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Supporting Information
for
The hydrolysis of geminal ethers: a kinetic appraisal of orthoesters and ketals

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Analytical data
Indicative plot of ln(integral) for 6 ($k_{obs} = 7 \times 10^{-4}; R^2 = 0.9944$), and 2 ($k_{obs} = 1.46 \times 10^{-5}; R^2 = 0.9932$), versus time (s).
Indicative stacked plot of 6 and 2 versus time (300 MHz $^1$H NMR in D$_2$O/CD$_3$CN (1:4), 625 s intervals, $T= 25$ °C, [HCl] = 9.56 x 10$^{-5}$ M).
Table S1: The concentration of acid catalyst used to determine values of $k_{H^+}$ for the following mixtures of reacting ortho esters.

| Reacting substrates | $[H^+] \times 10^{-4}$ M |
|---------------------|--------------------------|
| 6:2                 | 4.78                     |
| 3:2                 | 4.78                     |
| 6:13                | 1.98                     |
| 6:5                 | 1.98                     |
| 6:8                 | 1.98                     |
| 6:10:11:14          | 1.98                     |
| 6:16                | 0.125                    |
Table S2: Experimentally determined values of $k_{H^+}$ for the reacting mixtures of geminal ethers: $[6 + 2]$, $[3 + 2]$, $[6 + 13]$, $[6 + 5]$, $[6 + 8]$, $[6 + 10 + 11 + 14]$, $[6 + 16]$. 

The corresponding values of $k_{H^+}$ (including standard deviations) in Figure 1 (main article) were calculated from an average of these experiments. Thus, $k_{H^+}$ for 5 calculated using entries (x–xii). Also, $k_{H^+}$ for 6 calculated from entries (i–iii), (vii–ix), and (x–xxi) respectively, along with data from Table 1 of main article.

|    | 6     | 2     |
|----|-------|-------|
| (i) | 7.32  | 0.153 |
| (ii)| 6.74  | 0.145 |
| (iii)| 7.20  | 0.151 |

|    | 3     | 2     |
|----|-------|-------|
| (iv)| 1.650 | 0.147 |
| (v) | 1.675 | 0.155 |
| (vi)| 1.730 | 0.143 |
|   | 6       | 13       |
|---|---------|----------|
| (vii) | 6.91    | 19.44    |
| (viii) | 7.20    | 19.74    |
| (ix) | 6.89    | 21.18    |

|   | 6       | 5        |
|---|---------|----------|
| (x) | 7.50    | 6.70     |
| (xi) | 6.70    | 6.30     |
| (xii) | 7.20   | 6.60     |

|   | 6       | 8        |
|---|---------|----------|
| (xiii) | 6.84    | 9.77     |
| (xiv) | 6.99    | 10.00    |
| (xv) | 6.52    | 9.57     |
|     | 6   | 10  | 11  | 14  |
|-----|-----|-----|-----|-----|
| (xvi)| 7.07| 13.10| 13.99| 29.80 |
| (xvii)| 7.01| 11.76| 12.78| 27.38 |
| (xviii)| 6.90| 11.38| 12.07| 26.62 |

|     | 6   | 16  |
|-----|-----|-----|
| (xix)| 7.00| 70.63|
| (xx)| 7.20| 73.10|
| (xxi)| 6.74| 84.00|
Table S3: Corresponding values of \( k_{H^+} (\text{M}^{-1}\text{s}^{-1}) \) obtained from calibration of data obtained from different workers.

| Ortho ester | Relative rate\(^a\) | \( k_{H^+} (\text{M}^{-1}\text{s}^{-1}) \) |
|-------------|---------------------|--------------------------------------|
| 1           | 1                   | \( 4 \times 10^{-3b} \)            |
| 4           | 649                 | \( 2.79^b \)                         |
| 8           | 2270                | \( 9.78^c \)                         |
| 15          | 11351               | \( 48.90^a \)                        |

