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Short communication

SHORT COMMUNICATION

***In situ* generated hypiodous acid in an efficient and heterogeneous catalytic system for the homo-oxidative coupling of thiols**

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Abstract: Supported hydrogen peroxide on polyvinylpyrrolidone (PVPP–H₂O₂), silica sulfuric acid ([SiO₂]–OSO₃H) and catalytic amounts of potassium iodide (KI) was developed as a heterogeneous medium for the rapid oxidative coupling of thiols into symmetrical homodisulfides. This oxidizing system proceeds under extremely mild conditions and gives no other oxidized side products.

Keywords: supported hydrogen peroxide on polyvinylpyrrolidone; potassium iodide; silica sulfuric acid.

INTRODUCTION

In recent years, supported reagents on polymeric structures have become increasingly popular in organic synthesis,^{1–5} because of their mild and heterogeneous nature together with advantages of easy work-up of the products. The conversion of thiols to the corresponding disulfides is an important and interesting transformation in organic chemistry due to the central importance of this functional group in diverse areas of chemistry and biology,^{6–11} and oxidation is the most common methodology used for their preparation because of the commercial availability of thiols. A variety of oxidants have been reported for the conversion of thiols into disulfides, such as tributylammonium halochromates/silica gel,¹² Fe(HSO₄)₃ or Fe(HSO₄)₃/DMSO,¹³ Al(NO₃)₃·9H₂O/[SiO₂]–OSO₃H,¹⁴ (C₃H₇)₃NH[CrO₃X], (X = F or Cl)/Al₂O₃,¹⁵ *N*-bromosuccinimide,¹⁶ poly(4-vinylpyridinium nitrate),¹⁷ H₂O₂/NaI,¹⁸ urea–hydrogen peroxide/maleic anhydride,¹⁹ ethylenebis(*N*-methylimidazolium) chlorochromate,²⁰ manganese(III)

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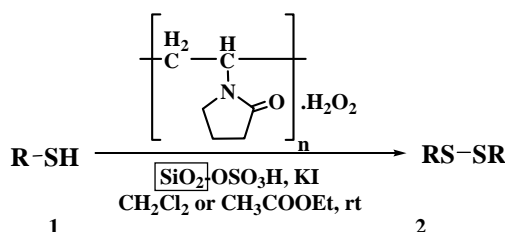
Schiff-base complexes,²¹ Au/CeO₂,²² Co(II) and Mn(II) salts of 4-aminobenzoic acid supported on silica gel²³ and Zn(II)–Al(III) double layer hydroxide with intercalated [Mo^{VI}O₂(O₂CC(S)Ph₂)₂]²⁻.²⁴ Some of these procedures suffer from one or more disadvantages, such as long reaction times, overoxidation, tedious work-up, low yields of the products, heavy metal contamination, harsh conditions, and expensive reagents or catalysts.

Hydrogen peroxide (H₂O₂) is a powerful oxidizing agent that has been used as an oxidant for the oxidation of different types of organic moieties,^{25,26} and in order to avoid the hazards connected with the use of concentrated solutions of hydrogen peroxide, this compound has been used supported on a carrier.^{25,27,28} In this regard, polyvinylpyrrolidone-supported hydrogen peroxide (PVPP–H₂O₂) has proved to be one of the most popular choices with its advantages of insolubility in organic solvents, easy work-up of products, non-toxic content and mild oxidizing properties. Therefore, it was decided to study the application of this polymeric reagent for the oxidative homocoupling of thiols in conjunction with silica sulfuric acid ($\text{[SiO}_2\text{]–OSO}_3\text{H}$) and catalytic amounts of potassium iodide (KI).

RESULTS AND DISCUSSION

In connection with an ongoing program related to the application of new reagents or reagent systems for organic functional group transformations,^{29–35} the preparation of polyvinylpyrrolidone-supported hydrogen peroxide (PVPP–H₂O₂) and its application to the synthesis of symmetrical disulfides from the corresponding thiols were considered of interest.

Therefore, in this study it was decided to design an efficient catalytic system including polyvinylpyrrolidone-supported hydrogen peroxide (PVPP–H₂O₂), silica sulfuric acid and potassium iodide (as catalyst) for the *in situ* generation of hypoiodous acid (IOH), as the active oxidant. A variety of aliphatic and aromatic thiols **1** were converted to the corresponding disulfides **2** using polyvinylpyrrolidone-supported hydrogen peroxide (PVPP–H₂O₂) and silica sulfuric acid ($\text{[SiO}_2\text{]–OSO}_3\text{H}$) in the presence of catalytic amounts of potassium iodide (KI) in dichloromethane or ethyl acetate (as solvent) at room temperature (Scheme 1). The results of this transformation are summarized in Table I.



