

17. F. F. Crim, *J. Phys. Chem.* **100**, 12725–12734 (1996).
18. B. Arnstrup, N. E. Henriksen, *J. Chem. Phys.* **97**, 8285–8295 (1992).
19. B. A. Heller, D. Holten, C. Kirmair, *Science* **269**, 940–945 (1995).
20. M. Shapiro, P. Brumer, *Rep. Prog. Phys.* **66**, 859–942 (2003).
21. V. I. Prokhorenko *et al.*, *Science* **313**, 1257–1261 (2006).
22. G. M. Roberts *et al.*, *Chem. Sci.* **4**, 993–1001 (2013).
23. S. S. Skourtis, D. H. Waldeck, D. N. Beratan, *J. Phys. Chem. B* **108**, 15511–15518 (2004).
24. D. Xiao, S. S. Skourtis, I. V. Rubtsov, D. N. Beratan, *Nano Lett.* **9**, 1818–1823 (2009).
25. H. Carias, D. N. Beratan, S. S. Skourtis, *J. Phys. Chem. B* **115**, 5510–5518 (2011).
26. Z. Lin *et al.*, *J. Am. Chem. Soc.* **131**, 18060–18062 (2009).
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.
28. C. J. Adams *et al.*, *Inorg. Chem.* **47**, 8242–8257 (2008).
29. J. M. Keller *et al.*, *J. Am. Chem. Soc.* **133**, 11289–11298 (2011).
30. P. A. Scattergood *et al.*, *Dalton Trans.* **43**, 17677–17693 (2014).
31. W. M. Kwok, D. L. Phillips, P. K. Yeung, V. W. Yam, *J. Phys. Chem. A* **101**, 9286–9295 (1997).
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.
33. P. Hamm, M. Zanni, *Concepts and Methods of 2D Infrared Spectroscopy* (Cambridge Univ. Press, Cambridge, 2011).
34. Pumping the C≡C $\nu = 0 \rightarrow 1$ transition with the IR pulse in DB⁺A⁺ is expected to populate $\nu = 1$. A bleach of the $\nu(0 \rightarrow 1)$ band and a corresponding $\nu(1 \rightarrow 2)$ transient signal anharmonically shifted to lower energies are expected, as well as similar signals for vibrational modes coupled to the C≡C mode. These signals are characteristic of two-dimensional IR (2DIR) and transient-2DIR spectra (33), which may use similar experimental setups. However, owing to vibronic interactions between different electronic states in **1**, the IR pump gives rise to signals associated with electronic states other than the pumped DB⁺A⁺.
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.
37. K. G. Spears, *J. Phys. Chem.* **99**, 2469–2476 (1995).
38. Y. Huang, C. T. Rettner, D. J. Auerbach, A. M. Wodtke, *Science* **290**, 111–114 (2000).
39. H. M. McConnell, *J. Chem. Phys.* **35**, 508–515 (1961).
40. M. D. Newton, *Chem. Rev.* **91**, 767–792 (1991).
41. I. A. Balabin, J. N. Onuchic, *Science* **290**, 114–117 (2000).
42. D. N. Beratan *et al.*, *Acc. Chem. Res.* **42**, 1669–1678 (2009).
43. Excitation of the high-frequency $\nu(\text{C}=\text{C})$ 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

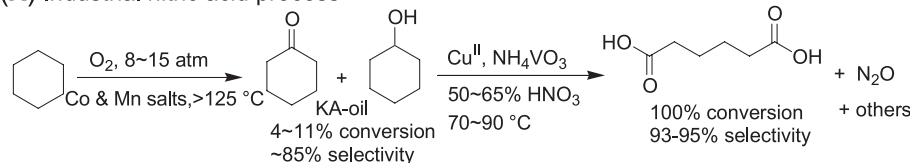
Kuo Chu Hwang* and Arunachalam Sagadevan

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.

