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 ^{1}H NMR spectra were measured in deuterated solvents on a Bruker AV400 spectrometer (^{1}H, 400 MHz). The ^{1}H NMR chemical shifts are expressed as δ downfield from tetramethylsilane (TMS) and calibrated to the residual proton of the deuterated solvent (δ = 7.26 ppm for chloroform-d). The ^{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_3PO_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$_3$) δ 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$_3$) δ 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$_3$) δ 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$_3$) δ 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$_3$) δ 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$_3$) δ 1.84 (s). Yield: 92 wt%.

Methyl tris(o-methoxyphenyl)phosphonium iodide (MTPP-(o-MeO)-I) (cation (6)): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.80 (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$_3$) δ 20.1 (s). Yield: 89 wt%.

Methyl tris(o-methylphenyl)phosphonium iodide (MTPP-(o-Me)-I) (cation (8)): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.73 (3H, t, J = 7.6 Hz), 7.55 (3H, t, J = 6.0 Hz), 7.43 (3H, t, J = 8.0 Hz), 7.23 (3H, dd, J = 15.2, 7.6 Hz), 3.20 (3H, d, J = 13.2 Hz), 2.40 (9H, s). ^{31}P NMR (161 MHz, CDCl$_3$) δ 21.7 (s). Yield: 86 wt%.

Methyl tris(*p*-methoxyphenyl)phosphonium iodide (MTPP-(*p*-MeO)-I) (cation (9)): ^{1}H NMR (400 MHz, CDCl$_3$) δ 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$_3$) δ 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$_3$) δ 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$_3$) δ 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$_3$) δ 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$_3$) δ 7.85 (s). Yield: 89 wt%.

Benzyl tris(*o*-methoxyphenyl)phosphonium chloride (BTPP-(*o*-MeO)-Cl) (cation (7)): ^{1}H NMR (400 MHz, CDCl$_3$) δ 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$_3$) δ 24.7 (s). Yield: 87 wt%.

Benzyl tris(*p*-methoxyphenyl)phosphonium chloride (BTPP-(*p*-MeO)-Cl) (cation 10): ^{1}H NMR (400 MHz, CDCl$_3$) δ 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$_3$) δ 21.1 (s). Yield: 92 wt%.

