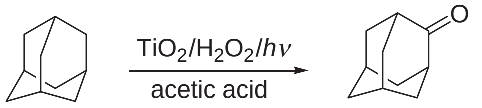
Highly Selective Production of 2-Adamantanone by Photocatalytic Oxidation of Adamantane

Sun-Jung Song,[1] Kyoung Seok Kim,[1,2] Kyung Hwan Kim,[1,2] Jong Beom Kim,[3] Jong-Ho Kim,[1,2,3]
Keun-Sik Kim,[4] Honghyun Shin,[5] and Dong Lyun Cho*[1,2]
[1]*Center for Functional Nano Fine Chemicals, Chonnam National University, Gwangju 500-757, Korea*
[2]*Center for Photonic Materials and Devices, Chonnam National University, Gwangju 500-757, Korea*
[3]*Photo & Environmental Technology Co., Ltd., Gwangju 500-460, Korea*
[4]*KS Laboratories, Sunchon 540-856, Korea*
[5]*Daelim Chemical Co., Ltd., Jinju, Korea*

(Received July 9, 2008; CL-080678; E-mail: dlcho@chonnam.ac.kr)

2-Adamantanone was selectively produced by photocatalytic oxidation of adamantane in acetic acid using TiO_2 powders. The reactions were carried out at ambient and acetic acid reflux temperatures with and without an oxidant. Adding oxidant in refluxing acetic acid under irradiation remarkably increased conversion and selectivity. Rutile TiO_2 powders showed better conversion and selectivity in the presence of H_2O_2. The total conversion was 67% and the highest selectivity of 2-adamantanone was 89%.

2-Adamantanone (2-ADO) and 2-adamantanol (2-ADOH) are useful oxidative derivatives of adamantane (ADH). In particular, 2-ADO is an important intermediate used for various pharmaceuticals such as neurological disorder drugs and therapeutic drugs for influenza.[1,2] Recently, the demand for 2-ADO has increased given its application in optical materials such as photoresists and functional materials for heat resistant plastics.[1,2] However, selective production of 2-ADO is difficult since it can only be obtained by oxidation of one of the most stable hydrocarbon compounds, ADH. In addition, several complicated steps are required to separate it from other oxidized products produced together with 2-ADO from this oxidation process, including 1-adamantanol, 2-adamantanol, 1,3-adamantanediol, and 1-hydroxy-4-adamantanone.[3,4] Among various developed processes for the selective production of 2-ADO, only one process in which ADH reacts with concentrated sulfuric acid at an elevated temperature was adapted as a commercial process. However, conversion is not high enough (≈50%) to be an economical process and separation and refinement of the products is still required. This is coupled with the various environmental and safety problems caused by the use of large amounts of 98% H_2SO_4 at high temperatures. As a consequence, improvement of the oxidation process has been attempted by using heterogeneous oxidative catalysts instead of concentrated sulfuric acid.[5–7] Recently, it was reported that TiO_2 photocatalytic oxidation of C–H bonds in alkanes and cyclic alkanes could produce alcohols or ketones,[8] with TiO_2-photocatalyzed oxidation of adamantane attempted to confirm potential of photo-oxidation capability of TiO_2.[9,10] However, the selectivity for 2-ADO was poor, as low as 10%, because other oxidized mixtures were obtained together with 2-ADO, however, TiO_2 showed photo-oxidation capability. In this study, the photocatalytic oxidation reaction of ADH with TiO_2 powders was attempted to selectively produce 2-ADO (eq 1). Photocatalytic oxidations of ADH (Wako Pure Chemical Industry Co.) were carried out with three types of TiO_2 powders: PC-500 (Millennium Co.); P-25 (Degussa Co.); and RT-1 (Photo & Environmental Technology Co.). The ratio of anatase:rutile in PC-100, P-25, and RT-1 was 100:0, 75:25, and 0:100, respectively. 30% H_2O_2 or O_3 was used as an oxidant.



(ADH) **(2-ADO)** (1)

The reactions were carried out in a 500-mL three-neck photochemical reactor equipped with a reflux condenser. After ADH (10.0 g, 0.07 mol) was dissolved in acetic acid (150 mL, 2.50 mol), TiO_2 powders (1.0 g/10.0 g of ADH), and 30% H_2O_2 (40.0 mL) were added. The solution was then irradiated with a 150-W Hg-lamp for 10 h at ambient temperature or refluxing acetic acid. After irradiation, the solution was kept at room temperature in acetic acid for 10 additional hours to raise selectivity for 2-ADO through further oxidation and disproportionation. Compounds in the product were identified by comparing with the GC chromatograms (Agilent 5890 series 2) of authentic compounds. Conversion and selectivity of the reaction were calculated based on the GC chromatograms.

