Electronic supplementary information

Structural effects on the bromination rate and selectivity of alkylbenzenes and alkoxybenzenes in aqueous solution[†]

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Includes 40 pages, 22 figures, and 18 tables.

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S1. Reagent Information

Table S1. Reagents list with corresponding purity and vendor information.

Reagent	Purity	Vendor
1,3,5-trimethoxybenzene	≥ 99%	Aldrich Chemistry
2-chlorobenzonitrile (CBN)	≥ 98%	Sigma-Aldrich
benzene	99.9%	Alfa Aesar
bromobenzene	99%	Acros Organics
chlorobenzene	≥ 99.0%	Mallinckrodt
ethoxybenzene	99%	Acros Organics
ethylbenzene	99%	Acros Organics
ethyl acetate	≥ 99.5%	Acros Organics
isooctane	≥ 95%	Acros Organics
isopropoxybenzene	97%	Oakwood Chemical
isopropylbenzene	99.9%	Acros Organics
methanol	99.9%	Fisher Scientific
nitric acid	ACS grade	Fisher Scientific
ortho-bromo-ethoxybenzene	99%	Oakwood Chemical
ortho-bromo-ethylbenzene	98%	Alfa Aesar
ortho-bromo-isopropoxybenzene	97%	Alfa Aesar
ortho-bromo-isopropylbenzene	97%	Alfa Aesar
ortho-bromo-*tert*-butoxybenzene	94% [a]	Novel Chemical Solutions
ortho-bromo-*tert*-butylbenzene	95%	Oakwood Chemical
para-bromo-ethoxybenzene	97%	Acros Organics
para-bromo-ethylbenzene	99%	Acros Organics
para-bromo-isopropoxybenzene	98%	Oakwood Chemical
para-bromo-isopropylbenzene	97%	Alfa Aesar
para-bromo-*tert*-butoxybenzene	98%	Alfa Aesar
para-bromo-*tert*-butylbenzene	97%	Oakwood Chemical
sodium bicarbonate	≥ 99.7%	Acros Organics
sodium bromide	99.5%	Sigma-Aldrich
sodium chloride	99.999%	Sigma-Aldrich
sodium hydroxide (aqueous)	50%	Ricca Chemical Company
sodium hypochlorite solution	5.65-6%	Fisher Scientific
sodium nitrate	≥ 99.0%	Sigma-Aldrich
sodium phosphate dibasic (anhydrous)	≥ 99.0%	Acros Organics
sodium sulfite (anhydrous)	≥ 98%	Acros Organics
sodium tetraborate decahydrate	99.5%	Acros Organics
sodium thiosulfate (anhydrous)	> 98%	Fisher Scientific
tert-butoxybenzene	98%	Alfa Aesar
tert-butylbenzene	99%	Aldrich Chemistry
tert-butyl methyl ether	99.9%	Fisher Scientific
toluene	99.9%	Fisher Scientific

[a] Purity determined via gas chromatography-mass spectrometry

S2. Liquid-Liquid Extraction of NaOCl to Remove Chloride Ion

Laboratory grade (5.65-6%) sodium hypochlorite (NaOCl) is typically manufactured by bubbling $Cl_2(g)$ into NaOH(aq), resulting in the formation of NaOCl and HCl at equimolar concentrations (~1 M). Reactions that were chloride-sensitive required the removal of chloride from the stock NaOCl solution by means of a liquid-liquid extraction. The extraction began with 50 mL of NaOCl(aq), 3.5 g $Na_2SO_4(s)$, 30 mL of ethyl acetate, and 3 mL of concentrated HNO_3 in a separatory funnel; the funnel was shaken vigorously, and air was periodically released from the stopcock. The low pH favored the formation of neutral free available chlorine (FAC) species (e.g., HOCl, Cl_2, and Cl_2O) and partitioning into the ethyl acetate (top layer). The bottom, aqueous layer was removed; 50 mL of 1.25 M NaOH(aq) was added to the separatory funnel and shaken vigorously. Under such conditions, virtually all of the FAC exists as OCl^- in the aqueous layer, which was removed from the funnel and stored in a plastic bottle wrapped in aluminum foil to minimize light exposure. To measure the success of the extraction, high performance liquid chromatography (HPLC) and a chloride selective electrode were employed as methods of analysis of FAC and Cl^- concentrations, respectively. Both analytical methods are described below.

Analysis of FAC in extracted NaOCl. 1,3,5-trimethoxybenzene (TMB) can react stoichiometrically (1:1) with FAC to give the chlorinated product, 2-chloro-1,3,5-trimethoxybenzene (Cl−TMB), that can be analyzed via HPLC.[1,2] Quantification of Cl−TMB serves as a surrogate method of analysis for [FAC]. Samples of extracted FAC required two dilution steps in order for TMB to be in sufficient excess to quench and form its mono-halogenated product (Cl−TMB). For the first dilution, 0.400 mL of extracted FAC was dissolved in 40 mL of 18 MΩ·cm water (Nanopure, Thermo Scientific) such that [FAC] ~ 0.01 M. For the second dilution, 0.250 mL of ~ 0.01 M FAC was added to a 25 mL buffer (sodium phosphate at 10 mM, adjusted to pH 7.00 using HNO_3). Three aliquots (1.00 mL each) of FAC in phosphate buffer were quenched in 2-mL HPLC autosampler vials pre-amended with TMB (0.333 mL at 2.624 mM, dissolved in methanol); vials were immediately capped and shaken for 10 s. After the FAC aliquot and TMB solution were combined, but prior to any reaction between them, theoretical concentrations of TMB and FAC were 650 μM and approximately 75 μM, respectively. Samples were analyzed via a Shimadzu HPLC with a diode array detector (DAD). The monitored wavelengths

on the DAD (corresponding the wavelengths of maximum absorbance) were 266 nm (for TMB) and 271 nm (for Cl-TMB). Separations were achieved using an Agilent Poroshell 120 column (50 mm length, 2.1 mm inner diameter, and 2.7 μm particle size) with an isocratic mobile phase consisting of 62 vol% 18 MΩ cm water (Nanopure, Thermo Scientific) and 38 vol% acetonitrile.

Analysis of chloride in extracted NaOCl. To 40 mL of 18 MΩ·cm water (Nanopure, Thermo Scientific, ionic strength adjusted to 100 mM using NaNO$_3$), 0.400 mL of the extracted NaOCl was added. This dilution allowed for the presumed [Cl$^-$] to be within the calibration range. A combination chloride selective electrode (Fisher Accumet AB 150) was used to measure the potential (mV) of samples and standards prepared using ultrahigh-purity (99.999%) NaCl.

S3. Gas Chromatography Methods

Samples were analyzed on an Agilent 7890A gas chromatograph (GC) interfaced with an Agilent 5975C mass spectrometer (MS). An Agilent DB-5MS+DG column (30 m + 10 m DuraGuard, 0.250 mm inner diameter, 0.25 μm film thickness) was used to effect separations. The inlet temperature was held at 280 °C and operated in splitless mode. The column flow rate was a constant 1 mL/min using ultra-high purity helium as the carrier gas. GC oven temperature programs and MS method details are provided below.

1. **Benzene Experiments.** The oven temperature program included an initial temperature of 35 °C (hold 2 min), ramp at 15 °C min^{-1} to 75 °C (no hold), ramp at 25 °C min^{-1} to 225 °C (no hold); the total analysis time was 10.7 min. Retention times and ions detected in selected ion monitoring (SIM) mode for each analyte are shown in **Table S2**.

Table S2. GC-MS SIM method for analyzing mono-halogenated products of benzene.

Analyte	SIM Group	Retention Time (min)	Quantitation Ion	Monitoring Ion
chlorobenzene	A	5.49	112 $M^{+\bullet}$	114 $M^+(^{37}Cl)$
bromobenzene	B	6.54	157 $M^{+\bullet}$	159 $M^+(^{81}Br)$
2-chlorobenzonitrile (internal standard)	C	8.93	137 $M^{+\bullet}$	102 $(M - Cl)^+$

2. **Alkylbenzene Experiments.** The oven temperature program included an initial temperature of 35 °C (no hold), ramp at 5 °C min^{-1} to 90 °C (no hold), ramp at 15 °C min^{-1} to 105 °C (no hold), ramp at 2 °C min^{-1} to 120 °C (no hold), ramp at 50 °C min^{-1} to 205 °C (no hold); the total analysis time was 21.2 min. Retention times and ions detected in SIM mode for each analyte are shown in **Table S3**.

Table S3. GC-MS SIM method details for analyzing alkylbenzenes and their *para*/*ortho*-brominated products.

Analyte	SIM Group	Retention Time (min)	Quantitation Ion	Monitoring Ion
ethylbenzene	A	6.41	106 M$^{+\bullet}$	91 (M – CH$_3$)$^+$
isopropylbenzene	B	7.85	120 M$^{+\bullet}$	105 (M – CH$_3$)$^+$
tert-butylbenzene	C	9.68	134 M$^{+\bullet}$	119 (M – CH$_3$)$^+$
ortho-bromo-ethylbenzene	D	13.90	184 M$^{+\bullet}$	169 (M – CH$_3$)$^+$
para-bromo-ethylbenzene	D	14.57	184 M$^{+\bullet}$	169 (M – CH$_3$)$^+$
ortho-bromo-isopropylbenzene	E	15.45	198 M$^{+\bullet}$	184 (M (^{81}Br) – ^{13}CH$_3$)$^+$
para-bromo-isopropylbenzene	E	16.35	198 M$^{+\bullet}$	185 (M (^{79}Br) – ^{12}CH$_3$)$^{+\,a}$
2-chlorobenzonitrile (internal standard)	F	17.78	137 M$^{+\bullet}$	102 (M – Cl)$^+$
para-bromo-*tert*-butylbenzene	G	18.69	212 M$^{+\bullet}$	197 (M – CH$_3$)$^+$
ortho-bromo-*tert*-butylbenzene	G	18.86	212 M$^{+\bullet}$	197 (M – CH$_3$)$^+$

[a] While typically m/z = 185 would be selected as the monitoring ion for *ortho*/*para*-bromo-isopropylbenzene, for most analyses herein, m/z = 184 was used.

3. **Alkoxybenzene Experiments.** The oven temperature program included an initial temperature of 60 °C (no hold), ramp at 10 °C min^{-1} to 110 °C (no hold), ramp at 20 °C min^{-1} to 160 °C (no hold), ramp at 18 °C min^{-1} to 196 °C (no hold), ramp at 30 °C min^{-1} to 241 °C (no hold); the total analysis time was 11 min. Retention times and ions detected in SIM mode for each analyte are shown in **Table S4**.

Table S4. GC-MS SIM method details for analyzing alkoxybenzenes and their *para*/*ortho*-brominated products.