Benzyl tris(*p*-methylphenyl)phosphonium chloride (BTPP-(*p*-Me)-Cl) (cation 11): ^{1}H NMR (400 MHz, CDCl$_3$) δ 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)-(l2) 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.
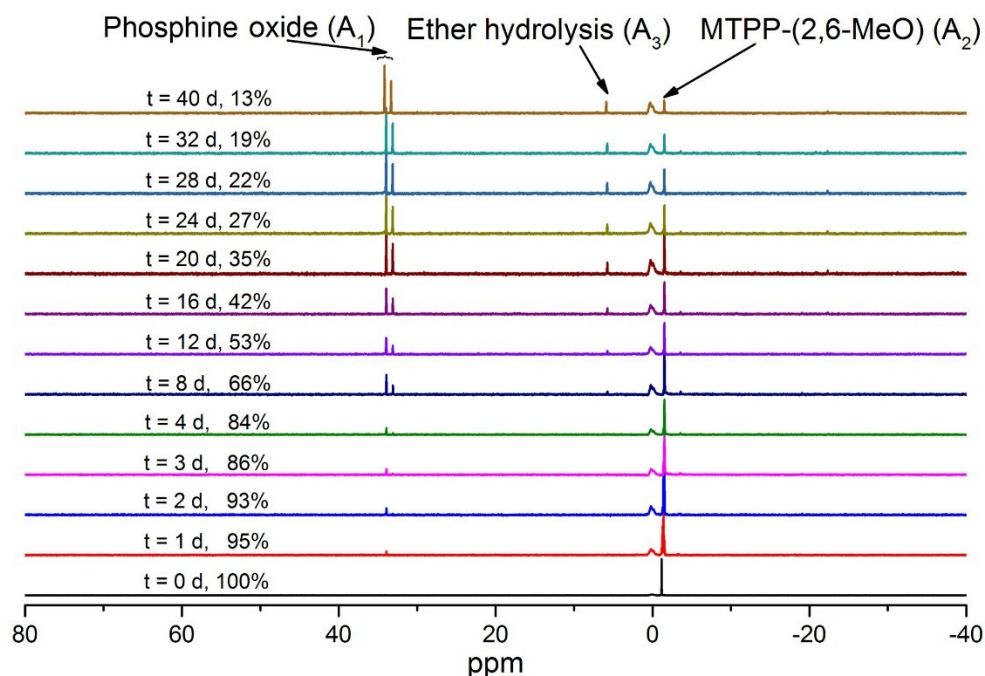
Figure S1. Time series of ^{31}P NMR spectra during durability test of MTPP-(2,6-MeO) (cation (4)) at 80 °C. Phosphoric acid as the external standard; 