Damage of polyesters by the atmospheric free radical oxidant NO$_3^\cdot$: a product study involving model systems

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Abstract
Manufactured polymer materials are used in increasingly demanding applications, but their lifetime is strongly influenced by environmental conditions. In particular, weathering and ageing leads to dramatic changes in the properties of the polymers, which results in decreased service life and limited usage. Despite the heavy reliance of our society on polymers, the mechanism of their degradation upon exposure to environmental oxidants is barely understood. In this work, model systems of important structural motifs in commercial high-performing polyesters were used to study the reaction with the night-time free radical oxidant NO$_3^\cdot$ in the absence and presence of other radical and non-radical oxidants. Identification of the products revealed ‘hot spots’ in polyesters that are particularly vulnerable to attack by NO$_3^\cdot$ and insight into the mechanism of oxidative damage by this environmentally important radical. It is suggested that both intermediates as well as products of these reactions are potentially capable of promoting further degradation processes in polyesters under environmental conditions.

Introduction
Polymers are without doubt the most important industrial materials, which have benefited our society in numerous ways. Improving the performance of polymers by making them long lasting and durable is therefore highly desirable not only for the consumer but also for the environment, because expensive waste removal strategies can be avoided or at least reduced. The most important way to improve polymer longevity is a detailed knowledge of the mechanism by which they undergo degradation upon exposure to the environment. It is quite surprising that, despite the heavy reliance of our society on polymeric materials, the chemical mechanism of polymer degradation is by far not fully understood.
It has generally been assumed that polymer degradation involves a radical-mediated autoxidation mechanism, which propagates through hydrogen abstraction by an intermediate peroxyl radical ROO•. Although this autoxidation mechanism was initially proposed only for a limited number of polymers that contain activated aliphatic hydrogen atoms (for example rubber materials) [1-5], it has been universally adapted as general mechanism for polymer degradation. However, recent comprehensive high-level theoretical studies by Coote et al. clearly revealed that polymers possessing only saturated alkyl chains, for example polyesters, will not propagate autoxidation, particularly because the ROO–H bond-dissociation energy (BDE) is usually less than the BDE for unactivated R–H bonds [6].

Polymer surface coatings, which are widely used in the building, automotive and aircraft industries to protect the underlying material from degradation, are commonly high-performing polyesters, which are exposed to significant environmental stress, in particular high temperatures, humidity and UV irradiation. These materials are in direct contact with the troposphere, which is the lowest part of the atmosphere and a highly oxidizing environment. While the oxidation power during daytime can be assigned to the presence of hydroxyl radicals, HO•, the highly electrophilic nitrate radical, NO3•, is responsible for the tropospheric transformation processes at night. NO3•, which is formed through reaction of the atmospheric pollutants nitrogen dioxide, NO2, with ozone, O3 (Scheme 1a) [7,8], reacts with organic compounds through various pathways, such as hydrogen abstraction (HAT) and addition to π systems. Most importantly, NO3• is one of the strongest free-radical oxidants known [E(NO3•/NO3−) = 2.3–2.5 V vs NHE] [9], and recent product studies by us revealed that NO3• readily damages aromatic amino acids and pyrimidine nucleosides through an oxidative pathway [10-13]. Thus, the ease by which model compounds of biologically important macromolecules are attacked by NO3• leads inevitably to the question, how resistant synthetic polymers are towards oxidative damage by this environmental free-radical species, in particular in conjunction with other atmospheric radical and non-radical oxidants, which are in direct contact with these materials. Is it possible that such reactions could lead to structural modifications in the polymer that may render the material more susceptible to further damage, for example through photodegradation and/or autoxidation? To our knowledge, the role of environmental free-radical oxidants as mediator of polymer degradation has barely been assessed so far.

In light of this, we have now performed the first product study of the reaction of NO3• with model substrates relevant to the polymeric structures in high-performing polyesters in the presence and absence of other oxidants, in particular NO2•, O2 and O3. This work not only reveals new insight into the degradation mechanism in polyesters upon exposure to important environmental oxidants, but it also enables identification of vulnerable sites (‘hot spots’) in the polymer, which could open up new pathways to polyester degradation under environmental conditions that have not been considered before. This study might therefore be regarded as a first step on a long journey towards a revised mechanistic scheme for polymer degradation, which is crucial for the development of improved materials.

**Results and Discussion**

**Experimental conditions**

The compounds that served in this work as models for substructures typically found in surface-coating polyesters are shown in Figure 1. These comprise aromatic moieties, such as phthalic and benzoic esters 1 and 3, respectively, as well as aliphatic diesters of type 2. The esters were used as methylates or neopentylates, where the latter provided a simplified model for diesters of neopentyl glycol, which is the commonly used diol component in such polyesters.

