Supporting Information

Relating alkaline stability to structure of quaternary phosphonium cations

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Materials and Characterization

All the chemicals were purchased from Sigma-Aldrich and used as received. The \textsuperscript{1}H NMR spectra were measured in deuterated solvents on a Bruker AV400 spectrometer (\textsuperscript{1}H, 400 MHz). The \textsuperscript{1}H NMR chemical shifts are expressed as \( \delta \) downfield from tetramethylsilane (TMS) and calibrated to the residual proton of the deuterated solvent (\( \delta = 7.26 \) ppm for chloroform-d). The \textsuperscript{31}P NMR spectra were measured in deuterated
solvents on a Bruker AV400 spectrometer ($^{31}$P, 161 MHz). The $^{31}$P NMR chemical shifts are expressed as downfield from external 85% H$_3$PO$_4$.

**General procedure for synthesizing methyl based quaternary phosphonium salts**
A mixture of the corresponding phosphine (10 mmol) and 2 mL iodomethane (32 mmol) was stirred at room temperature for 24 h. The precipitated product was collected by filtration, rinsed three times with THF, and dried under vacuum.[1]

Methyl tris(2,4,6-trimethyphenyl)phosphonium iodide (MTPP-(2,4,6-Me)-I) (cation (1)):
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.06 (6H, dd, $J = 84.0$, 3.2 Hz), 2.94 (3H, d, $J = 11.2$ Hz), 2.35 (18H, d, $J = 5.2$ Hz), 1.91 (9H, s). $^{31}$P NMR (161 MHz, CDCl$_3$) $\delta$ 6.53 (s). Yield: 95 wt%.

Methyl tris(2,4,6-trimethoxyphenyl)phosphonium iodide (MTPP-(2,4,6-MeO)-I) (cation (2)):
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.14 (6H, d, $J = 4.8$ Hz), 3.90 (9H, s), 3.61 (18H, s), 2.47 (3H, d, $J = 15.2$ Hz). $^{31}$P NMR (161 MHz, CDCl$_3$) $\delta$ 3.79 (s). Yield: 96 wt%.

Methyl tris(2,6-trimethoxyphenyl)phosphonium iodide (MTPP-(2,6-MeO)-I) (cation (4)):
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54 (3H, t, $J = 8.4$ Hz), 6.63 (6H, dd, $J = 8.8$, 5.6 Hz), 3.59 (18H, s), 2.60 (3H, d, $J = 15.2$ Hz). $^{31}$P NMR (161 MHz, CDCl$_3$) $\delta$ 1.84 (s). Yield: 92 wt%.

Methyl tris(2,6-trimethylphenyl)phosphonium iodide (MTPP-(2,6-Me)-I) (cation (8)):
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.73 (3H, t, $J = 7.6$ Hz), 7.25 (3H, t, $J = 6.4$ Hz), 7.13 (3H, td, $J = 7.6$, 2.8 Hz), 6.97 (3H, ddd, $J = 23.6$, 8.0, 1.6 Hz), 3.87 (9H, s), 2.74 (3H, d, $J = 15.2$ Hz). $^{31}$P NMR (161 MHz, CDCl$_3$) $\delta$ 20.1 (s). Yield: 89 wt%.
Methyl tris(\(p\)-methoxyphenyl)phosphonium iodide (MTPP-(\(p\)-MeO)-I) (cation (9)): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.59 (6H, dd, \(J = 12.8, 8.8\) Hz), 7.14 (6H, dd, \(J = 2.8\) Hz), 3.89 (9H, s), 2.93 (3H, d, \(J = 13.2\) Hz). \(^{31}\)P NMR (161 MHz, CDCl\(_3\)) \(\delta\) 18.8 (s). Yield: 91 wt%.

**General procedure for synthesizing benzyl based quaternary phosphonium salts**

A mixture of the corresponding phosphine (10 mmol) and 2.54 g benzyl chloride (20 mmol) in 10 mL THF was stirred at 60 °C for 24 h. The precipitated product was collected by filtration, rinsed three times with THF, and dried under vacuum.

Benzyl tris(2,4,6-trimethoxyphenyl)phosphonium chloride (BTPP-(2,4,6-MeO)-Cl) (cation (3)): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.05-7.03 (3H, m), 6.98-6.95 (2H, m), 6.04 (6H, d, \(J = 4.8\) Hz), 4.59 (2H, d, \(J = 17.2\) Hz), 3.85 (9H, s), 3.61 (18H, s). \(^{31}\)P NMR (161 MHz, CDCl\(_3\)) \(\delta\) 5.71 (s). Yield: 94 wt%.

Benzyl tris(2,6-trimethoxyphenyl)phosphonium chloride (BTPP-(2,6-MeO)-Cl) (cation (5)): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.45 (3H, t, \(J = 8.8\) Hz), 7.03-6.97 (5H, m), 6.53 (6H, dd, \(J = 8.4, 5.2\) Hz), 4.72 (2H, d, \(J = 17.6\) Hz), 3.61 (18H, s). \(^{31}\)P NMR (161 MHz, CDCl\(_3\)) \(\delta\) 7.85 (s). Yield: 89 wt%.