1 M KOD in CD_3OD/D_2O (5/1 vol) as the solvent. The degradation percentage is calculated by $A_2/(A_1 + A_2 + A_3)$. A_1 is the peak area of the phosphine oxide; A_2 is the peak area of cation (4); A_3 is the peak area of ether hydrolysis products.
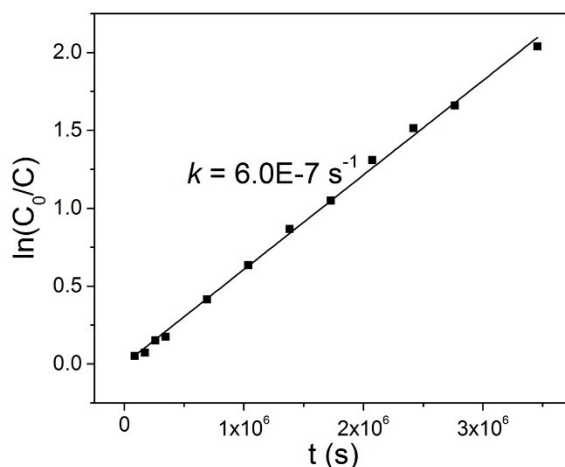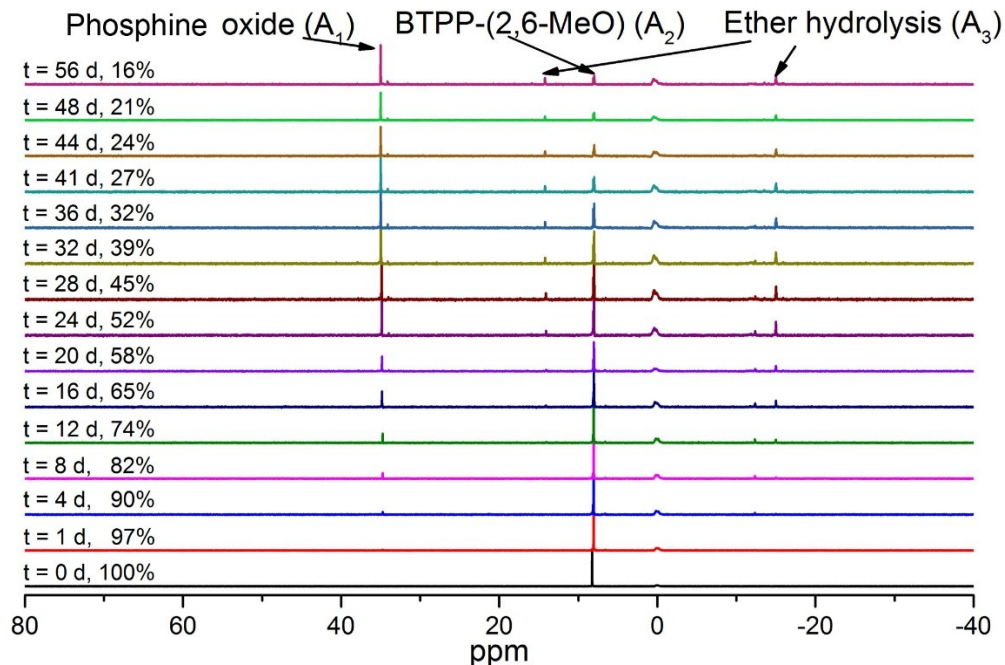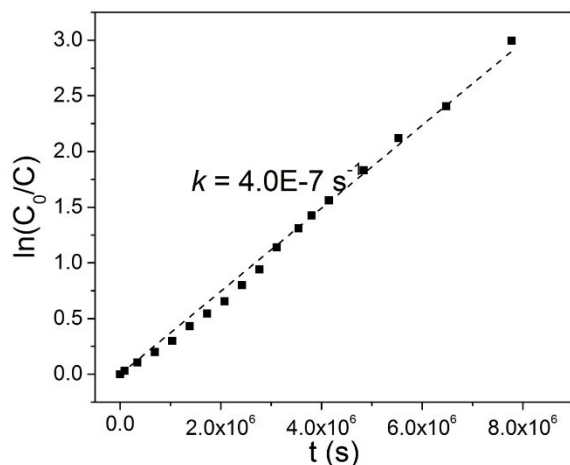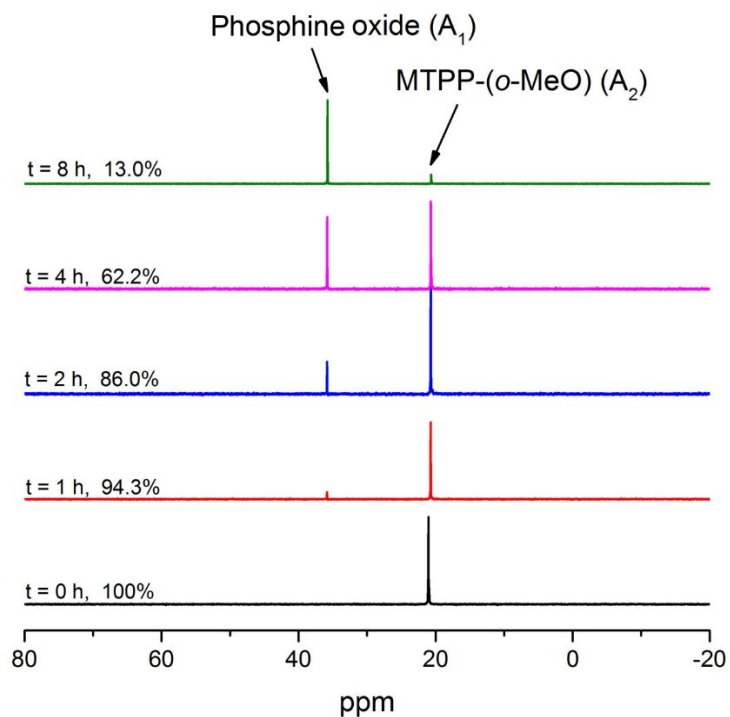

