This article was downloaded by: [Tomsk State University of Control Systems and Radio]
On: 18 February 2013, At: 13:27
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Application of Metal Nitrate Gic AS Nitration Reagent for Aromatic Compounds

E. Stumpp [a] & S. Ebinal [a]

[a] Technische Universität Clausthal, Institut für Anorganische und Analytische Chemie, Paul-Ernst-Str. 4, D-38670, Clausthal-Zellerfeld, GERMANY

Version of record first published: 23 Oct 2006.

To cite this article: E. Stumpp & S. Ebinal (1994): Application of Metal Nitrate Gic AS Nitration Reagent for Aromatic Compounds, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 245:1, 207-212

To link to this article: http://dx.doi.org/10.1080/10587259408051690

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever

caused arising directly or indirectly in connection with or arising out of the use of this material.

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:27 18 February 2013

Mol. Cryst. Liq. Cryst. 1994, Vol. 245, pp. 207–212
Reprints available directly from the publisher
Photocopying permitted by license only
© 1994 Gordon and Breach Science Publishers S.A.
Printed in the United States of America

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:27 18 February 2013

APPLICATION OF METAL NITRATE GIC AS NITRATION REAGENT FOR AROMATIC COMPOUNDS

E. STUMPP AND S. EBINAL
Technische Universität Clausthal, Institut für Anorganische und Analytische Chemie, Paul-Ernst-Str.4, D-38670 Clausthal-Zellerfeld, GERMANY

ABSTRACT Hitherto, certain metal nitrates were used as nitrating reagents for aromatic compounds. In this work $Zr(NO_3)_4$-GIC was used as nitrating reagent for toluene and phenol in different solvents to give the nitro products in various yields. The reaction products were separated and identified by gas chromatography. The GICs were examined by X-ray diffraction and thermogravimetric analysis. Depending on the solvent, the $Zr(NO_3)_4$-GIC showed a different reactivity towards the aromatic compounds .

INTRODUCTION

A variety of GICs has been used as reagents or catalysts in preparative chemistry[1]. The use of graphite nitrate and N_2O_5-graphite as nitrating reagents was already studied in a previous work [2]. The nitration of aromatic compounds with metal nitrates was studied in 1925 [3] and meanwhile various metal nitrates were used as nitrating reagents [4-6] to obtain the nitroproducts, sometimes in high yields and high selectivity. The nitration of aromatic compounds with $Zr(NO_3)_4$ in carbon tetrachloride was studied by Coombes and Russel[4]. They found an isomer distribution similar to conventional nitration. In this work the behaviour of $Zr(NO_3)_4$-GICs towards toluene and phenol in different solvents was investigated.

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:27 18 February 2013

EXPERIMENTAL

Preparation of $Zr(NO_3)_4$-GICs

The $Zr(NO_3)_4$-GICs were prepared by the reaction of anhydrous $Zr(NO_3)_4$ (resulting from the reaction of anhydrous $ZrCl_4$ with N_2O_5) [7,8] and graphite flakes (100-200μ) for 4 days at 100 °C. The required oxidizing reagent was $Zr(NO_3)_4$ itself or an excess of N_2O_5. The GICs were then washed with dilute nitric acid and acetone. The resulting $Zr(NO_3)_4$-GICs proved to be third stage samples with an interlayer distance of about 1783 pm. Despite of invariable reaction conditions the intercalate content was found to vary between $C_{36.6}Zr(NO_3)_{3.96}$ and $C_{46}Zr(NO_3)_{4.1}$. In some cases the chemical analysis of the GIC shows a nitrate : zirconium ratio lower than 4 which could be traced back to the partial formation of ZrO_2.

Reaction with the aromatics

The nitration reactions were carried out in a closed bulb at a temperature of 60 °C by adding 0.75 g GIC to a solution of the aromatic compound (215 mg respectively) in 5 ml solvent (nitromethane, carbon tetrachloride and without any solvent in the case of toluene). After stirring for 7 to10 days, the reaction was stopped, the GIC was separated from the reaction mixture by filtration and washed with the solvent and acetone. The reaction products were analyzed by gas chromatography (capillary columns: BP10 and HT5). When nitromethane was used as the solvent the formation of nitrogen oxides was observed. The resulting reaction mixture proved to consist partly of fine divided graphite. It was not possible to remove this part of graphite completely from the reaction mixture not even by filtration with a blue ribbon filter paper.

RESULTS AND DISCUSSION

Nitration of toluene and phenol

The reaction of $Zr(NO_3)_4$-GIC with toluene and phenol leads to the nitro products in an appreciable amount only when using nitromethane as the solvent. In carbon tetrachloride only an insignificant nitration reaction was observed. The results are given in Table 1. The isomer distributions were similar to those resulting from conventional nitration, which indicates an electrophilic substitution reaction of the aromatics with the $Zr(NO_3)_4$-GIC. During the reaction of the aromatics in nitromethane, the amount of obtained nitro products was determined at appointed time intervals.

The resulting course is represented in Figure 1 and shows an initial increase in both cases. The initial rate of reaction and the yield of nitro products depend on the amount of the intercalated metal nitrate.

