

Selective Oxidation of Glycerol to Formic Acid Catalyzed by Iron Salts
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Supplementary data

Experimental section

General

Reactions and manipulations were performed under air in a standard tube. All the chemicals were reagent grade and were used as received from the commercial suppliers.

Instrumental

^1H and ^{13}C NMR spectra were recorded on a Varian 500 spectrometer operating at 500 MHz and 125.68 MHz, respectively; chemical shifts were measured relative to the residual solvent signal. Assignments were verified by COSY and HSQC spectra.

The chemical yields of the catalytic reactions were determined by GC on an Agilent 6850 instrument with helium as carrier gas and a TCD detector. samples withdrawn from the reaction mixtures were injected without previous dilution at 100 °C into the cool on-column injector (programmed temperature in "track-oven") in a Restek Rtx[®]-Wax capillary column (30 m length, 0.32 mm ID, 0.5 μm df) protected by a Restek Hydroguard[®] FS precolumn (5 m length, 0.53 mm ID).

Electrospray mass spectra were obtained by an ion-trap instrument (ESI-MS Bruker Esquire 4000) equipped with an electrospray ion source. The instrument performed with 10.0 psi nebulizer pressure, end-plate offset -500V, capillary 4000V and capillary exit at 113.3V. The drying gas (N_2) flow was 5 L min^{-1} and the spectral range was from $m/z = 100$ to 1200.

Synthesis of the iron catalyst

Compound $[\text{Fe}(\text{BPA})_2(\text{OTf})_2]$ was prepared according to the reported procedure[Ref. 27].

Procedure for catalytic reactions

In a typical catalytic reaction in the presence of BPA as ligand, 3.54 mg (0.010 mmol) of $\text{Fe}(\text{OTf})_2$ were dissolved in an open vessel with 0.65 ml of MeCN to give a clear colourless solution; then 5.4 μl (0.030 mmol) of BPA were added through a micro-syringe leading to a deep orange solution. After 5 min, 0.35 ml of 1.0 M glycerol solution in water (0.35 glycerol mmol) were added without any change in the colour. Then H_2O_2 (100 μl , 30 wt % in H_2O 0.98 mmol) was slowly added dropwise (1 drop every 15 seconds, 4 minutes altogether) via micro-syringe under vigorous stirring until addition was complete. During the H_2O_2 addition the colour of the solution changed immediately to deep purple and then to become clearer with the addition going on; at the end the solution was brown-orange and clear. A light bubbling was observed as the first drops of H_2O_2 were added.

In a typical catalytic reaction without BPA, 3.54 mg (0.010 mmol) of $\text{Fe}(\text{OTf})_2$ were dissolved in 0.65 ml of MeCN; then 0.35 ml of 1.0 M glycerol solution in water (0.35 glycerol mmol) were added without any change in the colourless solution. Then H_2O_2 (150 μl , 30 wt % in H_2O 1.47 mmol) was slowly added dropwise (1 drop every 15 seconds, 6 minutes altogether) via micro-syringe under vigorous stirring until addition was complete. During the H_2O_2 addition the colour of the solution changed through clear yellow to dark brownish-yellow and then to become clearer with the addition going on; at the end the solution was clear orange. A light bubbling was observed as the first drops of H_2O_2 were added. Only when FeCl_2 was used as catalyst the reaction mixture showed from the beginning a very light solid powder clouding the yellowish suspension.

A series of reactions were performed in a vessel closed by a serum cap and kept at constant temperature (21 °C) in a thermostatted oil bath; in such case we monitored the evolution of the reaction mixture by collecting 5 specimens per minute after the H_2O_2 addition. Before the GC analyses the specimens were kept in liquid nitrogen to quench any possible reaction. The results were the same for all the specimens, confirming that all the reaction occurred during the H_2O_2 addition.

Analysis of the reaction mixtures

Qualitative analysis was accomplished by GC and NMR. The identification of FA, DHA, glyceraldehyde and glycerol was performed as described in our previous articles [Ref. #3,29]. Glycolic acid was identified by carrying out a large scale catalytic reaction in the presence of $\text{Fe}(\text{OTf})_2$ and BPA, *i.e.* the catalytic system which gave the highest yields of

such product; the identification was based on ^1H and ^{13}C NMR spectra of the reaction mixture and the data (NMR chemical shifts and GC retention times) were compared with those of authentic samples obtained by a commercial supplier (Sigma-Aldrich).