Analyte	SIM Group	Retention Time (min)	Quantitation Ion	Monitoring Ion
ethoxybenzene	A	5.35	122 $M^{+\bullet}$	94 $(M - CH_2CH_3)^+$
isopropoxybenzene	A	5.66	136 $M^{+\bullet}$	94 $(M - CH(CH_3)_2)^+$
tert-butoxybenzene	B	6.11	135 $(M - CH_3)^+$	94 $(M - C(CH_3)_3)^+$
2-chlorobenzonitrile (internal standard)	C	7.08	137 $M^{+\bullet}$	102 $(M - Cl)^+$
ortho-bromo-ethoxybenzene	D	7.81	200 $M^{+\bullet}$	172 $(M - CH_2CH_3)^+$
para-bromo-ethoxybenzene	D	7.98	200 $M^{+\bullet}$	172 $(M - CH_2CH_3)^+$
ortho-bromo-isopropoxybenzene	D	7.99	216 $M^{+\bullet}$	172 $(M - CH(CH_3)_2)^+$
para-bromo-isopropoxybenzene	E	8.24	214 $M^{+\bullet}$	172 $(M - CH(CH_3)_2)^+$
ortho-bromo-*tert*-butoxybenzene	E	8.39	213 $(M - CH_3)^+$	172 $(M - C(CH_3)_3)^+$
para-bromo-*tert*-butoxybenzene	E	8.61	213 $(M - CH_3)^+$	172 $(M - C(CH_3)_3)^+$

S4. Example Time Courses

Example time courses of bromination of alkyl- and alkoxybenzenes are given in **Figures S1** and **S2**, respectively.
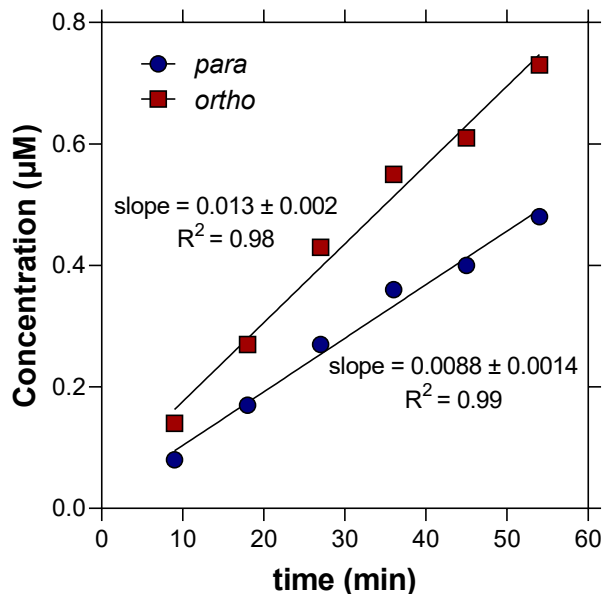
Figure S1. Example time course of ethylbenzene reacting with free bromine to produce *para-* and *ortho-*bromoethylbenzene. Solution conditions: $[Br^-]_o = 0.99$ mM, $[FAC]_o = 1.16$ mM, phosphate (20 mM) as pH buffer, pH = 6.30, [ethylbenzene]$_o$ = 16 µM, [NaCl] = 25 mM, [NaNO$_3$] = 75 mM, and T = 20.00 °C. Error estimates denote 95% confidence intervals.
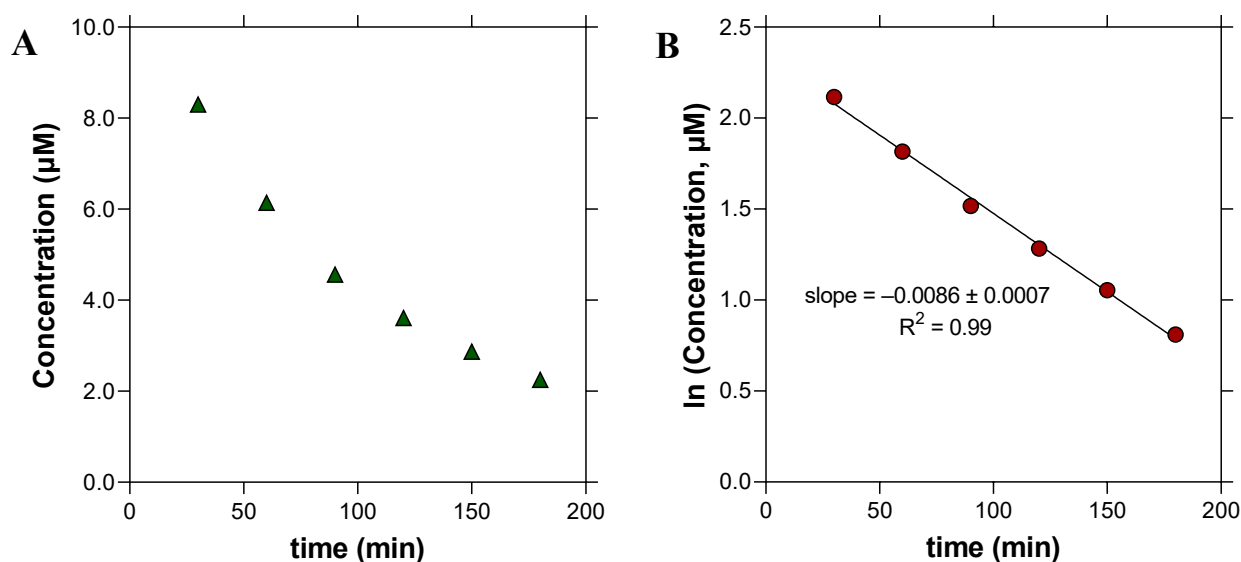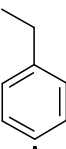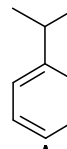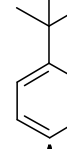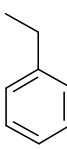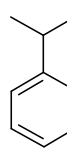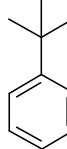
Figure S2. Example time course of ethoxybenzene bromination showing (**A**) loss of ethoxybenzene and (**B**) linear regression of ln[ethoxybenzene] over time. Solution conditions: $[Br^-]_o = 0.35$ mM, $[FAC]_o = 0.4$ mM, phosphate (20 mM) as pH buffer, pH = 7.0, [ethoxybenzene]$_o$ = 10 µM, [NaCl] = 10 mM, [NaNO$_3$] = 90 mM, and T = 20.00 °C. Error estimates denote 95% confidence intervals.

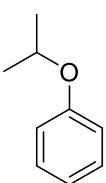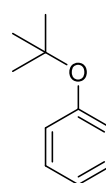# S5. Reactor Solution Conditions and Measured Rate Constants
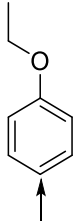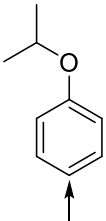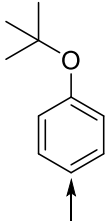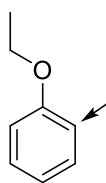
Varied Chloride. Solution conditions and pseudo-first-order rate constants for regiospecific bromination of alkylbenzenes and alkoxybenzenes as a function of the total chloride concentration ($[Cl^-]_{tot}$) are given in **Tables S5 and S6**, respectively.

Table S5. Pseudo-first-order rate constants (s^{-1}) for formation of *para*- and *ortho*-brominated alkylbenzenes via reactions with free bromine as a function of the total chloride concentration.[a]

$[Cl^-]_{tot}$ (mM)	$k_{obs,para}$	$k_{obs,para}$	$k_{obs,para}$	$k_{obs,ortho}$	$k_{obs,ortho}$	$k_{obs,ortho}$
17.0	$(5.2 \pm 0.5) \times 10^{-6}$	$(5.8 \pm 0.7) \times 10^{-6}$	$(3.0 \pm 0.5) \times 10^{-6}$	$(8.3 \pm 0.9) \times 10^{-6}$	$(9.8 \pm 1.4) \times 10^{-7}$	$(7.96 \pm 1.10) \times 10^{-8}$
26.9	$(8.0 \pm 0.5) \times 10^{-6}$	$(8.9 \pm 0.6) \times 10^{-6}$	$(4.6 \pm 0.3) \times 10^{-6}$	$(1.24 \pm 0.10) \times 10^{-5}$	$(1.50 \pm 0.14) \times 10^{-6}$	$(8.02 \pm 1.60) \times 10^{-8}$
36.9	$(9.9 \pm 1.0) \times 10^{-6}$	$(1.11 \pm 0.14) \times 10^{-5}$	$(5.6 \pm 0.6) \times 10^{-6}$	$(1.3 \pm 0.3) \times 10^{-5}$	$(1.9 \pm 0.3) \times 10^{-6}$	$(8.9 \pm 2.5) \times 10^{-8}$
46.8	$(1.3 \pm 0.2) \times 10^{-5}$	$(1.6 \pm 0.2) \times 10^{-5}$	$(7.9 \pm 1.1) \times 10^{-6}$	$(2.1 \pm 0.3) \times 10^{-5}$	$(2.6 \pm 0.4) \times 10^{-6}$	$(1.6 \pm 0.2) \times 10^{-7}$
61.7	$(1.7 \pm 0.2) \times 10^{-5}$	$(1.8 \pm 0.3) \times 10^{-5}$	$(9.3 \pm 1.4) \times 10^{-6}$	$(2.9 \pm 0.3) \times 10^{-5}$	$(2.8 \pm 0.5) \times 10^{-6}$	$(2.0 \pm 0.7) \times 10^{-7}$

[a] All reactors contained: $[FAC]_o = 1.16$ mM, phosphate (20 mM) as pH buffer, pH = 6.30, $[alkylbenzene]_o = 16$ μM for each parent compound, $[Br^-] = 0.99$ mM, $[NaCl] + [NaNO_3] = 100$ mM, and T = 20.00 °C. $[Cl^-]_{tot}$ is the contribution from all sources of Cl^-, including NaCl, added FAC, and generation of Cl^- during oxidation of Br^- by FAC. Error estimates denote 95% confidence intervals.
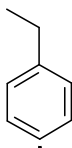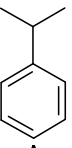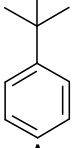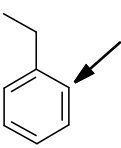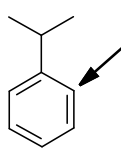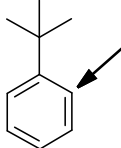
Table S6. Pseudo-first-order rate constants (s^{-1}) for formation of *para-* and *ortho*-brominated alkoxybenzenes via reactions with free bromine as a function of the total chloride concentration.[a]

$[Cl^-]_{tot}$ (mM)	$k_{obs,para}$	$k_{obs,para}$	$k_{obs,para}$	$k_{obs,ortho}$	$k_{obs,ortho}$	$k_{obs,ortho}$
10.0	(7.1 ± 0.6) $\times 10^{-3}$	(9.2 ± 0.8) $\times 10^{-3}$	(8.9 ± 1.7) $\times 10^{-4}$	(1.55 ± 0.13) $\times 10^{-3}$	(2.11 ± 0.19) $\times 10^{-3}$	(4.9 ± 0.9) $\times 10^{-4}$
20.0	(1.18 ± 0.19) $\times 10^{-2}$	(1.4 ± 0.3) $\times 10^{-2}$	(1.7 ± 0.3) $\times 10^{-3}$	(2.7 ± 0.4) $\times 10^{-3}$	(3.4 ± 0.8) $\times 10^{-3}$	(9.9 ± 1.4) $\times 10^{-4}$
30.0	(1.7 ± 0.4) $\times 10^{-2}$	(2.2 ± 0.8) $\times 10^{-2}$	(2.8 ± 0.4) $\times 10^{-3}$	(3.9 ± 0.9) $\times 10^{-3}$	(5 ± 2) $\times 10^{-3}$	(1.6 ± 0.2) $\times 10^{-3}$
40.0	(2.1 ± 0.4) $\times 10^{-2}$	(2.8 ± 0.7) $\times 10^{-2}$	(2.8 ± 0.3) $\times 10^{-3}$	(4.7 ± 0.9) $\times 10^{-3}$	(6.7 ± 1.6) $\times 10^{-3}$	(1.63 ± 0.16) $\times 10^{-3}$
50.0	(2.7 ± 0.9) $\times 10^{-2}$	(3.1 ± 1.6) $\times 10^{-2}$	(3.4 ± 0.3) $\times 10^{-3}$	(6 ± 2) $\times 10^{-3}$	(7 ± 4) $\times 10^{-3}$	(2.29 ± 0.19) $\times 10^{-3}$

[a] All reactors contained: $[FAC]_o = 0.4$ mM, phosphate (20 mM) as pH buffer, pH = 7.0, [alkoxybenzene]$_o$ = 10 µM for each parent compound, $[Br^-] = 0.35$ mM, $[NaNO_3] = 90$ mM, and T = 20.00 °C. $[Cl^-]_{tot}$ is the contribution from all sources of Cl^-, including NaCl, added FAC, and generation of Cl^- during oxidation of Br^- by FAC. Error estimates denote 95% confidence intervals.