It was observed that conversion of ADH and selectivity for 2-ADO in the TiO_2-photocatalyzed oxidation reactions were dependent on the type of TiO_2 powders. Figure 1 shows the conversions and selectivities for 3 different types of TiO_2 powders. Reactions were carried out at acetic acid reflux with 30% H_2O_2 as an oxidant. RT-1 shows the highest conversion and selectivity and PC-100 the lowest, indicating that the rutile structure has a higher photocatalytic activity than the anatase structure in this reaction. This result is consistent with previously reported results on the oxidation reactions of ADH in the presence of TiO_2

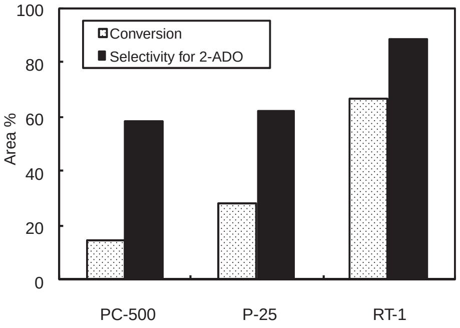


Figure 1. Conversions and selectivities of 2-ADO for 3 different types of TiO_2 powders by photocatalytic oxidation of ADH.

Table 1. Conversions and selectivities of 2-ADO by photo-oxidation of ADH for various combinations of oxidants and solvent

Combination	Conversion of ADH/%	Selectivity of 2-ADO/%
H_2O_2/acetic acid	12	52
$O_3{}^a$/acetic acid	5	8
TiO_2/acetic acid	trace	—
TiO_2/H_2O_2/acetic acid	64	89
TiO_2/O_3/acetic acid	12	62
$TiO_2/H_2O_2 + O_3$/acetic acid	33	69
TiO_2/H_2O_2/butyronitrile^b	30	12
$TiO_2/H_2O_2/CH_2Cl_2{}^b$	—	—
TiO_2/H_2O_2/toluene^b	—	—

$^a O_3$ was bubbled at a rate of 5 mL/min. ^{b}The amount of all solvents used was 2.50 mol.

photocatalyst, but inconsistent with the well-known fact that TiO_2 powders[9] with anatase structures have higher activities in photo-oxidation reactions than TiO_2 powders with rutile structures.[10] To ascertain the reason for this, a series of experiments were carried out for various combinations of oxidants and solvents with RT-1 TiO_2 powders. Conversions and selectivities obtained in the series of experiments are listed in Table 1. ADH was never oxidized in the dark and was hardly oxidized by TiO_2 powders alone without oxidants in spite of irradiation, but was oxidized, even without TiO_2 powders, when an oxidant such as H_2O_2 or O_3 was present in the solution under irradiation, although the conversion was very low. This implies that the OH or O radicals are responsible for the oxidation reaction since both are generated by dissociation of H_2O_2 and O_3 when irradiated with UV light.[11] The conversion increased to a large extent when TiO_2 powders were used together with an oxidant, especially H_2O_2, indicating that the role of the TiO_2 powders is to accelerate decomposition of H_2O_2 and O_3 to OH and O radicals. From this point of view, higher conversion by TiO_2 powders with rutile structures (RT-1) in Figure 1 may be explained by the decomposition characteristics of H_2O_2. In general, the lower photocatalytic activity of the rutile structures relative to anatase attributes to its lower band-gap energy (3.0 eV) than that of the anatase (3.2 eV). Considering that H_2O_2 can be decomposed simply by irradiation with UV light and the bond energy of O–O is as low as 145 kJ/mol, band-gap energy of the rutile structure seems to be high enough for the decomposition of H_2O_2. In addition, the lack of photocatalytic activity of the rutile structure probably prolongs the lifetime of the OH or O radicals. The selectivity of 2-ADO showed the close relationship with the conversion when acetic acid was used as a solvent. This may be explained by the oxidation of ADH to 2-ADO whereby the OH or O radicals generated on the TiO_2 surface attack the C–H bonds of the ADH, resulting in the formation of 1-adamantanyl and 2-adamantanyl radicals or 1-ADOH and 2-ADOH. In the beginning of the reaction, formation of 1-oxidated ADH derivatives is expected to be dominant because the tertiary carbon radical is the most stable intermediate. 2-ADO can then be formed through gradual disproportionation of the 1-oxidated ADH derivative and the further oxidation of 2-ADOH if OH or O radicals are still present in the solution. Therefore, not only the conversion, but also the selectivity of 2-ADO, can increase if more radicals are generated and sustained throughout the entire reaction.