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). After energy-consuming recovery and recycling, the amount of N₂O gas released to the atmosphere still accounts for ~5 to 8% of annual anthropogenic N₂O 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 N₂O. In 1998, Sato *et al.* reported a process using H₂O₂ as an oxidant to convert cyclohexene to adipic acid in the presence of a Na₂WO₄ catalyst and the phase-transfer reagent [CH₃(n-C₈H₁₇)₃N]HSO₄. 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 H₂O₂. The price of H₂O₂ is ~55% of the price of adipic acid. The requirement of 4 to 4.4 mol of H₂O₂ 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

(A) Industrial nitric acid process



(B) O₃-UV method

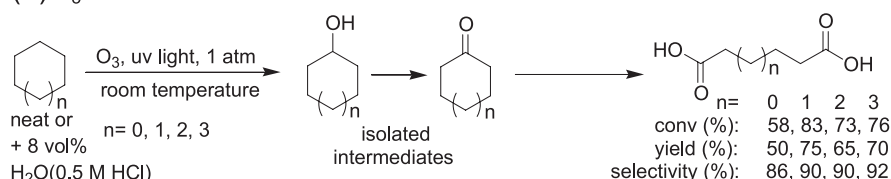


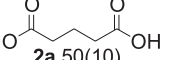
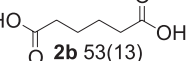
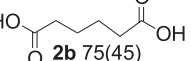
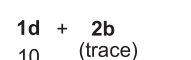
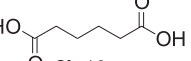
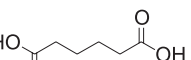
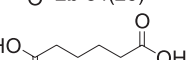
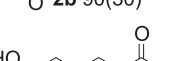
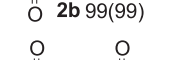
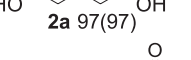
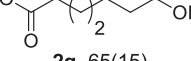
Fig. 1. Comparison of the industrial process and the method presented herein for production of adipic acid. (A) Industrial nitric acid process. (B) O₃-UV method.

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 standard 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 $-10^\circ C$) 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 $10^\circ C$ 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,

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/cm² 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 $-10^\circ C$) 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 $10^\circ C$.

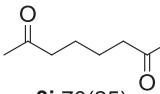
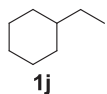
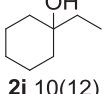
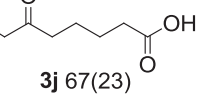
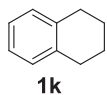
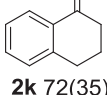
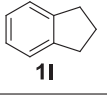
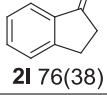
Substrates	Products %Yield	Time (h)	%Conversion	%Selectivity for 2	%Mass balance
 1a  1a' 8(12) +  2a 50(10)		10	58(22)	86(45)	58(25)
 1b  1d + 11(15)	 2b 53(13)	15	64(28)	84(46)	64(53)
 1b + 8 vol% aqueous 0.5 M HCl  1d + 8(10)	 2b 75(45)	15	83(55)	90(82)	83(55)
 1c +  1d +  2b 68 15 10 (trace)		0.5	25	—	93
 1c +  1d + 49 40	 2b 10	0.5	50	20	99
 1c +  1d + 10(15)	 2b 84(25)	8	94(40)	90(63)	98(96)
 1d + 6(65)	 2b 90(30)*	8	90(30)	99(99)	96(95)
 2b 99(99)  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 ₂ O	 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.

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 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/cm² 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 ¹H 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 ¹H 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 gen-

erate 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.

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(¹D) (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(¹D) 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 H₂O₂, 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(¹D) 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 H₂O₂ 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(¹D) or hydroxyl radical-mediated selective C-H bond functionalization.

REFERENCES AND NOTES

- Y. Wen *et al.*, *Green Chem.* **14**, 2868–2875 (2012).
- "Adipic acid (ADPA): 2014 world market outlook and forecast up to 2018" (Merchant Research and Consulting, Birmingham, UK, 2014).