Quantitative evaluation of product distributions was performed by GC with benzophenone as internal standard, using response factors previously determined by the analysis of standard solutions; the quantitative analysis thus performed allowed a reproducibility within $\pm 1\%$.

Typical gas-chromatograms were already reported in a previous paper (see ref. #29, Supplementary Information). Since the GC analysis of these reaction mixtures might be tricky, delivering misleading results [Ref. #6] and prone to give artefacts due to column contamination, particular care was taken to monitor the state of the analytical apparatus, which was periodically carried out by injecting standard solutions to confirm quantitative analysis and that no artefacts were resulting.

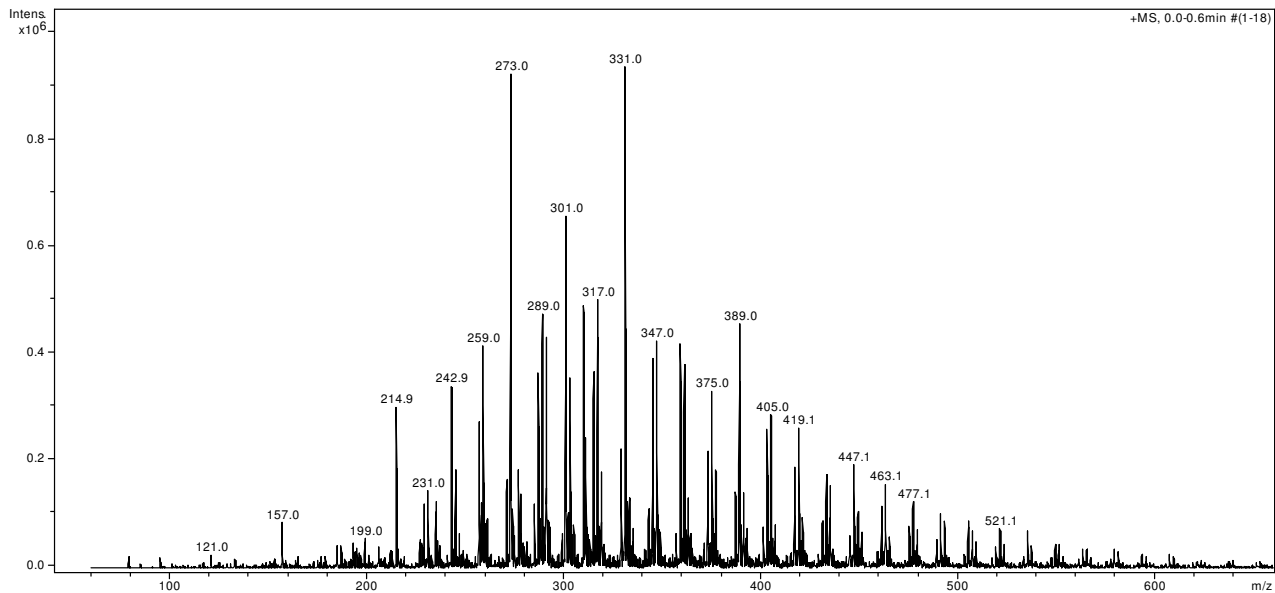
In order to check the possible formation of other products besides formic acid and glycolic acid, a typical catalytic reaction was carried out on a 10-fold scale (35.4 mg (0.10 mmol) of $\text{Fe}(\text{OTf})_2$, 322 mg, (3.5 mmol) of glycerol); at the end, a small specimen (0.2 μl) was injected for GC analysis confirming the expected results. The remaining part of the reaction mixture was evaporated to dryness at reduced pressure to isolate heavier compounds; thus the more volatile products, i.e.: formic acid and glycolic acid, already detected by GC were eliminated and 51 mg of oily, brownish residual was obtained. The oily residual was analysed by ESI-MS (see *infra* the ESI-MS section for the spectra). The spectra show a long series of peaks in the range 215-610 m/z , but the most intense ones (i.e. 215, 273, 331, 389, 447 m/z , etc. $\delta = 58 m/z$) are characterized by an isotopic distribution typical of iron containing compounds. Therefore, most of the residual after solvent evaporation are iron based products, probably containing oxygen atoms and glycerol moieties; as a consequence, and considering that initial loading of iron triflate amounted to 35.4 mg, we can conclude that the yield of oligo- and polymeric products was lower than 10 mg, i.e. 3% of the final mixture.