All experiments were performed in solution, using two different methods to produce NO3• in situ in the presence of the respective substrate 1-3. In experiments where NO3• was used in the absence of other radical and non-radical oxidants, NO3• was generated at room temperature from cerium(IV) ammonium nitrate (CAN) through photo-induced electron transfer at an irradiation wavelength of λ = 350 nm (Scheme 1b) [11-13].

In a typical experiment, the polyester-model substrate and four equivalents of CAN were dissolved in acetonitrile and the solu-
tions degassed by sonicating under a continuous argon stream, followed by irradiation and aqueous work-up. Control experiments performed under exclusion of light showed no reaction, which ensured that the observed products indeed resulted from the reaction involving NO$_3^-$ and not from CAN, which is also an oxidizing agent \[E^0(Ce^{4+/Ce^{3+}}) = 1.61\, V\, \text{vs. NHE}\] [14].

In another set of experiments, NO$_3^-$ was obtained through the reaction shown in Scheme 1a, where to a solution of the respective polyester-model substrate in anhydrous dichloromethane at 10 °C an excess of liquid NO$_2^-$ was added and ozonized O$_2$ was bubbled through the mixture at a low flow rate, followed by control work-up. Through control experiments it was revealed that none of the various polyester-model compounds reacted to a noticeable extent with NO$_2^-$ or ozonized O$_2$ in isolation. Reactions with this NO$_3^-$ source in acetonitrile gave identical products to those in dichloromethane. However, additional products were also obtained in small amounts, which could not be identified. It is possible that these resulted from hydrolysis of dinitrogen pentoxide, N$_2$O$_5$, which is formed through reversible recombination of NO$_2^-$ with NO$_3^-$, by trace amounts of water present in acetonitrile, but this was not further explored. By performing the radical reactions in dichloromethane, potentially interfering reactions involving the solvent, which could complicate the reaction outcome and mechanistic considerations, were avoided. It should also be noted that NO$_2^-$ is in equilibrium with its dimer dinitrogen tetroxide, N$_2$O$_4$. In solution the NO$_2^-$/N$_2$O$_4$ equilibrium constant favours the dimer [15], and N$_2$O$_4$ can be oxidized with O$_3$ to give N$_2$O$_5$. Gas-phase kinetic studies revealed that N$_2$O$_5$ reacts with unsaturated compounds several orders of magnitude slower than NO$_3^-$ [16] and does not readily nitrate deactivated aromatic compounds in solution [17].

In all experiments we have used NO$_3^-$ in excess in order to obtain sufficient amounts of material to enable product separation by preparative HPLC using UV detection at wavelengths of $\lambda = 214$ and 230 nm and identification by spectroscopic characterization. Details are given in the Experimental section. HPLC chromatograms of the relevant raw reaction mixtures are shown in Supporting Information File 1. Although under natural conditions NO$_3^-$ will be present in much lower concentrations compared to the polyester, our experimental procedure ensured that vulnerable sites in the polyester-model systems could be located with certainty. Due to the repeated purification by HPLC, yields could not be obtained for any of these reactions. However, since this study is aimed at obtaining insight into the nature of the products in order to qualitatively assess how such chemical modifications might affect polymer stability under environmental conditions, exact yields are not required. It is reasonable to assume that only very few damaged sites are initially required in the polyester to promote further degradation on a large scale through chain and other processes.

**Reaction of polyester-model compounds 1–3 with NO$_3^-$ from CAN photolysis**

Study of the products formed in the reaction of NO$_3^-$ obtained from CAN photolysis provides the opportunity to gain insight into the mechanism of oxidative damage in the absence of other radical and non-radical oxidants. In Scheme 2 the products of the reaction of the polyester-model compounds 1–3 with NO$_3^-$ are shown.

It was interesting to note that no reaction occurred with the isomeric phthalates 1 and the adipic acid derivatives 2. In the case of the former this could be explained by the fact that the aromatic ring is very deactivated due to the two electron-withdrawing ester substituents, so that oxidative electron transfer (ET) by NO$_3^-$ is not possible. Also, NO$_3^-$ induced HAT from the ester, particularly the neopentyl moiety, which is a potential pathway that should most likely occur at the methylene groups $\alpha$ to the ester oxygen atom [18-20], is apparently not a feasible pathway. This finding is of potential relevance for the autooxidation mechanism, which proposes hydrogen abstraction by ROO' as propagating step. Thus, although NO$_3^-$ is not only much more reactive than ROO' [7,8], and the BDE for the O$_2$NO–H bond is with 427 kJ mol$^{-1}$ also considerably higher than that of

![Scheme 2: Products of the reaction of polyester model compounds 1–3 with NO$_3^-$ in the absence of other radical and non-radical oxidants.](image-url)
the ROO–H bond (which is about 360 ± 20 kJ mol\(^{-1}\)) [21], the fact that no hydrogen abstraction from the ester units was observed in the reactions with NO\(_3^–\) demonstrates that saturated alkyl groups are quite inert to radical attack.