3. S. Van de Vyver, Y. Roma'n-Leshkov, *Catal. Sci. Technol.* **3**, 1465–1479 (2013).
4. A. Castellan, J. C. J. Bart, S. Cavallaro, *Catal. Today* **9**, 237–254 (1991).
5. A. Chauvel, G. Lefebvre, *Petrochemical Processes: Major Oxygenated, Chlorinated and Nitrated* (Editions Technip, Paris, 1989).
6. L. Schneider, M. Lazarus, A. Kollmuss, "Industrial N₂O projects under the CDM: Adipic acid - A case of carbon leakage?" Working paper WP-US-1006, Stockholm Environment Institute, Somerville, MA, 2010.
7. F. Cavani, J. H. Teles, *ChemSusChem* **2**, 508–534 (2009).
8. R. A. Reimer, C. S. Slaten, M. Seapan, M. W. Lower, P. E. Tomlinson, *Environ. Prog.* **13**, 134–137 (1994).
9. K. Sato, M. Aoki, R. Noyori, *Science* **281**, 1646–1647 (1998).
10. U. Schuchardt *et al.*, *Appl. Catal. A* **211**, 1–17 (2001).
11. M. N. Timofeeva, O. A. Kholdeeva, S. H. Jung, J. S. Chang, *Appl. Catal. A Gen.* **345**, 195–200 (2008).
12. Z. Bohström, I. Rico-Lattes, K. Holmberg, *Green Chem.* **12**, 1861–1869 (2010).
13. Y. Deng, Z. Ma, K. Wang, J. Chen, *Green Chem.* **1**, 275–276 (1999).
14. K. M. Draths, J. W. Frost, *J. Am. Chem. Soc.* **116**, 399–400 (1994).
15. H.-K. Fun, S. Chantrapromma, L.-H. Ong, *Molecules* **19**, 10137–10149 (2014).
16. B. Barletta *et al.*, *Ozone Sci. Eng.* **20**, 91–98 (1998).
17. Y. Matsumi *et al.*, *J. Geophys. Res.* **107**, 10.1029/2001JD000510 (2002).
18. Y. Matsumi, M. Kawasaki, *Chem. Rev.* **103**, 4767–4782 (2003).
19. P. Michaud, R. J. Cvetanovic, *J. Phys. Chem.* **76**, 1375–1385 (1972).
20. T. H. Varkony, S. Pass, Y. Mazur, *J. Chem. Soc. Chem. Commun.* **1975**, 457–458 (1975).
21. M. D. Hoops, B. S. Ault, *J. Mol. Struct.* **929**, 22–31 (2009).
22. I. Ignatyev, M. Montejo, P. G. R. Ortega, J. J. L. González, *Phys. Chem. Chem. Phys.* **13**, 18507–18515 (2011).
23. S. J. Blanksby, G. B. Ellison, *Acc. Chem. Res.* **36**, 255–263 (2003).
24. E. Reisz, W. Schmidt, H. P. Schuchmann, C. von Sonntag, *Environ. Sci. Technol.* **37**, 1941–1948 (2003).
25. B. J. Finlayson-Pitts, J. N. Pitts Jr., *Science* **276**, 1045–1052 (1997).
26. M. S. Chen, M. C. White, *Science* **318**, 783–787 (2007).
27. T. Newhouse, P. S. Baran, *Angew. Chem. Int. Ed.* **50**, 3362–3374 (2011).
28. H. M. L. Davies, T. Hansen, M. R. Churchill, *J. Am. Chem. Soc.* **122**, 3063–3070 (2000).
29. K. Chen, A. Eschenmoser, P. S. Baran, *Angew. Chem. Int. Ed.* **48**, 9705–9708 (2009) and references therein.
30. H. Varkony, S. Pass, Y. Mazur, *J. Chem. Soc. Chem. Commun.* **1974**, 437–438 (1974).
31. S. I. Chan *et al.*, *J. Catal.* **293**, 186–194 (2012).

