

## Anaerobic and Aerobic Oxidation of Styrene with the Cr(salen)/NO<sub>2</sub><sup>-</sup> System

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One of the problems in the oxidation of organic molecules catalyzed by soluble metal complexes [1–3] is the search for systems which can utilize cheap and easily available terminal oxidants, or, possibly, dioxygen itself. Among such oxidants, inorganic and organic nitrites have been little investigated [4–6]. In the course of our studies [7], we have found that NaNO<sub>2</sub> can oxidize styrene, stilbene and allyl alcohol, in the presence of [Cr(salen)(H<sub>2</sub>O)<sub>2</sub>]Cl [**1**, salen = *N,N'*-ethylenebis(salicylideneiminato)], and that this system can also use molecular dioxygen as the oxidant. Although conversions and yields are poor, we believe these observations are interesting, since they may lead to future applications upon appropriate modifications. We therefore wish to report some preliminary results on the oxidation of styrene which is the most reactive substrate.

### Experimental

[Cr(salen)(H<sub>2</sub>O)<sub>2</sub>]Cl (**1**) and [Cr(salen)(ONO)(H<sub>2</sub>O)] (**2**) were prepared according to refs. 8 and 9 respectively. Formaldehyde was determined by a colorimetric assay [10] and the other products by GLC analyses with naphthalene as the internal standard.

Oxidations with NaNO<sub>2</sub> were performed in CH<sub>2</sub>Cl<sub>2</sub>/water (5 ml/5 ml) mixtures; aerobic oxidations were carried out in 5 ml of methanol, in which **2** is soluble, under dry air or dry oxygen (1 atm). The GLC internal standard was added at the end of the reaction.

### Results and Discussion

Under both aerobic and anaerobic conditions, styrene is oxidized by NaNO<sub>2</sub> and in the presence of **1**, to styrene oxide, equimolar amounts of benzaldehyde and formaldehyde, and minor amounts (about 5% of the total conversion) of phenylacetaldehyde (probably derived from the epoxide [11]),

acetophenone and 1-phenyl-1,2-dihydroxyethane. Other substrates tested were: stilbene (which yields benzaldehyde and epoxide); allyl alcohol (epoxide); norbornene (only traces of epoxide). No reaction was observed with cyclohexene, *N,N*-dimethylaniline or thioanisole.

Oxidation of styrene with NaNO<sub>2</sub> was performed in a CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O mixture (Table 1, Nos. 1–10), in the absence of phase-transfer agents, since **1** possesses low but significant solubilities in both solvents. No reaction occurs either in the absence of NaNO<sub>2</sub> (No. 9) or if **1** is substituted by phase-transfer agents (i.e. NaNO<sub>2</sub> alone does not oxidize styrene under these conditions, No. 10). The product distribution depends on the presence of dioxygen (see Nos. 1–3), suggesting that two different processes (aerobic and anaerobic) are operative. Both processes are inhibited by the addition of naphtholes, which implies radical mechanisms, although we were not able to observe any ESR signal (apart from those of the Cr(III) complexes) in the reaction mixtures.

### Anaerobic Oxidations

This process (Nos. 4–8, Table 1) shows a rather low conversion, but the selectivity towards epoxide formation is higher than that of the aerobic case (Nos. 2, 3, 13–18), especially at a high oxidant/substrate ratio (No. 8). Reaction of **1** with NaNO<sub>2</sub> does not give the oxochromium(V) complex [CrO(salen)]<sup>+</sup> (which is known to epoxidize olefins [12]) but the known [9] Cr(III) *O*-bonded nitrito complex [Cr(salen)(ONO)(H<sub>2</sub>O)] (**2**). However, under rigorously anaerobic conditions, compound **2** is neither able to oxidize (stoichiometrically) styrene, nor to promote its oxidation with NaNO<sub>2</sub> (Nos. 11 and 12). At the moment we have no clue as to the mechanism of this anaerobic oxidation.

