

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

### **Accepted Article**

Title: Another Unprecedented Wieland Mechanism Confirmed: Hydrogen Formation from Hydrogen Peroxide, Formaldehyde, and Sodium Hydroxide

Authors: Robert Czochara, Grzegorz Litwinienko, Hans-Gert Korth, and Keith U. Ingold

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201800636 Angew. Chem. 10.1002/ange.201800636

Link to VoR: http://dx.doi.org/10.1002/anie.201800636 http://dx.doi.org/10.1002/ange.201800636

### WILEY-VCH

# Another Unprecedented Wieland Mechanism Confirmed: Hydrogen Formation from Hydrogen Peroxide, Formaldehyde, and Sodium Hydroxide

Robert Czochara, Grzegorz Litwinienko,\* Hans-Gert Korth,\* and Keith U. Ingold

This paper is dedicated to Alwyn Davies on the occasion of his 92<sup>st</sup> birthday.

**Abstract:** In 1923, Wieland and Wingler reported that in the molecular hydrogen producing reaction of hydrogen peroxide with formaldehyde in basic solution free hydrogen atoms (H<sup>•</sup>) are not involved. They postulated that bis(hydroxymethyl)peroxide, HOCH<sub>2</sub>OOCH<sub>2</sub>OH, is the intermediate that decomposes to yield H<sub>2</sub> and formate, proposing a mechanism which nowadays would be considered as a "concerted process". Since that time several other (conflicting) 'mechanisms' have been suggested. Our NMR and Raman spectroscopic and kinetic studies, particularly determination of the deuterium kinetic isotope effect (DKIE), now prove that in this base-dependent reaction both H atoms of H<sub>2</sub> derive from the CH<sub>2</sub> hydrogens of formaldehyde, not from the OH groups of HOCH<sub>2</sub>OOCH<sub>2</sub>OH or from water. Quantum-chemical CBS-QB3 and W1BD computations confirm that H<sub>2</sub> release proceeds through a concerted process, strongly accelerated by double deprotonation of HOCH<sub>2</sub>OOCH<sub>2</sub>OH, thereby ruling out a free radical pathway. Wieland's mechanism for H<sub>2</sub> evolution showed truly amazing chemical insight.

[\*] R. Czochara, Prof. G. Litwinienko,

Faculty of Chemistry, University of Warsaw Pasteura 1, 02-093 Warsaw, Poland E-mail: litwin@chem.uw.edu.pl

Dr. H.-G. Korth

Institut für Organische Chemie, Universität Duisburg-Essen Universitätsstraße 7, 45117 Essen, Germany E-mail: hans-gert.korth@uni-due.de

Dr. K. U. Ingold

National Research Council,

100 Sussex Dr., Ottawa, ON, Canada

E-mail: Keith.Ingold@nrc-cnrc.gc.ca

Supporting information and the ORCID identification numbers of the authors of this article can be found under:

https://doi.org/10.1002/anie2018xxxxx

Heinrich Wieland's mechanistic insight was unrivalled in peroxide chemistry. He was the first to identify any free radical rearrangement, viz.  $Ph_3CO^{\bullet} \rightarrow Ph_2C^{\bullet}OPh$ , during thermal decomposition of  $Ph_3COOCPh_3$ .<sup>[1]</sup> Decades later some of us<sup>[2]</sup> provided unequivocal evidence favoring this (disputed) isomerisation. This stimulated us to look for other questioned (or ignored) Wieland mechanistic proposals. We found the fast room temperature reaction:<sup>[3,4]</sup>

0.05 M H<sub>2</sub>O<sub>2</sub> + 0.1 M HCHO + 0.1 M NaOH 
$$\frac{H_2O, 25^{\circ}C}{\text{initial } \tau_{1/2} = 82 \text{ s}}$$
  
0.05 M H<sub>2</sub> + 0.1 M HCOO<sup>-</sup> Na<sup>+</sup> (1)

Wieland<sup>[3]</sup> postulated that bis(hydroxymethyl)peroxide (**H2P**)<sup>[5]</sup> was the intermediate that decomposed to give molecular hydrogen [reactions (2)–(4)], representing this process exactly as shown in Figure 1 and concluding that free H<sup>•</sup> atoms were not involved because methylene blue or iodine were not decolorized and *p*-benzoquinone was not hydrogenated.<sup>[6]</sup>

Wieland's genius is further attested to by his pioneering description of what later became known as the *solvent cage effect*.