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)
¹H and ¹³C NMR Data
¹H and ¹³C 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 + H₂O → CO₂ + H₂) 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, AuCl₃ 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 N₂O 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 co-workers (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-CeO₂, Au-FeO₂, and Au-TiO₂ 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

¹Department of Chemical and Biological Engineering, Tufts University, MA 02155, USA. ²Department of Chemical and Biological Engineering, University of Wisconsin-Madison, WI 53706, USA. ³Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803, USA. ⁴Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA. ⁵X-ray Science Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA. ⁶School of Chemical and Biomolecular Engineering, University of Sydney, NSW 2006, Australia.

*Corresponding author. E-mail: maria.flytzani-stephanopoulos@tufts.edu



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

This copy is for your personal, non-commercial use only.

If you wish to distribute this article to others, you can order high-quality copies for your colleagues, clients, or customers by [clicking here](#).

Permission to republish or repurpose articles or portions of articles can be obtained by following the guidelines [here](#).

The following resources related to this article are available online at www.sciencemag.org (this information is current as of December 18, 2014):

Updated information and services, including high-resolution figures, can be found in the online version of this article at:

<http://www.sciencemag.org/content/346/6216/1495.full.html>

Supporting Online Material can be found at:

<http://www.sciencemag.org/content/suppl/2014/12/17/346.6216.1495.DC1.html>

This article **cites 41 articles**, 3 of which can be accessed free:

<http://www.sciencemag.org/content/346/6216/1495.full.html#ref-list-1>

This article appears in the following **subject collections**:

Chemistry

<http://www.sciencemag.org/cgi/collection/chemistry>



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](#)).

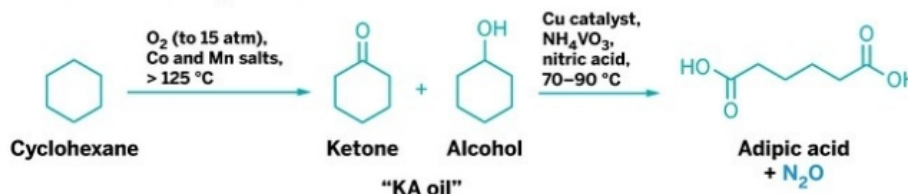
Ozone and UV light may be more economical than other routes. But using them as "reagents" is potentially problematic from a commodity-scale perspective, says [Thomas Boussie](#), cofounder of [Rennovia](#). His company is developing a commercial process to make N_2O -free adipic acid from glucose using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

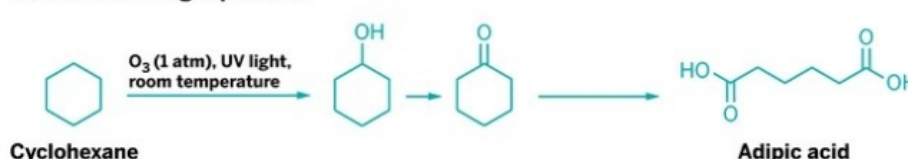
Hwang doesn't view those challenges as insurmountable. Any organic peroxides formed are short-lived, he says, and the engineering of photochemical reactors is improving with LED lighting. "We are optimistic," Hwang says.

[\[+\]Enlarge](#)

Industrial nitric acid process:



New ozone/UV light process:



As a chemical consultant are you covered?



MOST POPULAR

Viewed Commented Shared

[What Is Tinsel Made Of, And How Has It Changed Over The Years?](#)

[Texas Student Admits To Falsifying Data](#)

[Texas Student Falsified Data](#)

[Enzyme Catalysis Is A Moving Experience](#)

[Curiosity Confirms Organics On Mars](#)

*Most Viewed in the last 7 days

RELATED ARTICLES

[Biobased Polymers](#)

[Catalyzing Biobased Chemicals](#)

[Duo To Develop Biobased Adipic Acid](#)

[ADM Invests In Biotech Rennovia](#)

Advertisement

ScienceNews

MAGAZINE OF THE SOCIETY FOR SCIENCE & THE PUBLIC

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, O₃, and ultraviolet light. The ultraviolet light breaks the ozone gas into O₂ 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.

Source URL: <https://www.sciencenews.org/article/nylon-goes-green>