TABLE 1: Nitration of toluene and phenol with $Zr(NO_3)_4$-GIC

Aromatics/solvent	nitromethane	CCl_4	none
Toluene	ortho: 53.%	no significant	main product:
	meta: 4,6%	reaction	benzaldehyde
	para: 42.4%		
	Yield*: 9,7 %		
Phenol	ortho: 50-54 %		
	para: 46-50 %	< 5% nitro	
	yield*: 36%	products	

*Averaged values

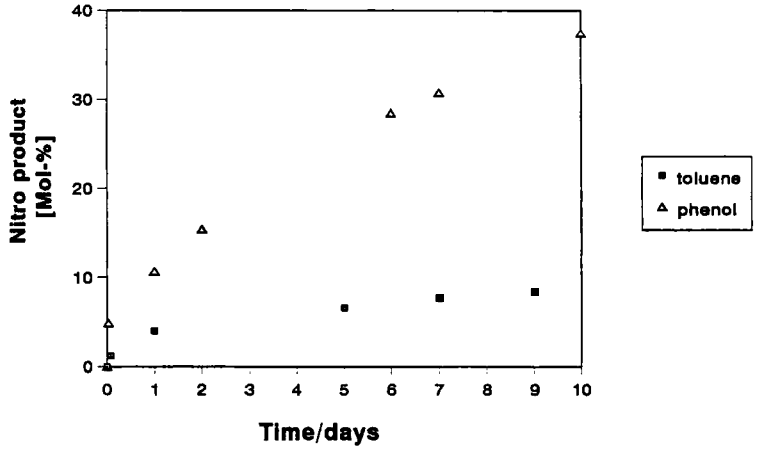

FIGURE 1: Course of the reaction of $Zr(NO_3)_4$-GIC with toluene and phenol

Coombes and Russell investigated the reaction of $Zr(NO_3)_4$ with aromatic and heteroaromatic compounds [4] and found high yields of the nitro products, in good aggreement with the reactions observed by Field and Hardy [9]. According to these results $Zr(NO_3)_4$-GIC should nitrate aromatics, however with less reactivity.

In contrast to this, the GIC was found to be stable towards toluene and phenol

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:27 18 February 2013

in carbon tetrachloride and to react with the aromatics only in nitromethane with its simultaneous destruction. Nitromethane is a solvent known to intercalate into GICs. Furthermore it is a good solvent for $Zr(NO_3)_4$. When the GIC was stirred in nitromethane without any aromatics under reaction conditions, the formation of NO_x was observed, indicating a partial decomposition of the $Zr(NO_3)_4$-GIC. Since nitromethane contains an acidic proton and Zr^{4+} is a strong Lewis acid, a reaction mechanism according to the following equation could be assumed:

$$Zr(NO_3)_4 + x\,H_3C\text{-}NO_2 \longrightarrow \underset{(I)}{Zr(NO_3)_{(4-x)}\text{-}(CH_2NO_2)_x} + xHNO_3 \quad (1)$$

This assumption is supported by the fact that the corresponding solutions as well as solutions of $Zr(NO_3)_4$ in nitromethane are acidic, in contrast to pure nitromethane. A similar reaction was investigated by Bauer and Foucault [9]. They found that hydrochloric acid was formed upon the reaction of the Lewis acid $AlCl_3$ with nitromethane . The formation of nitrogen oxides in the reaction above could occur by decomposition of the zirconium-nitromethane complex (I) to ZrO_2, NO_x and nitromethane derivatives.

Based on these considerations we suppose that during the reaction in nitromethane, HNO_3 formed according to equation (1) nitrate toluene and phenol. This could explain the low yields of nitrotoluenes and nitrophenols in comparison with conventional nitration reagents.

X-ray studies and thermogravimetric measurements

Upon the reaction with the aromatics in nitromethane one part of the $Zr(NO_3)_4$-GIC was disintegrated, whereas the other part still showed the original X-ray reflections. The X-ray diffraction of the original $Zr(NO_3)_4$-GIC is illustrated in Figure 2.

The thermogravimetric measurements were carried out in an oxygen stream to prevent sublimation of $Zr(NO_3)_4$, so that at approximately 400 °C the oxidation of graphite started. The resulting curve (Figure 3) shows a small weight loss at about 88 °C (1), which could correspond to the deintercalation of an excess of nitrate. The decomposition of the GIC (2) occurs at about 220 °C. The following step (3) was not found in all samples.

The chemical analysis (pyrohydrolysis followed by standard Kjeldahl technique) demonstrates that the nitrate content of the GIC equals the weight loss found upon thermal decomposition till 260°C.

