

# Acidic Activated Carbons: An Efficient Catalyst for the Epoxide Ring-Opening Reaction with Ethanol

Carlos J. Durán-Valle · Jesús A. García-Vidal

Received: 28 August 2008 / Accepted: 7 January 2009 / Published online: 23 January 2009  
© Springer Science+Business Media, LLC 2009

**Abstract** The epoxides (styrene oxide and 1,2-epoxyhexane) reaction with ethanol was carried out, catalysed with acidic activated carbons. The reactions were carried out under microwave irradiation. In the 1,2-epoxyhexane reaction, high yields were attained in some of the reaction conditions tested, although the regioselectivity was not high. For the styrene oxide reaction, the conversion was higher and the regioselectivity was high in most cases. For comparison, the reactions have been also performed in a batch reactor system under thermal activation.

**Keywords** Acidic carbons · Microwave irradiation · Epoxides · Ring-opening · Catalysis

## 1 Introduction

Activated carbons have been widely used in catalysis, although mainly as catalyst support [1]. Research carried out in recent decades about the chemistry and reactivity of activated carbon showed this is not an absolutely inert matter, their properties being able to be significantly modified. This allows to improve their application in different tasks, as is catalysis. In this way, they were at first being thought of just as a support for the active agent, while nowadays they are regarded as catalysts themselves.

Such materials are interesting for many reasons: they are heterogeneous catalysts which allow reducing energy consumption and solvents use in many reactions; they are

also easily handled, low contaminants, and those studied herein, of low cost. There is a significant opportunity to improve many of the chemical processes by replacing the current liquid-phase systems with acid-catalysts [2]. There are hardly any references on the use of activated carbons as catalysts in fine chemistry reactions, and most of them used basic carbons [3–5]. There are indeed references about the use of acidic activated carbons in environmental catalysis [6–8], but there are hardly any references on their use to obtain fine chemicals [9, 10].

Reactions of epoxides are key processes for the transformation of aliphatic and aromatic compounds. Epoxide ring-opening reactions are useful tools in organic chemistry [11, 12]. Epoxides used and  $\beta$ -alkoxy alcohols obtained are intermediates in organic [13–16] and inorganic [17, 18] synthesis. Also,  $\beta$ -alkoxy alcohols are used as solvents, as in silkscreen printing [19].

In this work, the epoxide ring-opening of styrene and 1,2-epoxyhexane when reacting with ethanol in the presence of acidic catalysts was studied.

## 2 Results and Discussion

### 2.1 Catalyst Characterization

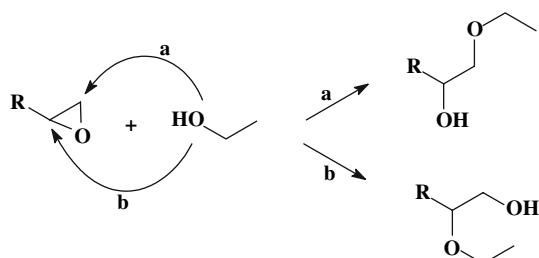
Table 1 shows the pH values for the catalysts. The pristine carbon, RX-1.5 EXTRA Norit, exhibits a slightly basic pH (7.4) behaviour. According to the treatment received, an increase in acidity was observed in the other carbons, being carbon B, the catalyst treated with sulfonitric mixture, the most acidic sample.

As can be observed, BET specific area is smaller for the treatment with sulfonitric mixture than that for the treatment with nitric acid only. The specific areas obtained were

C. J. Durán-Valle (✉) · J. A. García-Vidal  
Departamento de Química Orgánica e Inorgánica, Universidad de Extremadura, Avda. de Elvas s/n, E-06071, Badajoz, Spain  
e-mail: carlosdv@unex.es

**Table 1** Characterization of RX 1.5 EXTRA Norit and catalysts A and B

Sample	$S_{\text{BET}}$ ( $\text{m}^2 \text{ g}^{-1}$ )	pH
Norit RX 1.5	1,582	7.4
Catalyst A	1,523	3.9
Catalyst B	1,030	2.7

**Scheme 1** Reaction of epoxides with ethanol

very high, showing values higher than  $1,000 \text{ m}^2 \text{ g}^{-1}$  for all samples.

## 2.2 Catalytic Activity

When epoxides react with ethanol, two different reaction products can be obtained (Scheme 1).

Tables 2 and 3 show the results for the reactions carried out. When the reaction takes place with 1,2-epoxyhexane (**1**), 1-ethoxy-2-hexanol [**2** EI-MS:  $m/z$  87 (20%), 69 (100), 59 (74) and 41 (78)] is mainly obtained, while 2-ethoxy-1-hexanol (**3** EI-MS:  $m/z$  115 (51%), 87 (9), 69 (100), 61 (23) and 41 (71)) is obtained in a small proportion (Scheme 2). The less substituted carbon in the epoxide ring undergoes the attack in a higher extent. When the reaction was carried out with 1-butanol [9], however, the only product obtained was that resulting from the attack to the most substituted carbon.