 $H_2O_2 + HCHO \longrightarrow HOCH_2OOH$  (2)

$$HOCH_2OOH + HCHO \longrightarrow HOCH_2OOCH_2OH (H2P)$$
 (3)

$$HOCH_2OOCH_2OH + 2 NaOH \longrightarrow H_2 + 2 HCOONa + 2 H_2O$$
 (4)

$$\begin{array}{cccc} H(HO)C.O & O.C(OH)H \\ \hline H & & H \end{array} \longrightarrow 2 H(HO)C:O + H_{g}. \end{array}$$

*Figure* **1.** Mechanism of bis(hydroxymethyl)peroxide (**H2P**) decomposition proposed by Wieland and Wingler.<sup>[3]</sup> (H. Wieland, A. Wingler, Über den Mechanismus der Oxydationsvorgänge V. Zur Oxydation der Aldehyde, *Justus Liebigs Ann. Chem.* **1923**, *431*, 301–322.) Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

Reaction (1), first reported in 1898,<sup>[7]</sup> has been the subject of considerable mechanistic speculation, both before and after Wieland's Figure 1 proposal, but much of the speculation has ignored or overlooked established facts. The reaction has three times been reported to follow second-order kinetics. In the first of these studies,<sup>[8]</sup> the effect of added base (essential if the reaction is to proceed at a noticeable rate at or below 25 °C) was already recognized, but the evolved gas was assumed to be O<sub>2</sub>! The second work<sup>[9]</sup> explicitly incorporated base into a proposed mechanism. Unfortunately, it was concluded that the H<sub>2</sub> came from the two HO groups, viz. 2  $^{\circ}CH(OH)O^{-} \rightarrow 2$  $HCOO^{-} + H_2$ , despite an earlier study<sup>[10]</sup> in D<sub>2</sub>O in which the evolved hydrogen was converted to water, the density of which indicated that it was H<sub>2</sub>O, proving that the evolved hydrogen came from two non-exchangeable CH<sub>2</sub>, rather than the exchangeable OH groups.<sup>[11]</sup> In the third study<sup>[12]</sup>  $H_2O_2$  oxidation of HCHO in basic solution was suggested to proceed via the bis(hydroxymethyl)peroxide dianion ( $P^{2-}$ ) as an intermediate, and decomposition to H<sub>2</sub> and formate [reaction (5)] was proposed to be rate-limiting. However, H<sub>2</sub> release was not investigated.

$$\begin{array}{c} \text{-OCH}_2\text{OOCH}_2\text{O}^- \longrightarrow 2 \text{ HCOO}^- + \text{H}_2 \\ \mathbf{P}^{2^-} \end{array}$$
(5)

ccepted Manuscrip

We here confirm the peroxide's two CH<sub>2</sub> groups as the sole source of H<sub>2</sub> using Raman and NMR spectroscopy, see Figure 2 and Figures S14–S25 in the Supporting Information. In Ref. [9] it was also shown that the H<sub>2</sub> formation vs time curve at 0 °C using the concentrations given in reaction (1) was identical to that for an equivalent concentration of **H2P** with the appropriate [NaOH] added, reaction (4), see Figure S26. When the reaction is fast, e.g. reaction (1) conditions, the H<sub>2</sub> yield is 100% of theory,<sup>[3,9]</sup> but when slow (at pH ≤ 12), additional paths (see below) may make the yield appear to be <100%.<sup>[13]</sup>



*Figure 2.* A) <sup>1</sup>H NMR spectra of the gas generated from HCHO/H<sub>2</sub>O<sub>2</sub>/NaOH (4:1:2) in D<sub>2</sub>O (dotted) and from DCDO/H<sub>2</sub>O<sub>2</sub>/NaOH (4:1:2) in H<sub>2</sub>O (solid). Signals at 3.40 ppm: H<sub>2</sub>O vapor. The small signal (solid) at 7.29 ppm corresponds to the HCHO impurity of

the applied DCDO. B) <sup>2</sup>H NMR spectra of the gas generated from HCHO/H<sub>2</sub>O<sub>2</sub>/NaOH (4:1:2) in D<sub>2</sub>O (dotted; D<sub>2</sub> not detected; signal at 3.45 ppm: D<sub>2</sub>O vapor) and from DCDO/H<sub>2</sub>O<sub>2</sub>/NaOH (4:1:2) in H<sub>2</sub>O (solid; D<sub>2</sub> is detected at 7.17 ppm).