Varied Free Available Chlorine. Solution conditions and pseudo-first-order rate constants for regiospecific bromination of alkylbenzenes and alkoxybenzenes as a function of the initial FAC concentration are given in **Tables S7 and S8**, respectively. Effects of $[FAC]_o$ on regiospecific k_{obs} for alkylbenzenes are shown in **Figure S3**.

Table S7. Pseudo-first-order rate constants (s^{-1}) for formation of *para*- and *ortho*-brominated alkylbenzenes via reactions with free bromine as a function of free available chlorine concentration.[a]

$[FAC]_o$ (mM)	$k_{obs,para}$	$k_{obs,para}$	$k_{obs,para}$	$k_{obs,ortho}$	$k_{obs,ortho}$	$k_{obs,ortho}$
1.59	$(1.57 \pm 0.05) \times 10^{-6}$	$(1.64 \pm 0.06) \times 10^{-6}$	$(7.3 \pm 0.7) \times 10^{-7}$	$(2.54 \pm 0.14) \times 10^{-6}$	$(2.4 \pm 0.2) \times 10^{-7}$	$(1 \pm 2) \times 10^{-8b}$
2.47	$(1.53 \pm 0.07) \times 10^{-6}$	$(1.65 \pm 0.05) \times 10^{-6}$	$(7.4 \pm 0.6) \times 10^{-7}$	$(2.58 \pm 0.14) \times 10^{-6}$	$(2.56 \pm 0.12) \times 10^{-7}$	$(0.9 \pm 1.3) \times 10^{-9b}$
3.53	$(1.57 \pm 0.08) \times 10^{-6}$	$(1.63 \pm 0.07) \times 10^{-6}$	$(7.2 \pm 0.5) \times 10^{-7}$	$(2.2 \pm 0.3) \times 10^{-6}$	$(2.3 \pm 0.3) \times 10^{-7}$	$(0.9 \pm 3.4) \times 10^{-9b}$
4.48	$(1.63 \pm 0.04) \times 10^{-6}$	$(1.68 \pm 0.05) \times 10^{-6}$	$(7.3 \pm 0.3) \times 10^{-7}$	$(2.62 \pm 0.15) \times 10^{-6}$	$(2.63 \pm 0.18) \times 10^{-7}$	$(0.8 \pm 1.9) \times 10^{-9b}$
5.42	$(1.64 \pm 0.11) \times 10^{-6}$	$(1.67 \pm 0.09) \times 10^{-6}$	$(7.9 \pm 0.7) \times 10^{-7}$	$(2.6 \pm 0.2) \times 10^{-6}$	$(2.65 \pm 0.17) \times 10^{-7}$	$(1.0 \pm 1.9) \times 10^{-8b}$

[a] All reactors contained: phosphate (20 mM) as pH buffer, pH = 7.40, $[alkylbenzene]_o = 50$ μM for each parent compound, $[Cl^-]_o = 30.00$ mM, $[Br^-] = 1.00$ mM, $[NaNO_3] = 70$ mM, and T = 20.00 °C. $[Cl^-]_o$ represents the contribution from NaCl only. Error estimates denote 95% confidence intervals.
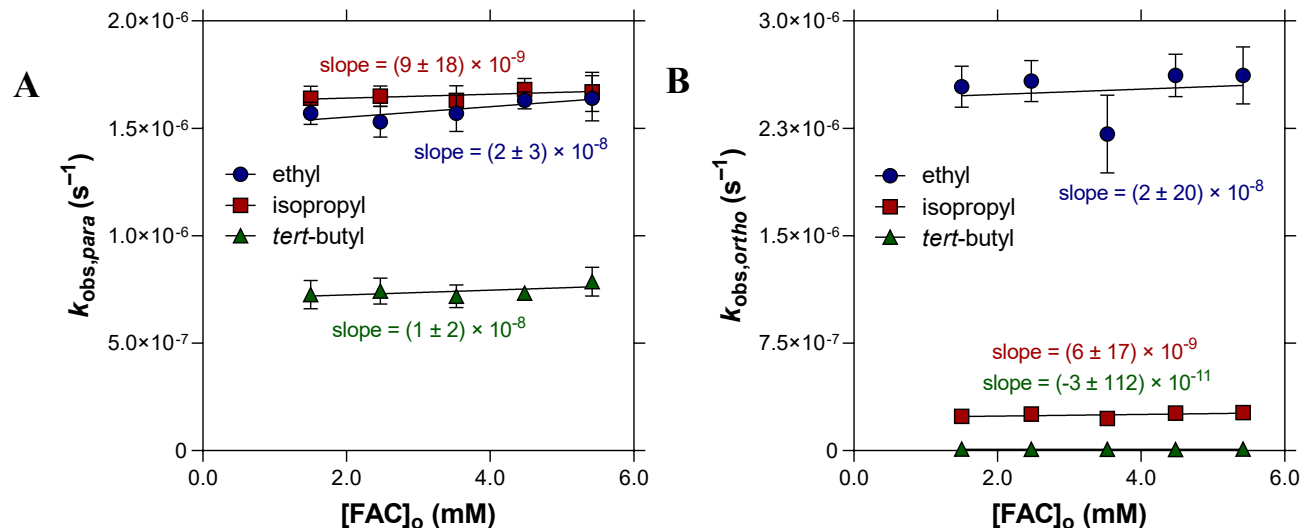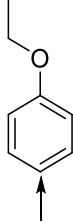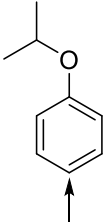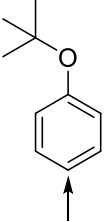
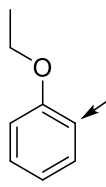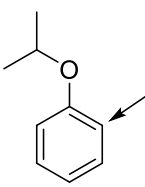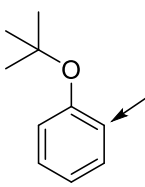[b] Not significantly different than zero.

Figure S3. Regiospecific pseudo-first-order rate constants for bromination of alkylbenzenes at the (A) *para* and (B) *ortho* positions as a function of free available chlorine (FAC) concentration. Solution conditions: $[FAC]_o$ ranged from 1.50 – 5.50 mM, $[Br^-] = 1.00$ mM, phosphate (20 mM) as pH buffer, pH = 7.40, $[alkylbenzene]_o = 50$ μM for each parent compound, $[Cl^-]_o = 30.00$ mM, $[NaNO_3] = 70$ mM, and T = 20.00 °C. $[Cl^-]_o$ represents the contribution from NaCl only. All error bars denote 95% confidence intervals.
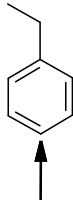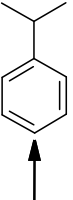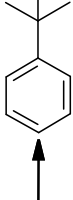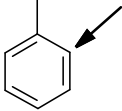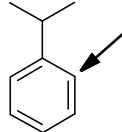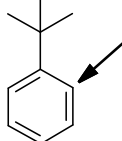
Table S8. Pseudo-first-order rate constants (s^{-1}) for formation of *para-* and *ortho-*brominated alkoxybenzenes via reactions with free bromine as a function of free available chlorine concentration.[a]

[FAC]$_0$ (mM)	$k_{obs,para}$	$k_{obs,para}$	$k_{obs,para}$	$k_{obs,ortho}$	$k_{obs,ortho}$	$k_{obs,ortho}$
0.40	$(4.8 \pm 0.5) \times 10^{-4}$	$(6.7 \pm 0.6) \times 10^{-4}$	$(8.4 \pm 1.2) \times 10^{-5}$	$(7.3 \pm 0.7) \times 10^{-5}$	$(9.9 \pm 0.9) \times 10^{-5}$	$(3.0 \pm 0.4) \times 10^{-5}$
0.50	$(5.5 \pm 0.7) \times 10^{-4}$	$(7.5 \pm 1.0) \times 10^{-4}$	$(8 \pm 2) \times 10^{-5}$	$(7.7 \pm 0.9) \times 10^{-5}$	$(1.05 \pm 0.14) \times 10^{-4}$	$(2.8 \pm 0.7) \times 10^{-5}$
0.60	$(5.9 \pm 0.5) \times 10^{-4}$	$(7.7 \pm 0.5) \times 10^{-4}$	$(9.7 \pm 1.0) \times 10^{-5}$	$(7.9 \pm 0.6) \times 10^{-5}$	$(1.03 \pm 0.07) \times 10^{-4}$	$(3.1 \pm 0.3) \times 10^{-5}$
0.70	$(6.5 \pm 0.7) \times 10^{-4}$	$(8.6 \pm 1.3) \times 10^{-4}$	$(1.06 \pm 0.09) \times 10^{-4}$	$(8.3 \pm 0.9) \times 10^{-5}$	$(1.11 \pm 0.17) \times 10^{-4}$	$(3.3 \pm 0.3) \times 10^{-5}$
0.80	$(7.1 \pm 0.6) \times 10^{-4}$	$(9.1 \pm 1.4) \times 10^{-4}$	$(1.14 \pm 0.06) \times 10^{-4}$	$(8.7 \pm 0.7) \times 10^{-5}$	$(1.14 \pm 0.17) \times 10^{-4}$	$(3.50 \pm 0.18) \times 10^{-5}$

[a] All reactors contained: borate (20 mM) as pH buffer, pH = 8.2, [alkoxybenzene]$_0$ = 10 µM for each parent compound, [Cl$^-$]$_0$ = 10 mM, [Br$^-$] = 0.35 mM, [NaNO$_3$] = 90 mM, and T = 20.00 °C. [Cl$^-$]$_0$ represents the contribution from NaCl only. Error estimates denote 95% confidence intervals.

Varied Bromide in the Presence of Excess FAC. Solution conditions and pseudo-first-order rate constants for regiospecific bromination of alkylbenzenes and alkoxybenzenes as a function of initial bromide concentration in the presence of excess FAC are given in **Tables S9 and S10**, respectively.
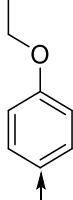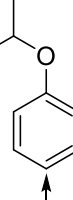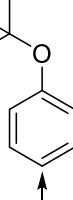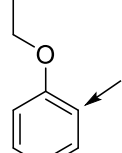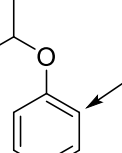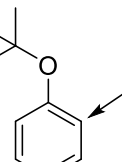
Table S9. Pseudo-first-order rate constants (s^{-1}) for formation of *para*- and *ortho*-brominated alkylbenzenes via reactions with free bromine as a function of initial bromide concentration in the presence of excess free available chlorine.[a]