On the other hand, in the case of neopentyl ester of m-toluic acid (3), which differs from the phthalates by replacement of one ester group by a \(\sigma\)-donating methyl group, reaction with NO\(_3^–\) leads to selective oxidative modification of the methyl side chain, while a reaction at the ester moiety was, again, not observed. Analytical HPLC of the raw reaction mixture recorded at \(\lambda = 230\) nm revealed besides unreacted starting material 3 (which was identified by comparison with an authentic sample but not isolated), nitrate 4, aldehyde 5 and carboxylic acid 6 as most important products (see Supporting Information File 1). Other products were formed in too minor amounts to enable isolation. Further, HPLC analysis revealed that shorter reaction times or a smaller excess of CAN shifted the product ratio towards the nitrate 4 at expense of the higher oxidized products 5 and 6 (data not shown).

The observed side-chain oxidation in 3 by NO\(_3^–\) is similar to the outcome of the reaction of thymidine nucleosides with NO\(_3^–\), where oxidative transformation of the methyl substituent in the heterocyclic base occurs exclusively [13]. Concentration–time profiles revealed for the latter reactions that formation of a nitrate occurs first, which is converted to an aldehyde and subsequently into a carboxylic acid [13]. It is not unreasonable to assume that such a step-wise oxidation also occurs in the reaction involving 3, which could be rationalized by the mechanism shown in Scheme 3.

Because of the high oxidation power of NO\(_3^–\), it is proposed that the reaction is initiated by ET at the aromatic ring through an addition–elimination pathway, as has been suggested from time-resolved transient spectroscopic studies for the reaction of NO\(_3^–\) with alkylaromatic compounds [22,23]. In the absence of any reactants the resulting radical cation 3\(^+\) undergoes deprotonation to give benzyl radical 7, in analogy to the mechanism of the NO\(_3^–\)-induced oxidation of aromatic amino acids and nucleosides [10-13]. This mechanism is supported by findings by Steenken et al., who showed that in the reaction of alkylaromatic compounds with NO\(_3^–\) ET and deprotonation can occur practically in a concerted fashion in the case of highly electron-rich arenes, while in the case of less activated alkylaromatic compounds the intermediate radical cation has a lifetime on the nanosecond time scale [23]. It was further demonstrated that deprotonation of arylic radical cations is accelerated by nitrate (NO\(_3^–\)) that is present in the reaction system as ‘byproduct’ of the oxidation process and as ligand in CAN, and which acts as a Brønsted base [23]. It is important to note that the formation of radical intermediate 7 could principally also occur in one step through NO\(_3^–\)-induced benzyl HAT in 3 (not shown). However, it appears from the outcome of the reactions with the neopentyl derivatives of 1 and 2 that HAT by NO\(_3^–\) is not competitive with NO\(_3^–\)-induced ET in these systems [7,8,24,25].

![Scheme 3: Proposed mechanism for the reaction of m-toluic acid neopentyl ester (3) with NO\(_3^–\) in the absence of radical and non-radical oxidants.](image-url)
An initial ET step and formation of an intermediate radical cation $3^{+*}$ is further supported by the outcomes of the reaction of 3 with NO$_3^-$ in the presence of NO$_2^-$, which will be outlined below.

Formation of nitrate 4 could principally occur via two different pathways, e.g. through direct trapping of 7 by NO$_3^-$ or in a two-step process by first NO$_3^-$ or CAN-induced ET, followed by quenching of the resulting benzyl cation 8 through ligand exchange from CAN. Although the nature of the intermediate was not further explored in this work, our previous experiments involving thymidines provided strong indications that the reaction likely involves a cationic intermediate [13].

Conversion of the nitrate ester 4 into the aldehyde 5 could proceed through either an intermediate benzyl radical 9, which could be formed through a direct HAT by NO$_3^-$ [26], or through a sequential ET–deprotonation pathway in analogy to the initial reaction step. The labile O–NO$_2$ bond in 9 is expected to undergo rapid β-scission to give aldehyde 5 with release of NO$_3^-$ [27,28]. The latter is too unreactive to initiate a radical process in this system, which has been confirmed through independent control experiments.

Oxidation of aldehyde 5 to the carboxylic acid 6 under the experimental conditions could be initiated through abstraction of the aldehyde hydrogen atom by NO$_3^-$ [29], followed by trapping of the resulting acyl radical 10 by NO$_3^-$ to give the mixed anhydride 11, which could be hydrolysed to the acid 6 during aqueous work-up and/or purification by HPLC.

The mechanism in Scheme 3 shows that more than one equivalent of NO$_3^-$ is required to produce the observed products 4–6. Such multiple attacks seem unlikely under environmental conditions, where [NO$_3^-$] is low [7,8]. However, from the previous work on NO$_3^-$-induced oxidative damage of biological molecules, it appears that an already damaged compound is more prone to attack by another NO$_3^-$ than an undamaged substrate [11–13].