Figure S2. The plot of $\ln(C_0/C)$ versus time of MTPP-(2,6-MeO) (cation (4)) at 80 °C. 1 M KOD in CD_3OD/D_2O (5/1 vol) as the solvent.

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_3OD/D_2O (5/1 vol) as the solvent. The degradation percentage is calculated by $A_2/(A_1 + A_2 + A_3)$. 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.
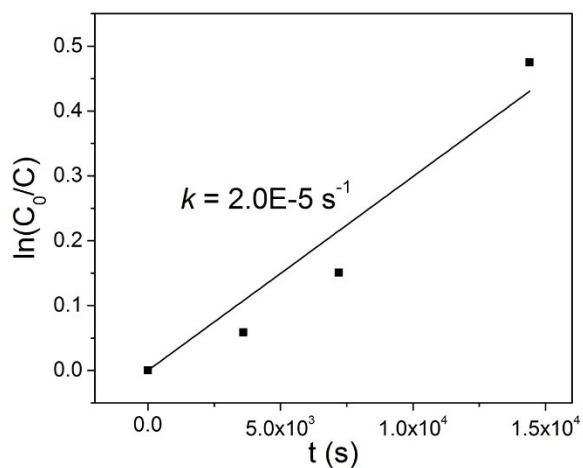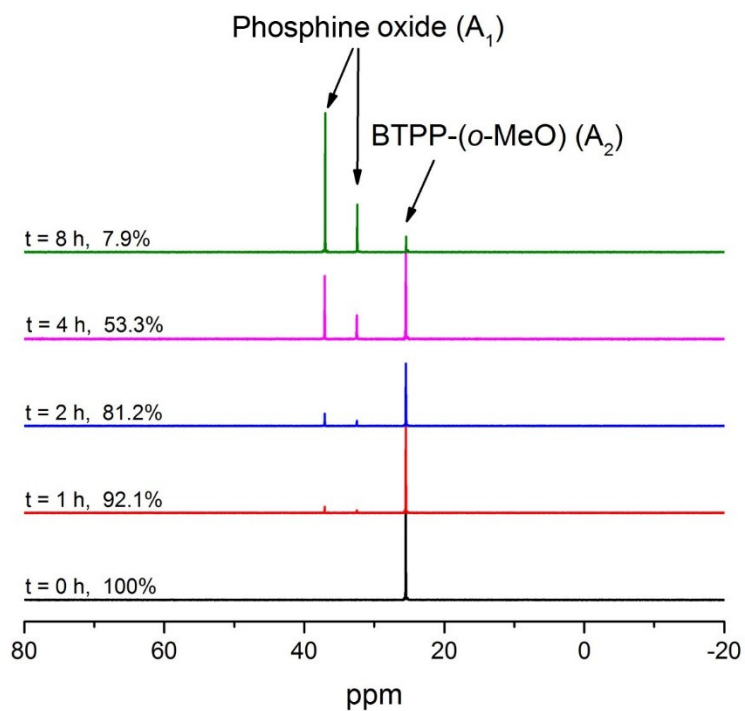

Figure S4. The plot of $\ln(C_0/C)$ versus time of BTPP-(2,6-MeO) (cation (5)) at 80 °C. 1 M KOD in CD_3OD/D_2O (5/1 vol) as the solvent.

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Figure S5. Time series of ^{31}P NMR spectra during durability test of MTPP-(*o*-MeO) (cation (6)) at 80 °C. Phosphoric acid as the external standard; 1 M KOD in CD_3OD/D_2O (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).
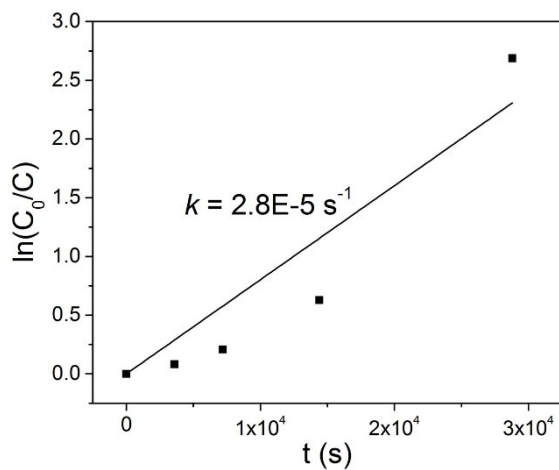

