reactors is improving with LED lighting. "We are optimistic," Hwang says.

[+]Enlarge



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News in Brief: Chemistry

Nylon goes green

Simple reaction makes manufacturing produce less greenhouse gas

By Beth Mole 2:00pm, December 18, 2014

Whether the world is better off from the invention of panty hose is debatable. But a new route toward making nylon — the polymer of many a sheer stocking — is decidedly better for the planet.

Using ozone bubbles and ultraviolet light, chemists can now make a precursor to nylon without the typical exhaust of greenhouse gas. The finding appears in the Dec. 19 *Science*.

Nylon is usually made from adipic acid, a zigzag molecule of six carbons bedecked with hydrogens and a few oxygens. To get adipic acid, scientists react hexagon-shaped carbon molecules with corrosive nitric acid. That reaction gives off nitrous oxide, which can harm the Earth's ozone layer and, molecule-for-molecule, has nearly 300 times the planet-warming capacity of carbon dioxide. Human activity produces more than 8 million metric tons of nitrous oxide each year and up to 8 percent of that comes from making nylon.

To avoid this, chemists Kuo Chu Hwang and Arunachalam Sagadevan of the National Tsing Hua University in Hsinchu, Taiwan, replaced the nitric acid with bubbles of ozone, O_3, and ultraviolet light. The ultraviolet light breaks the ozone gas into O_2 and a highly-reactive oxygen atom. Lone oxygen atoms then repeatedly attack and latch onto a hexagon-shaped carbon molecule, cyclohexane, until the ring breaks open, forming adipic acid.

Citations

K. Whang and A. Sagadevan. One-pot room-temperature conversion of cyclohexane to adipic acid by ozone and UV light. *Science*. Vol. 346, December 19, 2014, p. 1495. doi:10.1126/science.1259684.

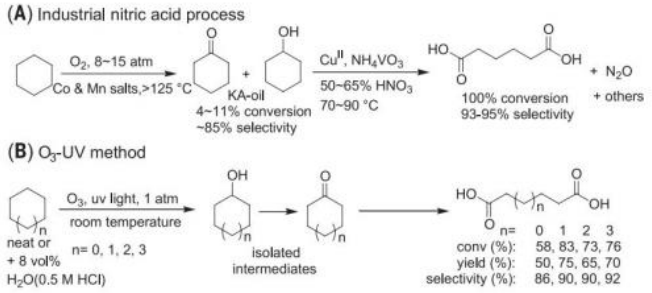
Further Reading

B. Mole. Fertilizer produces far more greenhouse gas than expected. Science News Online, June 9, 2014.

S. Perkins. An Ounce of Prevention. *Science News*. Vol. 158, July 15, 2000, p. 45.

Research pair devise a way to make nylon precursor that is less harmful to the ozone layer

19 December 2014, by Bob Yirka



Comparison of the industrial process and the method presented herein for production of adipic acid. (A) Industrial nitric acid process. (B) O3-UV method. Credit: *Science* 19 December 2014: Vol. 346 no. 6216 pp. 1495-1498. DOI: 10.1126/science.1259684

(Phys.org)—A pair of researchers working at National Tsing Hua University in Taiwan, has found a way to make a precursor to the synthetic polymer commonly known as nylon that doesn't cause the release of ozone damaging nitrous oxide. Kuo Chu Hwang and Arunachalam Sagadevan describe their process in a paper they've had published in the journal *Science* and explain why what they've discovered is important.

To make nylon, popularly used in panty hose, rope and a huge variety of other products, manufacturers first make adipic acid by mixing nitric acid with hexagon-shaped carbon molecules (cyclohexane) and other ingredients such as cobalt, copper, manganese, vanadate salts, and highly pressured oxygen. In addition to adipic acid, the process gives off nitrous oxide which is allowed to escape into the atmosphere where it harms the planet's ozone layer (it's also considered a greenhouse gas). So popular is nylon, and adipic acid (95 percent of it that's made is used to make nylon), that prior research has found that up to eight percent of the eight million metric tons of nitrous oxide released into the atmosphere each year, is the result of making adipic acid for nylon production. In this new effort, the pair of researchers describe a process they developed for creating adipic acid that doesn't release any nitrous oxide at all—it's also simpler and costs less.

Instead of adding nitric acid to cyclohexane (or cyclohexanol, or cyclohexanone) the two added ozone bubbles and ultraviolet light. The UV light caused the ozone to break down to O_2 releasing single highly reactive oxygen atoms. Those atoms attached themselves to the carbon molecules weakening their bonds and eventually causing the hexagon rings to break, which resulted in the formation of adipic acid. They note that the process doesn't require high pressure or any other new ingredients.

Excited by their discovery, the two researchers tried the same method on other, larger hydrocarbons—no report on what they found, but they imply that the possibilities are tantalizing, which suggests other researchers might be looking to do the same very soon—that could conceivably lead to the development of ways to create other common materials that aren't so harmful to the planet.

More information: One-pot room-temperature conversion of cyclohexane to adipic acid by ozone and UV light, *Science* 19 December 2014: Vol. 346 no. 6216 pp. 1495-1498. DOI: 10.1126/science.1259684

ABSTRACT

Nitric acid oxidation of cyclohexane accounts for ~95% of the worldwide adipic acid production and is also responsible for ~5 to 8% of the annual

worldwide anthropogenic emission of the ozone-depleting greenhouse gas nitrous oxide (N2O). Here we report a N2O-free process for adipic acid synthesis. Treatment of neat cyclohexane, cyclohexanol, or cyclohexanone with ozone at room temperature and 1 atmosphere of pressure affords adipic acid as a solid precipitate. Addition of acidic water or exposure to ultraviolet (UV) light irradiation (or a combination of both) dramatically enhances the oxidative conversion of cyclohexane to adipic acid.