| Ortho ester | \( k_{1H^+} \) ratios\(^a\) | \( k_{H^+} (\text{M}^{-1}\text{s}^{-1})\(^b\) | \( k_{H^+} (\text{M}^{-1}\text{s}^{-1})\(^c\) | \( k_{H^+} (\text{M}^{-1}\text{s}^{-1})\(^d\) |
|-------------|-------------------------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|
| 5           | 1                             | \( 6.53 \)                                  | \( – \)                                     | \( 6.5 \pm 0.2 \)                           |
| 6           | \( – \)                       | \( – \)                                     | \( – \)                                     | \( 7.0 \pm 0.2 \)                           |
| 7           | 2.0                           | \( \approx 13 \)                            | \( \approx 8 \)                             | \( – \)                                     |
| 9           | 2.6                           | \( \approx 17 \)                            | \( \approx 11 \)                            | \( – \)                                     |
| 12          | 3.4                           | \( \approx 22 \)                            | \( \approx 14 \)                            | \( – \)                                     |
| 16          | 18.8                          | \( \approx 123 \)                           | \( \approx 76 \)                            | \( 75.9 \pm 7.1 \)                          |
500 MHz $^1$H NMR spectrum of a mixture of 10, 11 and 14 in CD$_3$CN.
1D-NOESY $^1$H NMR spectrum of a mixture of 10, 11 and 14 (3:1:3.2, respectively) irradiated at 1.46 ppm.
1D-NOESY $^1$H NMR spectrum of a mixture of 10, 11 and 14 (3:1:3.2, respectively) irradiated at 1.44 ppm.
1D-NOESY $^1$H NMR spectrum of a mixture of 10, 11 and 14 (3:1:3.2, respectively) irradiated at 1.50 ppm.
MS(CI) spectrum of hydroxy ester the derived from 1,3-dioxolan-2-ylum cation $5^*$ and $H_2^{16/18}O$. 
MS(Cl) spectrum of the hydroxy ester derived from 1,3-dioxolan-2-ylium cation 16* and H$_2^{16/18}$O.
Partial $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of hydroxy ester derived from 16 illustrating resonances associated with $^{13}C=^{18}O$ ($\delta_C = 172.76$ppm) and $^{13}C=^{16}O$ ($\delta_C = 172.80$ ppm \textit{i.e., } $\Delta\delta_C = 0.04$ ppm) nuclei.
Full literature reference for Gaussian 09

**Gaussian 09**, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
Cartesian coordinates of conformer 16a

\[
\begin{array}{ccc}
C & -2.0318200 & -1.48965000 \\
C & -0.65026000 & 0.10995800 \\
C & -2.71696200 & -0.93745800 \\
H & -1.53976800 & -2.45194700 \\
H & -2.69624900 & -1.60348600 \\
H & -3.55058500 & -0.27027400 \\
H & -3.81079000 & -1.71225000 \\
O & -1.07539300 & -0.48067000 \\
O & -1.66994800 & -0.21260100 \\
C & 2.01132200 & -0.13827700 \\
C & -1.70594500 & 2.18082800 \\
C & 0.67229700 & 0.46586200 \\
H & 0.74833500 & -0.16286400 \\
H & 0.52920700 & -1.55318900 \\
C & 3.06375700 & -1.11795600 \\
H & 2.80847500 & -2.15785700 \\
H & 3.14739800 & -1.03077900 \\
H & 4.05146400 & -0.91215200 \\
C & 1.91375000 & 0.33679700 \\
H & 2.89471900 & -0.17794900 \\
H & 1.20598200 & 0.36262600 \\
H & 1.58261300 & -1.34987200 \\
C & 2.47793900 & 1.29981200 \\
H & 2.57498300 & 1.46087300 \\
H & 1.77454100 & 2.03795400 \\
H & 3.45981200 & 1.48242600 \\
O & -0.52029200 & 1.47759800 \\
H & -2.10822200 & 1.81140500 \\
H & -2.46727000 & 2.09899700 \\
H & -1.41375100 & 3.22613200
\end{array}
\]
Cartesian coordinates of conformer 16b

