A Journal of the Gesellschaft Deutscher Chemiker
Angewandte Chemie
GDCh
International Edition
www.angewandte.org

Title: Sustainable co-synthesis of glycolic acid, formamides and formates from 1,3-dihydroxyacetone by a Cu/Al2O3 catalyst with single active sites

Authors: Xingchao Dai, Sven Adomeit, Jabor Rabeah, Carsten Kreyenschulte, Angelika Brückner, Hongli Wang, and Feng Shi

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201814050
Angew. Chem. 10.1002/ange.201814050

Link to VoR: http://dx.doi.org/10.1002/anie.201814050
http://dx.doi.org/10.1002/ange.201814050

WILEY-VCH

Sustainable co-synthesis of glycolic acid, formamides and formates from 1,3-dihydroxyacetone by a Cu/Al_2O_3 catalyst with single active sites

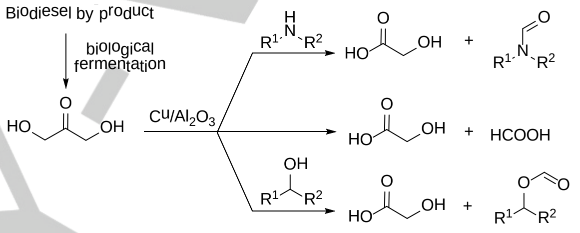
Xingchao Dai,+[a, c] Sven Adomeit,+[b] Jabor Rabeah,[b] Carsten Kreyenschulte,[b] Angelika Brückner,*[b] Hongli Wang,[a] and Feng Shi*[a]

Abstract: Glycolic acid (GA) as important building block of biodegradable polymers has been synthesized for the first time in excellent yields at room temperature by selective oxidation of 1,3-dihyroxyacetone (DHA) using a cheap supported Cu/Al_2O_3 catalyst with single active Cu^{II} species. By combining EPR spin-trapping and operando ATR-IR experiments, different mechanisms for the co-synthesis of GA, formates and formamides have been derived, in which •OH radicals formed from H_2O_2 via a Fenton-like reaction play a key role.

There is a rising demand for biodegradable polymers to be used, e. g., for packaging[1] and in biomedicine.[2] Especially polyglycolic acid (PGA) has attracted much attention. It is usually produced by carbonylation of formaldehyde (FAL)[3] or selective oxidation of ethylene glycol[4], yet these processes suffer from high pressure, corrosion of equipment as well as difficult workup. It would be very attractive to produce PGA by condensation of glycolic acid (GA) obtained from renewable biomass-based platform molecules such as 1,3-dihyroxyacetone (DHA). This is easily available from glycerol[5] being a by-product of biodiesel production with about 3 million tons per year.[6] Recently, the synthesis of glycolate from DHA has been reported[7], yet excess amounts of base are required and the glycolate needs to be acidized before further use, leading to much inorganic waste. With O_2 as oxidant, total oxidation of GA dominates.[8] Therefore, direct synthesis of GA from DHA with good enough yield would be a very attractive alternative.

Here we report for the first time the catalytic one-pot synthesis of GA and co-synthesis of formamides and formates from DHA as versatile building blocks without any added base (Scheme 1). With a non-noble metal Cu/Al_2O_3 catalyst and H_2O_2 as a clean oxidant, the C-C bond in DHA could be selectively cut to form GA in high yields at room temperature (RT).

Several supported catalysts with different metals and supports were tested in the solvent-free synthesis of GA from DHA at 25 °C (Table 1). Highest GA yield was obtained with Cu supported on Al_2O_3 (Entries 1, 10 and 11), known to be active in selective C-C bond cleavage.[9] Therefore, we focus only on Cu/Al_2O_3 in due course. With this catalyst, TOF values amounted to 159 h^{-1} (Entry 1). After 24 h, the desired GA could be obtained in up to 94% yield (Entry 10). However, only 41% yield of formic acid (FA) was obtained due to further oxidation to CO_2. Quantitative analysis of the gas phase after reaction revealed that 58% of FA was oxidized to CO_2. When bare Al_2O_3 or even no catalyst was applied, 83-85% DHA conversion was obtained but the yield of GA was only 24 % (Entries 12-13). This might be due to the non-selective oxidation of DHA by peroxide radicals generated from H_2O_2. ^1H-NMR analysis revealed 6% FA and 58% hydrated DHA while 18% of FA was oxidized to CO_2.



Scheme 1. One-pot synthesis of GA, formamides and formates with 1,3-dihydroxyacetone as a versatile building block.

