Supplemental Section

Derivation of the Rate Law in Terms of Solution Conductivity

The hydrolysis reaction for a *tert*-butyl halide is:

$$(CH_3)_3CX + H_2O \rightarrow (CH_3)_3COH + H^+ + X^- \qquad \text{S1}$$

Reactions involving *tert*-butyl halides generally follow unimolecular S_N1 or E1 mechanisms. The simplest form of the first-order rate law is in terms of the reactant concentration, i.e.:

$$\left[(CH_3)_3CX\right] = \left[(CH_3)_3CX\right]_0 e^{-kt} \qquad \text{S2}$$

in which $\left[(CH_3)_3CX\right]_0$ is the initial concentration. We monitored the hydrolysis reaction using a conductivity meter, so Equation (S2) is not in a useful form. The following paragraphs outline the reformulation of Equation (S2) in terms of conductivity.

Before delving into the kinetics analysis, we first examine the role of the autoionization equilibria associated with binary alcohol/water solvents. The protons that form in the hydrolysis reaction are quickly distributed as hydronium and alkyloxonium ions. The cross-protonation reaction between the two solvent components is:

$$ROH + H_3O^+ \rightleftharpoons ROH_2^+ + H_2O \qquad \text{S3}$$

in which ROH is the alcohol. The corresponding equilibrium constant expression is:

$$K_{cp} = \frac{\left[ROH_2^+\right]\left[H_2O\right]}{\left[ROH\right]\left[H_3O^+\right]} \qquad \text{S4}$$

in which K_{cp} is the cross-protonation equilibrium constant. The proportionality relationship between $\left[ROH_2^+\right]$ and $[H_3O^+]$ from Equation (S4) is:

$$\left[ROH_2^+\right] = \alpha_{cp}\left[H_3O^+\right] \qquad \text{S5}$$

in which $\alpha_{cp} = \frac{K_{cp}[ROH]}{\left[H_2O\right]}$. The autoionization reactions for the solvent components are:

$$2ROH \rightleftharpoons ROH_2^+ + RO^- \qquad \text{S6}$$

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \qquad \text{S7}$$

and the respective equilibrium constant expressions are:

$$K_{ROH} = \frac{\left[ROH_2^+\right]\left[RO^-\right]}{[ROH]^2}$$

S8

$$K_{H_2O} = \frac{\left[H_3O^+\right]\left[OH^-\right]}{\left[H_2O\right]^2}$$

S9

Combining Equations (S5), (S8), and (S9) yields the following proportionality between $[RO^-]$ and $[OH^-]$:

$$\beta\left[OH^-\right] = \left[RO^-\right] \qquad \text{S10}$$

in which $\beta = \dfrac{K_{ROH}[ROH]}{K_{cp}K_{H_2O}[H_2O]}$.

The ions present in the reaction solution include H_3O^+, OH^-, ROH_2^+, RO^-, and X^-. The concentrations of H_3O^+, ROH_2^+, and X^- increase with time, but the OH^- and RO^- concentrations asymptotically approach zero as the autoionization equilibria (Reactions (S6) and (S7)) shift further left during the reaction. If we identify an induction time, *t*′, at which these concentrations become negligible, then the time-dependent total proton concentration at *t*′ can be well approximated as:

$$\begin{aligned}[H^+] &= [(CH_3)_3CX]_0\left(1 - e^{-kt'}\right) - [HO^-]_0 - [RO^-]_0 \\ &= [(CH_3)_3CX]_0\left(1 - e^{-kt'}\right) - (1+\beta)[HO^-]_0 \end{aligned} \qquad \text{S11}$$

in which $[HO^-]_0$ is the initial hydroxide ion concentration. The total proton concentration must be substantially larger than $(1+\beta)[HO^-]_0$ to ensure the OH^- and RO^- concentrations are negligible. We will return to this issue later. Finally, the time-dependent halide ion concentration at *t*′ is:

