

Graphite oxide as an efficient solid reagent for esterification reactions

Maryam MIRZA-AGHAYAN^{1,*}, Rabah BOUKHERROUB², Mahshid RAHIMIFARD¹

¹Chemistry and Chemical Engineering Research Center of Iran (CCERCI), Tehran, Iran

²Institute of Interdisciplinary Research, Lille 1 University, Villeneuve d'Ascq, France

Received: 29.01.2014 • Accepted: 14.04.2014 • Published Online: 15.08.2014 • Printed: 12.09.2014

Abstract: Esterification of organic acids with alcohols under mild conditions in high yields using graphite oxide, a readily available and inexpensive material, as an effective reagent is described.

Key words: Acids, alcohols, esterification, graphite oxide, solid reagent

1. Introduction

Esters are a class of compounds widely distributed in nature. Esters encompass a large family of organic compounds with broad applications in medicine, biology, chemistry, and industry as plasticizers, solvents, perfumes, and flavor chemicals and also as precursors for a gamut of pharmaceuticals, agrochemicals, and other fine chemicals.¹

Esterification of alcohols by carboxylic acids using homogeneous acid catalysts is very well known.² However, the use of homogeneous acid catalysts for esterification like sulfuric acid and *p*-toluenesulphonic acid suffers from several drawbacks such as the occurrence of side reactions, corrosion of the equipment, and the need to deal with acidic wastes.³ The use of solid catalysts for chemical transformations has received increasing attention,^{4,5} and has the advantages of being easy to recover and reuse, as well as being compatible with environmental considerations.^{6–10}

Several authors have reported the utilization of solid acid porous materials such as zeolites,^{11–14} mesoporous materials,^{15,16} ion-exchange resins,¹⁷ and HO₃S-functionalized porous carbon^{18,19} for different reactions. For example, Amberlyst 15 is known as a catalyst with good properties in terms of its esterification efficiency.²⁰ Heteropoly acids (HPAs) supported on acid activated bentonite matrix (AT-GMB) act as stable solid acid catalysts for esterification of acetic acid with *n*-, *sec*-, and *tert*-butanol to produce their corresponding esters.²¹ More recently, Minakawa and co-workers have reported on the direct dehydrative esterification of alcohols and carboxylic acids with a macroporous polymeric acid catalyst at 50–80 °C after 12 h.²² Although most of the solid acid catalysts offer distinct advantages over conventional methods in terms of product separation and recycling, they suffer from certain drawbacks such as high cost, long reaction times, poor selectivity, and lower yields of the desired products.

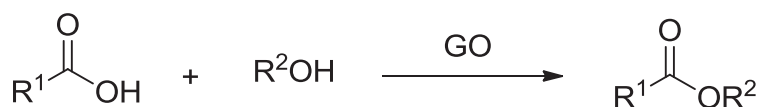
Graphite oxide (GO) has attracted much interest as a possible route for the large-scale production and manipulation of graphene,²³ a material with outstanding properties. GO and graphene oxide, prepared by exhaustive oxidation of graphite, have been explored as heterogeneous catalysts for various organic

*Correspondence: m.mirzaaghayan@ccerci.ac.ir

transformations.^{24–31} In spite of many successful examples of using GO or graphene oxide as a catalyst support in recent years,^{24–39} to the best of our knowledge there is still no report of using GO as an efficient solid acid catalyst.

2. Results and discussion

We previously reported that GO could be applied as an efficient oxidizing agent for the oxidative aromatization of Hantzsch derivatives.⁴⁰ More recently, we have shown the high performance of GO for oxidation of various alcohols into their corresponding aldehyde or ketone compounds under ultrasonic irradiation.⁴¹ In continuation of our investigation, herein we discuss the potential use of GO as a highly efficient reagent for the esterification of different carboxylic acids with various alcohols under mild conditions (Scheme).



Scheme. Esterification reaction of different carboxylic acids with various alcohols.

The GO utilized in this work was prepared according to a modified Hummers' method.^{41–44} The synthesized GO was characterized using UV/Vis spectroscopy, powder XRD, and FT-IR spectroscopy.^{24,41}

At an earlier stage of our work, the reaction of acetic acid (5 mmol), hexanol (5 mmol), and GO under different experimental conditions was examined with the aim to obtain the maximum yield of product. The results are presented in Table 1.