**Table 2** Yields for the reaction of 1,2-epoxyhexane with ethanol (Microwave reactions)

Catalyst	Conditions			Yields (%)			Regioselectivity (%)
	Irradiation power (W)	Irradiation time (min)	Amount of catalyst (g)	<b>2</b>	<b>3</b>	Total	
A	900	5	0.100	10	3	13	77
		2	0.100	9	3	12	77
		5	0.050	7	2	9	78
	700	5	0.100	9	3	12	76
		5	0.100	7	2	9	76
	400	5	0.100	7	2	9	76
B	900	5	0.100	64	36	100	64
		2	0.100	62	38	100	62
		5	0.050	62	38	100	62
	700	5	0.100	59	36	95	62
		5	0.100	57	36	93	61
	400	5	0.100	57	36	93	61

Total yield obtained for catalyst B is quite higher than that obtained for catalyst A. For the former, a smaller yield was only found when using low irradiation power (400 year 700 W). The worst results for catalyst A were obtained when using a very low irradiation power (400 W) or when reducing the amount of catalyst (from 0.100 to 0.050 g). Reducing irradiation time or using medium power (700 W) did not modify notably the conversion. Regioselectivity values measured were very similar for all reactions carried out with the same catalyst (77% with catalyst A and 62% with catalyst B). Yields can be related with the acidity of catalysts (Table 1). Also, the most acid catalyst (B) can accelerate other reactions giving lower regioselectivity.

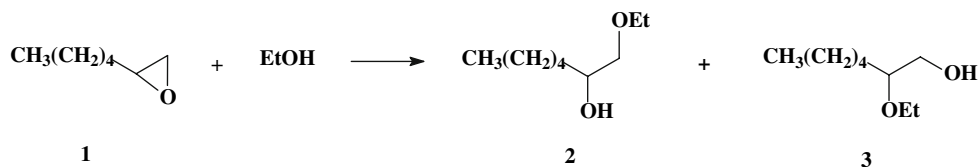
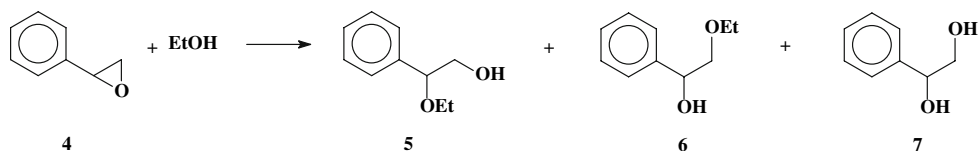
For the ethanol reaction with styrene oxide (**4**), four different compounds were found (Scheme 3):

- 2-Ethoxy-2-phenylethanol [**5** EI-MS:  $m/z$  135 (74%), 107 (73), 91 (15), 79 (100), 77 (50) and 51 (19)], resulting from the attack to the epoxide ring at the most substituted carbon, that—as in the reaction with 1-butanol [1] and opposite to the reaction of ethanol with 1,2-epoxyhexane—is the major product.
- 2-Ethoxy-1-phenylethanol [**6** EI-MS:  $m/z$  149 (4%), 121 (11), 103 (54), 91 (29), 75 (34), 65 (11) and 47 (100)], resulting from the attack of ethanol to the less substituted carbon in the epoxide ring. With catalyst A, this is either not detected or detected only as traces. With catalyst B, an amount between 2 and 6% was obtained, and thus this can be regarded as a minor compound.
- 1-Phenyl-1,2-ethanediol [**7** EI-MS:  $m/z$   $\text{M}^+$  (4%), 107 (100), 91 (6), 79 (81), 77 (66) and 51 (21)], resulting from the attack of a water molecule to the epoxide ring. This was always found in amounts lower than 3%.
- A product resulting from the attack of the hydroxyl group of 2-ethoxy-2-phenylethanol or 2-ethoxy-1-

**Table 3** Yields of reactions: styrene oxide with ethanol (Microwave reactions)

Catalyst	Conditions			Yields (%)			Regioselectivity (%)
	Irradiation power (W)	Irradiation time (min)	Amount of catalyst (g)	5	6	Total <sup>a</sup>	
A	900	5	0.100	90	0	92	99
		2	0.100	75	<1	85	88
		5	0.050	32	0	36	90
	700	5	0.100	92	<1	98	95
	400	5	0.100	55	0	79	70
B	900	5	0.100	92	3	99	93
		2	0.100	91	6	99	92
		5	0.050	93	2	99	94
	700	5	0.100	92	4	99	93
	400	5	0.100	82	4	98	84

