Catalysis Letters 33 (1995) 395–400

Photocatalytic oxidation of substituted toluenes with irradiated TiO_2 semiconductor. Effect of zeolite

Christine Bouquet-Somrani, Annie Finiels, Patrick Geneste, Patrick Graffin,
Alain Guida, Martine Klaver, Jean-Louis Olivé [1] and Ahmed Saaedan

Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique,
CNRS URA 418, Ecole Nationale Supérieure de Chimie de Montpellier,
8 rue de l'Ecole Normale, 34053 Montpellier Cedex 1, France

Received 17 January 1995; accepted 19 April 1995

Photocatalytic oxidation of substituted toluenes was investigated on irradiated TiO_2 and TiO_2 combined with HY_{15} and HY_{20} zeolites. In all cases the oxidation occurred in the first step exclusively on either one substituent or the other, but never on both simultaneously. In the presence of a zeolite, photooxidation conversion was higher than that obtained without zeolite.

Keywords: TiO_2; heterogeneous photocatalysis; oxidation; substituted toluenes; zeolites

1. Introduction

Heterogeneous photocatalysis, applied to the transformations of organic molecules, has become an exciting and rapidly growing area of research in the last few years.

The photocatalytic oxidation of alkylbenzenes and alkenylbenzenes has previously been reported [1,2]. The results concerning alkylbenzenes have shown a particular behaviour of toluene for which the reactivity was very low compared to longer chain monosubstituted benzenes [3].

In the literature, the heterogeneous photocatalytic oxidation of toluene [4–6] and 4-alkyltoluenes [7,8] (alkyl = methyl, ethyl, isopropyl or tert-butyl) have already been investigated over TiO_2 using different experimental conditions: liquid phase [4], without solvent [5,6] or gas phase [7] and for short irradiation times.

In this paper, we report investigations for the photocatalytic oxidation of 4-substituted toluenes compared to toluene, in liquid phase after prolonged irradiation times. As in the case of alkylbenzenes and alkenylbenzenes [1,2], the effect of a zeolite, an acid solid catalyst, added to TiO_2 on the oxidation of alkyltoluenes is also studied here.

---

[1] To whom correspondence should be addressed.

2. Experimental

Experiments were carried out with a Degussa P-25 TiO_2 (70% anatase and 30% rutile, specific surface area: $56\ m^2\,g^{-1}$, non porous). Organic substrates were reagent grade quality and employed as received. The zeolites used were HY type zeolites with different Si/Al ratios, 15 and 20 (HY_{15} and HY_{20}). The substrate (0.03 M) was added to a magnetically stirred TiO_2 (300 mg)-neat acetonitrile (360 ml) suspension and irradiated with a HPK 125 W mercury lamp ($\lambda = 330$ nm) as a central light source in a double-walled pyrex immersion well, surrounded with three similar lamps and cooled by water circulation. Samples were taken and analysed by FID gas chromatography (OV1-capillary column 25 m) and identified by GC-MS. In all cases obtained acids are not detected during irradiation time, but selectivity is calculated at the end of experiment and after evaporation of the solvent. When zeolite was employed, it was activated overnight at 400°C before use. This activated zeolite (300 mg) was added to the TiO_2–acetonitrile suspension.

3. Results and discussion

3.1. PHOTOCATALYTIC OXIDATION OF SUBSTITUTED TOLUENES OVER TiO_2

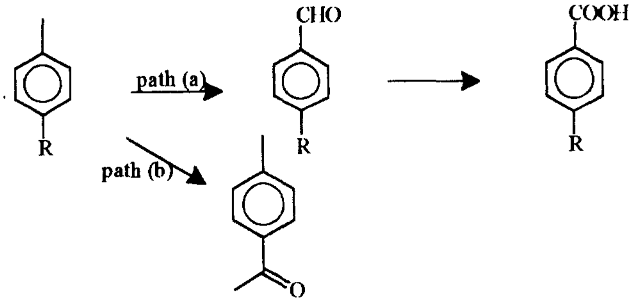
Photooxidations of various 4-substituted toluenes have been investigated. The results are reported in table 1. From consideration of this table, the following remarks can be made:

– In all cases, the initial step of the oxidation only affects side-chains on the aromatic nucleus.

– In the alkyltoluenes, two oxidation sites are possible: either the $-CH_3$ leading to the corresponding alkylbenzaldehydes which overoxidise into alkylbenzoic acids consecutively; or the para-alkyl group leading to the corresponding α-ketone. The oxidation never occurs on the two sites simultaneously on the same molecule.