As indicated in Table 1, when the esterification of acetic acid with 1-hexanol was performed in absence of GO, the reaction was very slow and gave only 6% of the corresponding ester after 2 h at 90 °C (Entry 1, Table 1). It should be noted that hexyl acetate was obtained in only 25% yield when the reaction of acetic acid, 1-hexanol, and 5 mg of GO was carried out at 50 °C (Entry 2, Table 1). Increasing the amount of GO to 50 mg and the temperature to 90 °C led to a significant increase in the yield of the corresponding ester to 93% (Entry 3, Table 1). However, it seems that 5 mg of GO was sufficient for this reaction as hexyl acetate was obtained in 81% yield after 2 h at 90 °C (Entry 4, Table 1).

In a similar fashion, various acids such as acetic acid, propionic acid, and butyric acid reacted smoothly with primary and secondary aliphatic alcohols (1-hexanol, 1-pentanol, 1-decanol, 1-butanol, 2-pentanol, and cyclohexanol) or benzyl alcohol in the presence of GO at 90 °C to afford the corresponding ester derivatives (Table 1). Under these experimental conditions, the reaction of 5 mmol of acetic acid with 5 mmol of 1-pentanol in the presence of 5 mg of GO gave pentyl acetate in 80% yield (Entry 5, Table 1). Similarly, the reaction of acetic acid with 1-decanol or benzyl alcohol afforded decyl or benzyl acetate in 85% and 80% yield, respectively (Entries 6 and 7, Table 1). High yields were also obtained for the esterification of propionic acid with 1-hexanol or 1-butanol: 80% and 92% yield, respectively (Entries 8 and 9, Table 1). In a similar fashion, hexyl butyrate, butyl butyrate, and benzyl butyrate were synthesized in 80% yield under otherwise similar experimental conditions (Entries 10–12, Table 1). In the case of secondary alcohols such as 2-pentanol, the yield of esterification was low when the reaction was performed under conditions similar to those for primary alcohols. An increase in the GO amount (from 5 mg to 10 mg) was required to achieve good yields (Entries 13 and 14, Table 1). Similar behavior was observed for secondary cyclic alcohols such as cyclohexanol (Entries 15–19, Table 1). 2-Pentyl acetate, cyclohexyl propionate, and cyclohexyl butyrate were obtained in 73%, 81%,

Table 1. Esterification of various acids with different alcohols in the presence of GO as solid reagent.

Entry	Acid	Alcohol	Time (h)	Temperature (°C)	GO (mg)	Yield ^a (%)
1	acetic acid	1-hexanol	2	90	—	6
2	acetic acid	1-hexanol	2	50	5	25
3	acetic acid	1-hexanol	2	90	50	93
4	acetic acid	1-hexanol	2	90	5	81
5	acetic acid	1-pentanol	2	90	5	80
6	acetic acid	1-decanol	2	90	5	85
7	acetic acid	benzyl alcohol	2	90	5	80
8	propionic acid	1-hexanol	2	90	5	80
9	propionic acid	1-butanol	2	90	5	92
10	butyric acid	1-hexanol	3	90	5	80
11	butyric acid	1-butanol	3	90	5	80
12	butyric acid	benzyl alcohol	2	90	5	80
13	acetic acid	2-pentanol	3	90	5	43
14	acetic acid	2-pentanol	3	90	10	73
15	propionic acid	cyclohexanol	2	90	5	35
16	propionic acid	cyclohexanol	3	90	5	50
17	propionic acid	cyclohexanol	6	90	10	81
18	butyric acid	cyclohexanol	3	90	5	50
19	butyric acid	cyclohexanol	6	90	10	75
20	benzoic acid	1-hexanol	3	90	—	-
21	benzoic acid	1-hexanol	24	90	—	6
22	benzoic acid	1-hexanol	3	90	10	37
23	benzoic acid	1-hexanol	24	90	10	73
24	benzoic acid	1-pentanol	24	90	10	70
25	4-nitrobenzoic acid	1-hexanol ^b	24	90	10	89
26	4-nitrobenzoic acid	1-pentanol ^b	24	90	10	86

(a)The products in these reactions were analyzed by gas chromatography (Varian CP-3800) with a flame ionization detector (FID), and *n*-hexane was used as an internal standard. (b) For 5 mmol of acid 10 mmol of alcohol was used.

and 75% yield using 10 mg of GO as reagent after 3 h, 6 h, and 6 h, respectively (Entries 14, 17, and 19, Table 1).