<sup>a</sup> This includes the two products shown, and also 1-phenyl-1,2-ethanediol (**7**) (0–4%) and the product resulting from the reaction of styrene oxide with one of the product shown in the table

**Scheme 2** Reaction of 1,2-epoxyhexane with ethanol**Scheme 3** Reaction of styrene oxide with ethanol

phenylethanol to the epoxide ring in styrene oxide. The structure of this compound could not be precisely determined, and is not shown in Scheme 2. It's found in low quantities, except when irradiating at low power (400 W).

The yields were higher for catalyst B than for catalyst A, although they were high in most conditions tested. With catalyst A, the yield reduced in a high extent when reducing catalyst amount (36% of total conversion) and it reduced slightly when reducing irradiation time. For both catalysts, the yield reduced when using a 400 W irradiation. In this case, a strong reduction in regioselectivity was also observed, as previously stated (last paragraph). For this product, a 22% yield was found when using catalyst A and a 10% yield when using catalyst B. The results obtained when carrying out the reactions with thermal activation are shown in Tables 4 and 5.

For the reaction of ethanol with 1,2-epoxyhexane, the catalyst B was again the most active one, attaining a 100% conversion at 333 K in 1 h. The results obtained for catalyst A were similar to those obtained with microwave irradiation, and they were better when carrying out the

**Table 4** Yields for the reaction of 1,2-epoxyhexane with ethanol (Batch reactions)

Catalyst	Conditions		Yields (%)			Regioselectivity (%)
	Temperature (K)	Time (h)	2	3	Total	
A	298	1	6	1	7	81
		2	6	2	8	74
		3	7	2	9	81
		4	10	3	13	76
	333	1	17	5	22	76
		2	19	7	26	75
		3	22	8	30	74
		4	26	9	35	74
B	298	1	52	26	78	65
		2	56	26	82	68
		3	57	27	84	68
		4	59	28	87	68
	333	1	67	33	100	67

**Table 5** Yields of reactions: styrene oxide with ethanol (Batch reactions)

Catalyst	Conditions		Yields (%)			Regioselectivity (%)
	Temperature (K)	Time (h)	5	6	Total	
A	298	1	72	6	83 <sup>a</sup>	86
		2	80	3	87 <sup>a</sup>	90
		3	82	2	88 <sup>a</sup>	93
		4	84	2	91 <sup>a</sup>	93
B	298	1	93	5	98	95

<sup>a</sup> Besides both expected products, 1-phenyl-1,2-ethanediol (**7**) was found (4–6%)

reaction at 333 K. However, for catalyst B, irradiating with microwaves is better than carrying out the reaction at room temperature. The same conversion was attained when irradiating for 2 min than when heating at 333 K for 1 h. The regioselectivity found was similar to that obtained using microwave irradiation.

When styrene oxide reacts with ethanol at room temperature, high yields were attained (higher for catalyst B). The regioselectivity and the yield were similar to those obtained with reactions carried out under microwave irradiation, although a longer time was required to get a similar conversion degree. For catalyst A, a higher proportion of 1-phenyl-1,2-ethanediol was found, but the product resulting from the attack of the hydroxyl group in 2-ethoxy-2-phenylethanol or 2-ethoxy-1-phenylethanol to the epoxide styrene ring in styrene oxide was not found. For catalyst B, none of both by-products were found.

### 3 Experimental

#### 3.1 Catalysts Preparation and Characterization

To prepare the catalyst A, 3 g of activated carbon Norit was treated with 30 mL of commercial nitric acid, with constant agitation in a fume hood. The catalyst B was obtained in the same way, but in this case, using a sulfonitric mixture (1:1) instead of nitric acid. Both processes were carried out at room temperature for 90 min. Then, catalysts were washed-out with distilled water in a proportion of 50 mL per gram of activated carbon treated, for about 18 h. After that, the catalyst was dried in an oven for about 24 h at 110 °C. The catalysts were crushed to powder.

The pristine carbon and the two catalysts (A and B) were characterized as follows: the pH of the samples was measured using a Crison pH-meter, model MicropH 2002. The quantity used for this measure was 0.5 g of catalyst

suspended in 50 mL of water, at room temperature and for 72 h. The specific surface areas of the samples were determined by N<sub>2</sub> adsorption isotherms at 77 K, applying the BET method in a Micromeritics ASAP 2010 Volumetric System.