Idividuals

- Members List

News

New Route To Adipic Acid Avoids Nitrous Oxide Production

A new route to adipic acid that uses ozone and ultraviolet light to eliminate the problematic nitrous oxide by-product has researchers intrigued. But once again, issues of scale-up and safety with a greener route to this chemical intermediate—used to make nylon, polyurethane, and plasticizers—temper the good news.

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Chemists have been exploring N_2O-free routes to adipic acid for years by using O_2 or H_2O_2 or employing enzymes. These methods tend to be more energy efficient, have better yields, and avoid corrosion problems from using nitric acid, but none has yet proven to be economical on a large scale.

Kuo Chu Hwang and Arunachalam Sagadevan of Taiwan's National Tsing Hua University have developed an approach that uses ozone and UV light at room temperature and pressure (Science 2014, DOI: 10.1126/science.1259684).

Ozone and UV light may be more economical than other routes. But using them as "reagents" is potentially problematic from a commodity-scale perspective, says Thomas Boussie, cofounder of Rennovia. His company is developing a commercial process to make N_2O-free adipic acid from glucose using an O_2 (air) oxidation process coupled with a hydrogenation step.

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Bringing science and development together through original news and analysis

Greener nylon production could cut costs and pollution

Image credit: Flickr/Shapeways

Speed read

- The new method uses far less energy than the existing one
- It is also produces little of the greenhouse gas nitrous oxide
- But there are fears that licensing costs could undermine its global take up

A greener and more-efficient way of making nylon set out in a recent paper could cut production costs, benefiting the developing nations that make and use the material.

Nylon is widely manufactured around the world, but current industrial production methods are responsible for five to eight per cent of global anthropogenic emissions of nitrous oxide, which depletes the atmosphere's ozone layer and has a greenhouse effect.

The new technique, developed by scientists from National Tsing Hua University in Hsinchu, Taiwan, promises to reduce harmful chemical emissions by using bubbles of ozone gas and ultraviolet light to produce adipic acid, a precursor to nylon.

"This new process produces next to no nitrous oxide gas and is far less energy demanding, but has higher overall reaction mass efficiency than the current industrial nitric acid oxidation process," says head researcher Kuo Chu Hwang.

According to Hwang, the low energy (http://www.scidev.net/global/environment/energy/) demand means the new process is also far more economical than traditional methods as it requires less energy — the process can be carried out at room temperature compared to the much higher temperatures needed for the traditional process — and a lower volume of chemicals to produce the same amount of nylon.

"There are many fantastic technologies that have the potential to revolutionise production processes, but the patents are owned by multinational companies in the developed world."

Scott Kelly, Centre for Climate Change Mitigation Research

As adipic acid is a key component for making plastics and polyurethane as well as nylon, developing nations could benefit from a more cost-effective approach that minimises pollution (http://www.scidev.net/global/environment/pollution/).

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Nylon production is high in South-East Asia and Bangladesh, but China is fast becoming the biggest producer and consumer of nylon products. According to the Taiwan Man-Made Fibre Industries Association, China produced more than 1.4 million tonnes of nylon in 2009.

But gaining access to this new technology (http://www.scidev.net/global/enterprise/technology/) could pose a challenge if developing countries are to "leapfrog from old dirty technologies that were the cornerstone of industrial development in the West", says Scott Kelly of the Centre for Climate Change Mitigation Research at the University of Cambridge, United Kingdom.

"There are many fantastic technologies that have the potential to revolutionise production processes, but the patents are owned by multinational companies in the developed world, and they are often reluctant to allow this technology to be used without an expensive licensing arrangement," he says.

"Often the licensing fees are too expensive and old existing technologies are used by developing countries in order to minimise costs."

The study was published last month (19 December) in Science.

> Link to full paper in Science (http://www.sciencemag.org/cgi/content/full/346/6216/1495?ijkey=BqpRiyeTT86pw&keytype=ref&siteid=sci)

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Science doi: 10.1126/science.1259684 (2014)

Africa: Africa: Greener Nylon Production Could Cut Costs and Pollution

2015/01/09

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The Greening of Nylon

by Catherine Nisbett Becker | January 2015

Nylon, invented in the 1930s, has become one of the most common polymers. An early use was for women's stockings—in fact, "nylons" came to be a synonym for "stockings." [See Wallace Carothers: Nylon Reshapes a Nation, September 2001.]

Seseg Zhigzhitova/EyeEm/Getty Images

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Now, nylon is found in a vast number of commercial products, from parachutes to tires, stringed instruments and carpets. Yet the production of nylon is inefficient and environmentally destructive. In particular, producing one of the key ingredients in nylon, a large, zigzag molecule called adipic acid, involves oxidizing nitric acid, which releases harmful nitrous oxide into the atmosphere. Not only does nitrous oxide deplete the ozone layer, it is a potent greenhouse gas, nearly 300 times more harmful than carbon dioxide.