Table 1: GA yields and TOF values for different catalysts.[a]

Entry	Cat.	Y [%]	TOF [h^{-1}]	Entry	Cat.	Y [%]	TOF [h^{-1}]
1	Cu/Al_2O_3	85	159	9	Cu/C	34	72
2	Ru/Al_2O_3	68	269	10[b]	Cu/Al_2O_3	94	59
3	Pd/Al_2O_3	42	121	11[b][c]	Cu/Al_2O_3	91/86[d] 85[e]/88[f]	57
4	Pt/Al_2O_3	--	--	12	--	24	--
5	Cu/Fe_2O_3	65	108	13	Al_2O_3	24	--
6	Cu/Ni_2O_3	74	138	14[g]	Cu/Al_2O_3	20	--
7	Cu/TiO_2	41	81	15	Cu/Al_2O_3-1%	57	22
8	Cu/SiO_2	46	86	16	Cu/Al_2O_3-H_2O	58	115

[a] Reaction conditions: 1 mmol 1,3-dihydroxyacetone, 3 equiv., H_2O_2, 25 mg catalyst, 25 °C, 8 h. [b] 24 h. [c] 1 equiv., H_2O_2. [d] Isolated yield. [e] Catalyst re-used in 2nd and [f] 3rd run. [g] The catalyst was removed by filtration after 3 h use and then the reaction was performed for another 5 h.

Based on the proposed mechanism in Scheme 2a (vide infra) and the stoichiometric balance (Fig. S1), conversion of 1 mmol DHA to GA requires at least 2 mmol of H_2O_2 (1 equiv.). Noteworthy, with 1 equiv. of H_2O_2 a similar GA yield like with 3 equiv. H_2O_2 was achieved (cf. Entry 10 and 11 in Table 1). The

---

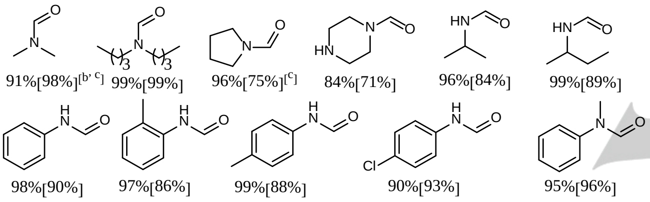
[a] Xingchao Dai,[+] Hongli Wang and Prof. Dr. Feng Shi, State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, No.18, Tianshui Middle Road, Lanzhou, 730000, China; E-mail: fshi@licp.cas.cn
[b] Sven Adomeit,[+] Dr. Jabor Rabeah, Dr. Carsten Kreyenshulte and Prof. Dr. Angelika Brückner, Leibniz-Institut für Katalyse e.V. an der Universität Rostock (LIKAT), Albert-Einstein-Str. 29a, 18059 Rostock, Germany, E-mail: angelika.brueckner@catalysis.de
[c] University of Chinese Academy of Sciences, No. 19A, Yuquanlu, Beijing, 100049, China
+ These authors contributed equally to this work

Supporting information for this article is given via a link at the end of the document.

desired GA could be easily isolated in high purity by removing water via simple distillation in up to 86% yield (Table 1, Entry 11 and Fig. S2). Estimation of residual H_2O_2 (SI, section 6)[10] indicated an H_2O_2 utilization efficiency of 91%. Pre-reduction of the catalysts had no positive effect since similar or lower GA yields were obtained in comparison to the active Cu/Al_2O_3 catalyst (cf. Table S1 and Table 1, entry 1).

Furthermore, the Cu/Al_2O_3 catalyst showed no deactivation in 3 subsequent runs after centrifugation, washing and drying (Table 1, Entry 11). Copper loadings of 0.17, 0.13, 0.14 and 0.13 wt.% (± 10% error) were detected in fresh Cu/Al_2O_3 and after 1st, 2nd and 3rd use. This shows that, apart from slight Cu leaching during the first run, the catalyst is stable. To test if the leached copper is responsible for the reaction, the catalyst was removed by filtration after 3 h use and only 10% conversion of DHA and 9% yield (≈ 90% selectivity) of GA were measured. When the reaction was run for another 5 h after catalyst removal, 95% conversion of DHA but only 20% yield of GA were obtained (Table 1, Entry 14). This result is similar to that of the blank test, indicating that supported copper is the active and selective species.