In a second test at 10-fold scale, the reaction was monitored to check the possible formation of CO_2 : the reaction was carried out in a two-neck closed vessel, having one neck closed by a serum cap and the second one connected to a vessel loaded with a saturated solution of $\text{Ba}(\text{OH})_2$. During the H_2O_2 addition we observed a weak, but constant gas bubbling in the $\text{Ba}(\text{OH})_2$ solution, but no formation of barium carbonate was observed. Thus, we can rule out a significative CO_2 production by the catalytic reaction.

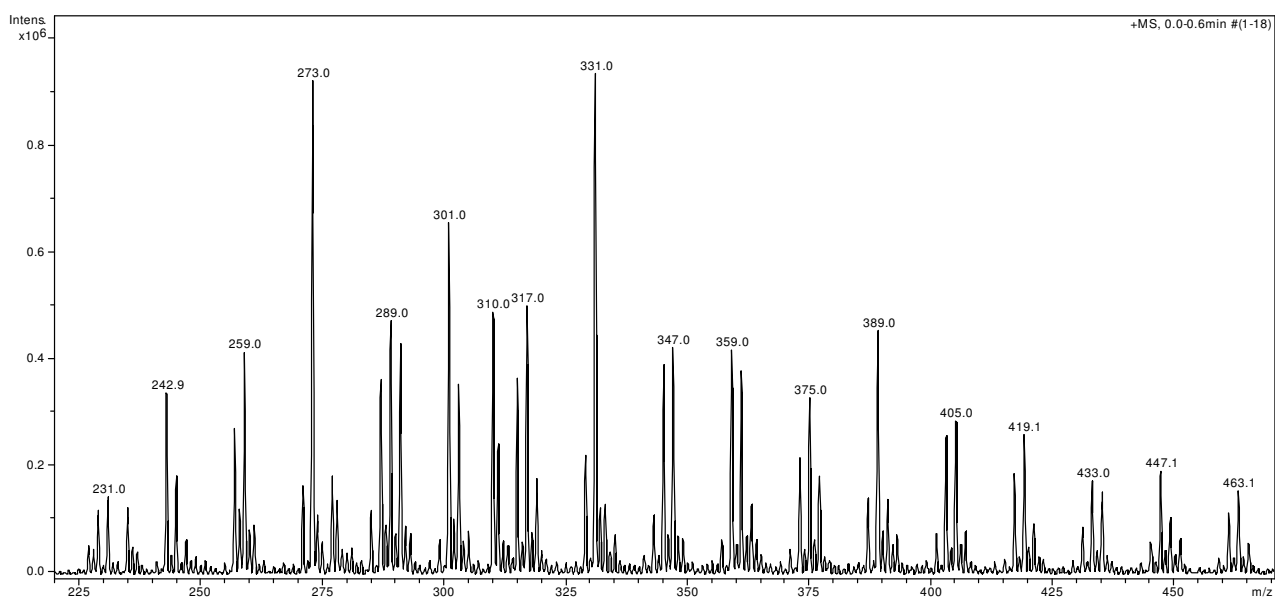
ESI-MS spectra

1) ESI-MS spectra of the oily residual at the end of the reaction reported above (see Analysis of the reaction mixtures)