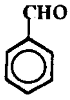
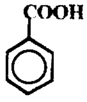
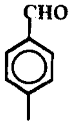
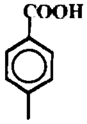
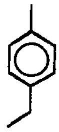
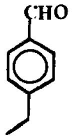
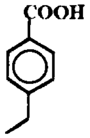
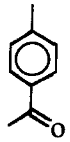
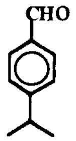
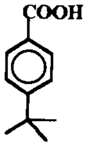
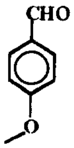
– The concentration profiles in the case of ethyltoluene disparition and formation of para-methylacetophenone and para-ethylbenzaldehyde are represented in fig. 1 for an example.

– According to this time course, the reaction scheme for alkyl toluenes oxidation may be the following:



R = H, CH_3, C_2H_5, i.C_3H_7, t.C_4H_9

Table 1
Selectivity of main photogenerated products by conversion at 48 h of various substrates

Substrate	Conversion (%)	Selectivity of main photogenerated products [a] (%)					
	30		12		33.5		
	50		40		20		
	63		12		19		33
	47		21.5		21.5		10.5
	30		60		7		
	75		60		13.5		

---

[a] In all cases, it can be noted that there are photodegradation of compounds (formation of CO_2 detected by conductimetry, about 10–15%) and adsorption of substrate and products onto surface of the solid particles, in the order of 8% (related to the substrate). Selectivity in acids is calculated at the end of experiment and evaporation of the solvent.

– The formation of benzoic acid, from benzaldehyde, could be explained by the autooxidation of benzaldehyde by direct reaction with molecular oxygen, which is very well known [9] and observed by Pichat et al. [7].

– These authors [7,8] also reported that only the $-CH_3$ group of 4-alkyltoluene was oxidised and consequently only the path (a) is proposed by these authors. For example, at room temperature and in liquid phase, the 4-tert-butyltoluene oxidation is very selective in 4-tert-butylbenzaldehyde; the tert-butyl group is not oxi-

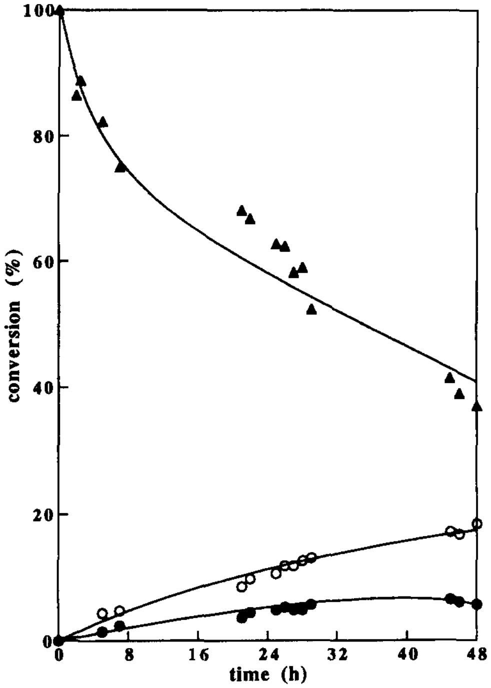


Fig. 1. Plots showing the disparition of para-ethyltoluene (▲) and formation of para-methylacetophenone (○) and para-ethylbenzaldehyde (●) versus reaction time.

dised [8]. Identical conclusions have been previously obtained by the same authors in the gas phase photocatalytic oxidation of 4-ethyl- and isopropyltoluenes.

In our experiments, we have followed the reaction up to 48 h. It was verified that the production of para-methylacetophenone does not occur in the absence of a semiconductor and consequently the path (b) is photocatalytic.

– As can be seen in table 2, the conversion increases from toluene, to *p*-xylene, to *p*-methoxytoluene. This result could be explained by considering the electron-donating substituent effect. This assumption is in agreement with the results reported by Baciocchi et al. [10] for the toluene, *p*-xylene and *p*-methoxytoluene photooxygenation. Better yields are obtained with more electron-rich substrates; that means, there is an increasing positive charge on the reaction center. This is then an argument in favour of the oxidation mechanism proposed (radical cation) in our previous papers [1,2] for alkylbenzenes.

Table 2
Influence of the electron-donating substituent effect on the conversion

Para substituent	σ_p^+	Conversion (%)
$-H$	0	30
$-CH_3$	−0.3	50
$-O-CH_3$	−0.78	75

