Selective oxidations by nitrosating agents
Part 2: Oxidations of alcohols and ketones over solid acid catalysts

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Abstract

The reactivity of a nitrosating agent (N_2O_3) on oxidations of alcohols and the methyl group of acetophenone were tested. Active electrophylic surface nitrosonium ions (NO^+) was detected on H_2SO_4/SiO_2 catalysts by Raman spectroscopy, suggesting a surface ionic mechanism of oxidation in agreement with the one proposed in acid aqueous solutions. Alcohols are selectively oxidized to ketones and aldehydes in high yield, useful for synthetic applications, at $25\,°C$ in 1,2-dichlorethane and using commercial sulfonated styrene divinyl benzene resins (Amberlyst 15®) as catalysts. In addition, nitrous acid ester has been observed as intermediates according to an ionic mechanism by surface NO^+. Under the same reaction conditions, acetophenone is selectively oxidized to benzoyl cyanide in high yield and selectivity. The comparison with oxidation carried out in aqueous solution of HNO_2, where benzoyl formic acid was obtained, suggests that the differences in the final products are likely due to the specific stabilizing effect of each solvent. Moreover, the reactivity of the intermediates isolated in aqueous systems implies that α-nitroso-acetophenone is a probable reaction intermediate also in aprotic heterogeneous systems.
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1. Introduction

In part 1, the selective oxidation of methyl and methylene groups of some enolizable ketones in aqueous acidic media has been reported [1]. For instance, benzoylformic acid from acetophenone and 1,2-cyclohexanedione from cyclohexanone are obtained in yields suitable for practical applications, employing HONO in aqueous sulfuric acid at $25\,°C$. The products are obtained in good yield only within selected acidity ranges, where activation of the reacting species by protonation, protonation–dehydration and ketoenol equilibria are occurring [1].

Since the early seventies, nitrogen oxides compounds (NO_x) have been studied mainly for their removal in gaseous emission (SCR $deNO_x$ process) rather then their oxidation properties [2]. Recently, a growing interest on nitrogen oxides as selective oxidant is due to the new process for phenol production by direct benzene oxidation [3]. In addition, the use of NO_x/O_2 mixture in catalysed gas phase nitration for environmentally benign nitro-aromatics syntheses increases the importance of these oxidants [4].

Heterogeneous gas/liquids reactions over solid catalysts give simplification in separation procedure and reduce environmental risks, compared to aqueous acid solutions. For instance, NO_x can be employed in organic solvents over solid acid catalysts instead of HONO in aqueous solutions; the latter reviewed in part 1 [1].

This paper deals with studies of non-aqueous solutions of the nitrosating species N_2O_3 in the presence of solid acid catalysts as selective oxidant for alcohols and ketones. The investigation of the surface moiety has been carried out to disclose the nature of the oxidant site in order relate the results

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with those obtained in aqueous solutions. The knowledge of the active species and their equilibria allows choosing the best conditions to attain desired products in high yield. However, the final aim of the work is the development of a versatile, selective and safe procedure for the oxidation of a large variety of substrates.

2. Experimental

2.1. Materials

Purified samples of SiO_2 (GRACE, 90 μm average particle size, 364 m^2/g (S_{BET}), 1.14 ml/g pore volume and 10 nm average pore diameter); TiO_2 (Fluka, 5 m^2/g (S_{BET}), 0.24 ml/g pore vol.); ZrO_2 (Fluka, 5 m^2/g (S_{BET}), 0.24 ml/g pore vol.); macroreticular sulfonated resin Amberlyst 15® (Aldrich, Amberlyst is a trade mark Rohm and Haas); H_2SO_4 95–97% (Riedel de Haen); H_3PO_4 85% RPE (Carlo Erba); CF_3SO_3H 99% (Acros); CH_3SO_3H 99% (Acros); *p*-toluenesulfonic acid monohydrate 98% (Aldrich); $NaNO_2$ P.A. (Fluka); $Ti(OPr)_4$ 98% technical (Fluka); $Zr(OPr)_4$ in isopropanol 70% P.A. (Fluka); $NaNO_2$ P.A. (Fluka); dichloromethane analar (BDH); 1,2-dichloroethane analar (BDH); ethanol analar (BDH). The starting ketones and alcohols (Aldrich) were purified by the appropriate procedure from commercially available products.

2.2. Preparations of solid acid catalysts

SiO_2–TiO_2 and SiO_2–ZrO_2 were prepared by polycondensation of $Ti(OPr)_4$ and $Zr(OPr)_4$ with H_2O over SiO_2; materials were obtained in EtOH employing a molar ratio $M/H_2O = 1/8$ (M = Ti or Zr) in the presence of a small amount of H_2SO_4.

Acid catalysts were prepared by mixing a known amount of solid materials with a known amount of aqueous acid solutions of appropriate concentrations. The slurries were stirred for 1 h, ca. and the surnatant solutions removed by filtration. The wet samples were dried at 105 °C in a stream of N_2 and stored in a dry apparatus.