Benzyl tris(\(o\)-methoxyphenyl)phosphonium chloride (BTPP-(\(o\)-MeO)-Cl) (cation (7)): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.77 (3H, t, \(J = 7.6\) Hz), 7.26 (3H, td, \(J = 12.8, 1.6\) Hz), 7.18-7.13 (9H, m), 6.97 (2H, dd, \(J = 17.6, 1.6\) Hz), 4.59 (2H, d, \(J = 16.0\) Hz), 3.66 (9H, s). \(^{31}\)P NMR (161 MHz, CDCl\(_3\)) \(\delta\) 24.7 (s). Yield: 87 wt%.

Benzyl tris(\(p\)-methoxyphenyl)phosphonium chloride (BTPP-(\(p\)-MeO)-Cl) (cation (10)): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.52-7.46 (6H, m), 7.22-7.17 (1H, m), 7.13-6.99 (10H, m), 4.96 (2H, d, \(J = 14.0\) Hz), 3.86 (9H, s). \(^{31}\)P NMR (161 MHz, CDCl\(_3\)) \(\delta\) 21.1 (s). Yield: 92 wt%.

Benzyl tris(\(p\)-methylphenyl)phosphonium chloride (BTPP-(\(p\)-Me)-Cl) (cation 11): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.57-7.51 (6H, m), 7.42-7.38 (6H, m), 7.24-7.19 (1H, m),
7.15-7.11 (2H, m), 7.08-7.05 (2H, m), 5.24 (2H, d, J=14.4 Hz), 2.46 (9H, s). $^{31}$P NMR (161 MHz, CDCl$_3$) δ 22.2 (s). Yield: 88 wt%.

Benzyl triphenylphosphonium chloride (BTPP-Cl) (cation 12): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.77-7.71 (9H, m), 7.63-7.59 (6H, m), 7.22-7.17 (1H, m), 7.13-7.07 (4H, m), 5.50 (2H, d, J=14.8 Hz). $^{31}$P NMR (161 MHz, CDCl$_3$) δ 23.3 (s). Yield: 85 wt%.

Alkaline stability tests of QP cations

1 M deuterated potassium hydroxide (KOD) in CD$_3$OD/D$_2$O (5/1 vol) solution was prepared by dissolving KOD (40 wt% in D$_2$O, 4.28 g, 30.0 mmol) in a mixture of deuterated methanol and heavy water (CD$_3$OD/D$_2$O) (25 mL/2.67 mL). QP cations (1.00 mmol) was added to the alkaline solution to obtain a molar ratio of 30 KOD : 1 model compound (i.e., 0.033 M). The mixture was placed in a fluoropolymer lined autoclave held at 80 °C. Before the test (t = 0), an aliquot of the testing solution was removed and analyzed by $^{31}$P NMR spectroscopy to determine the initial quantity of the QP cation. Then, the testing solution was held at 80 °C. Aliquots of the reaction mixture were removed periodically and analyzed by $^{31}$P NMR spectroscopy to determine the quantity of the QP cation remaining. A control sample with the same recipe but without adding KOD was prepared, and its $^{31}$P NMR were also measured.

Calculation of the degradation rate constants ($k$) of QP cations

$k_{80}$ (the degradation rate constant at 80 °C) of cation (1)-(3) and (10)-(12) have been discussed in our previous work.$^{[2]}$ $k_{80}$ of other cations studied in this work were calculated by correlating ln($C_0/C$) at 80 °C and time (Fig. S1-S12). Here, $C_0$ is the initial QP cation concentration, and C is the QP cation concentration at the sampling time.
Figure S1. Time series of $^{31}$P NMR spectra during durability test of MTPP-(2,6-MeO) (cation (4)) at 80 °C. Phosphoric acid as the external standard; 1 M KOD in CD$_3$OD/D$_2$O (5/1 vol) as the solvent. The degradation percentage is calculated by $\frac{A_2}{(A_1 + A_2 + A_3)}$. $A_1$ is the peak area of the phosphine oxide; $A_2$ is the peak area of cation (4); $A_3$ is the peak area of ether hydrolysis products.

Figure S2. The plot of ln($C_0/C$) versus time of MTPP-(2,6-MeO) (cation (4)) at 80 °C. 1 M KOD in CD$_3$OD/D$_2$O (5/1 vol) as the solvent.
**Figure S3.** Time series of $^{31}$P NMR spectra during durability test of BTPP-(2,6-MeO) (cation (5)) at 80 °C. Phosphoric acid as the external standard; 1 M KOD in CD$_3$OD/D$_2$O (5/1 vol) as the solvent. The degradation percentage is calculated by $\frac{A_2}{(A_1 + A_2 + A_3)}$. $A_1$ is the peak area of the phosphine oxide; $A_2$ is the peak area of cation (5); $A_3$ is the peak area of ether hydrolysis products.