$[Br^-]_o$ (mM)	$k_{obs,para}$	$k_{obs,para}$	$k_{obs,para}$	$k_{obs,ortho}$	$k_{obs,ortho}$	$k_{obs,ortho}$
5.87	$(1.40 \pm 0.06) \times 10^{-6}$	$(1.18 \pm 0.06) \times 10^{-6}$	$(1.15 \pm 0.06) \times 10^{-6}$	$(2.02 \pm 0.10) \times 10^{-6}$	$(1.84 \pm 0.11) \times 10^{-7}$	$(1.0 \pm 1.2) \times 10^{-8b}$
6.85	$(1.66 \pm 0.08) \times 10^{-6}$	$(1.37 \pm 0.09) \times 10^{-6}$	$(1.30 \pm 0.09) \times 10^{-6}$	$(2.31 \pm 0.14) \times 10^{-6}$	$(2.08 \pm 0.14) \times 10^{-7}$	$(1.2 \pm 1.6) \times 10^{-8b}$
7.81	$(2.12 \pm 0.03) \times 10^{-6}$	$(1.77 \pm 0.03) \times 10^{-6}$	$(1.57 \pm 0.06) \times 10^{-6}$	$(2.8 \pm 0.2) \times 10^{-6}$	$(2.51 \pm 0.08) \times 10^{-7}$	$(1.3 \pm 0.9) \times 10^{-8}$
8.78	$(3.06 \pm 0.07) \times 10^{-6}$	$(2.52 \pm 0.07) \times 10^{-6}$	$(2.4 \pm 0.2) \times 10^{-6}$	$(4.1 \pm 0.2) \times 10^{-6}$	$(3.64 \pm 0.15) \times 10^{-7}$	$(1.8 \pm 1.8) \times 10^{-8b}$
9.74	$(3.7 \pm 0.3) \times 10^{-6}$	$(3.1 \pm 0.2) \times 10^{-6}$	$(2.9 \pm 0.02) \times 10^{-6}$	$(5.0 \pm 0.3) \times 10^{-6}$	$(4.5 \pm 0.2) \times 10^{-7}$	$(2 \pm 2) \times 10^{-8b}$

[a] All reactors contained: $[FAC]_o = [Br^-]_o + 0.5$ mM, borate (20 mM) as pH buffer, pH = 8.00, [alkylbenzene]$_o$ = 50 µM for each parent compound, $[Cl^-]_o = 5.00$ mM, $[NaNO_3] = 95$ mM, and T = 20.00 °C. $[Cl^-]_o$ represents the contribution from NaCl only. Error estimates denote 95% confidence intervals.
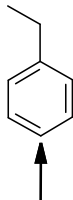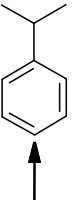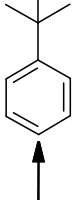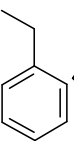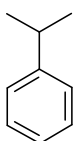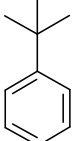[b] Not significantly different than zero.

Table S10. Pseudo-first-order rate constants (s^{-1}) for formation of *para*- and *ortho*-brominated alkoxybenzenes via reactions with free bromine as a function of initial bromide concentration in the presence of excess free available chlorine.[a]

$[Br^-]_o$ (mM)	$k_{obs,para}$	$k_{obs,para}$	$k_{obs,para}$	$k_{obs,ortho}$	$k_{obs,ortho}$	$k_{obs,ortho}$
0.15	$(3.9 \pm 0.4) \times 10^{-3}$	$(5.0 \pm 0.4) \times 10^{-3}$	$(5.2 \pm 1.0) \times 10^{-4}$	$(8.2 \pm 0.8) \times 10^{-4}$	$(1.12 \pm 0.09) \times 10^{-3}$	$(2.8 \pm 0.5) \times 10^{-4}$
0.20	$(4.4 \pm 0.2) \times 10^{-3}$	$(5.7 \pm 0.4) \times 10^{-3}$	$(5.3 \pm 0.6) \times 10^{-4}$	$(9.0 \pm 0.5) \times 10^{-4}$	$(1.25 \pm 0.09) \times 10^{-3}$	$(2.8 \pm 0.3) \times 10^{-4}$
0.25	$(4.8 \pm 0.8) \times 10^{-3}$	$(6.4 \pm 0.8) \times 10^{-3}$	$(7 \pm 2) \times 10^{-4}$	$(1.01 \pm 0.17) \times 10^{-3}$	$(1.42 \pm 0.17) \times 10^{-3}$	$(3.52 \pm 0.13) \times 10^{-4}$
0.30	$(6.2 \pm 0.8) \times 10^{-3}$	$(8.2 \pm 0.7) \times 10^{-3}$	$(9 \pm 5) \times 10^{-4}$	$(1.32 \pm 0.16) \times 10^{-3}$	$(1.82 \pm 0.16) \times 10^{-3}$	$(5.0 \pm 0.3) \times 10^{-4}$
0.35	$(5.76 \pm 0.16) \times 10^{-3}$	$(7.57 \pm 0.14) \times 10^{-3}$	$(7.8 \pm 0.9) \times 10^{-4}$	$(1.26 \pm 0.04) \times 10^{-3}$	$(1.70 \pm 0.03) \times 10^{-3}$	$(4.2 \pm 0.5) \times 10^{-4}$

[a] All reactors contained: $[FAC]_o = 0.4$ mM, phosphate (20 mM) as pH buffer, pH = 7.0, [alkoxybenzene]$_o$ = 10 µM for each parent compound, $[Cl^-]_o = 10$ mM, $[NaNO_3] = 90$ mM, and T = 20.00 °C. $[Cl^-]_o$ represents the contribution from NaCl only. Error estimates denote 95% confidence intervals.

Varied Excess Bromide. Solution conditions and pseudo-first-order rate constants for regiospecific bromination of alkylbenzenes and alkoxybenzenes as a function of excess bromide concentration are given in **Tables S11 and S12**, respectively. Effect of $[Br^-]_{xs}$ on bromination of alkyl- and alkoxybenzenes is shown in **Figures S4A** and **S4B**, respectively.

Table S11. Pseudo-first-order rate constants (s^{-1}) for formation of *para*- and *ortho*-brominated alkylbenzenes via reactions with free bromine as a function of excess bromide concentration.[a]

$[Br^-]_{xs}$ (mM)	$k_{obs,para}$	$k_{obs,para}$	$k_{obs,para}$	$k_{obs,ortho}$	$k_{obs,ortho}$	$k_{obs,ortho}$
0.96	$(4.20 \pm 0.13) \times 10^{-6}$	$(2.98 \pm 0.12) \times 10^{-6}$	$(1.53 \pm 0.05) \times 10^{-6}$	$(3.04 \pm 0.17) \times 10^{-6}$	$(4.54 \pm 0.16) \times 10^{-7}$	$(4.2 \pm 1.9) \times 10^{-8}$
1.96	$(5.9 \pm 0.2) \times 10^{-6}$	$(4.6 \pm 0.3) \times 10^{-6}$	$(2.3 \pm 0.2) \times 10^{-6}$	$(4.8 \pm 0.2) \times 10^{-6}$	$(6.3 \pm 0.4) \times 10^{-7}$	$(5.1 \pm 5.0) \times 10^{-8}$
2.95	$(7.1 \pm 0.6) \times 10^{-6}$	$(5.5 \pm 0.7) \times 10^{-6}$	$(2.9 \pm 0.3) \times 10^{-6}$	$(5.9 \pm 0.6) \times 10^{-6}$	$(7.7 \pm 0.7) \times 10^{-7}$	$(5.6 \pm 8.5) \times 10^{-8b}$
3.93	$(7.4 \pm 0.2) \times 10^{-6}$	$(6.1 \pm 0.4) \times 10^{-6}$	$(3.0 \pm 0.2) \times 10^{-6}$	$(6.4 \pm 0.3) \times 10^{-6}$	$(7.8 \pm 0.4) \times 10^{-7}$	$(5.1 \pm 4.9) \times 10^{-8}$
4.92	$(7.8 \pm 0.3) \times 10^{-6}$	$(6.5 \pm 0.7) \times 10^{-6}$	$(3.2 \pm 0.4) \times 10^{-6}$	$(6.9 \pm 0.5) \times 10^{-6}$	$(8.1 \pm 0.9) \times 10^{-7}$	$(5 \pm 11) \times 10^{-8b}$

[a] All reactors contained: $[FAC]_o = 1.00$ mM, $[Br^-]_{xs} = [Br^-]_o - [FAC]_o$, phosphate (20 mM) as pH buffer, pH = 6.30, [alkylbenzene]$_o$ = 16 μM for each parent compound, $[Cl^-]_o = 5.00$ mM, $[NaNO_3] = 95$ mM, $[Cl^-]_{tot} = 6.75$ mM, and T = 20.00 °C. $[Br^-]_{xs} = [Br^-]_o - [FAC]_o$. $[Cl^-]_o$ represents the contribution from NaCl only while $[Cl^-]_{tot}$ is the contribution from all sources of Cl^- (which includes NaCl, added FAC, and generation of Cl^- during oxidation of Br^- by FAC). Error estimates denote 95% confidence intervals.
[b] Not significantly different than zero.

Table S12. Pseudo-first-order rate constants (s^{-1}) for formation of *para*- and *ortho*-brominated alkoxybenzenes via reactions with free bromine as a function of excess bromide concentration.[a]

[Br⁻]$_{xs}$ (mM)	$k_{obs,para}$	$k_{obs,para}$	$k_{obs,para}$	$k_{obs,ortho}$	$k_{obs,ortho}$	$k_{obs,ortho}$
0.00	$(2.66 \pm 0.08) \times 10^{-4}$	$(3.82 \pm 0.11) \times 10^{-4}$	$(4.1 \pm 0.8) \times 10^{-5}$	$(3.11 \pm 0.09) \times 10^{-5}$	$(4.25 \pm 0.12) \times 10^{-5}$	$(1.1 \pm 0.2) \times 10^{-5}$
0.05	$(3.58 \pm 0.16) \times 10^{-4}$	$(5.1 \pm 0.2) \times 10^{-4}$	$(7.0 \pm 1.1) \times 10^{-5}$	$(3.35 \pm 0.15) \times 10^{-5}$	$(4.7 \pm 0.2) \times 10^{-5}$	$(1.7 \pm 0.3) \times 10^{-5}$
0.10	$(5.4 \pm 0.12) \times 10^{-4}$	$(7.3 \pm 0.6) \times 10^{-4}$	$(9.3 \pm 0.7) \times 10^{-5}$	$(4.24 \pm 0.09) \times 10^{-5}$	$(5.9 \pm 0.5) \times 10^{-5}$	$(1.98 \pm 0.15) \times 10^{-5}$
0.15	$(6.8 \pm 0.6) \times 10^{-4}$	$(9.6 \pm 1.1) \times 10^{-4}$	$(1.20 \pm 0.05) \times 10^{-4}$	$(4.7 \pm 0.4) \times 10^{-5}$	$(7.0 \pm 0.8) \times 10^{-5}$	$(2.37 \pm 0.11) \times 10^{-5}$
0.20	$(7.4 \pm 0.7) \times 10^{-4}$	$(1.07 \pm 0.16) \times 10^{-3}$	$(1.33 \pm 0.03) \times 10^{-4}$	$(4.6 \pm 0.4) \times 10^{-5}$	$(7.1 \pm 1.1) \times 10^{-5}$	$(2.49 \pm 0.05) \times 10^{-5}$