2.3. Characterizations of solid acid catalysts

Acid percentage compositions of the catalysts were determined by automatic potentiometric titration against standard solutions of NaOH and checked before use. The milli-equivalents of $H^+/g_{catalyst}$ of the catalysts obtained are: $H_2SO_4/ZrO_2 = 0.8$; $H_2SO_4/TiO_2 = 0.9$; $H_3PO_4/SiO_2 = 1.7$; H_2SO_4/SiO_2–$TiO_2 = 2.1$; H_2SO_4/SiO_2–$ZrO_2 = 2.3$; $H_2SO_4/SiO_2 = 8.6$. Similarly, the total ion exchange capacity in NaOH of Amberlyst 15 was measured by back titration with standard solutions of HCl and is 4.7 meq $H^+/g_{catalyst}$.

The samples of H_2SO_4/SiO_2 were also characterized by additional procedures [5,6]. The surface layer of the catalyst has been characterized by XPS measurements; after pyridine chemisorption the investigation of the N_{1s} XPS band shows a single peak at 401.4 eV, highlighting only the presence of rather strong Broensted acid sites [7].

Surface area and pore size distribution of the samples were determined by nitrogen adsorption isotherm. Samples with different acid loading show a continuous decrease of the BET area as the amount of sulfuric acid loaded on the solids increases. The observed values are between 247 and 108 m^2/g for samples with acid loading between 3.31 and 5.07 mmol $H_2SO_4/g_{catalyst}$. In any case, pore size distribution is unaffected by H_2SO_4 loading and average pore diameter remains almost unchanged (9 nm, ca.). The BET surface area of Amberlyst 15® 15 is 37 m^2/g with an average pore diameter of 21 nm.

Studies by UV–vis spectroscopy, used for testing the protonation of weak bases (B), show that chloronitro- and chlorodinitro-anilines can be progressively converted to their conjugated acid (BH^+) by using H_2SO_4/SiO_2 increasing acid loading [5,6].

2.4. Solutions of N_2O_3: preparation and spectroscopic measurements in gas liquid and solid phase

2.4.1. Preparation

A known amount of sodium (or potassium) nitrite was mixed with a known volume of 1,2-dichloroethane (or methylene chloride) and the resulting slurry was stirred under nitrogen flow for 1 h, ca. in order to remove the dissolved oxygen. After cooling to 0 °C, the mixture was added drop-wise to an outgassed aqueous solution of sulfuric acid at 60%, obtaining a deep blue solution of N_2O_3 in the organic phase. The organic layer was separated from the acid phase, dried over anhydrous sodium sulfate and 4 Å molecular sieve, then used immediately or stored under liquid nitrogen. The bleu solution is stable for some hours at 25 °C in a stopped vessel.

2.4.2. IR spectra

The solutions of N_2O_3 in different solvent (methylene chloride, chloroform and 1,2-dichloroethane) were analyzed employing a Nicolet Magna 750 FTIR in a PTFE cell (optical length 1 mm) with CaF_2 windows. Samples of the vapour in equilibrium with the blue solution of N_2O_3 in methylene chloride, chloroform and in 1,2-dichloroethane at the pressure of 25 Torr and at 25 °C were also obtained after the usual freezing–thaw cycles. The spectra were recorded by a Bruker Vector 22 FTIR, in a cell (optical length 160 mm) with KBr windows. The spectral trends of the samples in aprotic solvents and in the gas phase are shown in Figs. 1–3.

2.4.3. Raman spectra

Small amounts of the catalysts (i.e. samples of H_2SO_4/SiO_2 with 2.1 mmol $H_2SO_4/g_{catalyst}$) were added in a quartz cell to a solution of N_2O_3 in 1,2-dichloroethane at 25 °C and the acidic mixture analysed by Raman. The Raman spectra were in the standard 90° geometry using an argon-ion laser operating at 488 nm, vertically polarized and
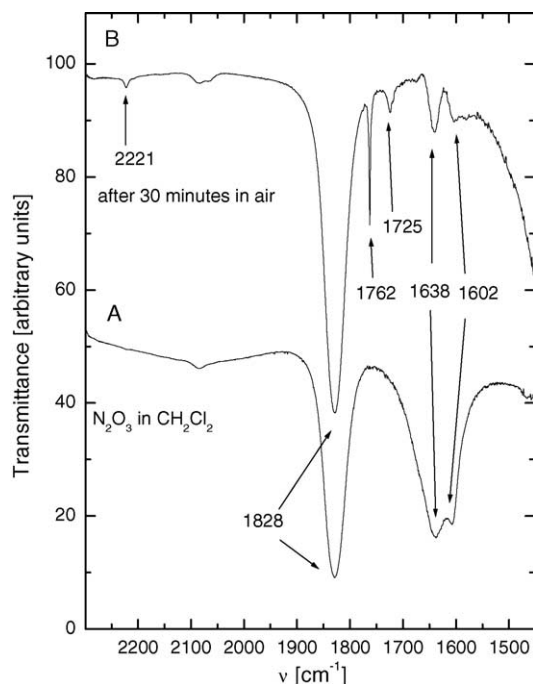
Fig. 1. Infrared spectra of N_2O_3 in dichloromethane.