**Reaction of polyester-model compounds 1–3 with NO$_3^-$ from NO$_2^-$/O$_3$**

Under environmental conditions, however, NO$_3^-$ is not an isolated reactant, but is always accompanied by other radicals and non-radical oxidants, such as NO$_2^-$, O$_3$, and O$_2$, respectively, which principally could become involved in these reactions through trapping of reactive intermediates. Thus, in order to explore the role of such additional reactants on the outcome of NO$_3^-$-induced oxidative damage of polyester-model compounds, we have used the reaction in Scheme 1a to produce NO$_3^-$. Similar to the reaction with NO$_3^-$ in isolation, no reaction of NO$_3^-$ with phthalates 1 and adipic esters 2 was observed in the presence of NO$_2^-$, O$_3$, and O$_2$, which is a further confirmation for the low reactivity of saturated alkyl chains. On the other hand, the reaction with the m-toluic acid ester 3 was very fast.

According to the HPLC spectrum of the raw reaction mixture (see Supporting Information File 1), the starting material was completely consumed and considerably more products were obtained in the presence of NO$_2^-$, O$_3$, and O$_2$ compared to the reaction of NO$_3^-$ in isolation.

The main reaction pathways lead to products possessing a nitroaromatic ring, such as the isomeric mono-nitroaromatic compounds 12a–d, the dinitrated product 13 and two isomeric species 14a,b, which carry both a nitro and a hydroxy substituent (Scheme 4). The nitro compound 15 appears to be the only product that results from oxidative modification of the methyl substituent at the aromatic ring. HPLC analysis indicated that additional products were formed in this reaction (see Supporting Information File 1), but their amounts were too small to enable isolation and identification. The proposed mechanism leading to the various products 12–15 is outlined in Scheme 5.

Similar to the mechanism shown in Scheme 3, initial ET should lead to the radical cation $3^{+*}$. However, in contrast to the reaction with NO$_3^-$ in isolation, where benzyl deprotonation occurred exclusively, in the presence of excess NO$_2^-$ the radical cation $3^{+*}$ is trapped prior to deprotonation to form the isomeric σ-complexes 16 [30]. The aromatic ring is restored through loss of a proton, which leads to the nitroaromatic products 12a–d. The proposed competition in radical cation $3^{+*}$ between trapping by NO$_2^-$ and benzyl deprotonation is supported by the fact that the nitromethylene compound 15 is obtained as byproduct in this reaction. The latter likely results from recombination of NO$_2^-$ with benzyl radical 7, which is obviously formed in small amounts. Thus, in contrast to the reaction of 3 with NO$_3^-$ in isolation, formation of stable reaction products in the presence of NO$_2^-$, O$_3$ and O$_2$, such as the nitroaromatic compounds 12, requires only one equivalent of NO$_3^-$ and should readily occur even at low atmospheric [NO$_3^-$].

Formation of the tetrasubstituted products 13 and 14 proceeds likely through a second NO$_3^-$-induced ET in the mono-nitrated compounds 12a,b, where the intermediately formed radical cation $12^{+*}$ can be trapped by NO$_2^-$ to give the dinitro compound 13 after deprotonation. This mechanism is supported by previous findings in the reaction of aromatic amino acids with NO$_3^-$ in the presence of NO$_2^-$, O$_3$, and O$_2$, where it was shown that dinitrated products result from a step-wise nitration of the aromatic ring [10]. On the other hand, to our knowledge, forma-
formation of hydroxylated products of type 14 in the reaction of NO$_3^\cdot$ with aromatic compounds is unprecedented. We propose that these compounds result from hydrolysis of the corresponding nitrates 18 during work-up and/or HPLC purification. Potential pathways to the latter could involve either trapping of the radical cation 12$^{\cdot+}$ by NO$_3^\cdot$, followed by deprotonation, or recombination of 12$^{\cdot+}$ with NO$_3^\cdot$ (the byproduct of the NO$_3^\cdot$-induced ET). The resulting radical adduct 17 could be oxidized in a subsequent step by either NO$_3^\cdot$ or NO$_2^\cdot$ [$E$(NO$_3^\cdot$/NO$_2^\cdot$) = 1.04 V vs NHE] [31], which is followed by deprotonation to restore the aromatic system.