|   |        |        |        |
|---|--------|--------|--------|
| C | 2.38968800 | -1.37618000 | -0.58742300 |
| C | 0.65369300 | 0.12175600 | -0.27113300 |
| C | 2.27342700 | -1.08285900 | 0.90637300 |
| H | 1.91707900 | -2.33428600 | -0.84817000 |
| H | 3.41693000 | -1.37254000 | -0.96145000 |
| H | 3.08183200 | -0.42462900 | 1.25333400 |
| H | 2.25165200 | -1.97980500 | 1.53181300 |
| O | 1.68860200 | -0.28655300 | -1.17061100 |
| O | 1.01185700 | -0.42378900 | 1.00060800 |
| C | -2.01088200 | -0.13476500 | 0.00804900 |
| C | 1.76908600 | 2.17713900 | 0.20309800 |
| C | -0.69264300 | -0.42218600 | -0.76409500 |
| H | -0.56063700 | -1.50891700 | -0.83061300 |
| H | -0.80096000 | -0.05593000 | -1.79119400 |
| C | -1.93898400 | -0.60490100 | 1.47351100 |
| H | -1.67068700 | -1.66512400 | 1.53981700 |
| H | -1.19613600 | -0.04224300 | 2.04237900 |
| H | -2.91421100 | -0.47521200 | 1.95722100 |
| C | -3.11714400 | -0.93625700 | -0.71278700 |
| H | -4.08823900 | -0.77068900 | -0.23356100 |
| H | -3.20829200 | -0.63589500 | -1.76296700 |
| H | -2.91244300 | -2.01286900 | -0.68825700 |
| C | -2.38886300 | 1.35911000 | -0.03438000 |
| H | -1.66131100 | 1.97239700 | 0.49890100 |
| H | -2.43886200 | 1.72540400 | -1.06596300 |
| H | -3.37390600 | 1.51031000 | 0.42230100 |
| O | 0.59430000 | 1.50544700 | -0.24707400 |
| H | 2.63111000 | 1.93027200 | -0.42475100 |
| H | 1.98820100 | 1.92961300 | 1.24752000 |
| H | 1.55567700 | 3.24418000 | 0.12297800 |
## Cartesian coordinates of conformer 16c

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| C    | 1.89106600 | -1.62860600| -0.60508300|
| C    | 0.70638100 | 0.24111600 | -0.17460500|
| C    | 2.00325600 | -1.31263500| 0.90460600 |
| H    | 1.68891600 | -2.68057200| -0.81852900|
| H    | 2.78172900 | -1.30766800| -1.15468900|
| H    | 3.02099100 | -1.02455900| 1.18911700 |
| H    | 1.67908700 | -2.14381600| 1.53859600 |
| O    | 0.75043600 | -0.87067000| -1.01760200|
| O    | 1.09432100 | -0.22422200| 1.10544500 |
| C    | -1.95450000| 0.02730500 | 0.03190700 |
| C    | 2.00317400 | 2.26227600 | 0.12712600 |
| C    | -0.67408400| 0.89747500 | -0.11627700|
| H    | -0.76624600| 1.50331000 | -1.0243600 |
| H    | -0.63111200| 1.59724500 | 0.72578800 |
| C    | -3.10852700| 0.99775800 | 0.36487900 |
| H    | -2.94503100| 1.49856400 | 1.32609400 |
| H    | -3.21411600| 1.77242400 | -0.40361600|
| H    | -4.06057800| 0.45932900 | 0.42632800 |
| C    | -1.83563600| -1.00419600| 1.16910700 |
| H    | -2.79635200| -1.51176700| 1.31362500 |
| H    | -1.08407200| -1.76409400| 0.94337400 |
| H    | -1.55599900| -0.52978700| 2.11497200 |
| C    | -2.29071700| -0.69270300| -1.28985000|
| H    | -2.42633500| 0.02729200 | -2.10541700|
| H    | -1.49754600| -1.38314400| -1.58032100|
| H    | -3.22472600| -1.25723200| -1.18760200|
| O    | 1.69011400 | 1.13564200 | -0.68186000|
| H    | 2.18922200 | 1.97067500 | 1.16665100 |
| H    | 1.20940700 | 3.02082400 | 0.10491700 |
| H    | 2.91130600 | 2.70023100 | -0.29357500|