kept at constant power (100 mW). The spectra were recorded by analysing the scattered light with polarization parallel to the one of the exciting beam. The signal was collected by a Jobin Yvon U 1000 double monochromator, and analysed by a photon-counting system. A resolution of $4\,cm^{-1}$ has been employed for all measurements. As already observed
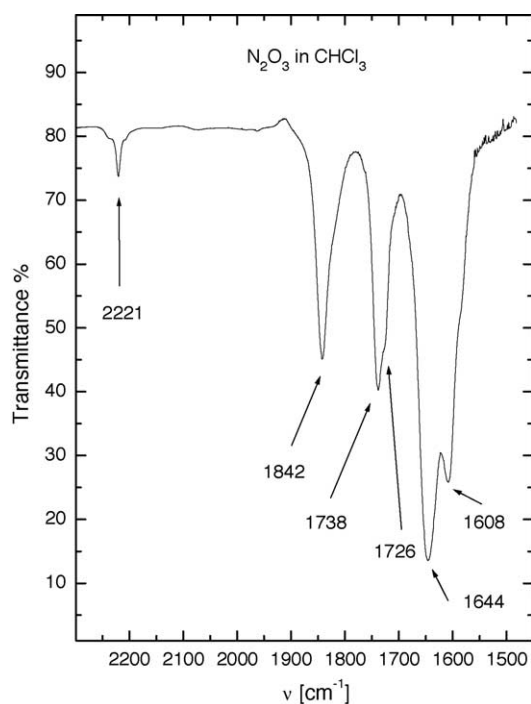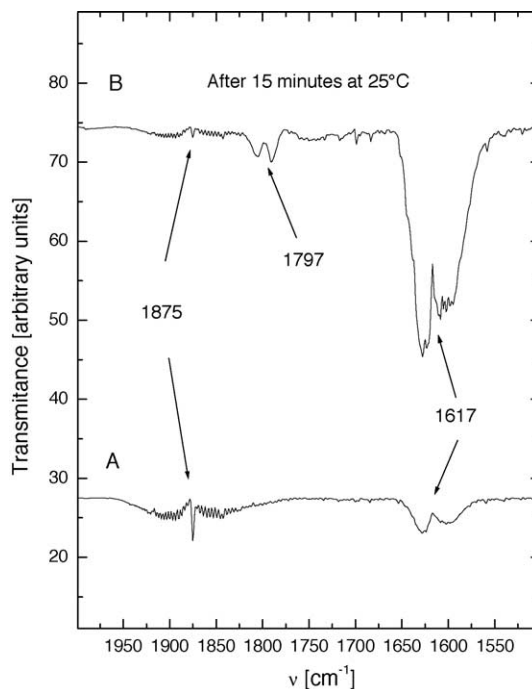

Fig. 2. Infrared spectra of N_2O_3 in chloroform.

Fig. 3. Gas phase infrared spectra of the vapor over the N_2O_3 solution in dichloromethane.

[8], strong luminescence of the solid samples was the main experimental difficulty which was strongly reduced in the presence of N_2O_3. The spectral trends of the nitrosating agent with and without catalyst are shown in Fig. 4.

2.4.4. Determination of the N_2O_3 concentration

The concentration of N_2O_3 (ca. $0.2\,mol\,l^{-1}$ of N_2O_3) was estimated by the molar extinction coefficient of N_2O_3 in 1,2-dichloroethane ($\varepsilon = 7.3\,l\,mol^{-1}\,cm^{-1}$, at $\lambda = 700\,nm$).

The unknown ε values of N_2O_3 in non-aqueous solvents were determined by extraction of the nitrosating agent with a titrated solution of sulfuric acid in the range where quantitative conversion $N_2O_3 \rightarrow NO^+$ (ca. 85%) occurs. In this way, the well-known UV–vis spectra of the aqueous solution of nitrosonium ions allow the determination of the unknown value of ε [9–13].