[a] All reactors contained: [FAC]$_o$ = 0.4 mM, borate (20 mM) as pH buffer, pH = 8.4, [alkoxybenzene]$_o$ = 10 μM for each parent compound, [Cl⁻]$_o$ = 10 mM, [NaNO$_3$] = 90 mM, and T = 20.00 °C. [Br⁻]$_{xs}$ = [Br⁻]$_o$ − [FAC]$_o$. [Cl⁻]$_o$ represents the contribution from NaCl only. Error estimates denote 95% confidence intervals.
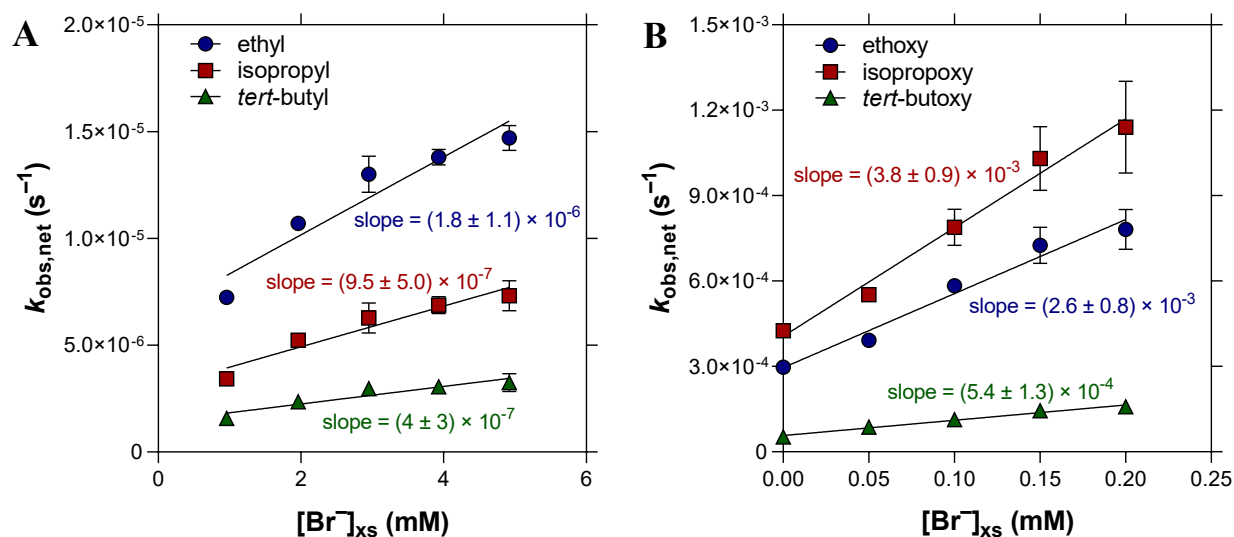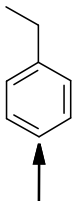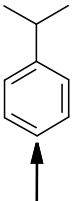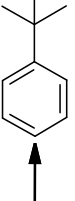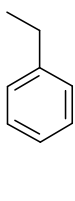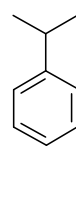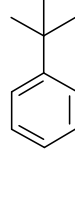

Figure S4. Pseudo-first-order rate constants for bromination of (A) alkyl- and (B) alkoxybenzenes as a function of excess bromide concentration ([Br⁻]$_{xs}$ = [Br⁻]$_o$ − [FAC]$_o$). Solution conditions: T = 20.00 °C, (A) [FAC]$_o$ = 1.00 mM, phosphate (20 mM) as pH buffer, pH = 6.30, [alkylbenzene]$_o$ = 16 μM, [Cl⁻]$_o$ = 5.00 mM, [NaNO$_3$] = 95 mM, and [Cl⁻]$_{tot}$ = 6.75 mM; (B) [FAC]$_o$ = 0.400 mM, borate (20 mM) as pH buffer, pH = 8.4, [alkylbenzene]$_o$ = 16 μM, [Cl⁻]$_o$ = 10 mM, and [NaNO$_3$] = 90 mM. [Cl⁻]$_o$ represents the contribution from NaCl only while [Cl⁻]$_{tot}$ is the contribution from all sources of Cl⁻ (which includes NaCl, added FAC, and generation of Cl⁻ during oxidation of Br⁻ by FAC). All error bars denote 95% confidence intervals (smaller than symbols when not shown).

Varied pH. Solution conditions and pseudo-first-order rate constants for regiospecific bromination of alkylbenzenes and alkoxybenzenes as a function of pH are given in **Tables S13 and S14**, respectively.
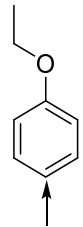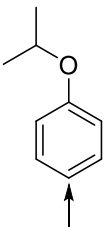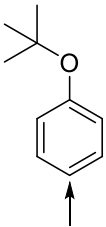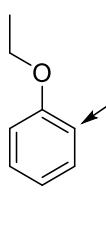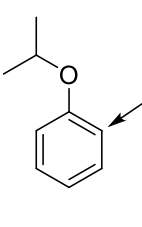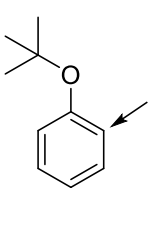
Table S13. Pseudo-first-order rate constants (s^{-1}) for formation of *para*- and *ortho*-brominated alkylbenzenes via reactions with free bromine as a function of pH.[a]

pH	$k_{obs,para}$	$k_{obs,para}$	$k_{obs,para}$	$k_{obs,ortho}$	$k_{obs,ortho}$	$k_{obs,ortho}$
5.31	$(3.5 \pm 0.3) \times 10^{-5}$	$(4.1 \pm 0.3) \times 10^{-5}$	$(2.11 \pm 0.09) \times 10^{-5}$	$(5.2 \pm 0.5) \times 10^{-5}$	$(6.2 \pm 0.4) \times 10^{-6}$	$(5 \pm 4) \times 10^{-7}$
5.54	$(2.62 \pm 0.11) \times 10^{-5}$	$(2.80 \pm 0.12) \times 10^{-5}$	$(1.40 \pm 0.07) \times 10^{-5}$	$(3.9 \pm 0.2) \times 10^{-5}$	$(4.3 \pm 0.2) \times 10^{-6}$	$(3 \pm 3) \times 10^{-7b}$
5.68	$(1.88 \pm 0.10) \times 10^{-5}$	$(2.13 \pm 0.12) \times 10^{-5}$	$(1.05 \pm 0.08) \times 10^{-5}$	$(3.0 \pm 0.3) \times 10^{-5}$	$(3.3 \pm 0.3) \times 10^{-6}$	$(2 \pm 3) \times 10^{-7b}$
6.00	$(9.8 \pm 1.5) \times 10^{-6}$	$(1.07 \pm 0.09) \times 10^{-5}$	$(5.4 \pm 1.5) \times 10^{-6}$	$(1.7 \pm 0.2) \times 10^{-5}$	$(1.62 \pm 0.10) \times 10^{-6}$	$(2.3 \pm 1.1) \times 10^{-7}$
6.25	$(3.1 \pm 0.3) \times 10^{-6}$	$(3.6 \pm 0.3) \times 10^{-6}$	$(1.7 \pm 0.3) \times 10^{-6}$	$(6.0 \pm 0.6) \times 10^{-6}$	$(6.1 \pm 0.8) \times 10^{-7}$	$(5 \pm 8) \times 10^{-8b}$
6.50	$(2.10 \pm 0.14) \times 10^{-6}$	$(2.13 \pm 0.14) \times 10^{-6}$	$(9.8 \pm 1.4) \times 10^{-7}$	$(3.4 \pm 0.4) \times 10^{-6}$	$(3.3 \pm 0.4) \times 10^{-7}$	$(4 \pm 5) \times 10^{-8b}$
6.75	$(1.14 \pm 0.09) \times 10^{-6}$	$(1.12 \pm 0.08) \times 10^{-6}$	$(6.4 \pm 0.3) \times 10^{-7}$	$(2.16 \pm 0.19) \times 10^{-6}$	$(2.02 \pm 0.08) \times 10^{-7}$	$(2.3 \pm 0.9) \times 10^{-8}$
7.00	$(8.7 \pm 0.3) \times 10^{-7}$	$(8.3 \pm 0.4) \times 10^{-7}$	$(4.2 \pm 0.4) \times 10^{-7}$	$(1.38 \pm 0.10) \times 10^{-6}$	$(1.34 \pm 0.06) \times 10^{-7}$	$(9 \pm 6) \times 10^{-9}$
7.25	$(6.4 \pm 0.3) \times 10^{-7}$	$(6.2 \pm 0.3) \times 10^{-7}$	$(3.6 \pm 0.3) \times 10^{-7}$	$(1.09 \pm 0.11) \times 10^{-6}$	$(1.02 \pm 0.06) \times 10^{-7}$	$(7 \pm 7) \times 10^{-9b}$
7.50	$(4.0 \pm 0.3) \times 10^{-7}$	$(4.3 \pm 0.3) \times 10^{-7}$	$(2.0 \pm 0.3) \times 10^{-7}$	$(7.9 \pm 1.0) \times 10^{-7}$	$(7.3 \pm 0.4) \times 10^{-8}$	$(9 \pm 4) \times 10^{-9}$
7.75	$(2.28 \pm 0.04) \times 10^{-7}$	$(2.19 \pm 0.06) \times 10^{-7}$	$(1.09 \pm 0.09) \times 10^{-7}$	$(3.6 \pm 0.5) \times 10^{-7}$	$(3.79 \pm 0.15) \times 10^{-8}$	$(2 \pm 3) \times 10^{-9b}$
8.00	$(1.24 \pm 0.03) \times 10^{-7}$	$(1.19 \pm 0.06) \times 10^{-7}$	$(6.0 \pm 0.7) \times 10^{-8}$	$(2.7 \pm 0.2) \times 10^{-7}$	$(2.14 \pm 0.14) \times 10^{-8}$	$(2.4 \pm 1.6) \times 10^{-9}$

[a] All reactors contained: $[FAC]_o = 1.50$ mM, $[Br^-]_o = 1.00$ mM, phosphate (20 mM) as pH buffer, $[alkylbenzene]_o$ = 50 μM for each parent compound, $[Cl^-]_o = 5.00$ mM, $[NaNO_3] = 95$ mM, and T = 20.00 °C. $[Cl^-]_o$ represents the contribution from NaCl only. Error estimates denote 95% confidence intervals.
[b] Not significantly different than zero.

Table S14. Pseudo-first-order rate constants (s^{-1}) for formation of *para*- and *ortho*-brominated alkoxybenzenes via reactions with free bromine as a function of pH.[a]