#### 3.2 Microwave-Activated Reactions

The reactions were carried out in a microwave oven. A microwave transparent, all-Teflon (PTFE) autoclave was used. The microwave equipment used in this work was a Moulinex CY3 microwave oven operated at a frequency of 2,450 MHz.

To carry out the reactions, 1 M epoxide solutions in ethanol were prepared. The catalyst (either 0.050 or 0.100 g) was placed inside the PTFE with 1 mL of the epoxide solution. Then, the PTFE autoclave was placed in the microwave oven (for either 2 or 5 min), at different powers (400, 700 or 900 W). After irradiation, samples were taken and filtered with a Swinney Millipore syringe with a Durapore 0.45 µm HV Millipore microfilter. The reaction was followed using a Konik KNK-3000-HRGC gas chromatograph (GC) equipped with a 60 m column (BP-1). Mass spectra of some samples were obtained on a Shimadzu GC-17A chromatograph with a QP-5000 mass detector. The reactivity was expressed in terms of the amount of products obtained, in mol%. Regioselectivity was expressed as the amount of main product divided by the amount of all final products.

#### 3.3 Thermal-Activated Reactions

Epoxide solution (1 M, 3 mL) in ethanol was heated (298 and 333 K) while stirring, in a batch reactor. Then, the catalyst was added (0.300 g) and the reaction time was set to start. Samples were taken at different times and treated following the same method as those in microwave-activated reactions.

### 4 Conclusions

Acidic activated carbons are efficient catalysts to obtain products with a high value added. The catalyst treated with sulfonitric mixture (B) is better than that treated with nitric acid (A). The catalyst's acidity is more important than its specific surface.

The use of microwave irradiation usually means a considerable saving in time and energy for this reaction.

Regioselectivity depends on several factors: the epoxide (better with styrene oxide than with 1,2-epoxyhexane), the alcohol (the regioselectivity when using ethanol is lower than that using 1-butanol) and the catalyst used (usually,

the most selective catalyst is the least active). But it does not depend on the method used for providing energy, or on the reaction conditions (temperature, amount of catalyst, reaction time, and, in most cases, irradiation power).

**Acknowledgments** Financial Support of this work by Spanish CICYT (project CTQ2004-00243/PPQ) is gratefully acknowledged. Norit pristine carbon has been kindly supplied by Norit Company.

## References

1. Rodríguez-Reinoso F (1998) *Carbon* 36:159
2. Corma A, García H (1997) *Catal Today* 38:257
3. Perozo-Rondón E, Calvino-Casilda V, Martín-Aranda RM, Casal B, Durán-Valle CJ, Rojas-Cervantes ML (2006) *Appl Surf Sci* 252:6080
4. Calvino V, Picallo M, López-Peinado AJ, Martín-Aranda RM, Durán-Valle CJ (2006) *Appl Surf Sci* 252:6071
5. Durán-Valle CJ, Fonseca IM, Calvino-Casilda V, Picallo M, López-Peinado AJ, Martín-Aranda RM (2005) *Catal Today* 107–108:500
6. Santiago M, Stüber F, Fortuny A, Fabregat A, Font J (2005) *Carbon* 43:2134
7. Huang H-H, Lu M-C, Chen J-N, Lee C-T (2003) *Chemosphere* 51:935
8. Stüber F, Font J, Fortuny A, Bengoa C, Eftaxias A, Fabregat A (2005) *Top Catal* 33:3
9. García-Vidal JA, Durán-Valle CJ, Ferrera-Escudero S (2006) *Appl Surf Sci* 252:P6064
10. Nevskaya DM, Martín-Aranda RM (2003) *Catal Lett* 87:143
11. Schneider C (2006) *Synthesis* 23:3919
12. Gracia R, Martínez M, Aracil J (1999) *Chem Eng Technol* 22:987
13. Kato N, Tomita D, Maki K, Kanai M, Shibasaki M (2004) *J Org Chem* 69:6128
14. Prestat G, Baylon C, Heck MP, Grasa GA, Nolan SP, Mioskowski C (2004) *J Org Chem* 69:5770
15. Bonini C, Chiummiento L, Pullez M, Solladie G, Colobert F (2004) *J Org Chem* 69:5015
16. Okazoe T, Watanabe K, Itoh M, Shirakawa D, Tatematsu S (2001) *J Fluorine Chem* 112:109
17. Pietrzykowski A, Skrok T, Pasynkiewicz S, Brzoska-Mizgalski M, Zachara J, Anulewicz-Ostrowska R, Suwinska K, Jerzykiewicz LB (2002) *Inorg Chim Acta* 334:385
18. Gärtner P, Letschnig M, Knollmüller M (2000) *Monatsh Chem* 131:867
19. Laitinen J, Liesivuori J, Harvima R (2006) *Toxicol Lett* 162:186