Table 2: Co-production of GA and formamides from DHA and different amines.[a]



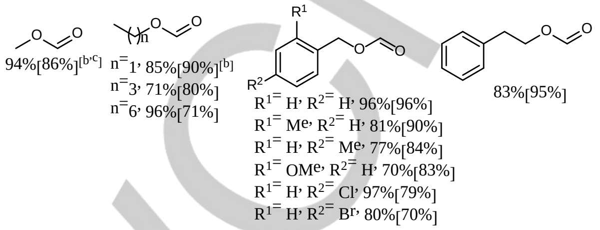
[a] 5 mmol amines, 1 mmol DHA, 1.5 equiv., H_2O_2, 25 mg Cu/Al_2O_3, 2 mL H_2O, reactions run at 25 °C for 24 h, respectively at 50 °C for 12 h. GA yields shown in brackets. [b] Dimethylamine gas as starting material. [c] 5 mL H_2O.

Together with GA, FA was formed (Scheme 1, determined by ^{1}H NMR), but only in 41 % yield, which might be due to over-oxidation to CO_2. Hence, to avoid waste of the carbon source and raise atom efficiency, a protocol for the co-production of GA and formamides or formates has been developed by trapping FA with amines or alcohols (Scheme 1). For this purpose, DHA was reacted with different amines in the presence of Cu/Al_2O_3 (Table 2). Remarkable formamide yields of 84-99% have been obtained with both aromatic and aliphatic amines, while GA was still generated in high yields (71-99%).

Besides amines, various alcohols were used as efficient trapping agents for FA (Table 3), forming up to 97% formates and 70-96% GA. GA and formates could be easily separated by simple distillation, leading to isolated GA yields of 71-81% with ethanol and benzyl alcohol.

To explore the correlation between structure and catalytic performance, the active Cu/Al_2O_3 catalyst was characterized comprehensively. The Cu loading dropped marginally from 0.17% in the fresh to 0.13% in the used catalyst, while BET surface area, pore volume and mean pore diameter remained constant at 146 m^2g^{-1}, 43.5 cm^3 g^{-1} and 6 nm, respectively, confirming that the catalyst is stable during reaction (Fig. S3). As expected for such low Cu contents, no signals of Cu species were observed, neither by XRD (Fig. S4) nor by XPS (not shown). HAADF-STEM (Fig. S5) of Cu/Al_2O_3 do not show any Cu containing particles although the EDX analysis in Fig. S6 points to the presence of Cu. If any, then only few very small CuO_x moieties can be seen (Fig. S5), suggesting that Cu is mainly present as single sites. This is evidenced, too, by the EPR spectrum of Cu/Al_2O_3 (Fig. S7) showing an axial signal of isolated Cu^{II} ions with spin hamiltonian parameters of $g_{\|}=2.349$, $g_{\perp}=2.078$ and $A_{\|}=142$ G[11] without significant superposition of a broad singlet expected for Cu_xO_y clusters, as observed for similarly prepared catalyst, yet with 1 wt.% of Cu deposited on Al_2O_3 (*vide infra*).

Table 3: Co-production of GA and formates from DHA and different alcohols.[a]



[a] 5 mmol alcohols, 1 mmol DHA, 1.5 equiv., H_2O_2, 25 mg Cu/Al_2O_3 catalyst, 80 °C, 24 h. [b] 50 °C. [c] 5 mL $CHCl_3$ as solvent. GA yield in brackets.

In the Cu K-edge EXAFS spectra, only a peak for a Cu-O coordination between 1.2 and 1.8 Å but no typical peak for a Cu-Cu shell between 2.2 and 2.8 Å was observed, neither in the fresh nor in the used catalysts (Fig. S8). This confirms clearly the dominance of Cu^{II} single sites attached to O atoms of the Al_2O_3 support surface.[12]

To find out whether it is indeed these Cu single sites that govern catalytic activity, we prepared a 1 wt.% Cu/Al_2O_3 catalyst by the same method, which showed a GA yield of only 57%, despite its five times higher Cu content (cf. Table 1, entry 1 and 15). In the EPR spectrum of this catalyst, Cu_xO_y clusters are clearly visible by the broad background signal superimposed on the hfs signal of the single Cu^{II} sites (Fig. S7), supporting clearly that it is indeed the single Cu^{II} species which are active in GA synthesis from DHA.

Besides acetone, also water was used as solvent in the impregnation procedure for catalyst synthesis. However, due to its low volatility, it had to be removed by rotary evaporation at 80 °C. This may have led to clustering of Cu sites. Only 58% GA yield was obtained in this case (Table 1, entry 16). Therefore, this synthesis method was disregarded.