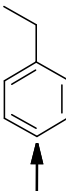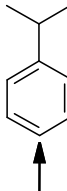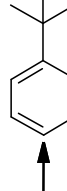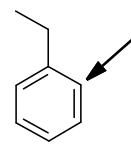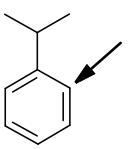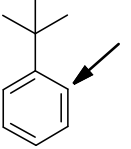| pH	$k_{obs,para}$	$k_{obs,para}$	$k_{obs,para}$	$k_{obs,ortho}$	$k_{obs,ortho}$	$k_{obs,ortho}$
6.53	$(2.1 \pm 1.2) \times 10^{-2}$	$(2.2 \pm 1.9) \times 10^{-2}$	$(1.01 \pm 0.09) \times 10^{-2}$	$(4.2 \pm 2) \times 10^{-3}$	$(5 \pm 4) \times 10^{-3}$	$(5.0 \pm 0.4) \times 10^{-3}$
6.76	$(1.6 \pm 0.3) \times 10^{-2}$	$(1.6 \pm 0.6) \times 10^{-2}$	$(8 \pm 3) \times 10^{-3}$	$(3.2 \pm 0.6) \times 10^{-3}$	$(3.6 \pm 1.3) \times 10^{-3}$	$(3.8 \pm 1.4) \times 10^{-3}$
6.94	$(9 \pm 3) \times 10^{-3}$	$(1.1 \pm 0.8) \times 10^{-2}$	$(1.76 \pm 0.09) \times 10^{-3}$	$(1.8 \pm 0.7) \times 10^{-3}$	$(2.4 \pm 1.7) \times 10^{-3}$	$(8.7 \pm 0.4) \times 10^{-4}$
7.20	$(6.6 \pm 0.8) \times 10^{-3}$	$(8.6 \pm 1.4) \times 10^{-3}$	$(1.0 \pm 0.4) \times 10^{-3}$	$(1.31 \pm 0.16) \times 10^{-3}$	$(1.8 \pm 0.3) \times 10^{-3}$	$(4.9 \pm 1.9) \times 10^{-4}$
7.34	$(5.3 \pm 0.8) \times 10^{-3}$	$(6.8 \pm 1.0) \times 10^{-3}$	$(6 \pm 3) \times 10^{-4}$	$(1.04 \pm 0.16) \times 10^{-3}$	$(1.4 \pm 0.2) \times 10^{-3}$	$(2.7 \pm 1.2) \times 10^{-4}$
7.50	$(2 \pm 4) \times 10^{-3\,b}$	$(2.7 \pm 0.7) \times 10^{-3}$	$3.6 \pm 0.3 \times 10^{-4}$	$(4.1 \pm 0.7) \times 10^{-4}$	$(5.7 \pm 1.5) \times 10^{-4}$	$(1.72 \pm 0.15) \times 10^{-4}$
7.68	$(1 \pm 3) \times 10^{-3\,b}$	$(1.9 \pm 0.6) \times 10^{-3}$	$(2.43 \pm 0.10) \times 10^{-4}$	$(2.7 \pm 0.5) \times 10^{-4}$	$(3.8 \pm 1.2) \times 10^{-4}$	$(1.09 \pm 0.04) \times 10^{-4}$
7.85	$(1.08 \pm 0.10) \times 10^{-3}$	$(1.4 \pm 0.2) \times 10^{-3}$	$(1.73 \pm 0.04) \times 10^{-4}$	$(1.92 \pm 0.18) \times 10^{-4}$	$(2.5 \pm 0.4) \times 10^{-4}$	$(7.240 \pm 0.015) \times 10^{-4}$
8.12	$(6.7 \pm 0.3) \times 10^{-4}$	$(9.2 \pm 0.4) \times 10^{-4}$	$(1.05 \pm 0.13) \times 10^{-4}$	$(1.07 \pm 0.05) \times 10^{-4}$	$(1.45 \pm 0.07) \times 10^{-4}$	$(4.0 \pm 0.5) \times 10^{-5}$
8.23	$(4.8 \pm 0.5) \times 10^{-4}$	$(6.7 \pm 0.6) \times 10^{-4}$	$(8.4 \pm 1.0) \times 10^{-5}$	$(7.2 \pm 0.7) \times 10^{-5}$	$(9.9 \pm 0.9) \times 10^{-5}$	$(3.0 \pm 0.4) \times 10^{-5}$
8.49	$(3.1 \pm 0.18) \times 10^{-4}$	$(4.40 \pm 0.18) \times 10^{-4}$	$(4.6 \pm 1.7) \times 10^{-5}$	$(3.8 \pm 0.2) \times 10^{-5}$	$(5.2 \pm 0.2) \times 10^{-5}$	$(1.3 \pm 0.5) \times 10^{-5}$
8.68	$(1.90 \pm 0.11) \times 10^{-4}$	$(2.73 \pm 0.15) \times 10^{-4}$	$(3.2 \pm 1.3) \times 10^{-5}$	$(2.15 \pm 0.13) \times 10^{-5}$	$(2.94 \pm 0.16) \times 10^{-5}$	$(8 \pm 3) \times 10^{-6}$
8.86	$(1.1 \pm 0.3) \times 10^{-4}$	$(1.8 \pm 0.3) \times 10^{-4}$	$(2.3 \pm 1.8) \times 10^{-5}$	$(1.2 \pm 0.3) \times 10^{-5}$	$(1.7 \pm 0.3) \times 10^{-5}$	$(6 \pm 4) \times 10^{-6}$
9.07	$(7 \pm 2) \times 10^{-5}$	$(1.09 \pm 0.16) \times 10^{-4}$	$(2.1 \pm 1.8) \times 10^{-5}$	$(7 \pm 2) \times 10^{-6}$	$(9.4 \pm 1.4) \times 10^{-6}$	$(5 \pm 4) \times 10^{-6}$
9.29	$(3.3 \pm 1.3) \times 10^{-5}$	$(5.2 \pm 1.5) \times 10^{-5}$	$(1.1 \pm 0.6) \times 10^{-5}$	$(3.1 \pm 1.2) \times 10^{-6}$	$(4.1 \pm 1.2) \times 10^{-6}$	$(2.9 \pm 1.7) \times 10^{-6}$
9.77	$(9 \pm 4) \times 10^{-6}$	$(1.1 \pm 0.3) \times 10^{-5}$	$(4 \pm 3) \times 10^{-6}$	$(1.3 \pm 0.6) \times 10^{-6}$	$(2.3 \pm 0.6) \times 10^{-6}$	$(1.3 \pm 0.9) \times 10^{-6}$
9.91	$(3.9 \pm 1.6) \times 10^{-6}$	$(1.2 \pm 0.7) \times 10^{-5}$	$(3.0 \pm 0.6) \times 10^{-6}$	$(7 \pm 3) \times 10^{-7}$	$(4 \pm 2) \times 10^{-6}$	$(1.1 \pm 0.2) \times 10^{-6}$
10.03	$(1.0 \pm 0.7) \times 10^{-5}$	$(9 \pm 5) \times 10^{-6}$	$(4 \pm 2) \times 10^{-6}$	$(2.3 \pm 1.6) \times 10^{-6}$	$(3 \pm 2) \times 10^{-6}$	$(1.1 \pm 0.6) \times 10^{-6}$

[a] All reactors contained: $[FAC]_o$ = 0.4 mM, $[Br^-]_o$ = 0.35 mM, borate and phosphate (20 mM each) as pH buffer, $[alkoxybenzene]_o$ = 10 μM for each parent compound, $[Cl^-]_o$ = 10 mM, $[NaNO_3]$ = 90 mM, and T = 20.00 °C. $[Cl^-]_o$ represents the contribution from NaCl only. Error estimates denote 95% confidence intervals.
[b] Not significantly different than zero.

S6. Determination and Modeling of Second-Order Rate Constants

For robust calculations of second-order rate constants, reactivity data were divided into bins (**Table S15** and **S16**) according to the regiospecific product and brominating agent that were anticipated to predominate under the specific solution conditions.

Table S15. Data bins used as input parameters to fit regiospecific second-order bromination rate constants for bromination of alkylbenzenes.

Brominating Agent	$k_{obs,para}{}^{a}$	$k_{obs,para}{}^{a}$	$k_{obs,para}{}^{a}$	$k_{obs,ortho}{}^{b}$	$k_{obs,ortho}{}^{b}$	$k_{obs,ortho}{}^{b}$
BrCl	Table S5					
Br_2O	Table S7					
Br_2	Table S9					
H_2OBr^+	not quantified ^{c}			Table S5 and S11 (pH = 5.31 – 6.48 only)		
HOBr	not quantified ^{d}					
BrOCl	not quantified ^{e}					
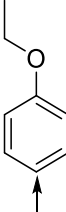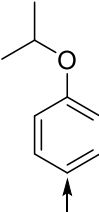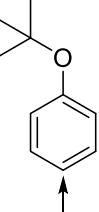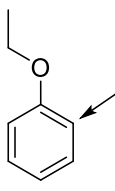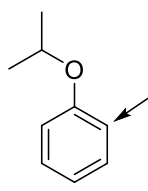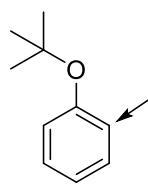
^{a} Order of optimization: BrCl, Br_2O, Br_2
^{b} Order of optimization: BrCl, Br_2O, Br_2, H_2OBr^+
^{c} Our results suggested H_2OBr^+ did not appreciably influence overall bromination rates of these compounds.
^{d} The contribution of HOBr to the overall regiospecific bromination rates was too small to quantify, although attempts were made to fit it concurrently with Br_2O.
^{e} Kinetic experiments suggested varying $[FAC]_o$ had no effect on the overall bromination rate; therefore, BrOCl was unable to be quantified.

Table S16. Data bins used as input parameters to fit regiospecific second-order bromination rate constants for bromination of alkoxybenzenes.^{a}

Brominating Agent	$k_{obs,para}$	$k_{obs,para}$	$k_{obs,para}$	$k_{obs,ortho}$	$k_{obs,ortho}$	$k_{obs,ortho}$
BrCl	Table S6					
Br_2O	Table S8					
Br_2	Table S10					
HOBr	Table S14 (pH = 8.49 – 9.29 only)					
BrOCl	Table S12					

^{a} Order of optimization: BrOCl and HOBr, BrCl and HOBr, Br_2 and Br_2O, HOBr

S7. Determination of Taft Parameters

Literature values for the polar substituent constants and steric substituent constants of alkyl and alkoxy substituent groups are shown in **Table S17**.

Table S17. Literature reported and normalized values for polar and steric substituent constants of substituted benzenes.[3]

Compound	Substituent	σ^*	E_s	Normalized $\sigma^{*\,a}$	Normalized $E_s{}^a$
benzene	–H	0.49	1.24	0.00	0.00
ethylbenzene	–C$_2$H$_5$	–0.10	–0.07	–0.59	–1.31
isopropylbenzene	–C$_3$H$_7$	–0.19	–0.47	–0.68	–1.71
tert-butylbenzene	–C$_4$H$_9$	–0.30	–1.54	–0.79	–2.78
methoxybenzene	–OCH$_3$	–0.22	0.99	–0.71	–0.25
ethoxybenzene	–OC$_2$H$_5$	–0.18	0.90	–0.67	–0.34

[a] Benzene was defined as the reference reaction, and values for both substituent constants were accordingly assigned as zero; substituent constants for other compounds were normalized by subtracting the corresponding value for benzene.

The predicted Taft parameters were compared to the experimental ratio of k_{BrCl} $\left(\log\left(\frac{k_{BrCl,s}}{k_{BrCl,H}}\right)\right)$, where $k_{BrCl,s}$ and $k_{BrCl,H}$ are the experimentally determined second order rate constants of BrCl towards the bromination of the substituted compound and benzene, respectively. Values for each examined subgroup of alkyl- and alkoxybenzenes and are shown in **Figures S5 – S8**.