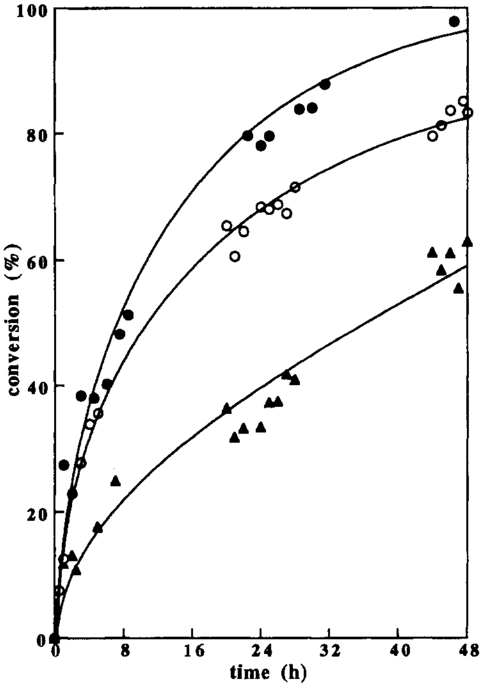


Fig. 2. Conversion of para-ethyltoluene versus reaction time over TiO_2 (▲) and both TiO_2/HY_{15} (○) and TiO_2/HY_{20} (●).

– For substrates having similar donor effect substituents (methyl, ethyl, isopropyl and tert-butyl, $\sigma_p^+ \approx -0.3$), it seems that two other factors could simultaneously occur on the reactivity: (i) The stability of the intermediate radical cation which leads to *p*-ethyltoluene more reactive than *p*-xylene more reactive than tert-butyltoluene. (ii) However, this only factor does not explain the higher reactivity of *p*-ethyltoluene compared to isopropyltoluene (secondary carbocation/tertiary carbocation). In this case, hyperconjugation [11] which needs parallel orientation of the σ-orbital of the C–H bond with p-orbitals of the aromatic ring could explain this result. The tertiary hydrogen on the isopropyl group is located in the node plane of the benzene ring where its interaction with the π system is minimized. On the other hand, the secondary hydrogens on the ethyl group can rotate more freely and consequently the probability to have an hydrogen nearly perpendicular to the ring plane is important.

3.2. PHOTOCATALYTIC OXIDATION OF SUBSTITUTED TOLUENES OVER BOTH TiO_2 AND ZEOLITE

Addition of the acidic zeolite (HY_{15} or HY_{20}) leads to an increased yield in both cases, for all the substrates. The selectivity in the different products is not changed. This effect seems to be related to the influence of the acidity on the reaction mechanism as in the case of alkylbenzenes [1,2]. For example, fig. 2 compares the conversion of *p*-ethyltoluene versus reaction time over TiO_2 and over both TiO_2 and zeolite.

4. Conclusion

Our results show that the electronic density on the reaction center and the hyperconjugative effect could play an important role in the oxidation rate of the studied substituted toluenes.

The addition of zeolites confirms our previous results, i.e. the oxidation rate is dependent on the acidity of the reaction mixture.

References

[1] O. Beaune, A. Finiels, P. Geneste, P. Graffin, J.L. Olivé and A. Saaedan, J. Chem. Soc. Chem. Commun. (1992) 1649.

[2] O. Beaune, A. Finiels, P. Geneste, P. Graffin, A. Guida, J.L. Olivé and A. Saaedan, in: *Heterogeneous Catalysis and Fine Chemicals III*, Studies in Surface Science and Catalysis, Vol. 78, eds. M. Guisnet, J. Barbier, J. Barrault, C. Bouchoule, D. Duprez, G. Pérot and C. Montassier (Elsevier, Amsterdam, 1993) p. 401.

[3] A. Saaedan, Doctoral Thesis, Ecole Nationale Supérieure de Chimie de Montpellier, Université de Montpellier, France (1992).

[4] M. Fujihira, Y. Satoh and T. Osa, Chem. Lett. (1981) 1053.

[5] M. Fujihira, Y. Satoh and T. Osa, J. Electroanal. Chem. 126 (1981) 277.

[6] J.A. Navio, M. Garcia Gomez, A. Pradera Adrian and J. Fuentas Mota, in: *Heterogeneous Catalysis and Fine Chemicals II*, Studies in Surface Science and Catalysis, Vol. 59, eds. M. Guisnet, J. Barrault, C. Bouchoule, D. Duprez, G. Pérot, R. Maurel and C. Montassier (Elsevier, Amsterdam, 1991) p. 445.

[7] M.N. Mozzanega, J.M. Herrmann and P. Pichat, Tetrahedron Lett. (1977) 2965.

[8] P. Pichat, J. Disdier, J.M. Herrmann and P. Vaudano, Nouv. J. Chim. 10 (1986) 548.

[9] N.S. Isaacs, *Reactive Intermediates in Organic Chemistry* (Wiley, New York, 1974).

[10] E. Baciocchi, G.C. Rosato, C. Rol and G.V. Sebastiani, Tetrahedron Lett. 33 (1992) 5437.

[11] A. Onopchenko, J.G.D. Schulz and R. Seekircher, J. Org. Chem. 37 (1972) 1414.