Considering all of the above (and other experimental facts) it would seem that Wieland's Figure 1 may be an acceptable approximation to the transition state of reaction (1), in particular if the two hydroxyl H atoms are replaced by two negative charges, viz.  $P^{2-}$ . This leaves two mechanistic possibilities: either, the rate controlling step could involve a *concerted* bond making/breaking (sigmatropic [2+2+2] elimination, as implied by Figure 1), or O–O bond scission is rate controlling, being followed by two fast in-cage C–H scissions to give a singlet pair of H<sup>•</sup> atoms that combine 'instantaneously', reaction (6).



It seemed likely that these two mechanisms could be readily distinguished by the HCHO/DCDO deuterium kinetic isotope effect (DKIE), which would be large for the concerted process but small for a simple O–O scission. Determining the (possibly small) DKIE demanded a careful kinetic study. In view of the earlier kinetic work,<sup>[9]</sup> we chose as our base the conditions indicated in reaction (1), kept to 25 °C and monitored H<sub>2</sub> evolution while varying the concentration of one reagent at a time. Experimental details and results are given in the SI, Tables S1–S18 and Figures S1–S13.

Reproducibility was less than we would have liked, but was quite sufficient for our purposes. We confirmed (approximate) second-order<sup>[14]</sup> H<sub>2</sub> evolution with 100% yield for fast reactions. At less than stoichiometric [HCHO] the rate was ~[HCHO]<sup>2</sup>, while excess HCHO roughly doubled the rate (Figure 3A). The rate slightly enhances with a small increase in [H<sub>2</sub>O<sub>2</sub>] (Figure 3B) but a stoichiometric excess of H<sub>2</sub>O<sub>2</sub> strongly retarded the reaction (because now hydroxymethyl hydroperoxide, HOCH<sub>2</sub>OOH, [reaction (2)] is favored over **H2P**).



**Figure 3**. Initial rates of H<sub>2</sub> evolution. A) 0.10 M NaOH and 0.05 M H<sub>2</sub>O<sub>2</sub> with varying amounts of HCHO (inset: initial rate as a function of [HCHO]<sup>2</sup>). B) 0.10 M NaOH and 0.10 M HCHO with varying amounts of H<sub>2</sub>O<sub>2</sub>. C) 0.10 M HCHO with 0.05 M H<sub>2</sub>O<sub>2</sub> with varying amounts of NaOH (expressed as pH). The arrow indicates the stoichiometric

8

10.1002/anie.201800636

HCHO: $H_2O_2$ :NaOH = 2:1:2 ratio. Empirical fits to the non-linear graphs are just intended to guide an eye.

The pH dependence of the initial rate of H<sub>2</sub> production is shown in Figure 3C. Clearly, the pK<sub>a</sub> of the species governing H<sub>2</sub> release must be around 13.5. Since the pK<sub>a</sub>'s of H<sub>2</sub>O<sub>2</sub> and HOCH<sub>2</sub>OOH are 11.6 (Table S19) and ~10 (estimated from computed deprotonation free energies, see Figure S27), respectively, these observations are not only consistent with earlier work<sup>[9,12]</sup> but also provide strong support for a rate-controlling *concerted* decomposition of **P**<sup>2-</sup> (formed via an extensive series of equilibria, see Scheme S1), i.e. HOCH<sub>2</sub>OH<sup>[15]</sup> and **HP**<sup>-</sup> (see Figure S28) are the only species present likely to have such a high pK<sub>a</sub>. The reaction rate was the same (to within one standard deviation) under O<sub>2</sub> as under N<sub>2</sub><sup>[16]</sup> and was also the same when NaOH was replaced by CsOH (Tables S10–S18).<sup>[17]</sup> The reaction exhibited a mean HCHO/DCDO DKIE of 6.9, which is fully consistent with a concerted elimination of H<sub>2</sub> from **P**<sup>2-</sup>. Facile H<sub>2</sub> elimination from **P**<sup>2-</sup> in water is consistent with a report<sup>[18]</sup> that decomposition of neutral **H2P** in the gas phase at 110–200 °C yields formic acid and H<sub>2</sub> *more slowly* than it yields HCHO and HOCH<sub>2</sub>OOH, i.e. reaction (–3) is favored over H<sub>2</sub> loss.