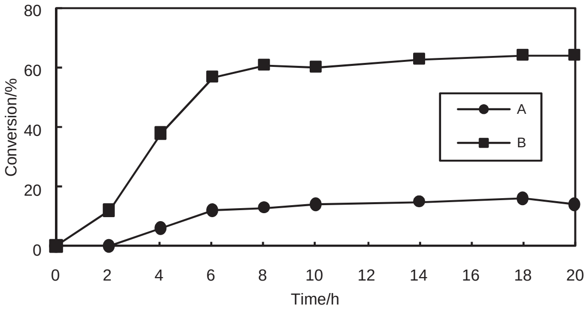


Figure 2. Conversions in photocatalytic oxidation of ADH as a function of time at 2 different temperature. Reaction mixture was irradiated for 10 h: (A) at room temperature and (B) at acetic acid reflux.

Acidic conditions seem to be preferable to the radicals. Four different solvents were tried in this study, but oxidation occurred only in acetic acid and butyronitrile. Selectivity of 2-ADO in butyronitrile was very low compared to the conversion level, implying that most of the radicals could not sustain for prolonged periods. In fact, it was reported that 2-ADO could be obtained from 1-ADOH through disproportionation (1,2-shift), with high yields in acidic solvents such as concentrated H_2SO_4 at 30 °C,[3] while formation of 2-ADOH from ADH by the oxidation process could be increased by heating the concentrated sulfuric acid.[4]

Reaction temperature during the Hg-lamp irradiation influenced the conversion. Figure 2 shows conversion as a function of time for 2 different temperatures. It is observed that the conversion is much higher at acetic acid reflux than at an ambient temperature.

In conclusion, 2-ADO was selectively produced by photocatalytic oxidation of ADH with TiO_2 powders as a catalyst. High conversion and selectivity of 2-ADO were obtained when TiO_2 powders with a rutile structure (RT-1) were used as a catalyst in acetic acid. Addition of an oxidant was essential for the photo-oxidation of ADH. Reaction at acetic acid reflux with H_2O_2 as an oxidant was preferable for high conversion and selectivity.

This work was supported by the Center for Photonic Materials and Devices at Chonnam National University and KRF-2007-412-J02002.

References

1 D. H. R. Barton, *Chem. Soc. Rev.* **1996**, *25*, 237.
2 M. J. Perkins, *Chem. Soc. Rev.* **1996**, *25*, 229.
3 H. W. Geluk, J. L. M. A. Schlatmann, *Tetrahedron* **1968**, *24*, 5361.
4 H. W. Geluk, J. L. M. A. Schlatmann, *Tetrahedron* **1968**, *24*, 5369.
5 A. Mazeaud, Y. Dromzee, R. Thouvenot, *Inorg. Chem.* **2000**, *39*, 4735.
6 B. J. S. Johnson, A. Stein, *Inorg. Chem.* **2001**, *40*, 801.
7 J. Wang, H.-O. Zhu, *Catal. Lett.* **2004**, *93*, 209.
8 P. Boarini, V. Carassiti, A. Maldotti, R. Amadelli, *Langmuir* **1998**, *14*, 2080.
9 T. Ohno, T. Mitsui, M. Matsumura, *J. Photochem. Photobiol., A* **2003**, *160*, 3.
10 H. Kominami, J. Kato, Y. Takada, Y. Doushi, B. Ohtani, S. Nishimoto, M. Inoue, T. Inui, Y. Ker, *Catal. Lett.* **1997**, *46*, 235.
11 J. R. Harbour, V. Chow, J. R. Bolton, *Can. J. Chem.* **1974**, *52*, 3549.

Published on the web (Advance View) September 6, 2008; doi:10.1246/cl.2008.1052