To explore the mechanism of GA formation from DHA, EPR spin trapping experiments and operando ATR-IR investigations were performed, in which conversion of DHA to GA is monitored by decreasing ν(C–OH) and ν(C=O) bands of DHA and rising ν(C=O) and ν(C-OH) bands of GA. EPR spectra in the presence of 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin trap have been recorded since formation of radicals during reaction was assumed.[13] Addition of H_2O_2 to Cu/Al_2O_3 + spin trap in aqueous solution leads to DMPO-OH and DMPO-OOH spin adducts (Fig. 1a and S9), indicating formation of 62.6% •OH and 37.4% •OOH radicals[14], derived by spectra simulation.

After adding DHA, a new EPR signal from a DMPO-R spin adduct appeared (Fig. 1a, top), indicating formation of a C-centered radical intermediate (•R ≈ 20% after 30 min). Probably •OH radicals attack DHA, leading to a drop of DMPO-OH from 62.6 to 40.1% while the amount of DMPO-OOH remained almost constant (Fig. 1b). In due course, DMPO-OH is formed again due to excess H_2O_2 while DMPO-R species decreased, suggesting that •R is converted into EPR silent species probably due to product formation.

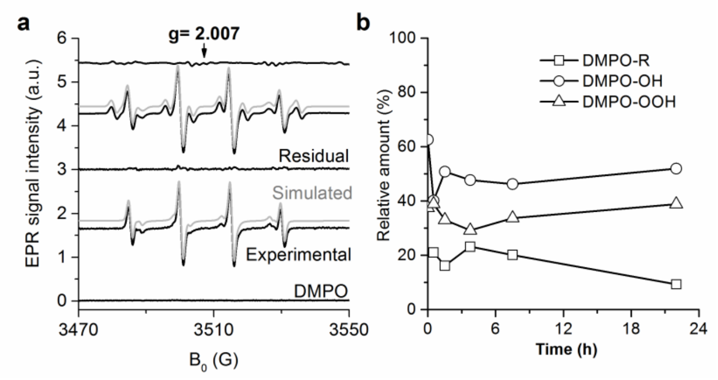


Fig. 1. a) Normalized EPR spectra of DMPO spin adducts (cf. Fig. S9) with Cu/Al_2O_3 and H_2O_2 before (bottom) and 90 min after addition of DHA (top). Hfs parameters: $A_N \approx A_H$ =14.9 G for •OH, A_N =14.3, $A_{\beta H}$ = 11.4, $A_{\gamma H}$ =1.2 G for •OOH, and A_N =15.9, A_H =22.7 G for •R. **b)** Relative amount of the DMPO-X spin adducts before (t=0) and after adding DHA.

Operando ATR-IR spectra were recorded in D_2O to avoid overlap of the ν(C=O) bands with the δ(O–H) vibration of H_2O (Fig. 2a, *cf.* Fig. S10). Initially, two ν(C–OH) bands of DHA at 1004 and 1064 cm^{-1} are seen, while the ν(C=O) band of DHA falls at 1736 cm^{-1}. After adding H_2O_2 these bands drop as DHA is consumed and new ν(C=O) and ν(C-OH) bands of GA appear at 1724 and 1092 cm^{-1} (*cf.* reference spectrum in Fig. S11).

Furthermore, a new $v_{as}(COO^-)$ band of carboxylate rises at 1590 cm^{-1}, suggesting partial deprotonation of the formed carboxylic acids. Due to overlap in the ν(C=O) region, different carbonyl compounds cannot be discerned in the absorption spectrum. However, the 2nd derivative shows at least two other ν(C=O) bands besides that of GA at 1709 cm^{-1} and 1693 cm^{-1} (Fig. S13). The former might arise from some small fraction of FA (*cf.* Fig. S11), the presence of which was also confirmed by ^{1}H-NMR (Fig. S15). Moreover, the formation of another C=O containing compound is evident from the slope of the peak heights at 1724,1092 and 1064 cm^{-1} in Fig. 2a (*cf.* Fig. S14). The band at 1724 cm^{-1}, reflecting GA + some other carbonyl species, rises faster than the GA band at 1092 cm^{-1} while the drop of the DHA band at 1064 cm^{-1} parallels the rise of the former.