Figure S6. The plot of $\ln(C_0/C)$ versus time of MTPP-(*o*-MeO) (cation (6)) at 80 °C. 1 M KOD in CD_3OD/D_2O (5/1 vol) as the solvent.
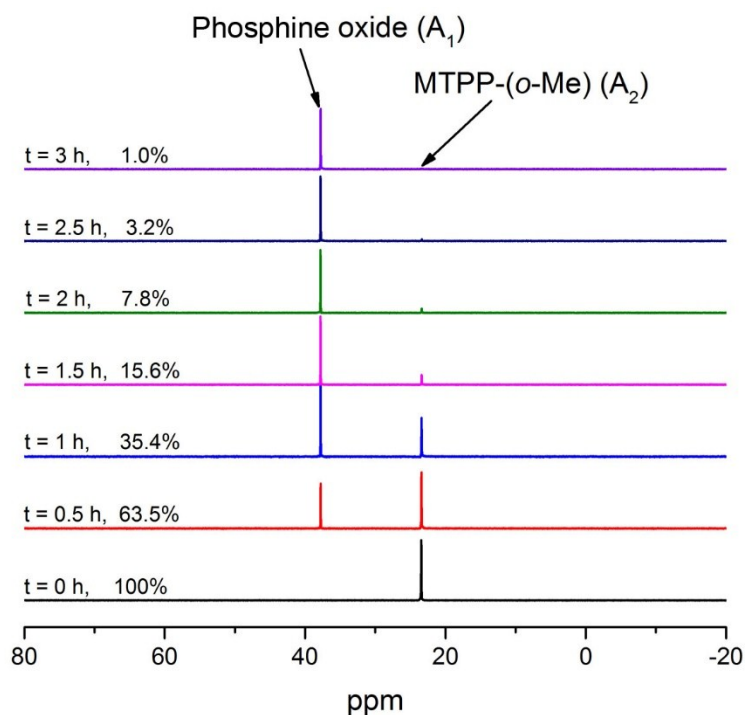
Figure S7. Time series of ^{31}P NMR spectra during durability test of BTPP-(o-MeO) (cation (7)) at 80 °C. Phosphoric acid as the external standard; 1 M KOD in CD_3OD/D_2O (5/1 vol) as the solvent. The degradation percentage is calculated by $A_2/(A_1 + A_2)$. A_1 is the peak area of the phosphine oxide; A_2 is the peak area of cation (7).
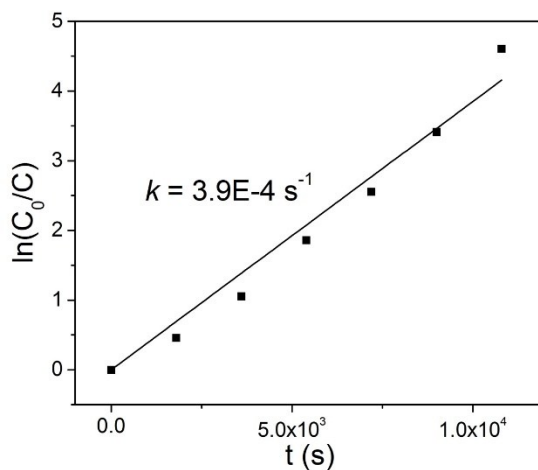

Figure S8. The plots of $\ln(C_0/C)$ versus time of BTPP-(o-MeO) (cation (7)) at 80 °C. 1 M KOD in CD_3OD/D_2O (5/1 vol) as the solvent.
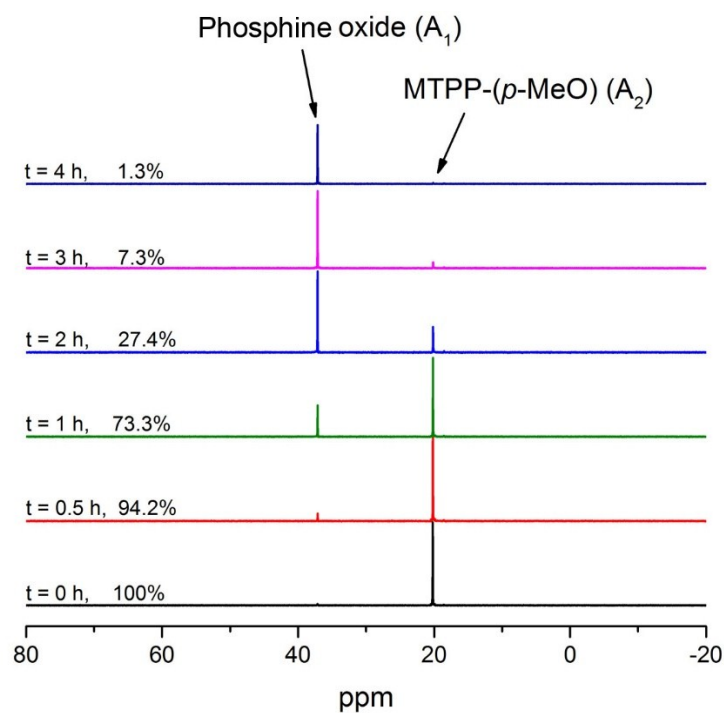
Figure S9. Time series of ^{31}P NMR spectra during durability test of MTPP-(o-Me) (cation (8)) at 80 °C. Phosphoric acid as the external standard; 1 M KOD in CD_3OD/D_2O (5/1 vol) as the solvent. The degradation percentage is calculated by $A_2/(A_1 + A_2)$. A_1 is the peak area of the phosphine oxide; A_2 is the peak area of (cation (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_3OD/D_2O (5/1 vol) as the solvent.