2.5. Oxidation of ketones and alcohols

The oxidations were performed at $25\,°C$ in a well-stirred thermostatted reactor containing weighted samples of solvent, reagents and catalysts. Aliquots of the solutions were drawn at different times and the samples, after dilution, analysed by HPLC using a Perkin-Elmer apparatus and a Lichrospher 100 (RP-18, $5\,\mu m$) column. At the end of the reaction the mixtures were also examined by GC (Agilent 6890) and GC–MS (HP 5890–5931) using an HP-5 capillary column ($300\,\mu m$, 30 m long). It is noteworthy that evolution of gas was observed during the course of reaction for every substrate.
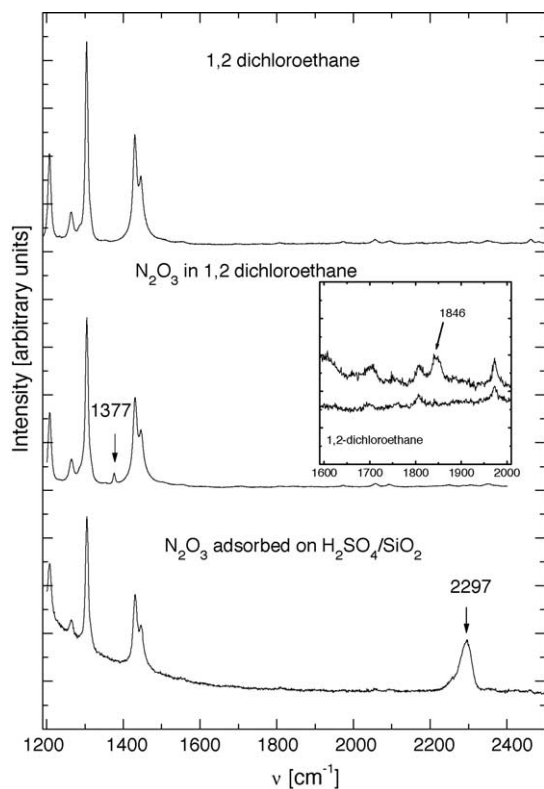
Fig. 4. Raman spectra of N_2O_3 in 1,2-dichloroethane in liquid phase and adsorbed on H_2SO_4/SiO_2 catalysts.

3. Results and discussion

In order to gain further insight into the features of the new catalytic systems, the state of the nitrosating agent in aprotic solvents was investigated as well as, in analogous solvents, the oxidation of alcohols, acetophenone and of the intermediates detected in the reactions carried out in aqueous acid solutions [1].

3.1. Spectroscopic analysis of the nitrosating agent

Thermodynamic and spectroscopic properties of nitrogen oxides have been the subject of several investigations since these compounds are commonly observed as a mixture of species involved in complex equilibria. In the vapour phase, for instance, NO, NO_2, N_2O_3, N_2O_4 were detected where the dissociations $N_2O_3 \rightleftharpoons NO + NO_2$ and $N_2O_4 \rightleftharpoons 2NO_2$ are occurring [12]. In solution, the relative stability of N_2O_3 and N_2O_4 depends on solvation phenomena [14–16]. Furthermore, the presence of nitrous acid cannot be excluded since traces of water may be present into the solvent ($NO + NO_2 + H_2O \rightleftharpoons 2HONO$) [17].

On the attempt to identify molecular and/or ionic species of the nitrosating agent, the main IR spectral features of the mixture in dichloromethane and in chloroform were investigated and reported in Figs. 1–3.

The trend, within the range 2250–1500 cm^{-1}, essentially shows the presence of asymmetric N_2O_3 (NO–NO$_2$) by the peak of the nitrosyl –NO stretching mode around at 1830–1845 cm^{-1} and by the one of the nitro-NO stretching mode around at 1600–1645 cm^{-1} (Fig. 1a) [17–28]. In the presence of O_2, spectral modifications were observed with time as well as additional peaks in the range 1725–1800 cm^{-1}, already assigned to N_2O_4 (Fig. 1b) [17,20,23,25–27]. Moreover, the extensive presence of N_2O_4 in freshly prepared solution of N_2O_3 in CHCl$_3$ (Fig. 2) suggests that chloroform is not a suitable solvent due to the intrinsic low stability of the oxidant. The spectral behaviour of the gas phase indicates that only NO and NO_2 are initially present (Fig. 3a) originated from the N_2O_3 decomposition ($N_2O_3 \rightleftharpoons NO + NO_2$), other nitrogen oxides (mainly N_2O_2, N_2O_4) are gradually formed (Fig. 3b).

Fig. 4 reports the Raman spectra of the nitrosating agent in 1,2-dichloroethane and over a solid acid catalyst. The Raman spectrum in 1,2-dichloroethane exhibits some weak bands due to a mixture of N_2O_3 and N_2O_4, observed respectively at 1850 cm^{-1} and at 1610 cm^{-1} for N_2O_3 [22,24] and at 1710 cm^{-1} for N_2O_4 [21,25,26]. This spectral trend disappears by addition of the H_2SO_4/SiO_2 catalyst and the spectrum of the solid phase exhibits only a strong band, at about 2300 cm^{-1}, already assigned to nitrosoniun ion of dinitrogen trioxide in sulfuric acid by Raman spectroscopy [29]. An analogous behavior has been reported by using nitrating agents over solid acids where the conversion HNO$_3 \rightarrow$ NO$_2{}^+$ has been detected by the Raman analysis of the band at 1300 cm^{-1} of undissociated nitric acid and of the band at 1400 cm^{-1} of nitronium ion [8].