GC-MS analysis detected only small amounts of FA, suggesting its formation *via* an intermediate such as FAL or formyl species. In aqueous media, FAL also shows a ν(C=O) band around 1730 cm^{-1}.[15] In view of up to 94% yield of GA (Table 1, entry 10), its conversion to FA can be basically excluded. Instead, the C_3 skeleton of DHA may undergo selective C-C cleavage to generate one C_2 product (GA) and one C_1 product (FA). Surprisingly, only 41% yield of FA was obtained. Given that H_2O_2 is in excess, this can be explained by oxygenolysis of FA as 0.58 mmol CO_2 was observed after reaction. The reaction of $H^{13}COOH$ with H_2O_2 under the same conditions confirmed this transformation (Scheme S2), in which $^{13}CO_2$ was detected (Fig. S16).

Based on all of these results, a reaction mechanism can be proposed (Scheme 2a). Cu/A_2O_3 activates H_2O_2 to form •OH radicals, which split a C-C bond in DHA resulting in the radical intermediates $•COCH_2OH$ and $•CH_2OH$. The latter react with •OH to the desired GA and a short-lived acetal intermediate that rapidly reacts with H_2O_2 to FA while H_2O is liberated. This is also evident from the rising intensity of the ν(O–H) vibration of H_2O at 1647 cm^{-1} (Fig. 2a). Finally, in excess H_2O_2, a part of FA can be further oxidized to CO_2 and H_2O.

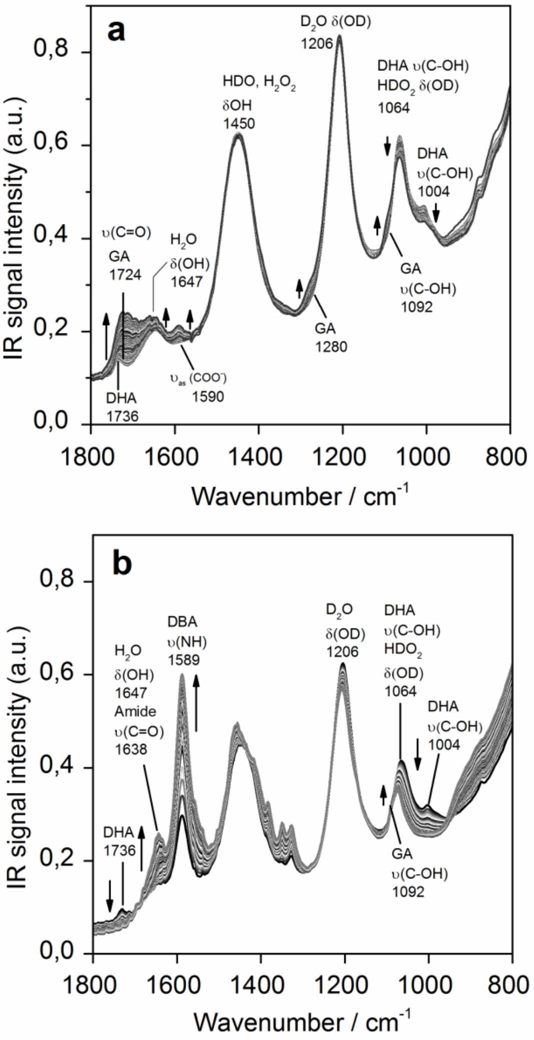


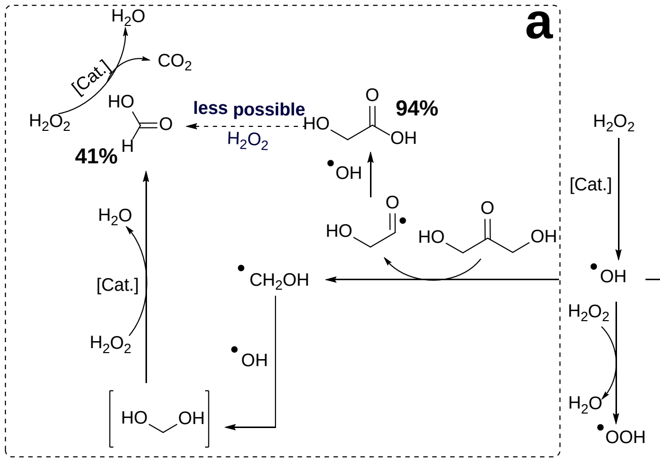
Fig. 2. Operando ATR-FTIR spectra during conversion of DHA to GA performed in D_2O a) without amines and b) with amines. (For detailed stepwise addition of H_2O_2 see Fig. S12).