**Conclusion**

We have shown for the first time that certain aromatic moieties in commercial polyesters (e.g. alkylated benzoic acid derivatives of type 3) are vulnerable to damage by the environmental free-radical oxidant NO$_3^\cdot$. The reaction is most likely initiated by ET to give a highly reactive aryl radical cation intermediate 3$^{\cdot+}$, whose fate depends strongly on the reaction conditions. In the absence of radical-trapping agents, in particular NO$_2^\cdot$, benzylic deprotonation is the exclusive pathway that ultimately leads to oxidative functionalization of the alkyl side chain through formation of nitrates 4, aldehydes 5 and carboxylic acids 6. In this work we have not specifically explored the role of O$_2$ on the reaction outcome, but our recent studies on the NO$_3^\cdot$-induced oxidative damage in thymidines showed that any residual O$_2$ present in the system solely accelerates production of the higher oxidized compounds 5 and 6, while no different products are formed [13]. It is reasonable to expect a similar outcome for the reaction of NO$_3^\cdot$ with 3 in the presence of O$_2$. On the other hand, when the reaction of NO$_3^\cdot$ with 3 is performed in the presence of NO$_2^\cdot$, benzylic deprotonation in radical cation 3$^{\cdot+}$ can hardly compete with trapping of the latter by NO$_2^\cdot$, which leads to formation of the isomeric nitroaromatic compounds 12a-d as well as the dinitro and hydroxylated products 13 and 14, respectively, that result from further NO$_3^\cdot$-induced oxidation of 12. An additional, however only minor pathway yields the nitromethylene compound 15, which
is formed via benzyl radical 7. Although we have not studied the nature of the reactive intermediates formed in these reactions, it is difficult to rationalize formation of the ring-substituted products 12–14 through a mechanism that involves benzyllic HAT by NO$_3^−$. The reaction must therefore be initiated by oxidation of the aromatic ring, which is in accordance with literature findings [22,23].

The different outcome of the reaction of NO$_3^−$ with 3 under the various conditions could be explained by the different concentration of NO$_2^−$ and NO$_3^−$ in these systems. Thus, CAN photolysis generates NO$_3^−$ in the presence of excess NO$_3^−$, which acts as Brønsted base and mediates deprotonation of the initial radical cation 3$^+$ to give benzyl radical 7 [23], followed by transformation to the products 4–6. In the NO$_2^−$/O$_3$ system, on the other hand, [NO$_3^−$] = [3$^+$] and deprotonation in 3$^+$ cannot complete with its trapping by excess NO$_2^−$, which leads to the nitroaromatic species 12–14.

In contrast to the high reactivity of the aromatic ring in 3, phthalate-building blocks as well as ester moieties possessing only saturated alkyl chains appear to be inert to attack by NO$_3^−$ through either ET or HAT, respectively, under the various conditions explored. Our observation that NO$_3^−$-induced HAT in the ester moieties does not occur, although NO$_3^−$ is much more reactive than ROO$^−$ and the O$_2$NO–H bond is considerably stronger than the ROO–H bond, could be taken as indication that an autoxidation mechanism involving ROO$^−$ as chain carrier cannot operate in intact polyester materials (however, it should be noted that these structural motifs may be formed in the polymer through degradation processes).

None of the various polyester-model compounds explored in this work reacted with NO$_2^−$ and O$_3$ in isolation. However, this outcome is not unexpected, since the reactivity of NO$_3^−$ is much lower than that of NO$_3^−$. In particular, the oxidation power of NO$_3^−$ is not sufficient to induce ET in deactivated aromatic compounds [31]. Likewise, although O$_3$ is a strong oxidant, it does not react via ET transfer. Rapid reactions are only expected for π systems, such as alkenes, which are not present in intact polyester materials (however, it should be noted that these structural motifs may be formed in the polymer through degradation processes).

What are the potential implications of NO$_3^−$-induced oxidative damage in aromatic building blocks for polyester stability? Although there are no experimental data available yet, it is possible to make some predictions from the outcome of this work, which can be used to guide future studies on polyester stability upon exposure to the environment. It is important to realize that under environmental conditions only few sites of initial damage are required to trigger degradation of the polymer material on a large scale. Identification of the reaction products using simplified model systems enables to obtain some general insight into the mechanism of radical-induced oxidative damage in these materials. Thus, in the reaction of the aromatic ester 3 with NO$_3^−$ it could be speculated that both intermediates as well as products could principally promote further damage in the polymer.

Of the various products formed in the reaction of NO$_3^−$ with 3 under the different reaction conditions, in particular the aldehyde 5 and the nitroaromatic species 12–14 are expected to be photochemically active compounds. Exposure of the carboxyl or nitro moieties to UV light leads to photoexcited intermediates, which are strong hydrogen-atom abstractors in Norrish-type II photoreactions [32,33]. In the polymer matrix, where the various polyester chains are tightly packed, both intra- and interstrand reactions are likely to occur, such as photo-induced hydrogen abstractions, which could provide pathways to C-radicals in unactivated alkyl chains that would usually be inert to attack by peroxy radicals.

To conclude, this work provides strong indications for a number of so far unexplored pathways that could promote degradation of high-performing polyesters under environmental conditions. It is obvious that detailed kinetic data and product analyses from exposure studies involving both simple as well as more complex model systems, including melamine cross-linker moieties, are required (for example from smog chamber experiments), to obtain further insight into the role of environmental free-radical oxidants, such as NO$_3^−$ and HO$^−$, in promoting polyester degradation.