$$[X^-] = [(CH_3)_3CX]_0\left(1 - e^{-kt'}\right) \qquad \text{S12}$$

The general expression for the solution conductivity, κ, for dilute solutions of ions is:

$$\kappa = \sum \lambda_i c_i \qquad \text{S13}$$

in which λ_i is the limiting molar conductivity for ion "i" and c_i is its molar concentration. This expression is based on Kohlrausch's law of independent ion migration. Following the formula in Equation (S13), the solution conductivity at $t \geq t'$ for the *tert*-butyl halide reaction is:

$$\begin{aligned}\kappa &= \lambda_{ROH_2^+}\left[ROH_2^+\right] + \lambda_{H_3O^+}\left[H_3O^+\right] + \lambda_{X^-}\left[X^-\right] \\ &= \left(\alpha_{cp}\lambda_{ROH_2^+} + \lambda_{H_3O^+}\right)\left[H_3O^+\right] + \lambda_{X^-}\left[(CH_3)_3CX\right]_0\left(1 - e^{-kt}\right)\end{aligned} \tag{S14}$$

The total time-dependent proton concentration is:

$$\begin{aligned}\left[H^+\right] &= \left[ROH_2^+\right] + \left[H_3O^+\right] \\ &= \left(1 + \alpha_{cp}\right)\left[H_3O^+\right]\end{aligned} \tag{S15}$$

Combining Equations (S11), (S14), and (S15), and then simplifying yields the following expression for the solution conductivity at *t*, for which *t* ≥ *t*′:

$$\kappa = \left(\frac{\alpha_{cp}\lambda_{ROH_2^+} + \lambda_{H_3O^+}}{1 + \alpha_{cp}} + \lambda_{X^-}\right)\left[(CH_3)_3CX\right]_0 - \left(\frac{\alpha_{cp}\lambda_{ROH_2^+} + \lambda_{H_3O^+}}{1 + \alpha_{cp}}\right)(1 + \beta)\left[HO^-\right]\left[(CH_3)_3CX\right]_0 e^{-kt} \tag{S16}$$

Equation (S16) can be recast in the following form to include the induction time:

$$\kappa = \left(\frac{\alpha_{cp}\lambda_{ROH_2^+} + \lambda_{H_3O^+}}{1 + \alpha_{cp}} + \lambda_{X^-}\right)\left[(CH_3)_3CX\right]_0 - \left(\frac{\alpha_{cp}\lambda_{ROH_2^+} + \lambda_{H_3O^+}}{1 + \alpha_{cp}}\right)(1 + \beta)\left[HO^-\right]\left[(CH_3)_3CX\right]_0 e^{-kt'} e^{-k\left(t - t'\right)} \tag{S17}$$

Each parameter in Equation (S17) depends on one or more of the following variables: T, X_{water}, $[(CH_3)_3CX]_0$, and $t^{'}$. As these parameters are all constant for any given kinetic trial, Equation (S17) can be readily simplified to the following "analysis-friendly" form:

$$\kappa(t) = C - Be^{-k(t-t^{'})} \qquad \text{S18}$$

in which the regression parameters are C, B, and k. The difference term, $t - t^{'}$, is not required to be zero for the first data point.

For our rate studies we used an Oakton conductivity meter, which displays the measurements to four digits. As such, Equation (S18) is precise within ±1 unit in the last digit if reaction monitoring begins when the time-dependent term, $(1+\beta)[HO^-]$, is less than four orders of magnitude smaller than the total proton concentration, and if $\lambda_{H_3O^+}$ and $\lambda_{ROH_2^+}$ are comparable to λ_{OH^-}. We estimate that this criterion is met when ~8% of the *tert*-butyl bromide has reacted. The maximum conductivity range, which depends primarily on the solution mole fraction, is between 340 and 590 μS. As standard protocol, we began monitoring the reactions when the conductivity was at least 50 μS.