Effect of copper salts on hydrothermal oxidative decarboxylation: a study of phenylacetic acid†

Xuan Fu,[a] Megan Jamison,[a] Aaron M. Jubb,[b] Yiju Liao,[a] Alexandria Aspin,[a] Kyle Hayes,[a] Christopher R. Glein[c] and Ziming Yang [ID] *[a]

Decarboxylation of carboxylic acids is favored under hydrothermal conditions, and can be influenced by dissolved metals. Here, we use phenylacetic acid as a model compound to study its hydrothermal decarboxylation in the presence of copper(II) salts but no O_2. Our results showed a strong oxidizing role of copper in facilitating oxidative decarboxylation.

Organic compound transformations in hydrothermal systems are of great importance to a wide range of chemical and geological processes, including degradation of sedimentary organic matter, metabolism in the subsurface biosphere, and the deep carbon cycle.[1–4] Unlike at ambient conditions, water at elevated temperatures and pressures assumes key properties that promote organic reactions. For example, hydrothermal water has a considerably lower dielectric constant but a higher dissociation constant (K_w) than ambient water, making it not only a good solvent for organic molecules but also providing Brønsted acid and base catalysts in the form of increased concentrations of H^+ and OH^-.[5,6] The chemistry of a variety of organic functional groups has been examined under hydrothermal conditions, and their reaction pathways and mechanisms have been elucidated.[7–12] In particular, reversible and irreversible interconversions between organic functional groups have been proposed in sedimentary basins,[1] and experimental data were collected showing the interconversions between alkanes, alkenes, alcohols, aldehydes/ketones, and carboxylic acids.[7,13] However, the hydrothermal chemistry of organic compounds can be influenced by the surrounding rocks and minerals, and water-rock interactions can release dissolved metal species that potentially dominate hydrothermal organic reactivity. Transformations of organic molecules could be promoted by the presence of minerals, and indeed some remarkable hydrothermal

redox reactions have been observed.[14–17] For example, reduction of ketones to alcohols can be facilitated by iron sulfide minerals,[15] oxidation of alcohols to aldehydes can be efficient in the presence of copper(II),[14] and selective reduction of alkenes to alkanes is feasible using Fe/Ni under hydrothermal conditions.[16]

Organic–inorganic hydrothermal reactions are also of growing interest to green chemistry. The concept of "geomimicry" has been proposed, which applies relatively benign and Earth-abundant materials (e.g., iron, copper, zinc) to organic synthesis, rather than the use of toxic or rare metal catalysts.[14,16] For example, copper salts have been used as effective catalysts for organic oxidation in green chemistry,[18,19] but the reactions usually require O_2 to be present as the oxidant.[20,21] In a previous study, we found that under hydrothermal conditions copper(II) chloride was an efficient oxidant for alcohols, even in the absence of O_2.[14] The oxidizing role of copper could create novel redox pathways for organic compounds in both natural and human-made hydrothermal systems. For example, deep-sea mining indicates that copper-bearing minerals were deposited at the seafloor from hydrothermal fluids,[22,23] and these minerals could release dissolved copper species that interact with organic carbon. Here we investigate the scope of hydrothermal organic oxidation using a suite of copper(II) salts, and we describe results that compare effects of different cupric salts in oxidative decarboxylation of carboxylic acids. Carboxylic acids are known to undergo decarboxylation under hydrothermal conditions,[12,24,25] but studies of hydrothermal interactions between carboxylic acids and inorganic species are few, and in particular, the effect of dissolved metal ions on acid decarboxylation is largely unknown. In this study, we use phenylacetic acid (PAA) as a model compound to examine the effects of cupric salts, based on its known hydrothermal chemistry and predictable decarboxylation pathways.[12,14] Results from this work may provide new insights into the roles of dissolved metal species in hydrothermal organic transformations.