As expected, the results are consistent with an acid catalysed ionization of the molecular species. On the other hand, the ionic dissociation constants (K^i) of neutral oxygenated nitrogen compounds in aprotic solvents were found to be very low [15,16]. The observed K^i values in sulfolane are 6.3×10^{-12} for the ionic dissociation of $N_2O_3 \rightleftharpoons NO^+ + NO_2$ and 7×10^{-8} for $N_2O_4 \rightleftharpoons NO^+ + NO_3$. In both cases, the concentrations of the ionic species are too low to be detected.

3.2. Oxidation of alcohols

Even though, N_2O_3 has been little employed it has interesting oxidant properties. For instances, it can be conveniently used instead of the well-known procedures based on chromium and selenium compounds [30,31].

The usual method of alcohol oxidation to ketone and aldehyde with chromium(VI) compounds gives acids as co-products and rarely the yield is higher than 60% [30,31]. In addition, the wastes disposal of chromium is not a problem of minor importance for the current environmental requirements.

Table 1 reports the results obtained in the oxidation of benzyl alcohols to benzaldehyde and of cyclohexanol to cyclohexanone with N_2O_3.

N_2O_3 is able to oxidize benzyl alcohol giving conversion to benzaldehyde without catalyst; however, poor yield and

Table 1
Oxidation of alcohols by N_2O_3 over solid acid catalysts at 25 °C

Catalysts	Meq H$^+$/g $_{catalyst}$	Ratio[a,b] alcohol/N_2O_3	Reaction time (h)	Conversion (%)	Yield (%) PhCHO	Yield (%) PhCH$_2$ONO[c]	Yield (%) PhCOOH
(A) Benzyl alcohol							
–	–	1:4	24	35	24	8	3
H$_3$PO$_4$/SiO$_2$	1.7	1:4	24	95	85	10	–
Amberlyst 15®	4.7	1:4	0.5	97	72	25	–
Amberlyst 15®	4.7	1:4	1	~99	~99	–	–
Amberlyst 15®	4.7	1:4	24	~99	~99	–	–
H$_2$SO$_4$/SiO$_2$	8.6	1:1	1	~99	~99	–	–
H$_2$SO$_4$/SiO$_2$	8.6	1:1	24	~99	57	–	42

Catalysts	Meq H$^+$/g$_{catalyst}$	Ratio[a] alcohol/N_2O_3	Reaction time (h)	Conversion (%)	Yield (%) cyclohexanone	Yield (%) cyclohexylnitrite	Yield (%) o.p.[d]
(B) Cyclohexyl alcohol							
–	–	1:4	2	45	1	44	–
–	–	1:4	24	42	1	40	1
H$_3$PO$_4$/SiO$_2$	1.7	1:1	24	38	27	–	11
Amberlyst 15®	4.7	1:1	1	>99	29	58	7
Amberlyst 15®	4.7	1:1	24	>99	86	10	4
Amberlyst 15®	4.7	1:4	1	>99	52	–	48
Amberlyst 15®	4.7	1:4	24	>99	–	–	>99
H$_2$SO$_4$/SiO$_2$	8.6	1:1	1/2	62	53	–	9
H$_2$SO$_4$/SiO$_2$	8.6	1:4	2	98	88	–	10
H$_2$SO$_4$/SiO$_2$	8.6	1:4	24	~99	83	–	16

[a] Solvent = 1,2-dichloroethane; [alcohol] and [N_2O_3] = 0.2 mol l^{-1}; catalyst = 0.5 g; reaction volume = 10 ml.
[b] *n*-Butanol; iso-butanol, 1-octanol over Amberlyst 15®, give mixtures of aldehydes, ketones, acids.
[c] Benzylnitrite.
[d] o.p. = products of cyclohexanone oxidation.

low selectivity are achieved (Table 1A). The consecutive reaction of benzaldehyde to benzoic acid is almost completely suppressed in the presence of Amberlyst 15 as acid catalyst. In 1 h, for instance, practically quantitative yield is achieved and after 24 h no further reactions occur (Table 1A). On the contrary, in the presence of H$_2$SO$_4$/SiO$_2$ the reaction proceeds to benzoic acid.

Cyclohexanol reacts with N_2O_3 giving merely cyclohexyl nitrite without catalyst. In the presence of solid acid catalysts, cyclohexanone is formed together with other products

(Table 1B). In this case, the selectivity to cyclic ketone is quite low (at most 87%) since condensation reactions catalysed by the solid acid may occur. This phenomenon is more marked with linear aliphatic alcohols. For instance, 1-octanol at room temperature gives a complex mixture of products due to the fast condensation and isomerization reactions.