**Experimental**

**General procedures**

The irradiations were performed under a continuous gas flow (argon) in a Rayonet photochemical reactor ($λ$ = 350 nm). Before the irradiations, residual oxygen was removed from the reaction mixture by bubbling argon through the solution while sonicating. $^1$H and $^{13}$C NMR spectra were taken on a Varian Unity Inova 500 spectrometer [500 MHz ($^1$H), 125 MHz ($^{13}$C)] or on an Agilent MR 400 spectrometer [400 MHz ($^1$H), 100 MHz ($^{13}$C)] in deuterated DMSO. If necessary the assignment of the chemical shifts was confirmed by utilising 2D NMR...
Reactions with NO$_3^-$ from CAN photolysis

In a typical experiment 1.0 mmol of the model substrate and 4.0 mmol of CAN were dissolved in 5 and 95 mL of absolute acetonitrile, respectively, and the individual solutions degassed by sonication under a continuous argon stream. The solutions were combined and irradiated (λ = 350 nm) for a period of 5 h at room temperature. The reaction was quenched by addition of brine (50 mL) and water (50 mL) and extracted with ethyl acetate. The combined organic fractions were dried (MgSO$_4$) and the solvent removed in vacuum. The crude product mixture was separated by reversed-phase HPLC.

Neopentyl 3-(nitratomethyl)benzoate (4): $^1$H NMR (DMSO-d$_6$, 500 MHz) δ 8.08 (td, J = 1.8, 0.6 Hz, 1H), 8.01 (ddd, J = 7.8, 1.8, 1.2 Hz, 1H), 8.75 (dd, J = 7.6, 1.2, 0.6 Hz, 1H), 7.60 (td, J = 7.7, 0.5 Hz, 1H), 5.66 (s, 2H), 3.99 (s, 2H), 0.99 (s, 9H); $^{13}$C NMR (DMSO-d$_6$, 125 MHz) δ 165.7, 134.5, 133.7, 130.7, 130.3, 130.2, 129.9, 74.9, 74.2, 31.8, 26.7; HRMS (m/z): calculated for C$_{13}$H$_{17}$NO$_3$ + H, 268.1185; found, 268.1181; HRMS (m/z): calculated for C$_{13}$H$_{17}$NO$_3$ + H, 269.1219; found, 269.1212.

Neopentyl 3-formylbenzoate (5): $^1$H NMR (DMSO-d$_6$, 500 MHz) δ 10.10 (s, 1H), 8.45 (td, J = 1.7, 0.5 Hz, 1H), 8.27 (ddd, J = 7.7, 1.8, 1.2 Hz, 1H), 8.17 (td, J = 7.7, 1.5 Hz, 1H), 7.77 (td, J = 7.7, 0.5 Hz, 1H), 4.02 (s, 2H), 1.00 (s, 9H); $^{13}$C NMR (DMSO-d$_6$, 125 MHz) δ 192.8, 164.9, 136.5, 134.5, 133.6, 130.7, 130.0, 129.9, 73.9, 31.4, 26.2; HRMS (m/z): calculated for C$_{15}$H$_{16}$O$_3$ + H: 221.1178. Found: 221.1170; HRMS (m/z): calculated for C$_{15}$H$_{16}$O$_3$ + H: 222.1211; found, 222.1204.

Neopentyl 3-carboxybenzoate (6): $^1$H NMR (DMSO-d$_6$, 500 MHz) δ 13.28 (s(br), 1H), 8.49 (td, J = 1.8, 0.5 Hz, 1H), 8.19 (d, J = 1.7 Hz, 1H), 8.18 (dd, J = 1.8, 0.5 Hz, 1H), 7.66 (td, J = 7.8, 0.6 Hz, 1H), 4.00 (s, 2H), 0.98 (s, 9H); $^{13}$C NMR (DMSO-d$_6$, 125 MHz) δ 166.9, 165.4, 134.2, 133.6, 131.9, 130.7, 130.1, 129.9, 74.2, 31.8, 26.7; HRMS (m/z): calculated for C$_{13}$H$_{11}$O$_4$ + Na, 259.0946; found, 259.0940; HRMS (m/z): calculated for C$_{13}$H$_{16}$O$_4$ + Na, 260.0980; found, 260.0974.

Reactions with NO$_3^-$ generated from NO$_2^-$/O$_3$

In a typical experiment 0.5 mL liquid NO$_2^-$ (15 mmol) was added to 1.00 mmol of the model substrate in anhydrous dichloromethane (15 mL) at 10 °C, and ozonised O$_3$ was bubbled through the mixture at a low flow rate. After 40 min the reaction was quenched by addition of 10 mLaq NaHCO$_3$, the phases were separated and the aqueous phase extracted with dichloromethane. The combined organic fractions were dried over MgSO$_4$, concentrated and the reaction products isolated and purified by repeated preparative HPLC. It was not possible to state the exact [NO$_2^-$] in these experiments, since an indeterminable amount evaporated prior to its reaction with O$_3$.