There are only three theoretical studies on (decomposition of) **H2P**.<sup>[19,20]</sup> Fleischmann and Cioslowski<sup>[19]</sup> recognized that H<sub>2</sub> must come from the dianion **P**<sup>2–</sup>. On the HF (MP2) level they located a "stretched" conformation ( $^{-}OCOO$  units *s-trans*) as the ground state structure, and gave barriers to internal rotation. No calculations being reported on H<sub>2</sub> loss or O–O bond cleavage. In two, essentially identical reports by Thiel (gas phase DFT calculations),<sup>[20]</sup> a 6-center cyclic transition structure of **H2P** is found from which H<sub>2</sub> can be extruded in a concerted process. The reported structures agree with the ones found

9

10.1002/anie.201800636

in this study, however, it was ignored that the release of H<sub>2</sub> in the gas phase or neutral aqueous solution is slow and the yield is not quantitative. In order to explore possible reaction paths of H<sub>2</sub> formation from H2P at neutral and basic pH, we carried out extensive gas phase and aqueous phase computations employing the composite (PCM)CBS-QB3 method.<sup>[21]</sup> Pivotal structures were additionally computed with the highaccuracy W1BD method, with aqueous solvation being modeled by the SMD approach. Structures and thermochemical data are collected in Figure S29 and Tables S20–S23. W1BD structures and activation data are displayed in Figure 4. With a few exceptions, identical structures were found with CBS-QB3 and W1BD in the gas and aqueous phase. Several ground state conformers and rotational transition states were located for H2P, HP<sup>-</sup> and P<sup>2-</sup> (Table S21). The lowest-energy structure of H2P (1/1a) has its OH groups mutually hydrogen bonded, thereby stabilizing an unfavorable arrangement for concerted H<sub>2</sub> elimination. Two conformeric TSs for concerted H<sub>2</sub> evolution were found, the lower (2/2a) of  $\Delta H^{\ddagger}(aq) = 27.8$  (CBS-QB3, 27.9) kcal mol<sup>-1</sup> activation enthalpy in water. A further transition structure (3/3a), leading to formic acid and dihydroxymethane (formaldehyde hydrate), was located, characterized by an elongated O-O bond combined with a simultaneous 1,3-shift of one of the CH<sub>2</sub> hydrogens to the remote peroxide oxygen. The >12 kcal  $mol^{-1}$  higher barrier, however, renders this path unimportant under normal conditions. Note that transition structures for simple O-O bond homolysis were not found (for bond dissociation energies see Table S23).

10

VIanusci

**\CCepted** 



*Figure 4*. (SMD)W1BD-computed lowest-energy aqueous phase structures and activation barriers  $\Delta H^{\ddagger}$  ( $\Delta G^{\ddagger}$ ) for bis(hydroxymethyl)peroxide (H2P) (left), its monoanion (HP<sup>-</sup>) (middle), and its dianion (P<sup>2-</sup>) (right) and related transition structures for concerted H<sub>2</sub> release and intramolecular hydrogen shift. For compound labelling and bond distances see Tables S20, S21 and Figure S29.

As expected, the ground state of the monoanion  $HP^-$  (4/4a) is intramolecularly strongly hydrogen-bonded ( $\Delta H_{HB} \leq -12$  kcal mol<sup>-1</sup>, cf. 18/18a, Table S21), again stabilizing an unfavorable conformation for concerted H<sub>2</sub> release. The related transition state (5/5a) is slightly lower than that of H2P (2/2a), both agreeing well with the

11

10.1002/anie.201800636

experiments in water,<sup>[8]</sup> see Figure S30. Interestingly, TS **6/6a** for decomposition to (initially) HCOOH and HOCH<sub>2</sub>O<sup>-</sup> now involves a 1,2-CH<sub>2</sub> hydrogen shift to the adjacent peroxide oxygen. This TS even lies below the barrier for concerted H<sub>2</sub> release, suggesting that at a pH where **HP**<sup>-</sup> exists, H<sub>2</sub> production will not be quantitative but accompanied by formation of HCOOH/HCOO<sup>-</sup> and HOCH<sub>2</sub>OH (= HCHO + H<sub>2</sub>O), as reported by Wieland.<sup>[3]</sup>