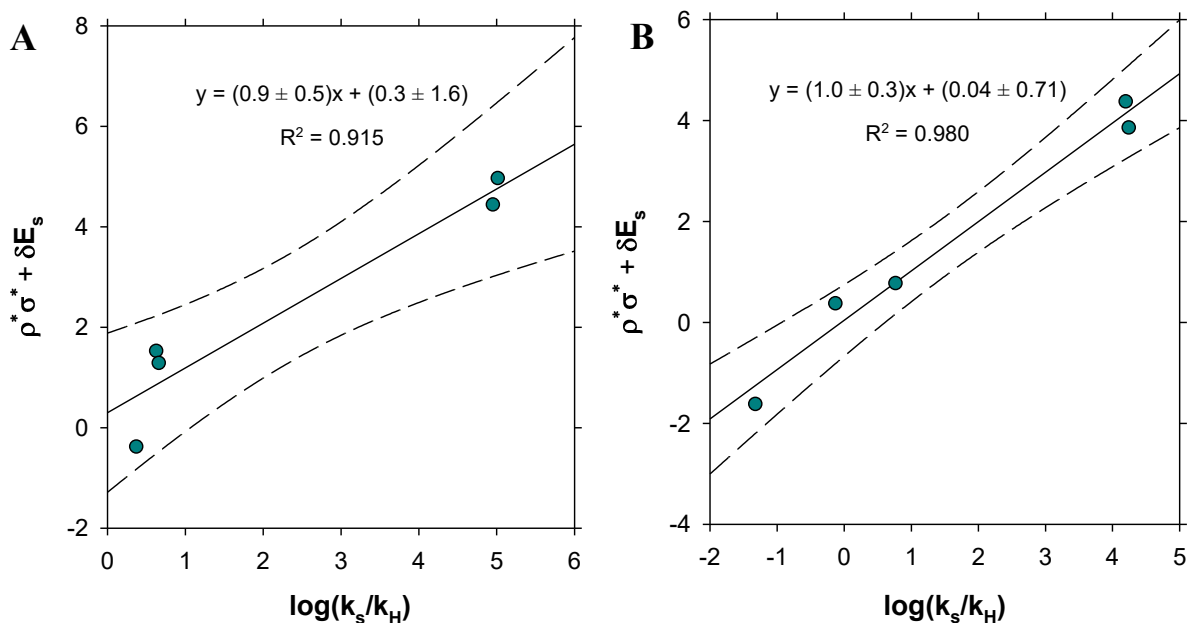**Figure S5.** Comparison of predicted Taft parameters to the experimental ratio of k_{BrCl} for (**A**) *para* and (**B**) *ortho* bromination of alkyl- and alkoxybenzenes. Dashed lines represent the 95% confidence interval of the linear regression.
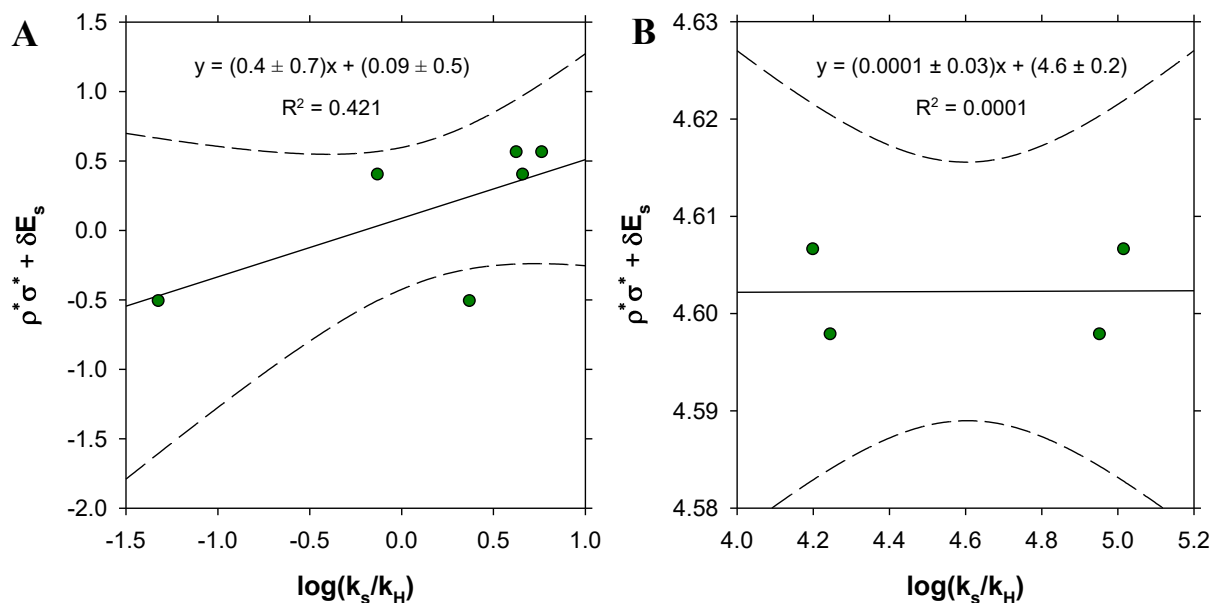
Figure S6. Comparison of predicted Taft parameters to the experimental ratio of k_{BrCl} for (**A**) alkyl- and (**B**) alkoxybenzenes. Dashed lines represent the 95% confidence interval of the linear regression.
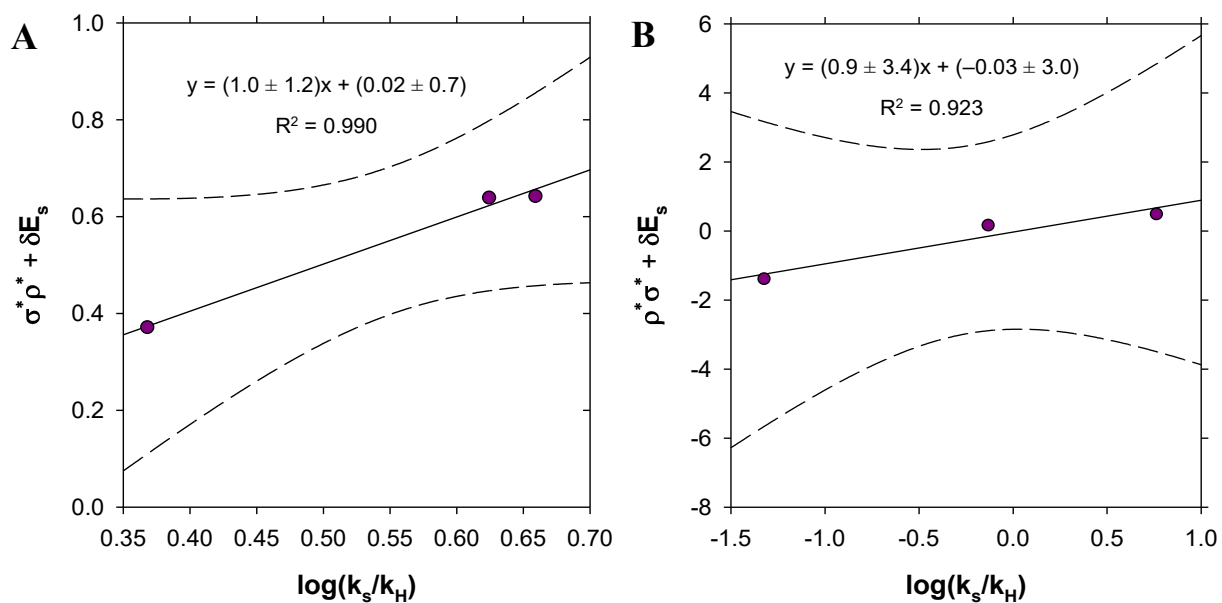

Figure S7. Comparison of predicted Taft parameters to the experimental ratio of k_{BrCl} for (**A**) *para*- and (**B**) *ortho*-bromination of alkylbenzenes. Dashed lines represent the 95% confidence interval of the linear regression.
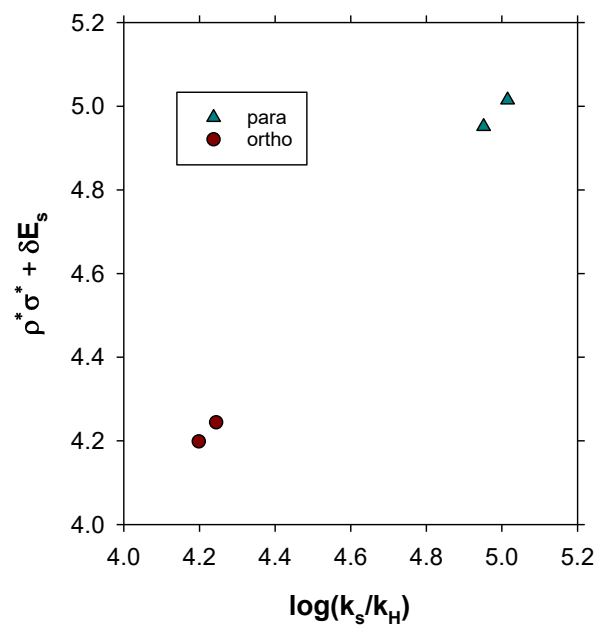
Figure S8. Comparison of predicted Taft parameters to the experimental ratio of k_{BrCl} for *para* and *ortho* bromination of alkoxybenzenes. Only two compounds (methoxybenzene and ethoxybenzene) were examined in each category, so 95% confidence intervals could not be calculated.

S8. Influence of Solution Conditions on Regioselectivity

The ratios of *para*-to-*ortho* brominates rates as a function of varied $[Cl^-]$, $[FAC]_o$, $[Br^-]_o$, $[Br^-]_{xs}$, and pH are given in **Figures S9** to **S13**.
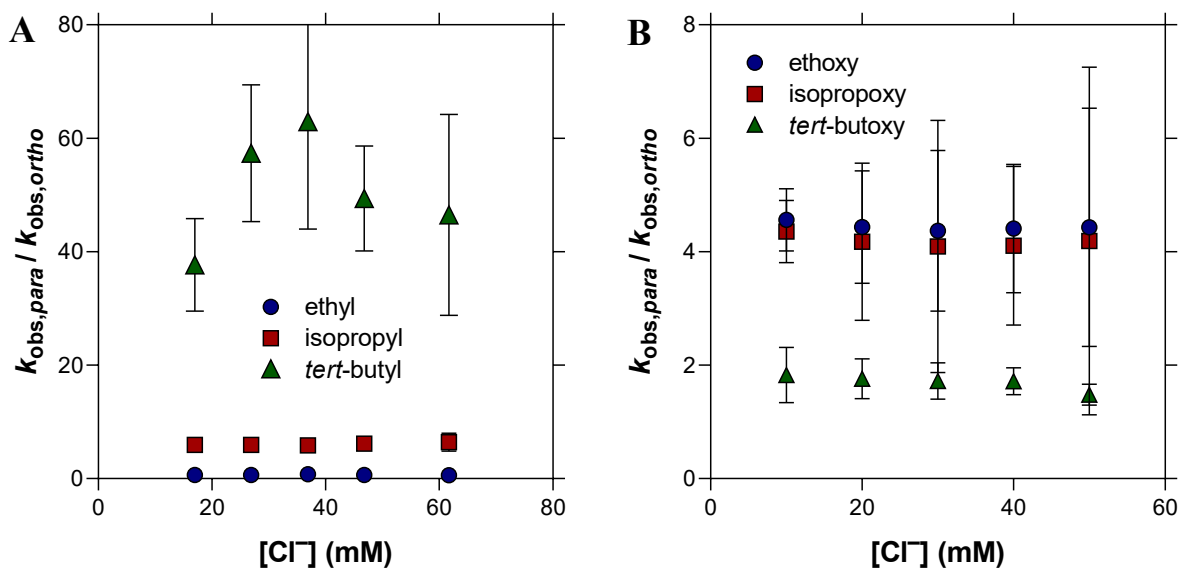

Figure S9. The ratio of $k_{obs,para}$ to $k_{obs,ortho}$ as a function of chloride concentration which corresponds to the rate of bromination at the *para* position relative to the *ortho* positions of the parent (A) alkyl- and (B) alkoxybenzenes. Conditions: (A) $[FAC]_o = 1.16$ mM, phosphate (20 mM) as pH buffer, pH = 6.30, $[alkylbenzene]_o = 16$ μM, $[Br^-] = 0.99$ mM, and $[NaCl] + [NaNO_3] = 100$ mM; (B) $[FAC]_o = 0.4$ mM, phosphate (20 mM) as pH buffer, pH = 7.0, $[alkoxybenzene]_o = 10$ μM, $[Br^-] = 0.35$ mM, and $[NaNO_3] = 90$ mM. Error bars denote 95% confidence intervals (smaller than symbols when not shown).
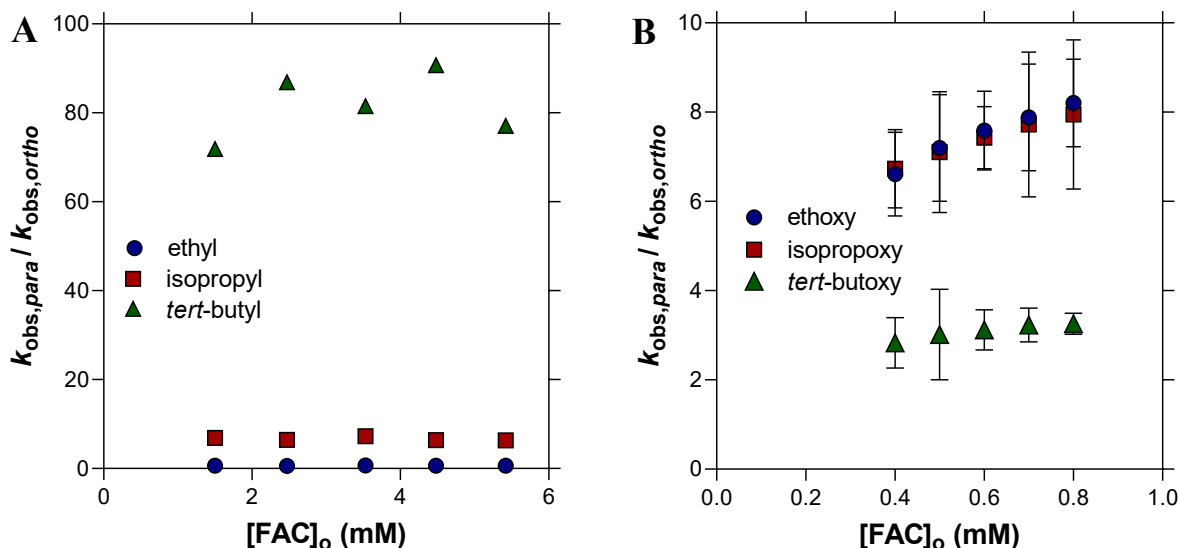
Figure S10. The ratio of $k_{obs,para}$ to $k_{obs,ortho}$ as a function of free available chlorine concentration which corresponds to the rate of bromination at the *para* position relative to the *ortho* positions of the parent (A) alkyl- and (B) alkoxybenzenes. Conditions: T = 20.00 °C, (A) [Br⁻] = 1.00 mM, phosphate (20 mM) as pH buffer, pH = 7.40, [alkylbenzene]ₒ = 50 µM, [Cl⁻]ₒ = 30.00 mM, [NaNO₃] = 70 mM; (B) [Br⁻] = 350 µM, borate (20 mM) as pH buffer, pH = 8.2, [alkoxybenzene]ₒ = 10 µM, [Cl⁻]ₒ = 10 mM, [NaNO₃] = 90 mM. [Cl⁻]ₒ represents the contribution from NaCl only. All error bars denote 95% confidence intervals (smaller than symbols when not shown). Error bars for *tert*-butyl benzene extend past the axes so are not shown.