### Aerobic Oxidations

Although **2** does not react with styrene, it is able to promote the oxidation of this substrate with dioxygen as the oxidant, also in the absence of NaNO<sub>2</sub> (Nos. 13–18, Table 1). Under these conditions the selectivity towards epoxide formation is low; benzaldehyde and formaldehyde are again formed in the ratio 1/1 and the yields of the oxidation products depend linearly on the concentration of **2** (Nos. 15–18). Dioxygen consumption (volumetric measurements) was found to be slightly larger than the sum of the oxygenated products, probably because of the formation of some by-product which could not be detected by GLC. Finally, from the reaction mixture we could recover the methanol solvate of **2** (characterized by elemental analyses and IR spectroscopy), which is also active and could be used for

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TABLE 1. Oxidation of styrene with the Cr(salen)/NaNO<sub>2</sub> system<sup>a</sup>

Entry No.	Complex (mmol)	NaNO <sub>2</sub> /styrene	Conditions	Yields (mmol) <sup>b</sup>	
				Benzaldehyde	Epoxide
1	1, 0.10	0.66	N <sub>2</sub> , D	0.020	0.020
2	1, 0.10	0.66	air, D	0.044	0.015
3	1, 0.10	0.66	O <sub>2</sub> , D	0.065	0.015
4	1, 0.05	0.14	N <sub>2</sub> , D	0.003	nm
5	1, 0.05	0.33	N <sub>2</sub> , D	0.005	0.003
6	1, 0.05	0.50	N <sub>2</sub> , D	0.006	0.005
7	1, 0.05	0.66	N <sub>2</sub> , D	0.008	0.006
8	1, 0.05	1.00	N <sub>2</sub> , D	0.010	0.010
9	1, 0.10	0	O <sub>2</sub> , D		
10	none <sup>c</sup>	1.00	O <sub>2</sub> , D		
11	2, 8.00	0	N <sub>2</sub> , M	nm	
12	2, 0.10	1.00	N <sub>2</sub> , M		
13	2, 0.10	0	air, M	0.200	0.004
14	2, 0.10	0	O <sub>2</sub> , M	0.500	0.015
15	2, 0.010	0	air, M	0.040	0.001
16	2, 0.037	0	air, M	0.123	0.003
17	2, 0.044	0	air, M	0.166	0.005
18	2, 0.062	0	air, M	0.211	0.010

<sup>a</sup>All reactions were carried out starting from 8 mmol of styrene. Nos. 1–14: 7 h at 26 °C; Nos. 15–18: 2.5 h at 35 °C. D = CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O mixture; M = methanol, see Experimental. <sup>b</sup>Formaldehyde and benzaldehyde were always formed in a 1/1 ratio, the former is not shown here for simplicity; nm = not measurable. <sup>c</sup>In the presence of trimethylbenzylammonium chloride.

other oxidation reactions. No oxidation of 2 to a nitrate or an oxo complex was observed.

Oxidation of organic substrates with dioxygen, catalyzed by metal nitro (*N*-bonded, M–NO<sub>2</sub>) complexes is a well-known reaction [13, 14], but, to our knowledge, no such reaction has ever been reported for *O*-bonded nitrito complexes\*. Coordination of the nitrite ion to Cr(III) seems to give rise invariably to nitrito (Cr–ONO) rather than nitro complexes which appear to be unknown for this metal ion [16]. Although isomerization to a transient Cr–NO<sub>2</sub> species cannot be ruled out, the reactivity pattern and products distribution of the M–NO<sub>2</sub> + O<sub>2</sub> oxidation reactions [13, 14, 17, 18] are usually different from those observed in the present work.

As for a possible mechanism of the dioxygen activation here described, we have noticed the analogy of our results to some reports on the oxidation of styrene and stilbene with ClO<sup>–</sup> [19], and PhIO [20, 21], catalyzed by some Ni(II) [19, 21] and Fe(III) [20] complexes. In fact, also in these systems, the presence of dioxygen increases the benzaldehyde/epoxide ratio, suggesting the occurrence of two different (aerobic and anaerobic) oxidation paths, the former deriving from the O<sub>2</sub> (rather than PhIO or ClO<sup>–</sup>) oxidation of the substrate [20, 21]. The proposed trapping of dioxygen in a ternary radical

catalyst–substrate–O<sub>2</sub> intermediate [21] could be a feature common to these and our systems, and work is being planned to test this hypothesis and to expand the scope of this oxidation system.

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\*Note, however, that the stoichiometric oxidation of ethylene by Pd(NO<sub>2</sub>)Cl(CH<sub>3</sub>CN)<sub>2</sub> has been proposed to occur via isomerisation to a transient PdONO species [15].

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