The ground state of dianion  $P^{2-}$  (7/7a) adopts the stretched conformation as found earlier.<sup>[19]</sup> This conformation can reasonably be attributed to Coulomb repulsion of the negatively charged oxygens. Two of the CH<sub>2</sub> hydrogens are now in a favorable orientation for concerted H<sub>2</sub> release [H–H distance 2.82 (g)/2.55 (aq) Å]. This results in a strongly decreased TS barrier (8/8a) with  $\Delta H^{\ddagger}(aq) = 13.1$  (CBS-QB3, 16.3) kcal mol<sup>-1</sup>. This  $\Delta H^{\ddagger}(aq)$  is close to the experimental "activation energy  $\Delta H_{a} = 14.5 \pm 0.3$  kcal mol<sup>-</sup> <sup>1</sup>",<sup>[9]</sup> which supports reaction (5) as the rate-determining step. The 1,2-H-shift TS **9/9a**, leading to (initally) HCOOH and  $^{-}OCH_2O^{-}$ , lies 7–8 kcal mol<sup>-1</sup> above TS 8/8a. This process thus would not compete noticeably with the concerted H<sub>2</sub> release. Internal reaction coordinate (IRC) computations (Figure S31) confirm the found transition states connect with the peroxidic educts (H2P, HP<sup>-</sup>, P<sup>2-</sup>) and the products (H<sub>2</sub> + HCOO<sup>-</sup> /HCOOH and HOCH<sub>2</sub>OH + HCOO<sup>-</sup>/HCOOH, respectively). Further, DKIEs for H<sub>2</sub> extrusion in the range 3.2-9.9 were computed (Table S21), in accord with the experimental values.<sup>[22]</sup> In toto, our computational findings are congruent with a baseinduced strong acceleration and quantitative evolution of H<sub>2</sub> from HCHO and H<sub>2</sub>O<sub>2</sub>, and support  $H_2$  evolution from  $P^{2-}$  in the rate-determining step.

Our conclusion is that Wieland's Figure 1 is an acceptable approximation to the transition state. *Hats off to Wieland!* 

#### Acknowledgements

We thank W. Siebrand for helpful discussions. This work was co-funded by the National Science Centre - Poland, decision no. 2014/15/B/ST4/04835.

#### **Conflict of interest**

The authors declare no conflict of interest.

Keywords: history of science • H<sub>2</sub>O<sub>2</sub>-formaldehyde reaction • hydrogen formation •

peroxides • reaction mechanisms

Accepted Manuscrip

- [1] H. Wieland, Ber. Dtsch. Chem. Ges. 1911, 44, 2550–2556.
- [2] G. A. DiLabio, K. U. Ingold, S. Lin, G. Litwinienko, O. Mozenson, P. Mulder, T. T. Tidwell Angew. Chem. Int. Ed. 2010, 49, 5982–5985; Angew. Chem. 2010, 122, 6118–6121.
- [3] H. Wieland, A. Wingler, Justus Liebigs Ann. Chem. **1923**, 431, 301–322.
- [4] Reaction follows second-order kinetics, so only first half-life is given.
- [5] First isolated by Legler (L. Legler, *Justus Liebigs Ann. Chem.* 1883, 217, 381) from *lampic acid* [Lampensäure] and first synthesized by Fenton [H. J. H. Fenton, *Proc. Roy. Soc. (London)* 1914, *A90*, 492–498].
- [6] The relevant sentence in Ref. [3] can be translated: The driving force for this peculiar decay reaction is the tendency of both escaping hydrogen atoms to combine to the molecule H<sub>2</sub>, a process which takes place before the molecular force field [molekulare Kraftfeld] is passed. This concept was foreshadowed by Wieland et al. (H. Wieland, E. Popper, H. Seefried, Ber. Dtsch. Chem. Ges., **1922**, 55B, 1816–1834) in a study of the Ph<sub>3</sub>CN=NPh → N<sub>2</sub> + Ph<sub>4</sub>C reaction: ... for a moment after their bond release, atoms or groups experience a kind of gravitation [with]in the force field of their [parent] molecules...
- [7] O. Blank, H. Finkenbeiner, Ber. Dtsch. Chem. Ges. 1898, 31, 2979–2981.
- [8] J. H. Kastle, A. S. Loevenhart, J. Am. Chem. Soc. 1899, 21, 262–276. Here it is reported that HCHO consumption in the presence of KOH or NaOH is about ten times faster than in the presence of NH₄OH, see Figure S30.