Inspired by this mechanism, we assumed that FA can react *in situ* with amines and co-produce GA and formamides, yet surprisingly dibutylamine and FA did not react to N,N-dibutylformamide but only to the ammonium salt of FA, while up to 99 % yield of N,N-dibutylformamide was obtained with FAL (Fig. S17). This suggests that FAL is a reaction intermediate. Furthermore, no FA has been detected by GC-MS and ^{1}H-NMR during reaction of DHA with H_2O_2 in the presence of N,N-dibutylamine (DBA), which implies that no $•CH_2OH$ was generated in this case. Thus, FA can be safely excluded as intermediate in the co-production of GA and formamides from DHA and amines.

To obtain more insight into the mechanism of formamide production, the reaction of DHA with H_2O_2 in the presence of

DBA was monitored by operando ATR-IR spectroscopy in D_2O (Fig. 2b). The ν(N-H) band of DBA at 1589 cm^{-1} increases with time reaching steady state after about 11 h (Fig. 2b). This is due to the fact that initially DBA forms a separate layer on top of the D_2O/H_2O_2 solution and dissolved in the latter only with time during reaction. Then a broad feature rises at 1640 cm^{-1}. From the 2nd derivative of the spectrum two bands at 1647 and 1638 cm^{-1} can be discerned (Fig. S13, right). While the former stems from δ(OH) of the formed H_2O, the latter is close to ν(C=O) of a tertiary formamide, i. e., the desired product.[16] Simultaneously, the small ν(C=O) band of DHA at 1736 cm^{-1} vanishes but no other carbonyl bands appeared, suggesting that the formed carboxylic acid intermediate reacts completely with the amine present in excess.

Based on these findings, we propose another reaction mechanism for the co-production of GA and formamides from DHA (Scheme 2b) which involves radical intermediates, too, as confirmed by in situ EPR measurements (Fig. 3).



Scheme 2. Proposed mechanism for the synthesis of GA from DHA in the absence (a) and in the presence (b) of amines .

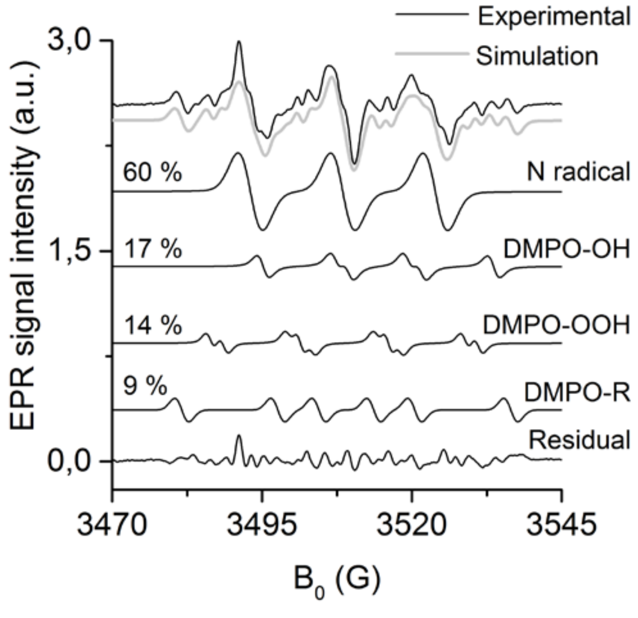


Fig. 3. EPR sum spectrum (top) of the organic phase, taken after 4.5 h from a reaction mixture containing Cu/Al_2O_3, H_2O_2, DHA and DBA after adding DMPO. The simulated spectrum was obtained by superimposing spectra of a $\bullet NR^1R^2$ radical (A_N =15.4 G) and DMPO adducts of •OH (A_N =12.1 G, A_H =14.2 G), •OOH (A_N =14.7 G, $A_{\beta H}$ =13.1 G, $A_{\gamma H}$ =2.1 G) and •R (A_N =16.0 G, A_H =22.9 G).

Since the reaction mixture of the Cu/Al_2O_3 catalyst, H_2O_2, DHA and DBA consists of an aqueous phase containing mainly H_2O_2 and DHA and an organic amine phase, the reaction might occur preferentially on the phase boundary. When a sample of the organic phase is mixed after 4.5 h with DMPO, the EPR spectrum shows signals from different DMPO adducts and an N–centered radical (Fig. 3), which reflect species proposed in the mechanism of Scheme 2b, namely •OH, •OOH, •C(O)CH_2OH and $\bullet NR^1R^2$. •OH and •OOH are formed from H_2O_2 over Cu/A_2O_3 via a Fenton's type reaction already without any substrate (Fig. 1a, bottom).[7b, 17] •OH can react with DHA in the aqueous phase to GA (Fig. 1a, top and Scheme 2a) and with the amine on the phase boundary to $\bullet NR^1R^2$ radicals (Fig. 3). These react with DHA on the phase boundary to the respective formamide (Scheme 2b), possibly *via* a hemiaminal radical that, however, cannot be discerned by EPR from other C-centered •R radicals. Thus, the •R component in Fig. 3 reflects all C-centered radicals postulated in Scheme 2.