**Figure S4.** The plot of ln(C$_0$/C) versus time of BTPP-(2,6-MeO) (cation (5)) at 80 °C. 1 M KOD in CD$_3$OD/D$_2$O (5/1 vol) as the solvent.
**Figure S5.** Time series of $^3\text{P}$ NMR spectra during durability test of MTPP-(ο-MeO) (cation (6)) at 80 °C. Phosphoric acid as the external standard; 1 M KOD in CD$_3$OD/D$_2$O (5/1 vol) as the solvent. The degradation percentage is calculated by $A_2/(A_1 + A_2)$. $A_1$ is the peak area of the phosphine oxide; $A_2$ is the peak area of cation (6).

**Figure S6.** The plot of ln(C$_0$/C) versus time of MTPP-(ο-MeO) (cation (6)) at 80 °C. 1 M KOD in CD$_3$OD/D$_2$O (5/1 vol) as the solvent.
**Figure S7.** Time series of $^{31}$P NMR spectra during durability test of BTPP-(o-MeO) (cation (7)) at 80 °C. Phosphoric acid as the external standard; 1 M KOD in CD$_3$OD/D$_2$O (5/1 vol) as the solvent. The degradation percentage is calculated by $A_2/(A_1 + A_2)$. $A_1$ is the peak area of the phosphine oxide; $A_2$ is the peak area of cation (7).

**Figure S8.** The plots of ln(C$_0$/C) versus time of BTPP-(o-MeO) (cation (7)) at 80 °C. 1 M KOD in CD$_3$OD/D$_2$O (5/1 vol) as the solvent.
Figure S9. Time series of $^{31}$P NMR spectra during durability test of MTPP-(o-Me) (cation (8)) at 80 °C. Phosphoric acid as the external standard; 1 M KOD in CD$_3$OD/D$_2$O (5/1 vol) as the solvent. The degradation percentage is calculated by $\frac{A_2}{(A_1 + A_2)}$. $A_1$ is the peak area of the phosphine oxide; $A_2$ is the peak area of (cation (8)).

Figure S10. The plot of ln($C_0/C$) versus time of MTPP-(o-Me) (cation (8)) at 80 °C. 1 M KOD in CD$_3$OD/D$_2$O (5/1 vol) as the solvent.

\[ k = 3.9E-4 \text{ s}^{-1} \]
**Figure S11.** Time series of $^{31}$P NMR spectra during durability test of MTPP-(p-MeO) (cation (9)) at 80 °C. Phosphoric acid as the external standard; 1 M KOD in CD$_3$OD/D$_2$O (5/1 vol) as the solvent. The degradation percentage is calculated by $A_2/(A_1 + A_2)$. $A_1$ is the peak area of MTPP-(p-MeO) oxide; $A_2$ is the peak area of (cation (9)).

**Figure S12.** Plots of ln (C$_0$/C) versus time of MTPP-(p-MeO) (cation (9)) at 80 °C. 1 M KOD in CD$_3$OD/D$_2$O (5/1 vol) as the solvent.
Figure S13. Oxide formation degradation pathway of QP cations in alkaline media.[3]

Figure S14. Ether hydrolysis degradation pathway of QP cations in alkaline media.[2]
Figure S15. Experimentally measured $\Delta G^\circ$ vs. DFT calculated $\Delta G^\circ$ using M06/6-311++G(2d,p) method and SMD solvation model.
Table S1. Degradation mechanisms of QP cations studied in this work.

| Degradation Mechanism       | Chemical Structures                                      |
|------------------------------|----------------------------------------------------------|
| **Oxidation formation**     | ![Chemical Structures](image1)                           |
| $k_{EH} \ll k_{OF}$         | $k = k_{OF}$                                             |
| $k = k_{EH} + k_{OF}$       | ![Chemical Structures](image2)                           |
| **Ether hydrolysis**        | ![Chemical Structures](image3)                           |
| $k_{EH} \gg k_{OF}$         | $k = k_{EH}$                                             |
REFERENCES

[1] Alyea, E. C.; Malito J., Non-metal Derivaries of the Bulkiest Known Tertiary Phosphine, Trimesitylphosphine. *Phosphorus Sulfur.* **1989**, *46*, 175-181.

[2] Zhang, B.; Kaspar, B. R.; Gu, S.; Wang, J.; Zhuang, Z.; Yan, Y., A New Alkali-stable Phosphonium Cation Based on Fundamental Understanding of Degradation Mechanisms. *Chemuschem* **2016**, *9*, 2374-2379.

[3] Zanger, M.; Vanderwerf, C. A.; McEwen, W. E.; Kinetic Study of the Decpmoision of Quaternary Phosphonium Hydroxide. *J. Am. Chem. Soc.* **1959**, *81*, 3806-3807.