Hydrothermal experiments were performed in fused silica glass tubes using a previously developed method.[26] Experiments were conducted under a hydrothermal condition of 200 °C and

[a] Department of Chemistry, Oakland University, Rochester, MI 48309, USA.
  E-mail: zimingyang@oakland.edu
[b] U.S. Geological Survey, 12201 Sunrise Valley Drive, Reston, VA 20192, USA
[c] Space Science and Engineering Division, Southwest Research Institute, San
  Antonio, TX 78228, USA
† Electronic supplementary information (ESI) available: Detailed experimental set ups and experimental materials. See DOI: 10.1039/c9cc09825a
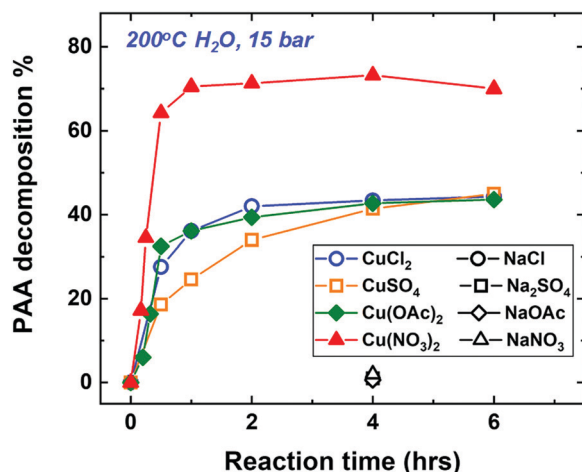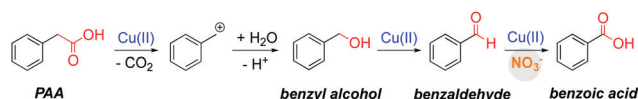
Fig. 1 Hydrothermal decarboxylation of phenylacetic acid (PAA) in the presence of copper or sodium salts at 200 °C and 15 bar (P_{sat}) for up to 6 hours.

15 bar (P_{sat}, calculated using SUPCRT92)[27] in the absence of O_2, and the effects of four copper(II) salts including $CuCl_2$, copper sulfate ($CuSO_4$), copper acetate [$Cu(OAc)_2$], and copper nitrate [$Cu(NO_3)_2$] were compared. At 200 °C, PAA reacted very slowly in pure hydrothermal water, with a < 2% decomposition after 6 hours. In the presence of the copper salts, however, more than 40% of the acid was degraded after 6 hours (Fig. 1). Time-series experiments showed that the decomposition of PAA mostly occurred in the first 2 hours and then reached a steady state (Fig. 1). Among the four copper(II) salts with the same concentration of copper (i.e., 0.2 molal), the trend in decomposing PAA followed as copper nitrate » copper chloride ≈ copper acetate > copper sulfate, with copper nitrate exhibiting the most significant effect (e.g., ~70% acid decomposition after 2 hours). Experiments with a lower molar ratio of 1 : 4 between PAA and copper(II) were also conducted, in which even higher decomposition of PAA was observed when larger amounts of copper(II) were used (Table S1, ESI†). In contrast, hydrothermal experiments with sodium salts with the same counterions showed negligible PAA decomposition (all below 2% after 4 hours) (Fig. 1), suggesting the reactions were not driven by the anions or nitrate alone. These results demonstrate different effects of copper salts on carboxylic acid decomposition, which could be attributed to the formation of different copper(II) complexes under the hydrothermal condition (see below).

Copper(II)-facilitated PAA hydrothermal transformation was proposed to undergo a series of oxidative steps starting with oxidative decarboxylation to form benzyl alcohol, then benzaldehyde, and benzoic acid (Scheme 1). In these steps, copper ions were proposed to serve as a reactive oxidant to promote acid decarboxylation and the following oxidation of primary products. UV-Vis spectroscopy analysis showed that the dissolved copper(II) was mostly consumed after the reaction (Fig. S3, ESI†), which verifies the oxidative role of copper(II) in this reaction scheme. Benzaldehyde and benzoic acid were formed as the major products of PAA, but their distributions were dependent on the type of copper(II) salts. As shown in Fig. 2, all copper experiments showed trends of increasing concentrations of benzaldehyde and benzoic acid over time, except for copper nitrate which showed a decreasing concentration of benzaldehyde that implies its further oxidation to benzoic acid after 0.5 hours. To compare the oxidizing effects between the copper salts, the ratio of benzoic acid to benzaldehyde was calculated. Fig. 2c shows that the acid:aldehyde ratios were between 0.3 and 2.3 in the presence of copper chloride/ sulfate/acetate, whereas the ratio in the copper nitrate experiment substantially increased to a value of 47.6 after 6 hours. This high acid:aldehyde ratio indicates that copper(II) nitrate was a much stronger oxidant than the other copper salts in hydrothermal transformation of carboxylic acids.