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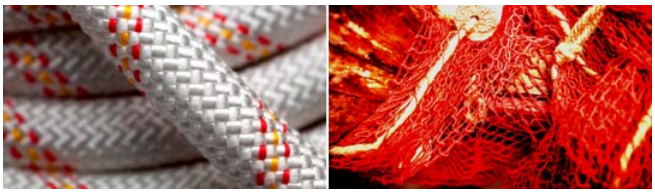

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Nylon is found in a vast number of commercial products, from parachutes to tires, stringed instruments and carpets. Yet the production of nylon is inefficient and environmentally destructive. ABOVE (clockwise from top left): parachute cloth, bike tires, nylon zipper, commercial fishing net, nylon rope, textile thread.

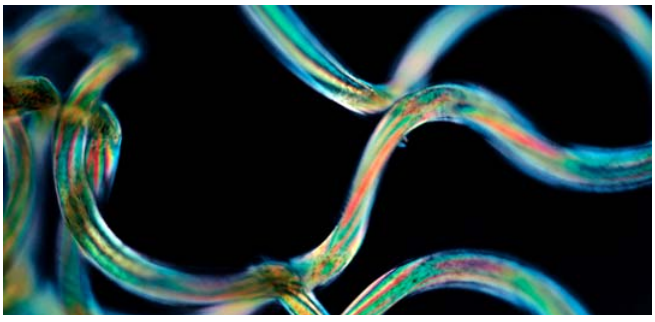
Though nylon production is not the only manufacturing process that releases nitrous oxide into the atmosphere, it is a major culprit. And because nylon is essential to so many manufactured goods, changing the way adipic acid is produced might benefit the environment and reduce man-made climate change. Recently, Kuo Chu Hwang and Arunachalam Sagadevan of the National Tsing Hua University in Taiwan may have set the stage for such a development. Using only ozone gas and ultraviolet (UV) light, they were able to create adipic acid far more efficiently than by oxidizing nitric acid. They published their results in the December 19, 2014 issue of *Science*.

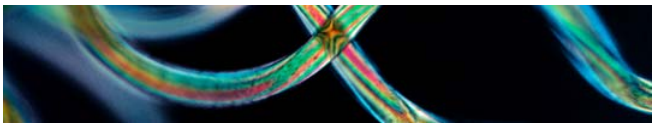
Using Nitric Acid Oxidation

In 2013, over 3.5 million metric tons of adipic acid were created in the production of nylon. And currently 95 percent of adipic acid is made using nitric acid oxidation, a toxic and inefficient method. In the first stage of a two-step process, cyclohexane, a hexagonal, carbon-based molecule, is oxidized in the air. The reaction requires temperatures of 125 to 165º C and pressures of between 8 and 15 atmospheres (multiples of the air pressure at sea level). The result is KA (ketone-alcohol) oil, a mix of cyclohexane and cyclohexanol, where one carbon atom in the cyclohexane hexagon is replaced by oxygen and hydrogen. This first step converts only between 4 and 11 percent of the products, making it particularly inefficient.

In the second step, nitric acid oxidizes the KA oil. Though all the products are converted in this step, a great deal of nitric acid is needed. The ratio of nitric acid to KA oil is 40 to 1. The process is energy intensive, and nitric acid is difficult to work with—the reaction vessels tend to corrode because it is so caustic.

However, the worst part is the emission of ozone-depleting nitrous oxide. For every kilogram of adipic acid produced through nitric acid oxidation, almost a third of a kilogram of nitrous oxide is also produced. The nylon industry employs energy-consuming recovery and recycling methods to prevent the gas from escaping into the atmosphere. Nevertheless, it is estimated that nylon production alone accounts for between 5 and 8 percent of the amount of nitrous oxide that humans emit worldwide—a total of more than 8 million metric tons each year.





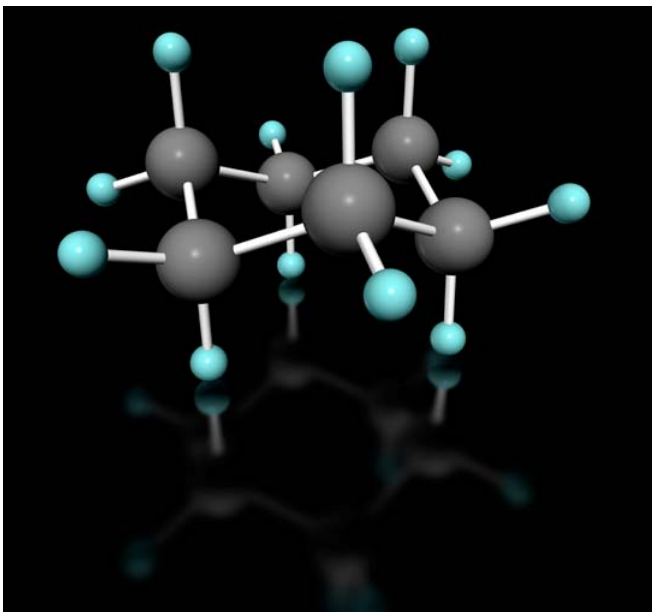
Michael Abbey/Science Source/Getty Images

Nylon production accounts for between 5 and 8 percent of the amount of nitrous oxide that humans emit worldwide—a total of more than 8 million metric tons each year.

Although there have been efforts to make the process more efficient and more environmentally friendly, their cost has been prohibitive.