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_3OD/D_2O (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)).
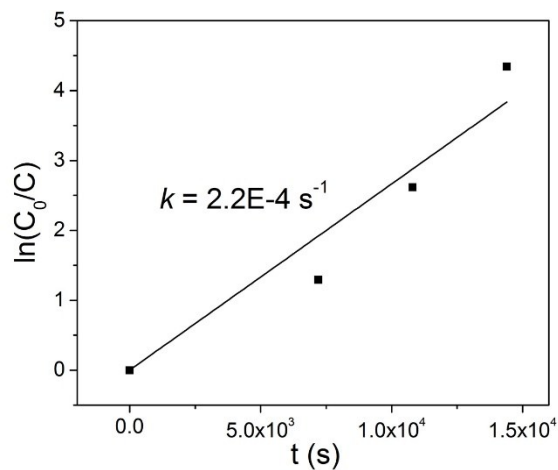

Figure S12. Plots of ln (C_0/C) versus time of MTPP-(p-MeO) (cation (9)) at 80 °C. 1 M KOD in CD_3OD/D_2O (5/1 vol) as the solvent.
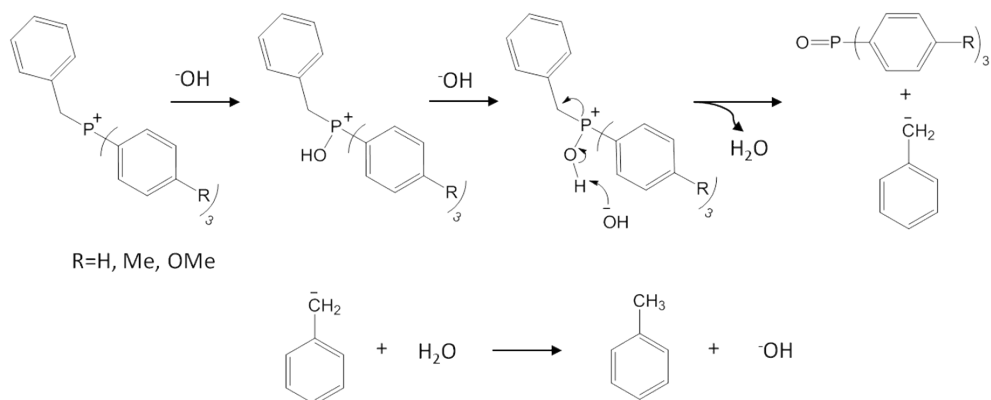
10