Neopentyl 5-methyl-2-nitrobenzoate (12a): $^1$H NMR (DMSO-d$_6$, 500 MHz) δ 7.95 (d, J = 8.3 Hz, 1H), 7.65 (dd, J = 1.8, 0.9 Hz, 1H), 7.60 (ddd, J = 8.3, 1.9, 0.9 Hz, 1H), 3.94 (s, 2H), 2.45 (s, 3H), 0.92 (s, 9H); $^{13}$C NMR (DMSO-d$_6$, 100 MHz) δ 165.4, 145.2, 133.3, 130.5, 127.1, 124.6, 75.5, 31.6, 26.5, 21.2. The signal of the carbon atom carrying the nitro substituent (C-2) could not be observed; MS (EI, 70 eV) m/z (%): 251.1 (1) [M$^+$], 164.1 (100) [M$^+$ − OCH$_2$C(CH$_3$)$_3$], 57.2 (31) [C(CH$_3$)$_3$]$^+$; IR (cm$^{-1}$): 2960, 1730, 1527, 1367, 1347, 1257,1200, 1072, 833.

Neopentyl 5-methyl-3-nitrobenzoate (12b): $^1$H NMR (DMSO-d$_6$, 500 MHz) δ 7.89 (d, J = 7.7 Hz, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.67 (d, J = 7.7 Hz, 1H), 3.95 (s, 2H), 2.30 (s, 3H), 0.94 (s, 9H); $^{13}$C NMR (DMSO-d$_6$, 100 MHz) δ 163.6, 136.7, 131.4, 130.7, 129.2, 123.1, 75.5, 31.6, 26.5, 16.8. The signal of the carbon atom carrying the nitro substituent (C-2) could not be observed; MS (EI, 70 eV) m/z (%): 251.1 (1) [M$^+$], 164.1 (100) [M$^+$ − OCH$_2$C(CH$_3$)$_3$], 57.1 (40) [C(CH$_3$)$_3$]$^+$; IR (cm$^{-1}$): 2958, 1727, 1533, 1369, 1287.

Neopentyl 3-methyl-4-nitrobenzoate (12c): $^1$H NMR (DMSO-d$_6$, 500 MHz) δ 8.08 (d, J = 8.5 Hz, 1H), 8.06 (d, J = 1.5 Hz, 1H), 8.00 (dd, J = 8.5, 1.9 Hz, 1H), 4.03 (s, 2H), 2.56 (s, 3H), 1.01 (s, 9H); $^{13}$C NMR (DMSO-d$_6$, 100 MHz) δ 164.7, 152.2, 138.8, 133.7, 133.5, 128.4, 125.3, 74.6, 31.8, 26.7, 19.5; MS (EI, 70 eV) m/z (%): 251.1 (4) [M$^+$], 164.1 (100) [M$^+$ − OCH$_2$C(CH$_3$)$_3$], 57.1 (90) [C(CH$_3$)$_3$]$^+$; IR (cm$^{-1}$): 2960, 1723, 1526, 1259,1192, 118, 1026, 839, 735.

Neopentyl 5-methyl-3-nitrobenzoate (12d): $^1$H NMR (DMSO-d$_6$, 500 MHz) δ 8.45 (m, 1H), 8.35 (ddd, J = 2.5, 1.5,
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References