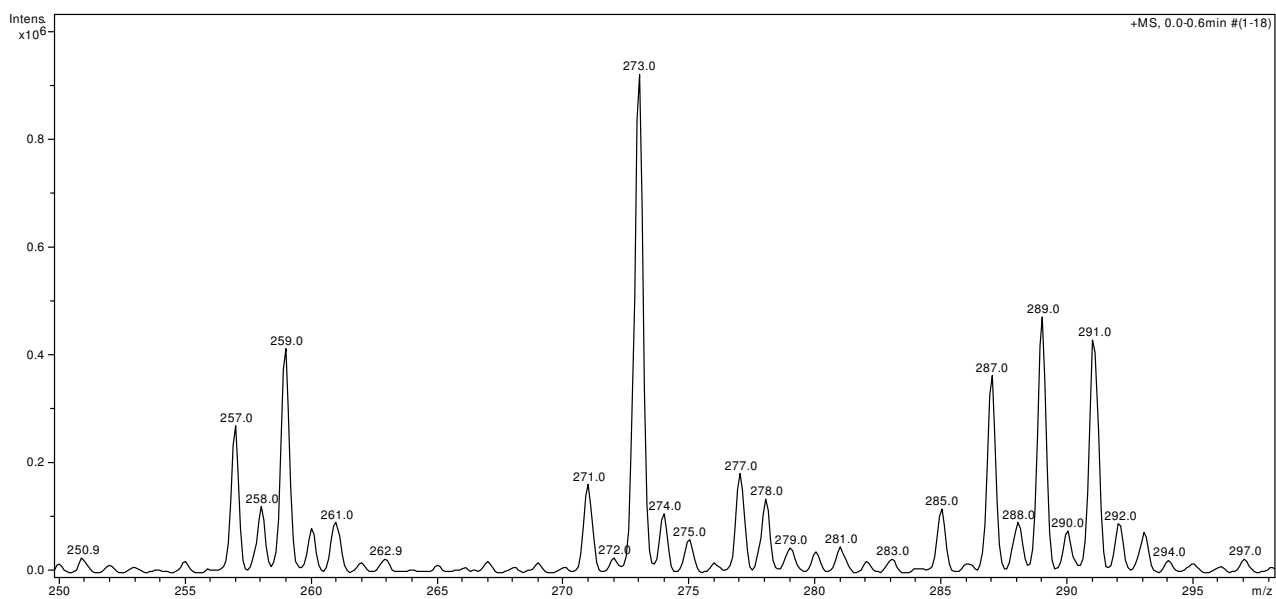
1a) positive



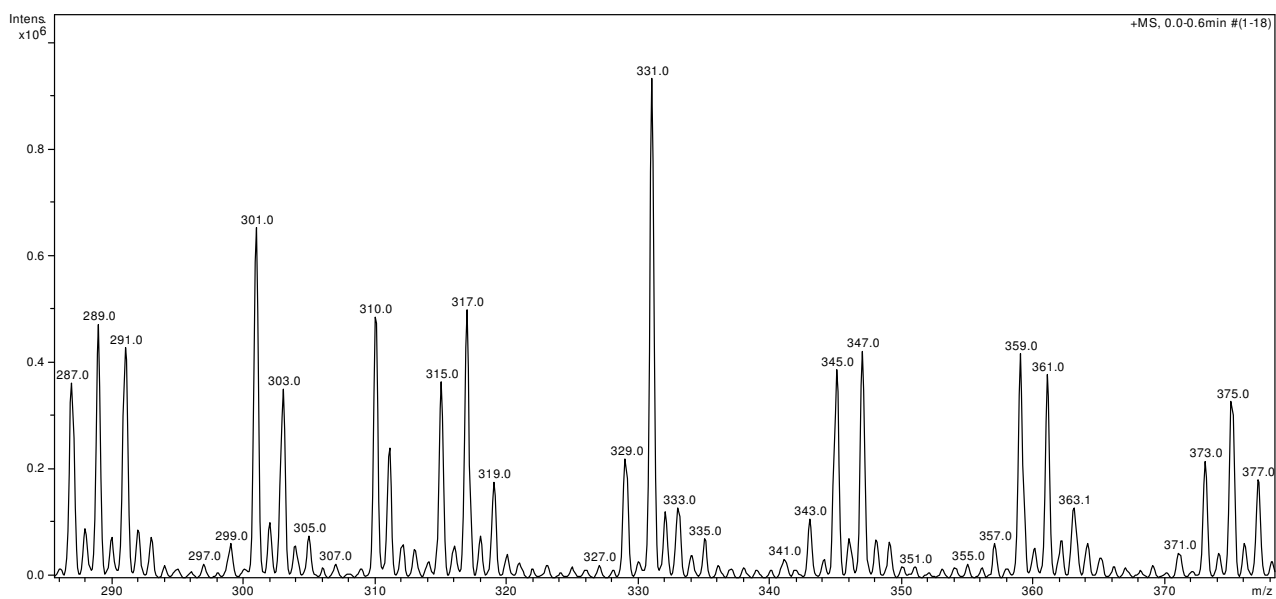
1b) enlargement of 1a).



1c) enlargement of 1a).



1d) enlargement of 1a).



2a) negative