Breaking the Loop

The key to creating adipic acid is to break open cyclohexane's carbon ring. Cyclohexane is part of a class of organic molecules called hydrocarbons that exist in the atmosphere. Hwang and Sagadevan wanted to study whether ozone gas (O3) and ultraviolet (UV) light were responsible for the oxidative degradation of these hydrocarbons. When UV light shines on ozone gas, it breaks it into inert oxygen gas (O2) and a single, highly reactive oxygen atom. Oxygen has only six electrons in its outer, valence shell, which means that it needs two more to become nonreactive. Hwang and Sagadevan wanted to know whether the oxygen atom breaks open the carbon skeleton of hydrocarbons to bond with carbon atoms in the molecules. They realized that the process they were studying might also oxidize cyclohexane.



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The key to creating adipic acid is to break open cyclohexane's carbon ring.

To test the hypothesis, they devised a simple experiment. First, they put 6.5 milliliters of cyclohexane in a test tube equipped with a small tube. They pumped ozone (O3) through the tube so that it bubbled up through the liquid. The effect was similar to blowing through a straw into a glass of water. Then they shone UV light on the test tube. The UV light split the ozone gas into O2 and O. And the individual oxygen atoms latched onto the cyclohexane ring until it broke open, forming a new molecule.

Over the course of the reaction, ranging from 2 to 8 hours, Hwang and Sagadevan saw a white precipitate collect at the bottom of the test tube. They took this pasty, wet solid and purified it, dried it, and subjected it to a variety of tests aimed at discovering its identity. It turned out to be adipic acid. Their yield was about 53 percent.

Further tests showed that they could increase the efficiency of the reaction by increasing the intensity of the UV light or by letting the reaction run for a longer period. When they mixed a weak hydrochloric acid into the cyclohexane, the reaction reached 75 percent efficiency.

Hwang and Sagadevan realized that the upper efficiency limit of their setup was about 90 percent, because as the precipitate fell to the bottom of the test tube, it trapped bubbles of cyclohexane that then could not react with the ozone. If the reaction chamber could somehow remove precipitate as the reaction proceeded, the researchers thought they might be convert the entire sample into adipic acid. To date, however, they have not done so.

Taking the Next Step

Hwang and Sagadevan were not initially interested in nylon production methods, so they have not designed a way to scale up their method to industrial needs. However, they did advance our understanding of how organic molecules oxidize in the atmosphere. Their method has worked equally well in oxidizing other carbon-based molecules.

Discussion Questions

How might you design an experimental setup that removes the precipitate from the bottom of the test tube while the reaction continues running?

Journal Articles and Abstracts

(*Researchers' own descriptions of their work, summary or full-text, on scientific journal websites*)

Hwang, Kuo Chu and Sagadevan, Arunachalam. "One-pot room-temperature conversion of cyclohexane to adipic acid by ozone and UV light." *Science*, December 14, 2014: www.sciencemag.org/content/346/6216/1495.figures-only.

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Extance, Andy. "Chemistry from the skies promises low-emission nylon raw material." *Chemistry World* (December 22, 2014) [accessed December 26, 2014]: www.rsc.org/chemistryworld/2014/12/xhemistry-skies-promises-low-emission-nylon-raw-material-adipic-acid.

Hwang, Kuo Chu and Sagadevan, Arunachalam. "One-pot room-temperature conversion of cyclohexane to adipic acid by ozone and UV light." *Science* (December 14, 2014) [accessed December 26, 2014]: www.sciencemag.org/content/346/6216/1495.figures-only.

Mole, Beth. "Nylon goes green." *Science News* (December 18, 2014) [accessed December 26, 2014]: www.sciencenews.org/article/nylon-goes-green.

Keywords

nylon, adipic acid, nitric acid oxidation, cyclohexane, carbon-molecule oxidation, ozone gas and UV light, Kuo Chu Hwang, Arunachalam Sagadevan

Citation Information (●) MLA ( ) APA ( ) Chicago Manual of Style

Nisbett Becker, Catherine. "The Greening of Nylon." *Today's Science.* Infobase Learning, Jan. 2015. Web. 2 Feb. 2015. <http://tsof.infobaselearning.com/recordurl.aspx?wid=10835&ID=32012>.

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SYNTHESIZING ADIPIC ACID WITHOUT GENERATING N2O

By Paul Grad | February 1, 2015

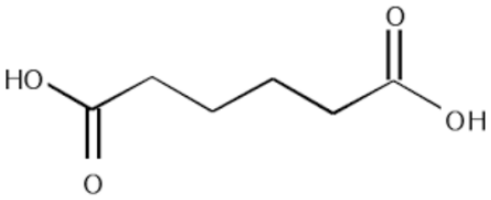
0

Adipic acid, a precursor for the synthesis of nylon, is usually produced through nitric acid oxidation of cyclohexane, a process which has disadvantages, such as the emission of nitrous oxide — a greenhouse and ozone-depleting gas — as well as low product yield, high energy consumption, and corrosion of reaction vessels by nitric acid. The amount of N_2O thus released into the atmosphere accounts for up to 8% of annual anthropogenic N_2O emission worldwide. An alternative adipic-acid route that eliminates the use of HNO_3 and thus the associated corrosion problems and N_2O emissions, has been discovered by professor Kuo Chu Hwang and researcher Arunachalam Sagadevan at National Tsing Hua University (Hsinchu, Taiwan; www.nthu.edu.tw). The researchers were inspired by reports that ozone and ultraviolet (UV) irradiation were primarily responsible for oxidative degradation of most hydrocarbons in the atmosphere, and decided to see whether both treatments in combination could oxidize cyclohexane, which exclusively contains unactivated sp^3 C–H bonds. By bubbling O_3 gas through cyclohexane with concurrent UV irradiation at room temperature, a solid reaction product precipitated at the bottom of the reaction vessel after 2–8 h. The solid...