In summary, the biomass-based platform molecule DHA has been catalytically activated and directly converted with amines and alcohols to highly valuable GA, formamides and formates in excellent yields at room temperature by a simple supported non-noble metal Cu/Al_2O_3 catalyst. To the best of our knowledge, this is the first demonstration that DHA can behave as a versatile building block to synthesize selectively various valuable molecules. The new concept of effectively converting DHA to value-added molecules by a simple and inexpensive supported Cu/Al_2O_3 catalyst could open new opportunities for the valorization of other biomass-based platform molecules and, thus, makes a significant contribution to sustainable chemical production.

Acknowledgements

We acknowledge financial support by the National Key Research and Development Program of China (2017YFA0403100), NSFC (21633013) Key Research Program of Frontier Sciences of CAS (QYZDJ and SSW-SLH051). We thank Prof. Dr. Lirong Zheng (Institute of High Energy Physics, Chinese Academy of Sciences) for helping us to perform the EXAFS analysis.

Keywords: glycolic acid • 1,3-dihydroxyacetone • formamides and formates • biomass conversion • EPR spectroscopy

[1] a) W. D. Luzier, *Proc. Natl. Acad. Sci.* **1992**, *89*, 839-842; b) Z. Li, X. Gu, S. Lou, Y. Zheng, *Biomaterials* **2008**, *29*, 1329-1344; c) B. Eling, S. Gogolewski, A. J. Pennings, *Polymer* **1982**, *23*, 1587-1593; d) X.-N. Gu, Y.-F. Zheng, *Front. Mater. Sci. China* **2010**, *4*, 111-115; e) R. Zhao, P. Torley, P. J. Halley, *J. Mater. Sci.* **2008**, *43*, 3058-3071.

[2] a) H. Kobayashi, K. Shiraki, Y. Ikada, *J. Biomed. Mater. Res.* **1992**, *26*, 1463-1476; b) D. Hutmacher, J. Goh, S. Teoh, *Ann. Acad. Med. Singap.* **2001**, *30*, 183-191; c) R. C. Mundargi, V. R. Babu, V. Rangaswamy, P. Patel, T. M. Aminabhavi, *J. Controlled Release* **2008**, *125*, 193-209; d) K. A. Athanasiou, G. G. Niederauer, C. M. Agrawal, *Biomaterials* **1996**, *17*, 93-102.

[3] M. T. Shattuck, in *US Patent, Vol. 2443482*, Pont DU. , United States, **1948**.

[4] a) T. van Haasterecht, T. W. van Deelen, K. P. de Jong, J. H. Bitter, *Catal. Sci. Technol.* **2014**, *4*, 2353-2366; b) C. Bianchi, F. Porta, L. Prati, M. Rossi, *Top. Catal.* **2000**, *13*, 231-236; c) M. B. Griffin, A. A. Rodriguez, M. M. Montemore, J. R. Monnier, C. T. Williams, J. W. Medlin, *J. Catal.* **2013**, *307*, 111-120.

[5] a) R. M. Painter, D. M. Pearson, R. M. Waymouth, *Angewandte Chemie International Edition* **2010**, *49*, 9456-9459; b) D. Hekmat, R. Bauer, J. Fricke, *Bioproc. Biosyst. Eng.* **2003**, *26*, 109-116.

[6] M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi, C. Della Pina, *Angew. Chem. Int. Ed.* **2007**, *46*, 4434-4440.

[7] a) P. Pullanikat, S. J. Jung, K. S. Yoo, K. W. Jung, *Tetrahedron Lett.* **2010**, *51*, 6192-6194; bV. Maksimović, M. Mojović, G. Neumann, Ž. Vučinić, *Ann. N.Y. Acad. Sci.* **2005**, *1048*, 461-465.