From a mechanistic point of view, the isolation of the nitrous ester as intermediate and the formation of the electrophylic species NO$^+$ on the catalyst surface are the key steps for this reaction. Such evidences, together with the evolu-
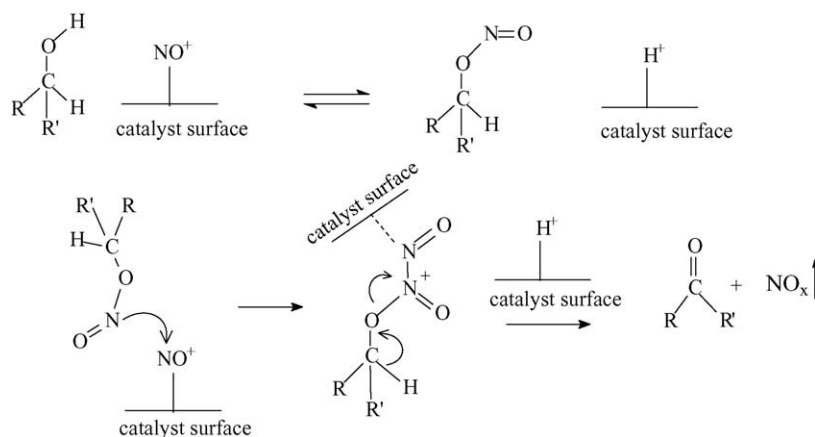
Scheme 1.

Table 2
Acid catalysed oxidations of alcohols by N_2O_3 in 1,2-dichloroethane at 25 °C

Acid[a,b]	Conversion (%)	Yield (%) PhCHO	Yield (%) PhCOOH
(A) Benzyl alcohol			
p-CH$_3$PhSO$_3$H	~99	~99	–
CF$_3$SO$_3$H	~99	58	41
CH$_3$SO$_3$H	~99	95	2
–	35	24	–

Acid[a]	Conversion (%)	Yield (%) cyclohexanone	Yield (%) other products[b]
(B) Cyclohexyl alcohol			
p-CH$_3$PhSO$_3$H	58	15	43
CF$_3$SO$_3$H	75	64	11
CH$_3$SO$_3$H	48	9	39
–	42	1	41[c]

[a] Solvent = 1,2-dichloroethane; [ArCOCH$_3$] = [N$_2$O$_3$] = [acid] 0.2 mol l^{-1}; reaction time = 20 h; reaction volume = 10 ml.
[b] Other products.
[c] 40% of nitrous esters has been detected.

tion of gas (see Section 2) are in agreement with the mechanism reported in Scheme 1. In addition, a similar explanation is given for the oxidation of alcohols with Cr(VI) where a chromic acid ester is involved [31].

Oxidations of the same alcohols in 1,2-dichloroethane in the presence of homogeneous acid catalysts are reported in Table 2. The same products of the heterogeneously catalysed reactions have been obtained, but the selectivity to ketones in homogeneous systems is lower than in heterogeneous ones (compare Tables 1 and 2). Such a phenomenon may be ascribed to the different reactivity of free molecules compared to the adsorbed ones. It is likely that sterical hindering on the catalyst surface leads to an increase of the selectivity.

3.3. Oxidation of ketones

In part 1 of the present investigation we have shown that PhCOCH$_3$ is selectively oxidized in aqueous sulfuric acid solution of HNO$_2$ to PhCOCOOH (yield > 95%) [1,30]. In such a system the oxidation of the methyl group

is related to the protonation of the carbonyl group as well as to the equilibrium of the electrophylic species (NO$^+$).

The results obtained with N$_2$O$_3$ in 1,2-dichloroethane over solid acid catalysts are reported in Table 3. It is noteworthy that the oxidation product is PhCOCN (benzoyl nitrile) rather than PhCOCOOH. The conversion and the selectivity to nitrile are strictly related to the PhCOCH$_3$/N$_2$O$_3$ ratio and to the nature of the catalyst. For instance, yield of PhCOCN (95%) useful for synthetic applications is obtained with a ratio PhCOCH$_3$/N$_2$O$_3$ = 1/4 and over sulfonated resins (Amberlyst 15®) as catalyst.

In order to gain new insights on the mechanism of the catalyzed heterogeneous reactions in non-aqueous solvent, the reactivity of the intermediates, previously isolated in aqueous solutions, are investigated. The results reported in Table 4 shows that PhCOCH$_2$NO (α-nitroso-acetophenone) is not stable in the presence of solid acid catalysts. For instance, with Amberlyst 15® as catalyst the reaction proceeds slightly giving 5% of PhCOCN, while H$_2$SO$_4$/SiO$_2$ promotes the formation of benzoic acid (yield 85%) with whole conversion.