1. Bolland, J. L. Proc. R. Soc. London, Ser. A 1946, 186, 218–236. doi:10.1098/rspa.1946.0040
2. Bolland, J. L.; Gee, G. Trans. Faraday Soc. 1946, 42, 244–252. doi:10.1039/tf9464200244
3. Bolland, J. L.; ten Have, P. Discuss. Faraday Soc. 1947, 2, 252–260. doi:10.1039/df4700200252
4. Bateman, L. Q. Rev., Chem. Soc. 1954, 8, 147–167.
5. Bolland, J. L.; Gee, G. Trans. Faraday Soc. 1946, 42, 236–243. doi:10.1039/tf4642000236
6. Grylnova, G.; Hodgson, J. L.; Coote, M. L. Org. Biomol. Chem. 2011, 9, 480–490. doi:10.1039/b00599g
7. Wayne, R. P.; Barnes, I.; Biggs, P.; Burrows, J. P.; Canosa-Mas, C. E.; Hjorth, J.; Le Bras, G.; Moorftal, G. K.; Perner, D.; Restelli, G.; Sidebottom, H. Atmos. Environ., Part A 1991, 25, 1–203. doi:10.1016/0960-1686(91)90192-A
8. Wayne, R. P.; Barnes, I.; Biggs, P.; Burrows, J. P.; Canosa-Mas, C. E.; Hjorth, J.; Le Bras, G.; Moorftal, G. K.; Perner, D.; Restelli, G.; Sidebottom, H. The Nitrate Radical. Physics, Chemistry and the Atmosphere - Air Pollution Report 31; CEC: Brussels, 1991.
9. Neta, O.; Huie, R. E. J. Phys. Chem. 1986, 90, 4644–4648. doi:10.1021/j100410a035
10. Goechsen, C.; Wilbowo, N.; White, J. M.; Wille, U. Org. Biomol. Chem. 2011, 9, 3380–3385. doi:10.1039/cob01186b
11. Sigmund, D. C. E.; Wille, U. Chem. Commun. 2008, 2121–2123. doi:10.1039/b803456g
12. Goechsen, C.; White, J. M.; Gable, R. W.; Wille, U. Aust. J. Chem. 2012, 65, 427–437. doi:10.1071/CH111446
13. Wille, U.; Goechsen, C. Aust. J. Chem. 2011, 64, 833–842. doi:10.1071/CH111102
14. Nair, V.; Deepthi, A. Chem. Rev. 2007, 107, 1862–1891. doi:10.1021/or068048n
15. Redmond, T. F.; Wayland, B. B. J. Phys. Chem. 1968, 72, 1626–1629. doi:10.1021/j100851a040
16. Pfang, C.; Martin, R. S.; Canosa-Mas, C. E.; Wayne, R. P. Phys. Chem. Chem. Phys. 2008, 10, 354–363. doi:10.1039/b510835g
17. Bak, R. R.; Smallridge, A. J. Tetrahedron Lett. 2001, 42, 6767–6769. doi:10.1016/s0040-4039(01)01378-8
18. Lindsay Smith, J. R.; Nagatomi, E.; Stead, A.; Waddington, D. J.; Bèvère, S. D. J. Chem. Soc., Perkin Trans. 2 2000, 1193–1198. doi:10.1039/b00507j
19. Lindsay Smith, J. R.; Nagatomi, E.; Waddington, D. J. J. Chem. Soc., Perkin Trans. 2 2000, 2248–2258. doi:10.1039/b004589f
20. Lindsay Smith, J. R.; Nagatomi, E.; Stead, A.; Waddington, D. J. J. Chem. Soc., Perkin Trans. 2 2001, 1527–1533. doi:10.1039/b003555j
21. Luo, Y. R. Comprehensive Handbook of Chemical Bond Energies; CRC Press: Boca Raton, Florida, 2007. doi:10.1201/9781420027282
22. Ito, O.; Akio, S.; Iino, M. J. Org. Chem. 1989, 54, 2436–2440. doi:10.1021/jo00271a038
23. Del Giacco, T.; Bacicocchi, E.; Steenken, S. J. Phys. Chem. 1993, 97, 5451–5456. doi:10.1021/j100123a003

Supporting Information

Supporting Information File 1
HPLC chromatograms of raw reaction mixtures.
[http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-9-225-S1.pdf]
24. Atkinson, R. J. Phys. Chem. Ref. Data 1991, 20, 459–507. doi:10.1063/1.555887
25. Wayne, R. P. Experimental study of the nitrate radical. In N-Centered Radicals; Alfassi, Z. B., Ed.; John Wiley & Sons: New York, 1998; pp 207–258.
26. Shono, T.; Yamamoto, Y.; Takigawa, K.; Maekawa, H.; Ishifune, M.; Kashimura, S. Chem. Lett. 1994, 23, 1045–1048. doi:10.1246/cl.1994.1045
27. Wille, U. J. Phys. Org. Chem. 2011, 24, 672–681. doi:10.1002/poc.1808
28. Wille, U. Chem. Rev. 2013, 113, 813–853. doi:10.1021/cr100359d
29. D’Anna, B.; Andresen, Ø.; Gefen, Z.; Nielsen, C. J. Phys. Chem. Chem. Phys. 2001, 3, 3057–3063. doi:10.1039/b103623h
30. Suzuki, H.; Mori, T. J. Chem. Soc., Perkin Trans. 2 1997, 1265–1274. doi:10.1039/a700326i
31. Shafirovich, V.; Cadet, J.; Gasparutto, D.; Dourandin, A.; Geacintov, N. E. Chem. Res. Toxicol. 2001, 14, 233–241. doi:10.1021/tr000204t
32. Takami, M.; Matsuura, T.; Saito, I. Tetrahedron Lett. 1974, 15, 661–662. doi:10.1016/S0040-4039(01)82298-X
33. Petersen, W. C.; Letsinger, R. L. Tetrahedron Lett. 1971, 12, 2197–2200. doi:10.1016/S0040-4039(01)96818-2

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