Finally, we investigated the esterification reaction of aromatic acids such as benzoic and 4-nitrobenzoic acid with 1-hexanol or 1-pentanol. When the esterification of benzoic acid with 1-hexanol was performed in the absence of GO, the reaction was very slow and gave only 6% of the corresponding ester after 24 h at 90 °C (Entries 20 and 21, Table 1). Addition of 10 mg of GO to the reaction mixture led to the successful formation of hexyl benzoate in 73% yield after 24 h (Entry 23, Table 1). Similarly, the reaction of benzoic acid with 1-pentanol, and 4-nitrobenzoic acid with 1-hexanol or 1-heptanol gave the corresponding esters: pentyl benzoate, hexyl 4-nitrobenzoate, and pentyl 4-nitrobenzoate in 70%, 89%, and 86% yield after 24 h, respectively (Entries 24–26, Table 1). However, it should be noted that the esterification of aromatic acids needed a long reaction time and the yields were moderate.

Next, we examined the reusability of the GO for the esterification of acetic acid with 1-hexanol. After completion of the reaction, GO was removed by filtration. The GO was dried and reutilized for 3 consecutive

esterification reactions. The results in Table 2 indicate a loss of activity of the recycled GO after each reaction. Hexyl acetate was obtained in 81%, 39%, and 14% yield after the 1st, 2nd, and 3rd run, respectively (Table 2).

Table 2. Reusability of GO for the esterification of acetic acid with 1-hexanol.

Entry	Yield ^a (%)	Time (h)	Run
1	81	2	First
2	39	2	Second
3	14	2	Third

^aDetermined by GC. Reaction conditions: acetic acid (5 mmol), 1-hexanol (5 mmol), and GO (5 mg) at 90 °C.

3. Conclusion

The esterification reaction in the presence of a solid acid, GO, in a solvent-free system proved to be highly efficient on the investigated substrates. The esterification of aliphatic and aromatic acids with aliphatic and aromatic alcohols afforded the corresponding esters in the presence of GO. This method has several advantages as the reaction occurs in solvent-free conditions, and takes place in short reaction times and mild conditions. The yield was good for esterification of aliphatic acids with primary alcohol compounds. However, an increase in the amount of GO for secondary acyclic and cyclic alcohols was required to obtain comparable yields. The esterification of aromatic acids required a long reaction time and the yields were moderate. Furthermore, GO is a cost effective material that may be easily removed from the reaction mixture by simple filtration.

4. Experimental

4.1. General remarks

All compounds were obtained from Merck and used without further purification. GC/MS analysis was performed on a FISON GC 8000 series TRIO 1000 gas chromatograph equipped with a capillary column CP Sil.5 CB, 60 m × 0.25 mm ID. ¹H NMR spectra were recorded on a Bruker 80 spectrometer using TMS as internal standard.

4.2. Preparation of GO

Eight grams of graphite was added to a mixture of 14 mL of sulfuric acid (98%), 4 g of potassium persulfate, and 4 g of phosphorus pentoxide with stirring. The mixture was kept at 80 °C for 6 h. The resulting product was washed with water and dried. CAUTION: 8 g of preoxidized product was added to 180 mL of sulfuric acid (98%), followed by the slow addition of 24 g of potassium permanganate with the temperature maintained below 20 °C in order to avoid overheating and explosion. The temperature was increased to 35 °C and maintained for 2 h. Next 400 mL of water was added over 15 min. A further 1.1 L of water was added to dilute the solution, and 20 mL of hydrogen peroxide (30%) was added to the solution to quench the excess potassium permanganate. A brown solution was obtained and was washed with a 2-L solution of 1:10 hydrogen chloride (37%):water in order to remove metal ions and finally washed with 2 L of water. Dried GO was obtained by centrifugation followed by dehydration on a rotary evaporator under vacuum.^{41–44}