- [9] J. B. Jaillet, C. Ouellet, *Can. J. Chem.* **1951**, *29*, 1046–1058. Similar to the present study, kinetics were determined from monitoring H<sub>2</sub> release by means of a pressuregauge albeit at a ~110-fold higher volume.
- [10]K. Wirtz, K. F. Bonhoeffer, Z. Phys. Chem. 1936, B32, 108–112.
- [11]Cited [10] but mistranslated, viz.<sup>[9]</sup> ...que l'oxygen dégagé provident uniquement de la formaldehyde... "oxygen" should have been "hydrogen".
- [12] J. S. Do, C. P. Chen, Ind. Eng. Chem. Res. 1994, 33, 387–394.
- [13]The Wieland mechanism has also been adopted for H<sub>2</sub> production from HCHO and H<sub>2</sub>O<sub>2</sub> in *acidic* solution: B. L. Dunicz, D. D. Perrin, D. W. G. Style, *Trans. Faraday Soc.* **1951**, *47*, 1210–1215. The overall process is proton-catalyzed (Scheme S2), but H<sub>2</sub> release from **H2P** is an acid-independent first-order reaction ( $E_a$  = 24.9 kcal mol<sup>-1</sup>).
- [14]The rates of H<sub>2</sub> evolution during reaction differ slightly from pure second-order in [HCHO], see Figures S9–S13, in agreement with Ref. [8], see Figure S30. We neglect this small effect because of clear dependence of the initial rates on [HCHO]<sup>2</sup> (see inset in Figure 3A).
- [15]For HOCH<sub>2</sub>OH a pK<sub>a</sub> range of 12.5–14.0, focusing on 13.3, is given in the literature, see: Y. I. Tur'yan, *Croat. Chem. Acta* 2000, 73, 625–641.
- [16]Supporting the absence of free H<sup>•</sup> atoms and an H<sup>•</sup> atom chain, H<sup>•</sup> +  $P^{2-} \rightarrow H_2$  + HCO<sub>2</sub><sup>-</sup> + <sup>•</sup>OCH<sub>2</sub>O<sup>-</sup>  $\rightarrow$  H<sup>•</sup> + HCO<sub>2</sub><sup>-</sup>.
- [17] In the presence of a heavy ion like Cs<sup>+</sup> a singlet H<sup>•</sup> pair should evolve to a triplet pair more rapidly, enhancing H<sup>•</sup> escape from the cage. This free H<sup>•</sup> could react rapidly with O<sub>2</sub> and lower the rate of H<sub>2</sub> formation.

[18] A. D. Jenkins, D. W. G. Style, J. Chem. Soc. 1953, 2337-2340.

- [19]E. D. Fleischmann, J. Cioslowski, Chem. Phys. Lett. 1990, 168, 265–268.
- [20]a) W. R. Thiel, Eur. J. Org. Chem. 2004, 3108–3112; b) W. R. Thiel, J. Mol. Catal. A: Chem. 2006, 251, 229–233.
- [21] Gaussian 09, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009; see SI, p. S-4 for full references.
- [22] A contribution by hydrogen-tunneling to the rate constants has to be expected for such type of reaction, see footnotes to Tables S20, S21. Detailed investigation of the tunneling contribution, however, is beyond the scope of our paper.

#### **Entry for the Table of Contents**

#### COMMUNICATION



*Hats off to Wieland!* Heinrich Wieland's 1923 foreseeing of a 'concerted' mechanism for the release of molecular hydrogen from reaction of hydrogen peroxide with formaldehyde in basic solution via a bis(hydroxymethyl)peroxide intermediate has been confirmed. Kinetics, spectroscopy, and quantumchemical computations prove both  $H_2$  hydrogens derive from formaldehyde's  $CH_2$  group. Free radicals are not involved.

Robert Czochara, Grzegorz Litwinienko,\* Hans-Gert Korth,\* Keith U. Ingold

Page No. – Page No.

Another Unprecedented Wieland Mechanism Confirmed: Hydrogen Formation from Hydrogen Peroxide, Formaldehyde, and Sodium Hydroxide