Table 3
Oxidation of acetophenone by N_2O_3 over solid acid catalysts at 25 °C

Catalysts[a]	Meq H$^+$/g $_{catalyst}$	Ratio ArCOCH$_3$/N$_2$O$_3$	Conversion (%)	Yield (%) PhCOCN	Yield (%) PhCOOH	Yield (%)[b] other products
–	–	1:1	8	8	–	–
HPMo/SiO$_2$[c]	–	1:1	31	2	24	5
H$_2$SO$_4$/ZrO$_2$	0.8	1:1	5	1	2	2
H$_2$SO$_4$/TiO$_2$	0.9	1:1	19	16	2	1
H$_3$PO$_4$/SiO$_2$	1.7	1:1	47	34	8	5
H$_3$PO$_4$/SiO$_2$	1.7	1:4	91	63	10	18
Amberlyst 15	4.7	1:1	29	11	2	16
Amberlyst 15	4.7	1:4	~99	95	2	2
H$_2$SO$_4$/SiO$_2$	8.6	1:1	68	55	10	3
H$_2$SO$_4$/SiO$_2$	8.6	1:4	~99	81	18	1

[a] Catalyst = 0.6 g; [ArCOCH$_3$] = 0.05–0.2 mol l^{-1}; [N$_2$O$_3$] = 0.2 mol l$^-$; solvent = 1,2-dichloroethane; reaction volume = 10 ml; reaction time = 24 h.
[b] Products identified in part.
[c] HPMo = phosphomolybdic acid 1%.

Table 4
Reactivity of α-nitroso-acetophenone, phenylglyossal and benzoylformic acid over solid acid catalysts without and with nitrosating agents at 25 °C

Compounds[a,b]	N_2O_3	Catalysts[c]	Reaction time (h)	Conversion (%)	Yield (%) PhCOCN	Yield (%) PhCOOH	Yield (%)[d,e,f] other products
α-NO-acetophenone	–	Amberlyst 15®	1	5	5	–	1[d]
α-NO-acetophenone	–	Amberlyst 15®	24	5	5	–	1[d]
α-NO-acetophenone	–	H_2SO_4/SiO_2	1	70	16	52	2[d]
α-NO-acetophenone	–	H_2SO_4/SiO_2	24	∼99	13	84	2[d]
α-NO-acetophenone	N_2O_3	–	1	∼99	6	3	90[e]
α-NO-acetophenone	N_2O_3	Amberlyst 15®	1	98	15	–	83[e]
α-NO-acetophenone	N_2O_3	Amberlyst 15®	24	∼99	65	–	34[e]
α-NO-acetophenone	N_2O_3	H_2SO_4/SiO_2	1	∼99	30	2	67[e]
α-NO-acetophenone	N_2O_3	H_2SO_4/SiO_2	24	∼99	38	26	35[e]
Phenylglyossal	–	Amberlyst 15®	1	15	–	14	1[d]
Phenylglyossal	–	Amberlyst 15®	24	45	–	14	31[d]
Phenylglyossal	–	H_2SO_4/SiO_2	24	45	–	41	4[d]
Phenylglyossal	N_2O_3	Amberlyst 15®	1	65	–	53	12[f]
Phenylglyossal	N_2O_3	Amberlyst 15®	6	∼99	–	∼99	–
Phenylglyossal	N_2O_3	–	1	1	–	1	–
Phenylglyossal	N_2O_3	–	6	15	–	15	–
Benzoylformic acid	–	Amberlyst 15®	24	–	–	–	–
Benzoylformic acid	–	H_2SO_4/SiO_2	24	1	–	1	–
Benzoylformic acid	N_2O_3	Amberlyst 15®	2	∼99	–	∼99	–
Benzoylformic acid	N_2O_3	–	2	∼99	–	∼99	–

[a] Run without N_2O_3: catalysts = 0.6 g; [substrates] = 0.05 mol l^{-1}; solvent = 1,2-dichloroethane; reaction volume = 10 ml.
[b] Run with N_2O_3: catalysts = 0.6 g; [compounds] = 0.05 mol l^{-1}; [N_2O_3] = 0.2 mol l^{-1}; solvent = 1,2-dichloroethane; reaction volume = 10 ml.
[c] Amberlyst 15®+ = 4.7 meq H$^+$/g$_{catalyst}$; H_2SO_4/SiO_2 = 8.6 meq H$^+$/g$_{catalyst}$.
[d] Unknown products.
[e] α-Dinitroso- and α-trinitroso-; plus unknown products.
[f] Benzoylformic acid as coproduct.

In the presence of N_2O_3, PhCOCH$_2$NO reacts completely even in the absence of catalyst. The selectivity to PhCOCN is related to the catalyst nature, while Amberlyst 15® leads to 65% of PhCOCN only, H_2SO_4/SiO_2 gives a mixture of PhCOOH and PhCOCN.

PhCOCHO (phenylglyoxal) and PhCOCOOH react readily with N_2O_3 to give quantitatively PhCOOH with or without catalysts, no traces of PhCOCN being observed.

Based on the previous evidences it is likely that the reaction follows Scheme 2.