4.3. Typical procedure for esterification

To a solution of acid (5 mmol) and alcohol (5 mmol) was added GO (5 mg). The resulting mixture was stirred at 90 °C for the indicated time in Table 1 prior to GC analysis. The mixture was filtered and purified with

fractional distillation. The spectroscopic data of the obtained esters were compared with those of authentic samples.^{45–48}

References

- Zaidi, A.; Gainer, J. L.; Carta, G. *Biotechnol. Bioeng.* **1995**, *48*, 601–605.
- Patai, S. (Ed.), *The Chemistry of Carboxylic Acid and Esters*. Wiley: New York, NY, USA, 1969.
- Vogel, A. I.; Furniss, B. S. *Vogel's Textbook of Practical Organic Chemistry*. Longman: London, UK, 1989.
- Kantam, M. L.; Bhaskar, V.; Choudary, B. M. *Catal. Lett.* **2002**, *78*, 185–188.
- Liu, W.-T.; Tan, C.-S. *Ind. Eng. Chem. Res.* **2001**, *40*, 3281–3286.
- Collignon, F.; Loenders, R.; Martens, J. A.; Jacobs, P. A.; Poncelet, G. *J. Catal.* **1999**, *182*, 302–312.
- Kim, H.-J.; Kang, B.-S.; Kim, M.-J.; Kim, D.-K.; Lee, J.-S.; Lee, K.-Y. *Stud. Surf. Sci. Catal.* **2004**, *153*, 201–204.
- Kim, H.-J.; Kang, B.-S.; Kim, M.-J.; Park, Y. M.; Kim, D.-K.; Lee, J.-S.; Lee, K.-Y. *Catal. Today* **2004**, *93–95*, 315–320.
- Marchetti, J. M.; Miguel, V. U.; Errazu, A. F. *Fuel* **2007**, *86*, 906–910.
- Park, Y.-M.; Lee, D.-W.; Kim, D.-K.; Lee, J.-S.; Lee, K.-Y. *Catal. Today* **2008**, *131*, 238–243.
- Corma, A. *Chem. Rev.* **1995**, *95*, 559–614.
- Davis, M. E. *Nature* **2002**, *417*, 813–821.
- Liu, F.; Meng, X.; Zhang, Y.; Ren, L.; Nawaz, F.; Xiao, F.-S. *J. Catal.* **2010**, *271*, 52–58.
- Jones, C. W.; Tsuji, K.; Davis, M. E. *Nature* **1998**, *393*, 52–54.
- Melero, J. A.; van Grieken, R.; Morales, G. *Chem. Rev.* **2006**, *106*, 3790–3812.
- De Vos, D. E.; Dams, M.; Sels, B. F.; Jacobs, P. A. *Chem. Rev.* **2002**, *102*, 3615–3640.
- Barbaro, P.; Liguori, F. *Chem. Rev.* **2009**, *109*, 515–529.
- Hara, M.; Yoshida, T.; Takagaki, A.; Takata, T.; Kondo, J. N.; Hayashi, S.; Domen, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 2955–2958.
- Toda, M.; Takagaki, A.; Okamura, M.; Kondo, J. N.; Hayashi, S.; Domen, K.; Hara, M. *Nature* **2005**, *438*, 178–178.
- Park, J.-Y.; Kim, D.-K.; Lee, J.-S. *Bioresource Technol.* **2010**, *101*, S62–S65.
- Bhorodwaj, S. K.; Dutta, D. K. *Appl. Clay Sci.* **2011**, *53*, 347–352.
- Minakawa, M.; Baek, H.; Yamada, Y. M. A.; Wook Han, J.; Uozumi, Y. *Org. Lett.* **2013**, *15*, 5798–5801.
- Choi, W.; Lee, J.-W. *Graphene: Synthesis and Applications*; CRC Press: Boca Raton, FL, USA, 2011.
- Vijay Kumar, A.; Rama Rao, K. *Tetrahedron Lett.* **2011**, *52*, 5188–5191.
- Dreyer, D. R.; Jia, H.-P.; Bielawski, C. W. *Angew. Chem., Int. Ed.* **2010**, *49*, 6813–6816.
- Dreyer, D. R.; Bielawski, C. W. *Chem. Sci.* **2011**, *2*, 1233–1240.
- Jia, H.-P.; Dreyer, D. R.; Bielawski, C. W. *Tetrahedron* **2011**, *67*, 4431–4434.
- Jia, H.-P.; Dreyer, D. R.; Bielawski, C. W. *Adv. Synth. Catal.* **2011**, *353*, 528–532.
- Dreyer, D. R.; Jia, H.-P.; Todd, A. D.; Geng, J.; Bielawski, C. W. *Org. Biomol. Chem.* **2011**, *9*, 7292–7295.
- Dreyer, D. R.; Jarvis, K. A.; Ferreira, P. J.; Bielawski, C. W. *Polym. Chem.* **2012**, *3*, 757–766.
- Dreyer, D. R.; Jarvis, K. A.; Ferreira, P. J.; Bielawski, C. W. *Macromolecules* **2011**, *44*, 7659–7667.
- Xiong, Z.; Zhang, L. L.; Zhao, X. S. *Chem. Eur. J.* **2011**, *17*, 2428–2434.
- Zhang, H.; Lv, X.; Li, Y.; Wang, Y.; Li, J. *ACS Nano* **2010**, *4*, 380–386.
- Severin, N.; Kirstein, S.; Sokolov, I. M.; Rabe, J. P. *Nano Lett.* **2009**, *9*, 457–461.