[8] a) Y. Nakagawa, D. Sekine, N. Obara, M. Tamura, K. Tomishige, *ChemCatChem* **2017**, *9*, 3412-3419; b) S. Lee, H. J. Kim, E. J. Lim, Y. Kim, Y. Noh, G. W. Huber, W. B. Kim, *Green Chem.* **2016**, *18*, 2877-2887; c) X. Liang, A. Rahubadda, B. S. Haynes, A. Montoya, *Ind. Eng. Chem. Res.* **2015**, *54*, 8437-8447; d) Z. Tang, W. Deng, Y. Wang, E. Zhu, X. Wan, Q. Zhang, Y. Wang, *ChemSusChem* **2014**, *7*, 1557-1567; e) J. Xu, Y. Zhao, H. Xu, H. Zhang, B. Yu, L. Hao, Z. Liu, *Appl. Catal. B: Environ.* **2014**, *154-155*, 267-273; f) J. Xu, H. Zhang, Y. Zhao, B. Yu, S. Chen, Y. Li, L. Hao, Z. Liu, *Green Chem.* **2013**, *15*, 1520-1525.

[9] a) L. Gu, C. Jin, H. Zhang, L. Zhang, *J. Org. Chem.* **2014**, *79*, 8453-8456; b) L. Gu, C. Jin, *Chem. Commun.* **2015**, *51*, 6572-6575; c) C. Tang, N. Jiao, *Angew. Chem. Int. Ed.* **2014**, *25*, 6528-6532; d) S. Chiba, L. Zhang, G. Y. Ang, B. W.-Q. Hui, *Org. Lett.* **2010**, *12*, 2052-2055.

[10] Q. Chang, K. Deng, L. Zhu, G. Jiang, C. Yu, H. Tang, *Microchim. Acta* **2009**, *165*, 299.

[11] a) A. Gervasini, M. Manzoli, G. Martra, A. Ponti, N. Ravasio, L. Sordelli, F. Zaccheria, *J. Phys. Chem. B* **2006**, *110*, 7851-7861; b) P. M. Schosseler, B. Wehrli, A. Schweiger, *Geochimica et Cosmochimica Acta* **1999**, *63*, 1955-1967.

[12] a) A. Didier, L. Feng, A. J. Ruiz, *Angew. Chem. Int. Ed.* **2005**, *44*, 7852-7872; b) S. Sankaranarayanapillai, S. Volker, T. W. R., *Angew. Chem. Int. Ed.* **2010**, *49*, 3428-3459; c) X.-F. Yang, A. Wang, B. Qiao, J. Li, J. Liu, T. Zhang, *Acc. Chem. Res.* **2013**, *46*, 1740-1748; d) L. Suxia, H. Ce, S. Yantao, *ChemCatChem* **2015**, *7*, 2559-2567.

[13] R. V. Lloyd, P. M. Hanna, R. P. Mason, *Free Radical Biol. Med.* **1997**, *22*, 885-888.

[14] K. Makino, T. Hagiwara, A. Murakami, *Int. J. Radiat. Appl. Instrum., Part C* **1991**, *37*, 657-665.

[15] D. Begue, S. Elissalde, E. Pere, P. Iratcabal, C. Pouchan, *J. Phys. Chem. A* **2006**, *110*, 7793-7800.

[16] C. Kruk, K. Spaargaren, *Spectrochimica Acta Part A: Molecular Spectroscopy* **1971**, *27*, 77-80.

[17] A. N. Pham, G. Xing, C. J. Miller, T. D. Waite, *J. Catal.* **2013**, *301*, 54-64.

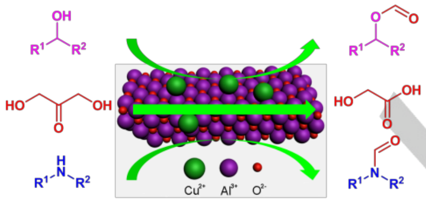
Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Clean and green by radicals

1,3-dihydroxylacetone, a biomass-based platform molecule has been oxidized with 100% carbon atom efficiency at room temperature to valuable glycolic acid, formamides and formates by a cheap non-noble metal catalyst. Radical-based mechanisms were discovered by in situ EPR with spin traps and operando ATR-IR spectroscopy.



Xingchao Dai, Sven Adomeit, Jabor Rabeah, Carsten Kreyenshulte, Angelika Brückner, Hongli Wang, and Feng Shi**

Page No. – Page No.

Sustainable co-synthesis of glycolic acid, formamides and formates from 1,3-dihydroxyacetone by a Cu/Al$_2$O$_3$ catalyst with single active sites