Scheme 1. Oxidative coupling of thiols.

TABLE I. Oxidative coupling of thiols into disulfides using PVPP-H₂O₂ and [SiO₂]-OSO₃H in the presence of a catalytic amount of KI at room temperature

Entry	Substrate	Product ^a	Time, min	Yield, % ^b	Melting point, °C		Ref.
					Found	Reported	
1			40	99	55–58	59–61	34
2			15	99	91–93	89–92	17
3			1440	54 ^c	91–93	89–92	17
4			1440	91 ^d	91–93	89–92	17
5			60	86	288–292	273–285	17
6			30	99	40–43	39–42	17
7			30	83	–	–	19
8			30	97	93–98	84–88	17
9			40	95	174–177	177–179	17
10			40	99	135–138	141–144	17
11	HSCH ₂ CH ₂ OH	HOCH ₂ CH ₂ S–SCH ₂ CH ₂ OH	20	82	^e	/	34
12	HSCH ₂ COOH	HOOCCH ₂ S–SCH ₂ COOH	20	98	/	/	17

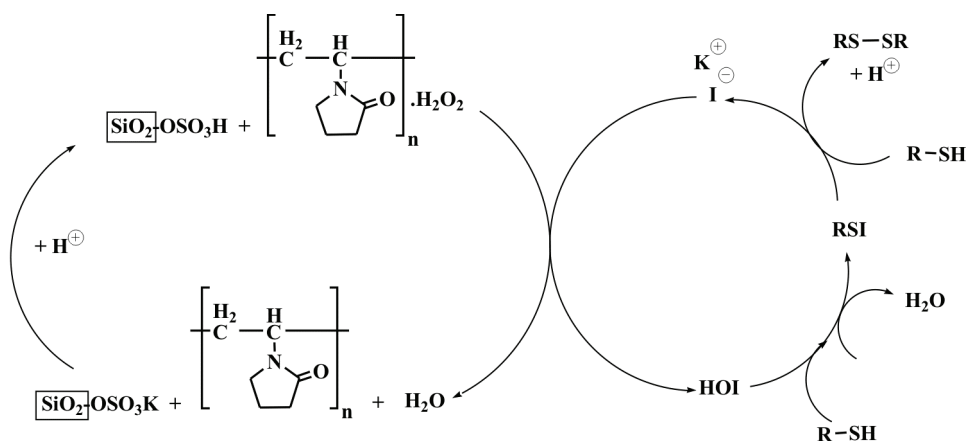
^aSubstrate/PVPP-H₂O₂/[SiO₂]-OSO₃H/KI = 1 mmol/0.175 g/0.1 g/0.02 mmol; ^bisolated yield; ^cin the absence of KI; ^din the absence of silica sulfuric acid; ^eoil

All of the coupling reactions were realized under completely heterogeneous conditions in which the product was easily obtained by simple filtration, washing the filtrate with an organic solvent and evaporation. Subsequent TLC and ¹H-NMR spectroscopic analysis of the residue in each case revealed purity to be > 95 %.

In order to demonstrate the role of potassium iodide as catalyst in the described system, it was decided to design a reaction in the absence of this compound. Therefore, 4-bromothiophenol was reacted with polyvinylpyrrolidone-supported hydrogen peroxide and silica sulfuric acid in the absence of potassium iodide. As is evident from Table I (entry 3), 1,2-bis(4-bromophenyl)disulfane was obtained in 54 % yield after 24 h, which is much less efficient than with the potassium iodide (15 min, 99 % yield). In addition, in order to study the role of the acid, 4-bromothiophenol (as a typical example) was subjected to oxidative coupling by PVPP-H₂O₂ and catalytic amounts of KI in the absence of silica sulfuric acid. In this case, it was observed that the reaction time was increased to 24 h and 1,2-bis(4-bromophenyl)disulfane was obtained in 91 % yield (Table I, entry 4). Thus, it was concluded that the presence of both the acid and potassium iodide was necessary for the rapid and efficient conversion of a thiol

into the corresponding disulfide by polyvinylpyrrolidone-supported hydrogen peroxide (PVPP-H₂O₂). A range of thiols were converted and a range of functional groups are chemoselectively tolerated (HO, CO₂H, heteroaromatic).