The mechanism on the catalyst surface is analogous to the one proposed in aqueous solutions, the difference on the final product is essentially due to the different stabilizing effect of the solvent on the products. The steps implicated in the formation of benzoic acid are not clear, and the involvement of PhCOCHO and PhCOCOOH together with other complex reaction pathway cannot be ruled out.

Homogeneous acid catalysed oxidation of acetophenone by N_2O_3 in 1,2-dicholroethane is reported in Table 5. It is noteworthy that the catalytic activity of each acid in the acetophenone oxidation as well as the selectivity to benzoylnitrile is related to their protonating ability (CF$_3$SO$_3$H > p-CH$_3$ArSO$_3$H > CH$_3$SO$_3$H) [32]. Furthermore, in 1,2-dichloroethane benzoylformic acid and phenylglyoxal are quantitatively converted to benzoic acid. Such evidence suggests that the different reactivity between
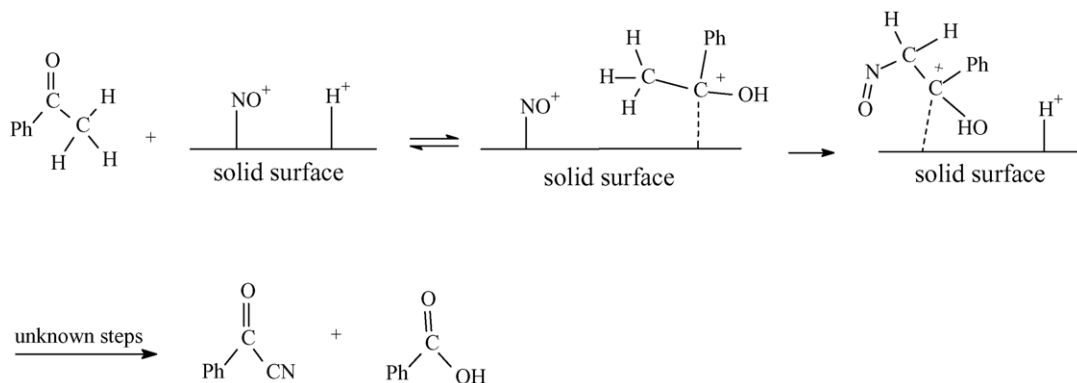

Scheme 2.

Table 5
Acid catalysed oxidations of ketones by N_2O_3 in 1,2-dichloroethane at 25°

Compounds[a]	Catalysts	Conversion (%)	Yield (%) PhCOCN	Yield (%) PhCOOH
Acetophenone	CF_3SO_3H	87	86	1
Acetophenone	CH_3SO_3H	36	26	9
Acetophenone	p-CH_3ArSO_3H	58	55	2
α-NO-acetophenone	CF_3SO_3H	>99	65	31
α-NO-acetophenone	CH_3SO_3H	>99	66	30
α-NO-acetophenone	p-CH_3ArSO_3H	>99	65	31
ArCOCN	CF_3SO_3H	5	–	–
ArCOCN	CH_3SO_3H	–	–	–
ArCOCN	p-CH_3ArSO_3H	–	–	–
ArCOCHO	CF_3SO_3H	>99	–	>99
ArCOCHO	CH_3SO_3H	>99	–	>99
ArCOCHO	p-CH_3ArSO_3H	>99	–	>99
ArCOCOOH	CF_3SO_3H	>99	–	>99
ArCOCOOH	CH_3SO_3H	>99	–	>99
ArCOCOOH	p-CH_3ArSO_3H	>99	–	>99

[a] [compounds] = 0.05 mol l^{-1}; [N_2O_3] = 0.2 mol l^{-1}; [AH] = 0.01 mol l^{-1}; solvent = 1,2- dichloroethane; reaction volume = 10 ml; reaction time = 20 h.

aqueous and non-aqueous solvent is mainly due to the stabilization of the products in the reaction environment and to the interaction with different catalysts.

4. Conclusions

Heterogeneously acid catalysed alcohols and ketones oxidation with N_2O_3 in non-aqueous solvent appear to be a practical and safe procedure applicable to large variety of substrates. The method allows a simple and safe replacement of the classical process with Cr_2O_3 and with SeO_2, avoiding the co-production of highly toxic wastes. Moreover, gaseous nature of the oxidant and solid catalysts allow easy separation procedures.

It is noteworthy that the one step formation of bezoyl nitrile from acetophenone in high yield is important from a synthetic point of view, since nitriles are versatile intermediates in many processes. Differently of what has been observed in part 1 benzoyl formic acid is not a reaction product due to the inherent higher stability of the nitrile, in non-aqueous media, in comparison with the corresponding acid.

The spectroscopic investigations on the adsorbed species give new insight on the nature of the reaction mechanism. Evidence of ionic NO^+ species on catalyst surface suggests the key role played by the nitrosonium ion as electrophile.

In conclusion, the attractive oxidation properties of N_2O_3 will be object of further investigations over various substrates and under different experimental conditions.

Acknowledgements

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