Because sodium salts did not show any oxidizing effects under the same hydrothermal condition (Fig. 1), we hypothesize that the main driver of oxidative decarboxylation could be complexes between copper(II) and the anions, rather than freely solvated copper(II). Indeed, thermodynamic calculations on copper speciation under similar hydrothermal conditions (e.g., 250 °C and 40 bar) suggested that the dominant forms of aqueous copper species were copper complexes (e.g., with chloride or acetate) instead of uncomplexed copper(II).[14] To investigate the effect of the nitrate complex, other divalent but non-oxidizing metal ions including magnesium (Mg^{2+}), zinc (Zn^{2+}), and nickel (Ni^{2+}) were studied in the form of nitrate salts to react with PAA at 200 °C for 4 hours, respectively. Compared to sodium nitrate, magnesium nitrate, zinc nitrate, and nickel nitrate all increased the PAA conversion by 10–15%, with benzaldehyde and benzoic acid formed as the major products (Fig. 3). Since these metals are non-oxidizing, forming the oxidation products implies a potential oxidizing role of divalent metal–nitrate complexes in the hydrothermal system. Interestingly, all three metal nitrates yielded more benzoic acid than benzaldehyde (acid/aldehyde ratio between 3.6 and 4.5), indicating the oxidation step from benzaldehyde to benzoic acid was promoted by the presence of nitrate. However, the PAA decomposition with non-oxidizing metal nitrates was not comparable to that with copper nitrate (Fig. 3), suggesting that the oxidative decarboxylation was mainly driven by the copper(II) complexes, whereas the oxidation of benzaldehyde was facilitated by the nitrate (Scheme 1).

To further study the copper complexation, Raman spectroscopy analysis was also performed for hydrothermal experiments with PAA and with PAA + $CuCl_2$, respectively. Raman spectra were collected every 30 minutes during a 2 hour hydrothermal reaction of PAA at 200 °C, and the peaks were assigned according to Lin-Vien et al. (1991).[28] No obvious changes were observed in the PAA alone experiment (Fig. 4a), which is consistent with the low reactivity of PAA under the hydrothermal condition. In the presence of $CuCl_2$, however, several significant changes are

Scheme 1 Proposed hydrothermal oxidative decarboxylation pathway from phenylacetic acid (PAA) to benzyl alcohol, benzaldehyde, and benzoic acid in the presence of copper(II).
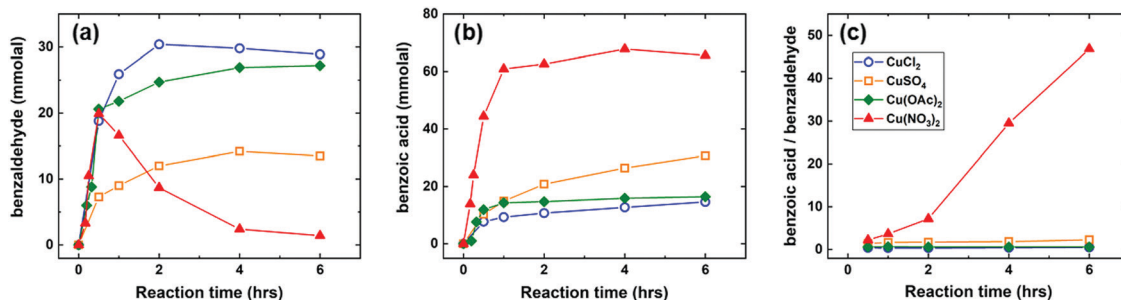
Fig. 2 Concentrations (mmolal) of major product benzaldehyde (a) and benzoic acid (b), and ratios of benzoic acid/benzaldehyde (c) vs. time in hydrothermal experiments of PAA with copper chloride (blue circles), copper sulfate (orange squares), copper acetate (green diamonds), and copper nitrate (red triangles) at 200 °C and 15 bar (P_{sat}).
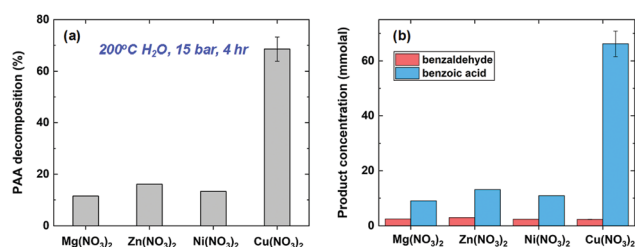