A plausible mechanism for this conversion is outlined in the catalytic cycle shown in Scheme 2 based on previously reported work.^{18,31,32,36} The key is the production of hypoiodous acid (HOI) as the active oxidant to form a sulfonyl iodide RSI as an intermediate. Coupling of this with another molecule of thiol produces the homodisulfide with formation of HI, which exchanges with the potassium salt of silica-sulfuric acid (Scheme 2) to regenerate KI. In this way, HI is not built up in the reaction.



Scheme 2. Mechanism of coupling of thiols by *in situ* generated iodine.

EXPERIMENTAL

Materials and methods

All chemicals and solvents were purchased from Fluka, Merck or Aldrich and were used without further purification. Polyvinylpyrrolidone-supported hydrogen peroxide (PVPP-H₂O₂) was prepared *via* the procedure reported by Pourali and Ghanei.^{37,38} Silica sulfuric acid was prepared *via* the procedure by reported Zolfigol.³⁹ All the prepared disulfides are known and were characterized by comparison of their spectral (IR, ¹H-NMR or ¹³C-NMR) and physical data with those of authentic samples.

General procedure for the oxidative coupling of thiols using PVPP-H₂O₂/[SiO₂]-OSO₃H/KI

To a suspension of polyvinylpyrrolidone-supported hydrogen peroxide (0.175 g), silica sulfuric acid (0.1 g) and potassium iodide (0.02 mmol) in dichloromethane or ethyl acetate (5 mL) was added a thiol (1 mmol), and the mixture was stirred at room temperature for the specified time (Table I). The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was filtered and the residue washed with CH₂Cl₂ (20 mL), (the residue of entry 5 was washed with ethanol). Finally, the organic solvent was evaporated and pure product was obtained as judged by TLC and ¹H-NMR spectroscopy.

CONCLUSIONS

In summary, it was demonstrated in this research that polyvinylpolypyrrolidone-supported hydrogen peroxide (PVPP-H₂O₂) is a practical and versatile oxidizing polymer, which is able to convert a variety of thiols into disulfides in the presence of an acid and iodide salt. The presence of silica sulfuric acid and potassium iodide was found to be critical for the conversion, and the isolation of the product was facile.

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ИЗВОД

IN SITU СТВАРАЊЕ ХИПОЈОДАСТЕ КИСЕЛИНЕ У ЕФИКАСНОМ ХЕТЕРОГЕНОМ КАТАЛИТИЧКОМ СИСТЕМУ ЗА ХОМО-ОКСИДАТИВНО КУПЛОВАЊЕ ТИОЛА

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Развијен је хетероген систем који садржи водоник-пероксид на поливинилполипириролидину (PVPP-H₂O₂), сумпорну киселину на силика-гелу ($[\text{SiO}_2]\text{-OSO}_3\text{H}$) и каталитичку количину калијум-јодида (KI). Овакав хетероген систем успешно генерише каталитичке количине хипојодасте киселине за брзо оксидативно купловање тиола до симетричних хомодисулфида. Оксидациони систем је ефикасан при благим реакционим условима и не производи друге споредне производе оксидације.

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REFERENCES

1. M. A. Karimi-Zarchi, B. F. Mirjalili, Z. Shamsi-Kahrizsangi, M. Tayefi, *J. Iran. Chem. Soc.* **7** (2010) 455
2. A. Ghorbani-Choghamarani, Z. Chenani, S. Mallakpour, *Synth. Commun.* **39** (2009) 4264
3. M. A. Chari, K. Syamasundar, *Catal. Commun.* **6** (2005) 67
4. N. Iranpoor, B. Tamami, K. Niknam, *Can. J. Chem.* **75** (1997) 1913
5. V. Mirkhani, M. Moghadam, S. Tangestaninejad, S. Hajibagheri, *J. Iran. Chem. Soc.* **7** (2010) 641
6. J. M. Herrmann, F. Kauff, H. E. Neuhaus, *Biochim. Biophys. Acta – Mol. Cell Res.* **1793** (2009) 71
7. B. A. Maron, Y. Y. Zhang, D. E. Handy, A. Beuve, S. S. Tang, J. Loscalzo, J. A. Leopold, *J. Biol. Chem.* **284** (2009) 7665
8. S. Fukuzawa, E. Shimizu, Y. Atsuumi, M. Haga, K. Ogata, *Tetrahedron Lett.* **50** (2009) 2374
9. Y. H. Seoa, K. S. Carroll, *Proc. Natl. Acad. Sci. USA* **106** (2009) 16163
10. C. Tidei, M. Piroddi, F. Galli, C. Santi, *Tetrahedron Lett.* **53** (2012) 232
11. D. Witt, *Synthesis* (2008) 2491
12. M. K. Mohammadi, S. Ghamamy, S. Zarrinabadi, M. H. Farjam, B. Sabayan, *Chin. J. Chem.* **28** (2010) 2199
13. H. Eshghi, M. Bakavoli, H. Moradi, A. Davoodnia, *Phosphorus Sulfur Silicon Relat. Elem.* **184** (2009) 3110