PAK CHEMICAL ENGINEERS

NITROUS OXIDE FREE SYNTHESIS OF ADIPIC ACID

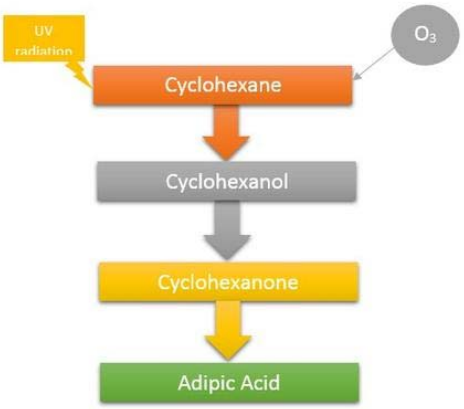
(Research by professor Kuo Chu Hwang and researcher Arunachalam Sagadevan at National Tsing Hua University)



Adipic acid is the require material for the synthesis if nylon, it is produce by the oxidation of cyclohexane with nitric acid, but during this oxidation nitrous oxide which is a greenhouse and ozone depleting gas is emitted also this process is high energy consuming and give low yield in comparison the use of energy.
The amount of N2O thus released into the atmosphere accounts for up to 8% of annual anthropogenic N2O emission worldwide.
An alternative route that eliminates the bad effects of adipic acid is discover by professor Kuo Chu Hwang and researcher Arunachalam Sagadevan at National Tsing Hua University.

They were inspired by reports that ozone and ultraviolet (UV) irradiation were primarily responsible for oxidative degradation of most hydrocarbons in the atmosphere, and decided to see whether both treatments in combination could oxidize cyclohexane, which exclusively contains un-activated sp3 C-H bonds. An alternative route that eliminates the bad effects of adipic acid is discover by professor Kuo Chu
Hwang and researcher Arunachalam Sagadevan at National Tsing Hua University. They were inspired by reports that ozone and ultraviolet (UV) irradiation were primarily responsible for oxidative degradation of most hydrocarbons in the atmosphere, and decided to see whether both treatments in combination could oxidize cyclohexane, which exclusively contains un-activated sp3 C-H bonds. A stronger UV light and a longer irradiation time generally lead to higher adipic acid yields.

Mechanism of adipic acid formation is shown in below figure;



3 Ways Researchers Have Found to Make Plastic Greener

by Kevin Mathews | July 8, 2015 | 9:00 am

Plastics: when they're not poisoning our bodies, they're ruining our planet. Although it would be for the best to get rid of plastics altogether, our dependence on the material makes that change unlikely any time soon. If we're going to continue manufacturing plastic goods, at the very least, we need to start being smarter (and environmentally-conscious!) in how we make it. That's precisely why these recently discovered plastic advancements are so important to our future:

1. Making Plastic More Recyclable

A lot of people have the mentality that plastic is fine for the environment because it's recyclable, yet only 7 percent of all plastic gets turned into a new goods. Plastic recycling is underutilized for two main reasons: First, it's expensive. Second, due to its reduced quality, no more than 20 percent of a new item is composed of recycled plastic, meaning that even "recycled" items are mostly new plastic.

All that could change, however. Two students at UC Davis, Akshay Sethi and Victor Awad, "thought outside of the box" if you will and discovered a new way to recycle plastic. They use enzymes to reduce PET plastic back into chemical matter, which can more easily be molded into new, stronger quality plastic.

The students took this potential advancement and created a company, Ambercycle. Though the pair have smaller goals for the company in the short term, they acknowledge that in the long term, this manner of recycling plastics could revolutionize the plastics industry.

2. Dropping the Cost of Biodegradable Plastic

For years, we've had the capability of making biodegradable plastics using polylactic acid (PLA). The green alternative has never managed to replace usual plastics, though, because the process is time consuming and the cost to produce PLA is too exorbitant.

Fortunately, this month, researchers at KU Leuven announced that they discovered a chemical process that speeds up the creation of PLA. "We produce more PLA with less waste and without using metals," said scientists Michiel Dusselier. "In addition, the production process is cheaper because we can skip a step."

Though it is unlikely that all plastics will shift to a biodegradable variety, having more of this on the market will be a win for the environment. The researchers have already sold the patent for their discovery to a company that wants to mass produce PLA.

3. Eliminating Nitrous Oxide From Nylon

You can't make nylon without adipic acid and, similarly, you can't make adipic acid without releasing a bunch of harmful nitrous oxide into the air. However, two researchers in Taiwan, Arunachalam Sagadevan and Kuo Chu Hwang, appear to have stumbled on a way to create adipic acid without generating so much

greenhouse gas, reports Scientific American.

The pair weren't originally trying to revolutionize plastic – instead they attempted to see whether ozone and UV light could divide compounds. They were pleasantly surprised to see that, under the right conditions, ozone and UV light could create adipic acid much more cleanly than the traditional method.

Though the finding is exciting and shows proof of a better way of creating nylon, at the moment, the technique is not financially feasible on a widespread level. Hwang admits that "many things have to be overcome and optimized" still, but that he's hopeful this discovery can lead to a green change in plastic.