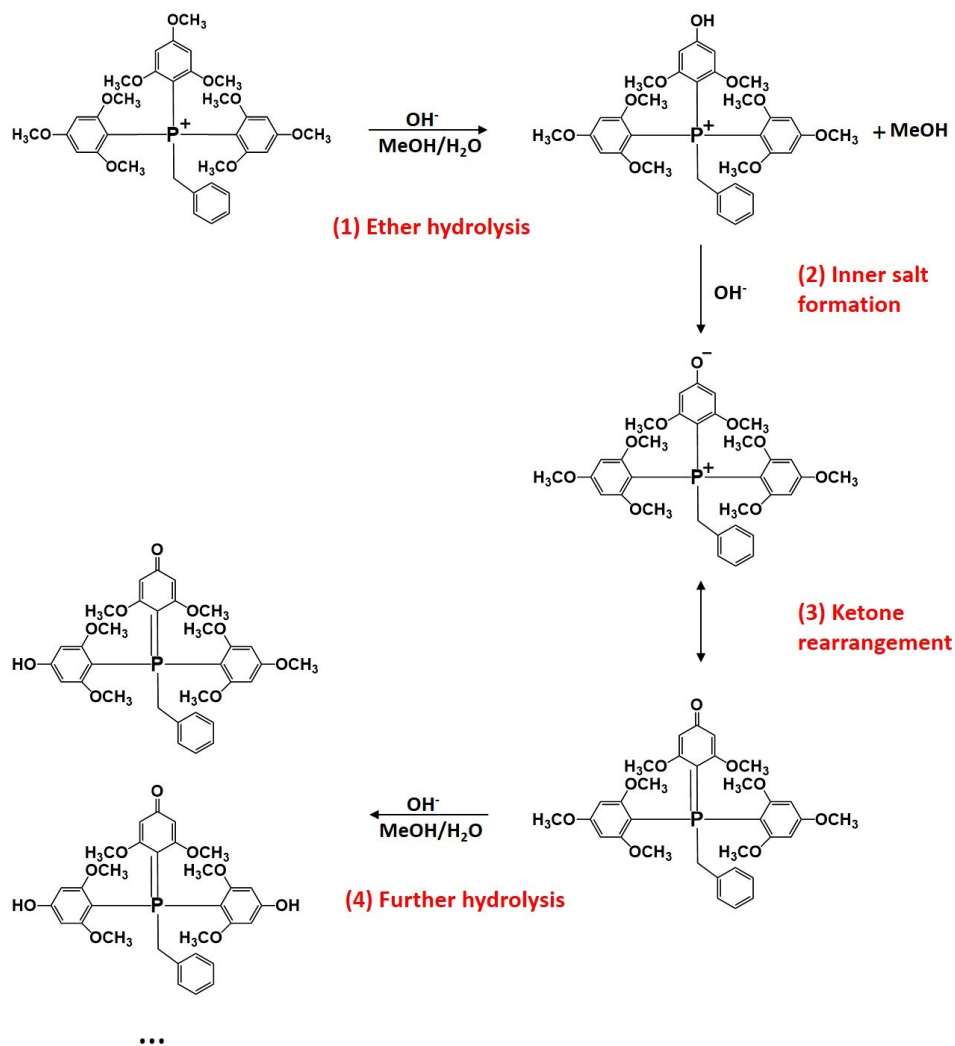**Figure S13.** Oxide formation degradation pathway of QP cations in alkaline media.[3]

Figure S14. Ether hydrolysis degradation pathway of QP cations in alkaline media.[2]
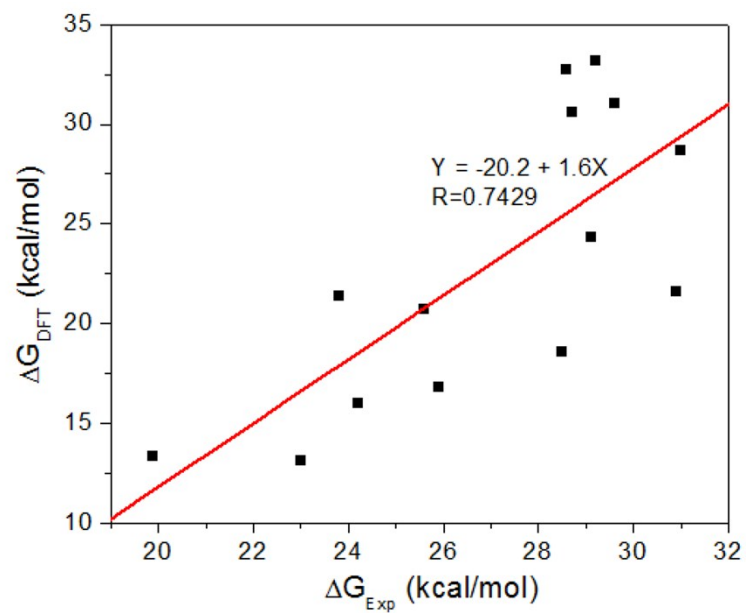
Figure S15. Experimentally measured *ΔG‡ vs.* DFT calculated *ΔG‡* using M06/6-311++G(2d,p) method and SMD solvation model.

Table S1. Degradation mechanisms of QP cations studied in this work.

Oxidation formation $k_{EH} \ll k_{OF}$ $k = k_{OF}$	
Oxidation formation & Ether hydrolysis $k = k_{EH} + k_{OF}$	
Ether hydrolysis $k_{EH} \gg k_{OF}$ $k = k_{EH}$	

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[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. *Chemsuschem* **2016**, *9*, 2374-2379.

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