35. Ide, Y.; Nakasato, Y.; Ogawa, M. *J. Am. Chem. Soc.* **2010**, *132*, 3601–3604.
36. Zhou, Y.-G.; Chen, J.-J.; Wang, F.-B.; Sheng, Z.-H.; Xia, X.-H. *Chem. Commun.* **2010**, *46*, 5951–5953.
37. Sutter, P. W.; Flege, J.-I.; Sutter, E. A. *Nat. Mater.* **2008**, *7*, 406–411.
38. Tang, Z.; Shen, S.; Zhuang, J.; Wang, X. *Angew. Chem., Int. Ed.* **2010**, *49*, 4603–4607.
39. Scheuermann, G. M.; Rumi, L.; Steurer, P.; Bannwarth, W.; Müllhaupt, R. *J. Am. Chem. Soc.* **2009**, *131*, 8262–8270.
40. Mirza-Aghayan, M.; Boukherroub, R.; Nemati, M.; Rahimifard, M. *Tetrahedron Lett.* **2012**, *53*, 2473–2475.
41. Mirza-Aghayan, M.; Kashef-Azar, E.; Boukherroub, R. *Tetrahedron Lett.* **2012**, *53*, 4962–4965.
42. Zhou, X.; Huang, X.; Qi, X.; Wu, S.; Xue, C.; Boey, F. Y. C.; Yan, Q.; Chen, P.; Zhang, H. *J. Phys. Chem. C* **2009**, *113*, 10842–10846.
43. Wang, Z.; Zhou, X.; Zhang, J.; Boey, F.; Zhang, H. *J. Phys. Chem. C* **2009**, *113*, 14071–14075.
44. Kovtyukhova, N. I.; Ollivier, P. J.; Martin, B. R.; Mallouk, T. E.; Chizhik, S. A.; Buzaneva, E. V.; Gorchinskiy, A. D. *Chem. Mater.* **1999**, *11*, 771–778.
45. Pouchert, C. J.; Behnke, J. *The Aldrich Library of ¹³C and ¹H FT NMR Spectra*; Vol. 1–3; Aldrich Chemical Company: Milwaukee, WI, USA, 1993.
46. Gowrisankar, S.; Neumann, H.; Beller, M. *Angew. Chem. Int. Ed.* **2011**, *50*, 5139–5143.
47. Won, J.-E.; Kim, H.-K.; Kim, J.-J.; Yim, H.-S.; Kim, M.-J.; Kang, S.-B.; Chung, H.-A.; Leeb, S.-G.; Yoon, Y.-J. *Tetrahedron* **2007**, *63*, 12720–12730.
48. Xue-Shun, J.; Hai-Long, W.; Qing, H.; Ling-Long, K.; Wei-He, Z. *J. Chem. Res.* **2006**, *2*, 135–138.