Read more: environment, green, plastic, plastics, pollution, research, science, waste

Photo credit: Thinkstock

41 comments


Sarah H.

3:54am PDT on Sep 14, 2015

I much preferred those brown paper bags.

SEND


Kamia T.

1:44pm PDT on Jul 24, 2015

I don't care WHAT they do to make plastics more "recyclable." The sad truth is that they simply aren't. They accumulate waste molecules, and should be banned. Period. End of Statement!

SEND

Nikki D.

4:32pm PDT on Jul 20, 2015

Thanks for this informative article.

SEND


Fi T.

4:07am PDT on Jul 12, 2015

Feasible and effective???

SEND


Marie W.

10:10pm PDT on Jul 11, 2015

Stop using so much is better.

SEND


Ruhee B.

5:37pm PDT on Jul 10, 2015

Sadly this won't help with all the junk that's already out there!

SEND

Catrin N.

6:38am PDT on Jul 10, 2015

A step in the right direction.

SEND

Lorraine A.

4:16am PDT on Jul 10, 2015

When plastic was first invented, people thought it is was the best thing since sliced bread. You could bring your groceries home in something other than a brown paper bag. I even remember them advertising a whole room made of plastics from the walls to the furniture, that could just be hosed off when it got dirty. That was not that many years go really, maybe 50, and look what plastic has done to our planet in that short a time. It has to go.

SEND

Roro I.

3:00am PDT on Jul 10, 2015

Thanks

SEND

Hussein K.

12:17am PDT on Jul 10, 2015

thanks

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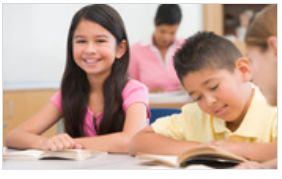

'Evolution, Not Creationism!' For England's 10-Year-Olds

Children

Australian School Teacher Avoids Jail After Child Porn Scandal

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NNadir (21,430 posts) Sat Feb 17, 2018, 03:58 AM

Can we eliminate the emissions of the greenhouse and ozone depleting gas N2O from nylon manufacture?

Nitrous oxide, N2O, aka "laughing gas" is no laughing matter.

Other than carbon dioxide, it is the atmospheric pollutant that most troubles me, not just because it is a profound greenhouse gas with a climate forcing potential 120 times as large as carbon dioxide, but also because it is an ozone depleting agent.

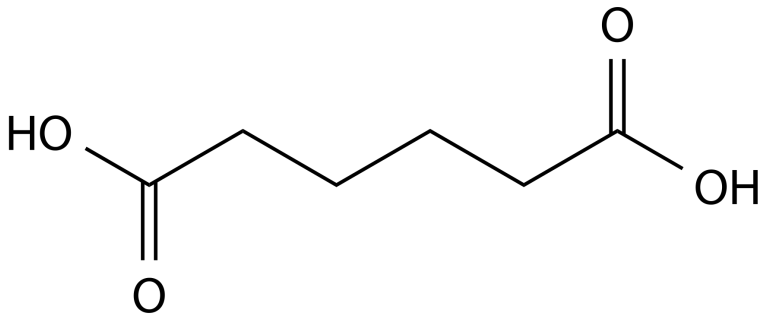
There is no really great way to eliminate human emissions - like carbon dioxide it has always been a natural component of the atmosphere, but anthrogenic emissions have swamped natural emissions - because the emission of nitrous oxide is an inevitable consequence of fertilizing soil for agriculture, without which a huge fraction of the planet's population would literally need to starve to death.

However, going through some scientific literature I collected a few years back but never properly filed in my computer's filing system, I was surprised to learn that between 5 to 8% of nitrous oxide emissions are an industrial side product of nylon manufacture.

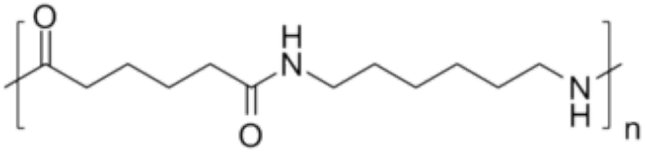
The paper to which I refer is here: One-pot room-temperature conversion of cyclohexane to adipic acid by ozone and UV light

(Kuo Chu Hwang*, Arunachalam Sagadevan, Science 19 Dec 2014:
Vol. 346, Issue 6216, pp. 1495-1498)

A key intermediate in the manufacture of the nylon polymer is the diacid adipic acid which has the following structure:



Nylon 66 has this structure:



Adipic acid is made from a constituent of the dangerous fossil fuel petroleum, cyclohexane, by oxidation with pressurized oxygen at 125C over a manganese and cobalt catalyst to give a mixture of cyclohexanol and cyclohexanone. These are passed over ammonium vanadate and cupric catalysts in the presence of 65% nitric acid (itself made by oxidation of ammonia prepared using dangerous natural gas) to give adipic acid.

During this process, the reductant is nitric acid, which is converted to N2O, which is then dumped into our favorite waste dump, the planetary atmosphere.

World production of adipic acid is on the order of a billion kg.