14. A. Ghorbani-Choghamarani, M. Nikoorazm, H. Goudarziafshar, B. Tahmasbi, *Bull. Korean Chem. Soc.* **30** (2009) 1388
15. A. Hassani-Joshaghani, S. Ghammamy, S. Bagi, A. Moghimi, Z. Javanshir, *Phosphorus Sulfur Silicon Relat. Elem.* **184** (2009) 164
16. H. Ghafari, M.M. Hashemi, *J. Sulfur Chem.* **30** (2009) 578
17. A. Ghorbani-Choghamarani, S. Sardari, *J. Sulfur Chem.* **32** (2011) 63
18. M. Kirihara, Y. Asai, S. Ogawa, T. Noguchi, A. Hatano, Y. Hirai, *Synthesis* (2007) 3286
19. B. Karami, M. Montazerzohori, M. H. Habibi, *Molecules* **10** (2005) 1358
20. R. Hosseinzadeh, M. Tajbakhsh, H. Khaledi, K. Ghodrati, *Monatsh. Chem.* **138** (2007) 871
21. H. Golchoubian, F. Hosseinpoor, *Catal. Commun.* **8** (2007) 697
22. A. Corma, T. Rodenas, M. J. Sabater, *Chem. Sci.* **3** (2012) 398.
23. M. M. Hashemi, Z. Karimi-Jaberi, *Monatsh. Chem.* **135** (2004) 41.
24. A. Cervilla, A. Corma, V. Fornes, E. Llopis, P. Palanca, F. Reyy, A. Ribera, *J. Am. Chem. Soc.* **116** (1994) 1595.
25. S. P. Mardur, G. S. Gokavi, *J. Iran. Chem. Soc.* **7** (2010) 441
26. A. Hasaninejad, M. A. Zolfigol, G. Chehardoli, M. Mokhlesi, *J. Serb. Chem. Soc.* **75** (2010) 307
27. M. A. Zolfigol, P. Salehi, S. E. Mallakpour, M. Torabi, *Bull. Chem. Soc. Japan* **76** (2003) 1673
28. B. Karimi, D. Zareyee, *J. Iran. Chem. Soc.* **5** (2008) S103
29. G. Chehardoli, M. A. Zolfigol, *Phosphorus Sulfur Silicon Relat. Elem.* **185** (2010) 193
30. A. Ghorbani-Choghamarani, M. Hajjami, H. Goudarziafshar, M. Nikoorazm, S. Mallakpour, F. Sadeghizadeh, G. Azadi, *Monatsh. Chem.* **140** (2009) 607
31. A. Ghorbani-Choghamarani, M. Abbasi, *Chin. Chem. Lett.* **22** (2011) 114
32. H. Goudarziafshar, A. Ghorbani-Choghamarani, M. Nikoorazm, Z. Naserifar, *Chin. J. Chem.* **27** (2009) 1801
33. A. Ghorbani-Choghamarani, M. Nikoorazm, H. Goudarziafshar, L. Shiri, Z. Chenani, *Bull. Korean Chem. Soc.* **30** (2009) 972
34. A. Ghorbani-Choghamarani, H. Goudarziafshar, S. Rezaee, S. S. Mortazavi, *Chin. Chem. Lett.* **20** (2009) 415
35. A. Ghorbani-Choghamarani, M. A. Zolfigol, M. Hajjami, S. Rastgoo, S. Mallakpour, *Lett. Org. Chem.* **7** (2010) 249
36. A. Ghorbani-Choghamarani, S. Sardari, *Chin. J. Catal.* **31** (2010) 1347
37. R. Ozenl, F. Aydin, *Monatsh. Chem.* **137** (2006) 307
38. A. R. Pourali, M. Ghanei, *Bull. Korean Chem. Soc.* **27** (2006) 1674
39. M. A. Zolfigol, *Tetrahedron* **57** (2001) 9509.