Fig. 3 Hydrothermal decarboxylation of PAA (a) and its product distribution (b) in the presence of magnesium nitrate, zinc nitrate, nickel nitrate, and copper nitrate at 200 °C and 15 bar (P_{sat}) after 4 hours.
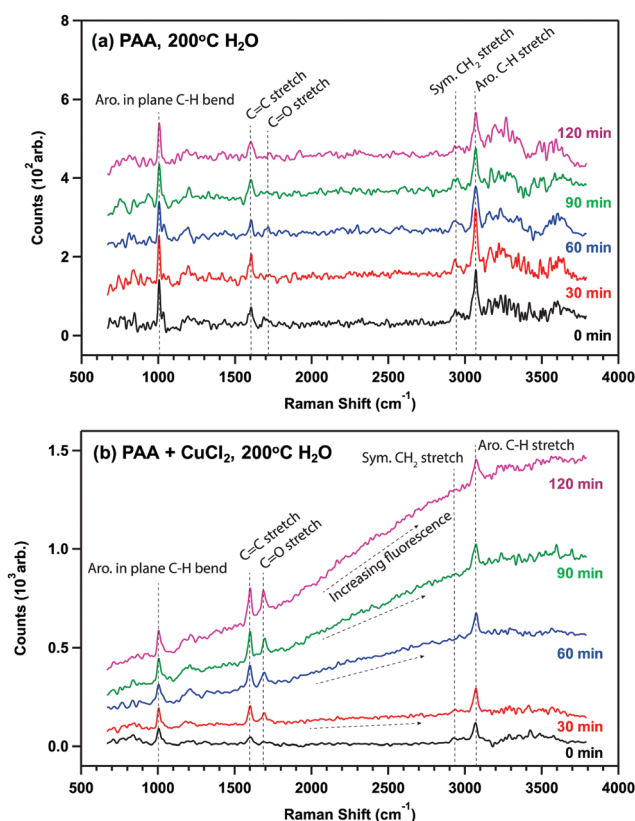

Fig. 4 Time-series Raman spectroscopy analysis (every 30 minutes) on hydrothermal decarboxylation of PAA (a) and PAA with copper chloride (b) at 200 °C and 15 bar (P_{sat}) for up to 2 hours. Dashed lines indicate major peaks with assignments taken from Lin-Vien et al. (1991). Aro = aromatic, sym = symmetric.

observed in the spectra (Fig. 4b). The C=O group became more abundant through the hydrothermal process, which is consistent with the production of benzaldehyde and benzoic acid from PAA. The intensity of a Raman response is equal to the product of the input laser energy, the number of oscillators, and the Raman cross-section of the vibration;[28] the Raman cross-section is proportional to the change in polarizability induced during the vibration. The increased C=O and C=C (from the benzene ring) intensities in Fig. 4b could be explained by a higher cross-section of the vibration in benzaldehyde and benzoic acid than that in PAA, since an increased proximity of the aromatic ring to the C=O moiety may induce a greater change in polarizability during vibration. More interestingly, an increasing fluorescence was detected over the reaction time, which may suggest the formation of copper-coordinated complexes in the system.[29–31] These Raman results provided additional evidence for the presence of copper complexes in the PAA experiments.

Copper(II) nitrate is a readily available cupric salt and has emerged as a versatile reagent for organic synthesis.[32] It has been used as an oxidizing agent and also a Lewis acid catalyst. For example, an organic synthesis study showed that copper nitrate allows facile oxidative decarboxylation of benzoyl formic acid to form benzonitrile in the presence of aqueous ammonium and O_2,[33] although the reaction conditions were quite different from the current work. To investigate whether copper nitrate played a role of Lewis acid in this decarboxylation, we chose another common Lewis acid – copper(II) triflate [$Cu(OTf)_2$] to study. The triflate ion is weakly nucleophilic, which makes the cupric ion more cationic and $Cu(OTf)_2$ a stronger Lewis acid than $Cu(NO_3)_2$.[34] At the same

experimental conditions at 200 °C, however, we found the conversions of PAA after 1 and 2 hours were $4.4 \pm 0.2\%$ and $14.6 \pm 0.3\%$, respectively, which were much lower than those in the $Cu(NO_3)_2$ experiments (Fig. 1). In contrast, experiment of PAA with a mixture of $Cu(OTf)_2$ and $NaNO_3$ yielded similar conversion to that with $Cu(NO_3)_2$ (Table S1, ESI†). These results further suggest that the complexation, instead of Lewis acidity, is more important to enhance the oxidative ability of copper(II).