Some brief excerpts from the text:

> Adipic acid is a precursor for the synthesis of the nylon-6,6 polymer and, as such, is one of the most important industrial chemical intermediates. More than 3.5 million metric tons of adipic acid were produced in 2013, reflecting a ~5% growth rate per year over the past 5 years (1, 2). Nearly 95% of the worldwide industrial production of adipic acid employed the nitric acid oxidation method (3). The first step is air oxidation of cyclohexane under high temperatures (125° to 165°C) and high pressure (8 to 15 atm) to produce KA oil (i.e., a mixture of cyclohexanone and cyclohexanol) with 4 to 11% conversion and ~85% selectivity (4, 5). In the second step, nitric acid is applied as an oxidant: the conversion is ~100%, and the selectivity for adipic acid is 93 to 95% with some other short-chain acids as side products (see Fig. 1A). The process requires the nitric acid–to–KA oil ratio to be maintained at 40:1. Disadvantages of the current industrial process include low overall product yield; corrosion of reaction vessels by nitric acid; emission of the ozone-depleting greenhouse gas N2O; and high energy consumption. It was estimated that ~0.3 kg of N2O gas is formed per kilogram of adipic acid produced (6, 7)...

> ...Inspired by literature reports that ozone and ultraviolet (UV) irradiation are primarily responsible for oxidative degradation of most hydrocarbons in the atmosphere, we sought to investigate whether both treatments in combination could oxidize cyclohexane, which exclusively contains unactivated sp3 C-H bonds. In a simple experiment, ozone gas was bubbled through neat cyclohexane with concurrent UV irradiation at room temperature. No metal catalyst or solvent was used. After 2 to 8 hours, a solid product gradually precipitated to the bottom of the reaction vessel (see Fig. 1B and fig. S1 for reaction scheme and pictures, respectively). A portion of the liquid cyclohexane evaporated due to the O3 gas bubbling. The solid oxidation product of cyclohexane was subjected to 1H nuclear magnetic resonance (NMR) and 13C NMR analysis (in deuterated chloroform) for structure characterization and proven to be adipic acid.

UV radiation can be continuously supplied by exposing BaF2, barium fluoride, to a gamma emitting radioactive substance, these being available in large quantities from used nuclear fuel. There are many ways to generate ozone, although the usual method is to generate it electrochemically.

I have no idea if there has been any effort to industrialize this most interesting bench chemistry, but this is a beautiful, if esoteric environmental idea.

I can't believe I overlooked this very beautiful paper for a couple of years.

Have a very pleasant weekend.

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Can we eliminate the emissions of the	NNadir	Feb 17	OP
What's the quantum yield ? That's	eppur_se_muova	Feb 17	#1
Well, as far as rules of industrial	NNadir	Feb 17	#2

eppur_se_muova (27,958 posts) Response to NNadir (Original post)
Sat Feb 17, 2018, 11:31 AM

1. What's the quantum yield ? That's the problem with any photochemical step.

First rule of photochemical synthesis: never make anything by a photochemical synthesis if you can make it another way. This rule was formulated by specialists in photochemical synthesis, so I take it seriously.

There's other, catalytic ways to make adipic acid, usually from cyclohex**ene**. H2O2 and a tungstate catalyst is one I've used in UG labs. I'm really surprised someone hasn't tried O2/Co+2 in acid solution. This can oxidize aralkyl side chains. Would be interested to see if it cleaves C=C in cyclohexene or does allylic oxidation.

It's interesting that they did succeed in oxidizing a saturated hydrocarbon. Saves a step, it's true.

I suppose the cyclohexanol/one mixture that's used industrially is ultimately a cheaper intermediate than cyclohexene, or more tolerant of impurties, or some such. On such tiny differences in cost are the decisions to use the more polluting method chosen. Invariably, it seems.

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NNadir (21,430 posts) Response to eppur_se_muova (Reply #1)
Sat Feb 17, 2018, 02:32 PM

2. Well, as far as rules of industrial chemistry go, one should be careful about how broadly one...

...applies them.

I once worked on a drug that was out-licensed by its discovering company on the grounds that it failed most of the Lipinski rules and anyway was impossible to make,

except that I was personally involved in the synthesis of hundreds of metric tons of the stuff.

I'll excerpt the mechanistic comments below.

Let me say a few other things first.

This is benchtop chemistry. If one was going to fill a reactor with cyclohexane and an ozone/oxygen mixture, one of course, would be making a bomb. This reaction is in fact, partial combustion - arrested combustion or controlled partial combustion of cyclohexane.

This said, it may be amenable to flow chemistry, about which I'll say a little more below.

As for the rule you describe, which I've not heard before, but seems reasonable, I would suspect that it applies to selectivity more than anything else. It applies less here because of the symmetry of cyclohexane: It doesn't matter on which carbon the reaction takes place, the result is the same. Since selectivity is not an issue, a free radical reaction is less limited than in other applications. Industrial scale free radical reactions are very common with symmetric molecules, polyethylene is such a case.

Additional process value is conceivable because the reaction product is insoluble in the liquid starting material.

One could imagine a flow system into which low amounts of ozone suspended in an inert carrier gas, argon perhaps, is introduced at a controlled rate in such a way that adipic acid is simply filtered from the flow.

Someone here recently remarked that most of my posts - probably one would not be far off if one said *all* of my posts in the environmental group and your science group are related to nuclear energy, and this is true here. An economic limitation of photochemistry is the energy required to run the initiator lamps but a continuous UV source is available from any gamma source coupled to an energy level transformer, to which I alluded above, is available with barium fluoride.