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:27 18 February 2013

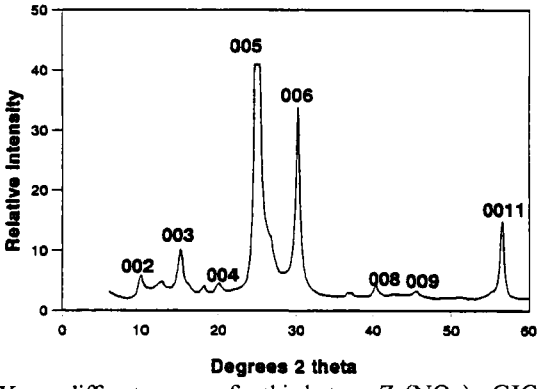

FIGURE 2: X-ray diffractogram of a third stage $Zr(NO_3)_4$-GIC (d_i =1783 pm)

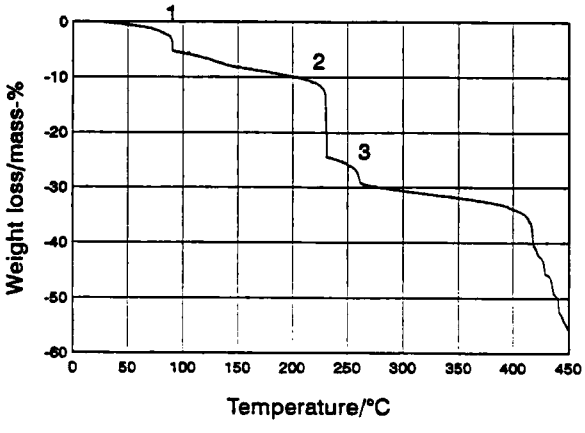

FIGURE 3: Thermogravimetric curve of a third stage $Zr(NO_3)_4$-GIC

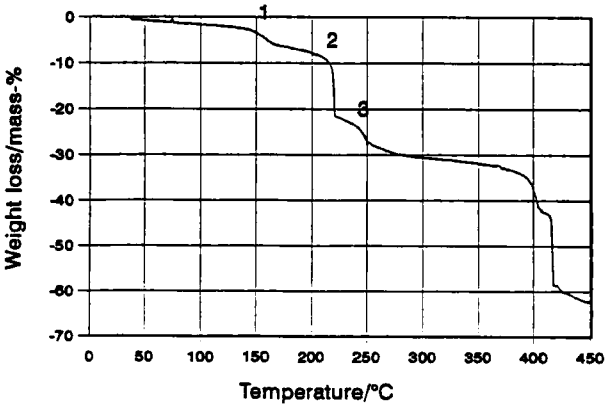

FIGURE 4: Thermogravimetric curve of the $Zr(NO_3)_4$-GIC after stirring in nitromethane under reaction conditions

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:27 18 February 2013

The X-ray reflections of the GIC treated with nitromethane under reaction conditions were similar to that of the pristine GIC, whereas the thermogravimetric curve (Figure 4) shows a further decomposition reaction beginning at about 150 °C (1) which could correspond to the deintercalation of nitromethane.

TABLE 2: Results of the chemical analysis of the GICs

GIC	Aromatic	Solvent	GIC after reaction
$C_{36.4}Zr(NO_3)_{3.96}$		nitromethane	$C_{39.1}Zr(NO_3)_{3.6}$ *
$C_{46}Zr(NO_3)_{4.1}$		"	$C_{51.5}Zr(NO_3)_{3.24}$
$C_{46}Zr(NO3)_{4.1}$	toluene	"	$C_{50.9}Zr(NO_3)_{3.45}$
$C_{40.4}Zr(NO3)_{4.1}$	toluene	"	$C_{47.7}Zr(NO_3)_{3.2}$
$C_{44.5}Zr(NO3)_{4.2}$	phenol	"	$C_{51.8}Zr(NO_3)_{3.2}$
$C_{36.4}Zr(NO3)_{3.96}$	phenol	"	$C_{40.8}Zr(NO_3)_{3.6}$

* The total nitrate content of the samples includes the small amount of cointercalated nitromethane

By chemical analysis of the GICs treated with nitromethane a lower zirconium content as well as a lower nitrate content compared with the starting GIC were found. The amount of nitrate was in a good agreement with the weight loss detected by thermogravimetric measurements till 250 °C. This observation was recognized in all treated samples.

REFERENCES

1. R. Setton, Synth .Met., 23, 467 and 519 (1988)
2. S. Ebinal, E. Stumpp, H.-J. Hummel and H.Griebel, Mat. Sci. Forum, 91-93, 787 (1992)
3. J.B. Menke, Rec. Trav. Chim, 44, 141 (1925)
4. R.G. Coombes and L.W. Russel, J. Chem. Soc. Perkin I, 1751 (1974)
5. D.W. Amos, D.A. Baines and G.W.Flewett, Tetrahedron Lett., 34, 3191 (1973)
6. J.-M. Poirier and C. Vottero, Tetrahedron, 45(5), 1415 (1989)
7. P. Scharff, E. Stumpp, C. Creutzburg and G. Nietfeld, Proc. Int. Coll. on Layered Compounds (Pont-à-Mousson) 65 (1988)
8. B. O. Field and C. J. Hardy, Proc. Chem. Soc., 76 (1962)
9. D. Bauer and A. Foucault, C. R. Acad. Sc. Paris, Ser. C, 272, 192 (1971)

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:27 18 February 2013