Copper nitrate experiments with substituted phenylacetic acids, including p-tolylacetic acid and p-fluorophenylacetic acid, were also
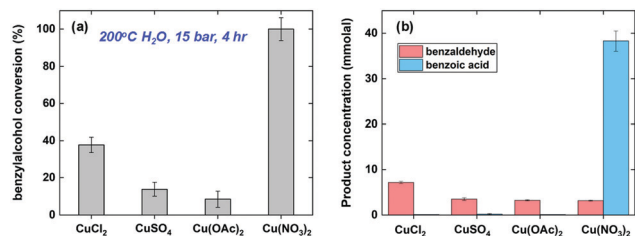
Fig. 5 Hydrothermal transformation of benzyl alcohol (a) and its product distribution (b) in the presence of the copper salts at 200 °C and 15 bar (P_{sat}) after 4 hours.

conducted to further clarify the decarboxylation mechanism. At 200 °C, the acid conversions after 1 hour were $42.1 \pm 0.3\%$ and $13.6 \pm 0.2\%$ for p-tolylacetic acid and p-fluorophenylacetic acid, respectively, while the conversion for parent PAA was $36.1 \pm 0.1\%$. This conversion trend (p-tolylacetic acid > PAA > p-fluorophenyl-acetic acid) thus suggests a carbocation intermediate (in Scheme 1), since the electron-donating substituent (–CH$_3$) on the benzene ring accelerated the reaction, whereas the electron-withdrawing substituent (–F) slowed down the reaction. In addition, experiments starting with benzyl alcohol were also performed, and results showed that benzaldehyde and benzoic acids were formed as the major products (Fig. 5), which further support the reaction steps proposed in Scheme 1. Specifically, in the presence of CuCl$_2$, CuSO$_4$, and Cu(OAc)$_2$, the benzyl alcohol conversions were below 40% with an acid:aldehyde ratio <0.1, while in the presence of Cu(NO$_3$)$_2$ the conversion was nearly 100%, with a ratio increased to $15:1$. These observations are also consistent with the PAA experiments, in which copper nitrate behaved as the strongest oxidant.

In conclusion, the fact that the organic reactivity and product distribution were dependent on the type of copper salts highlights a selective role of metal ions/complexes in hydrothermal organic redox transformations. The unique properties of water at high temperatures and pressures not only allow organic reactions to occur in aqueous medium, but also influence the speciation and complexation of dissolved metals, which can selectively control organic redox transformations in hydrothermal environments. While the majority of hydrothermal organic geochemistry research have been focusing on organic-mineral interactions, this work provides new insights into the hydrothermal interactions between organic and dissolved metal species, which are important to further our understanding of hydrothermal systems, as well as to discover more "geomimicry" approaches in green chemistry.[14,16]