If one notes that this reaction is catalyst free one might also wonder if a catalyst might be added. I would particularly be interested in the very interesting ceramic radiocesium titanate (perhaps in a nanostructured system with barium fluoride) because of the reaction mechanism, and the properties of titanates in photochemical-like systems. (Radiocesium titantanates have historically been synthesize as "waste forms" but I don't believe in "waste." I consider radiocesium titatanate to be one of the most potentially useful fission product based materials imaginable; it's a shame about fear and ignorance, which will prevent the exploration of this material's utility until a less stupid generation comes along.)

Such a system would effectively require no energy input other than the decay of radiocesium and a source of cyclohexane.

(I may post over in your Science Group some interesting physical chemistry connected with the conversion of high energy radiation to light energy that was just published in one of the journals I am coming to love, using one of my

favorite elements, uranium.)

Here is a discussion of the mechanism (and the quantum yield) from the original paper:

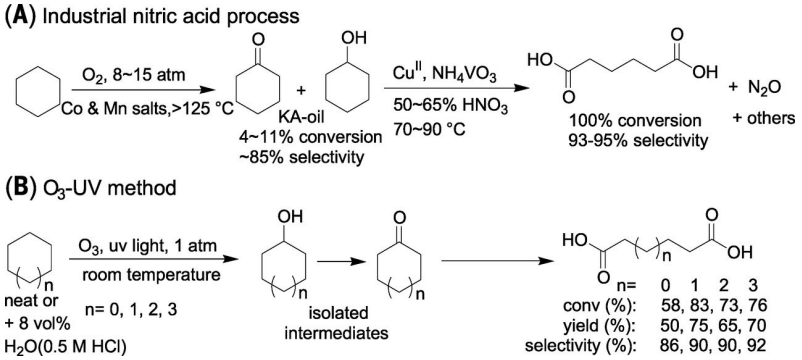
> It is well established that upon UV (306 to 328 nm) irradiation, ozone decomposes to generate singlet 1O2 and a singlet O(1D) atom with a quantum yield of 0.79 (17, 18). The singlet O(1D) atom is highly reactive and can insert into C-H bonds of hydrocarbons to form C-O-H bonds in the gas phase with the conservation of total spin angular momentum (19, 20). Our control experiments show that exposure of cyclohexane to singlet 1O2 (by photoirradiation of cyclohexane in the presence of photosensitizers) does not generate adipic acid, suggesting that the formation of adipic acid is mainly due to chemical reactions between atomic O(1D) with cyclohexane, cyclohexanol, and cyclohexanone. A possible reaction pathway for the neat cyclohexane-ozone-UV system is proposed in fig. S4(i) to account for formation of adipic acid via selective C-H bond oxidation of cyclohexane by O(1D). First, direct C-H bond insertion of O(1D) into cyclohexane would lead to the formation of cyclohexanol (21), which is further oxidized by O(1D) at the weakest methine C-H bond to form a geminal diol, 1,1′-dihydroxycyclohexane. Geminal diols are known to be very unstable and will rapidly undergo dehydration to form stable ketones (22). The bonding energies of methine C-H, methylene C-H, and O-H bonds are ~96, ~99, and ~105 kcal/mol, respectively (23). Insertion of O(1D) into a C-H bond in cyclohexane requires cleavage of one C-H bond and formation of two bonds (i.e., C-O and O-H), which are exothermic and thermodynamically favored. Subsequent insertion of O(1D) into the methine C-H bond of cyclohexanol is also thermodynamically favored. Both cyclohexanol and cyclohexanone were isolated as stable intermediates upon short-time UV irradiation of cyclohexane in the presence of ozone. The conversion of cyclohexanone to adipic acid by reaction with a singlet O(1D) atom probably proceeds via dihydroxylation at the α-C-H bond adjacent to the ketone functionality, because the α-C-H bond is weaker than other remote methylene C-H bonds.

The mechanism is pictured in the supplemental information which may be open sourced; I don't know, I'm writing in a library. The supplement also contains very nice photographs of the reaction, as well as full experimental details.

It's here: SI of the paper.

One may imagine other sources of singlet oxygen, of course, than ozone, but to the extent that they involve the addition of other reagents they may complicate the reaction.

Here is a scheme comparing the current industrial reaction with the proposed reaction:



The big problem with this whole scheme is, to my mind, the source of cyclohexane, which currently is obtained from dangerous and environmentally unacceptable petroleum.

I'm only interested in these kinds of reactions to the extent that polymers represent a path to sequestering carbon in an economically viable way. It is easy to imagine chemistry that forms butadiene from glyoxal, and glyoxal from the electrolytic (or catalytic) reduction of carbon dioxide, and ethylene from the partial hydrogenation of acetylene, acetylene being prepared from biomass and metallic calcium. These two compounds of course can be subject to [4 + 2] cycloaddition (Diels Alder) chemistry to give cyclohexene, which as you note, is a little further along on the path to adipic acid.

If I recall correctly I may have read in many places that adipic acid is also available from the various furan diacids, mixed acid/aldehydes and diacids of furan formed by the dehydration of biomass. A lot has been written about this kind of chemistry in recent years, mostly in connection with fuels, but also in connection with synthetic intermediates.

This may be superior chemistry; I don't know, at least where the goal is to economically remove carbon dioxide from the air; something humanity *must* do at some point owing the criminal negligence of my generation in putting that carbon dioxide there in the first place while praying insipidly for whirlygigs and glass coated with toxins to save the day.

Nevertheless, this is beautiful chemistry, and it struck me last night while I was struggling with insomnia and came across the paper in my files.

Thanks for your interesting comment.

Have a nice weekend.

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