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 J. S. Seewald, *Nature*, 2003, **426**, 327–333.
2 I. M. Head, D. M. Jones and S. R. Larter, *Nature*, 2003, **426**, 344–352.
3 T. M. McCollom and J. S. Seewald, *Chem. Rev.*, 2007, **107**, 382–401.
4 D. A. Sverjensky, V. Stagno and F. Huang, *Nat. Geosci.*, 2014, **7**, 909–913.
5 N. Akiya and P. E. Savage, *Chem. Rev.*, 2002, **102**, 2725–2750.
6 M. Watanabe, T. Sato, H. Inomata, R. L. Smith, K. Arai, A. Kruse and E. Dinjus, *Chem. Rev.*, 2004, **104**, 5803–5822.
7 Z. Yang, I. R. Gould, L. B. Williams, H. E. Hartnett and E. L. Shock, *Geochim. Cosmochim. Acta*, 2012, **98**, 48–65.
8 C. Bockisch, E. D. Lorance, H. E. Hartnett, E. L. Shock and I. R. Gould, *ACS Earth Space Chem.*, 2018, **2**, 821–832.
9 K. M. Fecteau, I. R. Gould, C. R. Glein, L. B. Williams, H. E. Hartnett and E. L. Shock, *ACS Earth Space Chem.*, 2019, **3**, 170–191.
10 K. J. Robinson, I. R. Gould, K. M. Fecteau, H. E. Hartnett, L. B. Williams and E. L. Shock, *Geochim. Cosmochim. Acta*, 2019, **244**, 113–128.
11 Z. Yang, E. D. Lorance, C. Bockisch, L. B. Williams, H. E. Hartnett, E. L. Shock and I. R. Gould, *J. Org. Chem.*, 2014, **79**, 7861–7871.
12 C. R. Glein, I. R. Gould, E. D. Lorance, H. E. Hartnett and E. L. Shock, *Geochim. Cosmochim. Acta*, 2020, **269**, 597–621.
13 E. L. Shock, P. Canovas, Z. Yang, G. Boyer, K. Johnson, K. Robinson, K. Fecteau, T. Windman and A. Cox, *Rev. Mineral. Geochem.*, 2013, **76**, 311–350.
14 Z. Yang, H. E. Hartnett, E. L. Shock and I. R. Gould, *J. Org. Chem.*, 2015, **80**, 12159–12165.
15 Z. Yang, I. R. Gould, L. B. Williams, H. E. Hartnett and E. L. Shock, *Geochim. Cosmochim. Acta*, 2018, **223**, 107–126.
16 C. Bockisch, E. D. Lorance, G. Shaver, L. B. Williams, H. E. Hartnett, E. L. Shock and I. R. Gould, *Green Chem.*, 2019, **21**, 4159–4168.
17 J. A. Shipp, I. R. Gould, E. L. Shock, L. B. Williams and H. E. Hartnett, *Proc. Natl. Acad. Sci. U. S. A.*, 2014, **111**, 11642–11645.
18 P. Gamez, P. G. Aubel, W. L. Driessen and J. Reedijk, *Chem. Soc. Rev.*, 2001, **30**, 376–385.
19 J. Liu, X. Zhang, H. Yi, C. Liu, R. Liu, H. Zhang, K. Zhuo and A. Lei, *Angew. Chem., Int. Ed.*, 2015, **54**, 1261–1265.
20 S. E. Allen, R. R. Walvoord, R. Padilla-Salinas and M. C. Kozlowski, *Chem. Rev.*, 2013, **113**, 6234–6458.
21 S. D. McCann and S. S. Stahl, *Acc. Chem. Res.*, 2015, **48**, 1756–1766.
22 J. R. Hein, K. Mizell, A. Koschinsky and T. A. Conrad, *Ore Geol. Rev.*, 2013, **51**, 1–14.
23 K. A. Miller, K. F. Thompson, P. Johnston and D. Santillo, *Frontiers in Marine Science*, 2018, **4**, 418.
24 J. B. Dunn, M. L. Burns, S. E. Hunter and P. E. Savage, *J. Supercrit. Fluids*, 2003, **27**, 263–274.
25 T. M. McCollom and J. S. Seewald, *Geochim. Cosmochim. Acta*, 2003, **67**, 3625–3644.
26 Z. Yang and X. Fu, *JoVE*, 2018, e58230.
27 J. W. Johnson, E. H. Oelkers and H. C. Helgeson, *Comput. Geosci.*, 1992, **18**, 899–947.
28 D. Lin-Vien, N. B. Colthup, W. G. Fateley and J. G. Grasselli, *The handbook of infrared and Raman characteristic frequencies of organic molecules*, Academic Press, 1991.
29 M. H. Lim and S. J. Lippard, *J. Am. Chem. Soc.*, 2005, **127**, 12170–12171.
30 R. Krämer, *Angew. Chem., Int. Ed.*, 1998, **37**, 772–773.
31 X.-M. Chen and M.-L. Tong, *Acc. Chem. Res.*, 2007, **40**, 162–170.
32 M. Gao, R. Ye, W. Shen and B. Xu, *Org. Biomol. Chem.*, 2018, **16**, 2602–2618.
33 P. K. Arora and L. M. Sayre, *Tetrahedron Lett.*, 1991, **32**, 1007–1010.
34 C. Hertweck, *J. Prakt. Chem.*, 2000, **342**, 316–321.