Figure S11. The ratio of $k_{obs,para}$ to $k_{obs,ortho}$ as a function of initial bromide concentration in the presence of excess FAC which corresponds to the rate of bromination at the *para* position relative to the *ortho* positions of the parent (A) alkyl- and (B) alkoxybenzenes Conditions: T = 20.00 °C, (A) [FAC]ₒ = [Br⁻]ₒ + 0.5 mM, borate (20 mM) as pH buffer, pH = 8.00, [alkylbenzene]ₒ = 50 µM, [Cl⁻]ₒ = 5.00 mM, and [NaNO₃] = 95 mM; (B) [FAC]ₒ = 0.4 mM, phosphate (20 mM) as pH buffer, pH = 7.0, [alkoxybenzene]ₒ = 10 µM, [Cl⁻]ₒ = 10.0 mM, [NaNO₃] = 90 mM. [Cl⁻]ₒ represents the contribution from NaCl only. Error bars denote 95% confidence intervals (smaller than symbols when not shown). Error bars for *tert*-butyl benzene extend past the axes so are not shown.
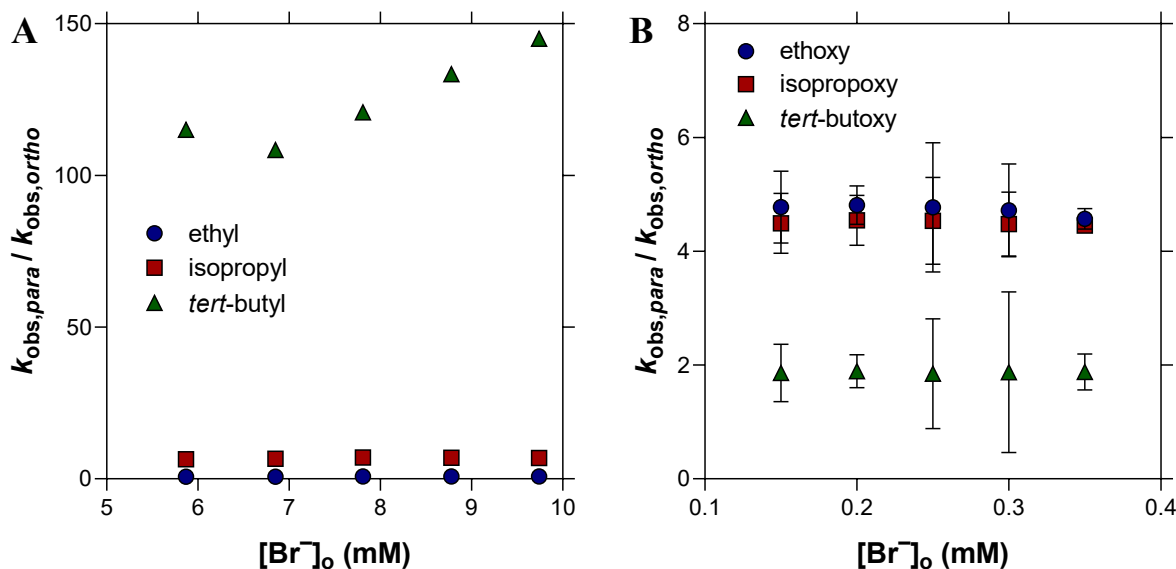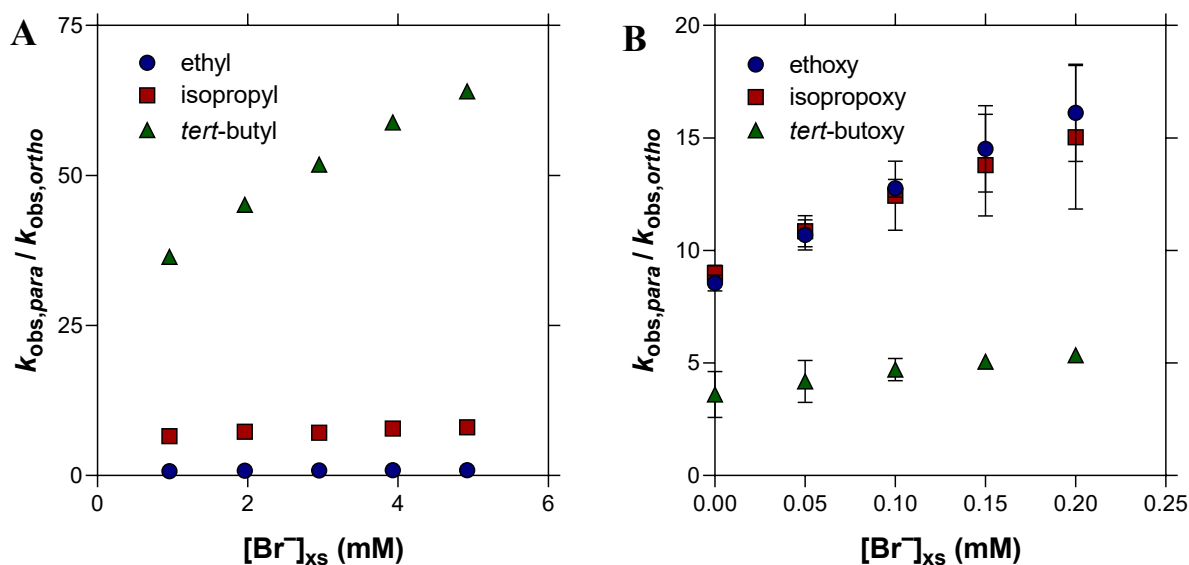
Figure S12. The ratio of $k_{obs,para}$ to $k_{obs,ortho}$ as a function of excess bromide concentration ($[Br^-]_{xs} = [Br^-]_o - [FAC]_o$) which corresponds to the rate of bromination at the *para* position relative to the *ortho* positions of the parent (A) alkyl- and (B) alkoxybenzenes. Conditions: T = 20.00 °C, (A) $[FAC]_o$ = 1.00 mM, phosphate (20 mM) as pH buffer, pH = 6.30, $[alkylbenzene]_o$ = 16 μM, $[Cl^-]_o$ = 5.00 mM, $[NaNO_3]$ = 95 mM, and $[Cl^-]_{tot}$ = 6.75 mM; (B) $[FAC]_o$ = 0.400 mM, borate (20 mM) as pH buffer, pH = 8.4, $[alkylbenzene]_o$ = 16 μM, $[Cl^-]_o$ = 10 mM, and $[NaNO_3]$ = 90 mM. $[Cl^-]_o$ represents the contribution from NaCl only while $[Cl^-]_{tot}$ is the contribution from all sources of Cl^- (which includes NaCl, added FAC, and generation of Cl^- during oxidation of Br^- by FAC). Error bars denote 95% confidence intervals (smaller than symbols when not shown). Error bars for *tert*-butyl benzene extend past the axes and are not shown.
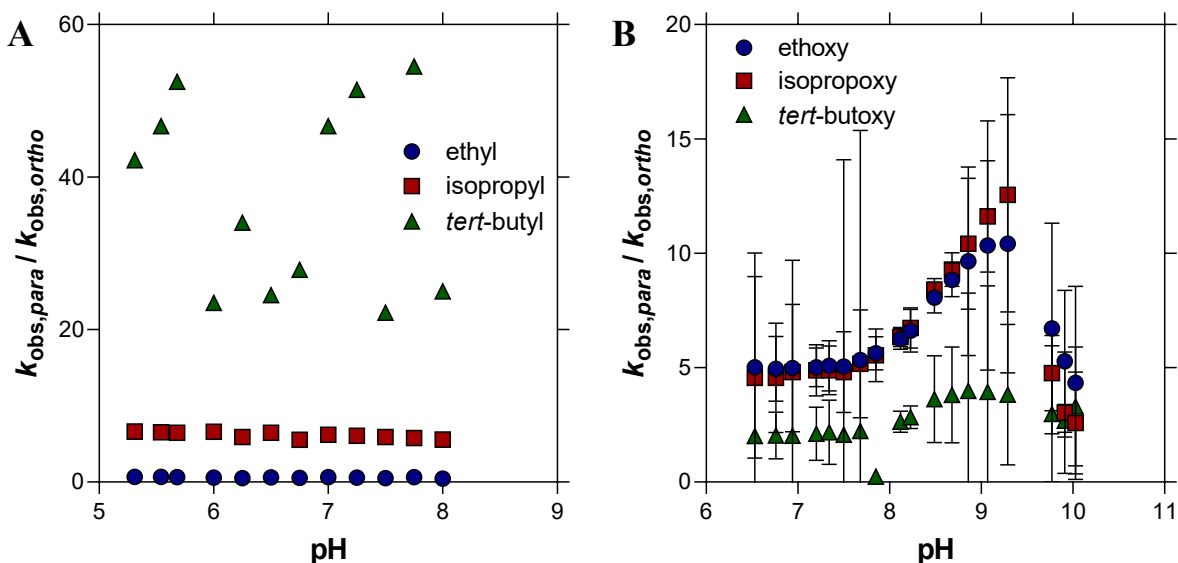

Figure S13. The ratio of $k_{obs,para}$ to $k_{obs,ortho}$ as a function of pH, corresponding to the rate of bromination at the *para* position relative to the *ortho* positions of the parent (A) alkyl- and (B) alkoxybenzenes. Conditions: T = 20.00 °C, (A) $[FAC]_o$ = 1.50 mM, $[Br^-]_o$ = 1.00 mM, phosphate (20 mM) as pH buffer, $[alkylbenzene]_o$ = 50 μM, $[Cl^-]_o$ = 5.00 mM, and $[NaNO_3]$ = 95 mM; (B) $[FAC]_o$ = 400 μM, $[Br^-]_o$ = 350 μM, borate and phosphate (20 mM each), $[alkoxybenzene]_o$ = 10 μM, $[Cl^-]_o$ = 10 mM, $[NaNO_3]$ = 90 mM. $[Cl^-]_o$ represents the contribution from NaCl. Error bars denote 95% confidence intervals (smaller than symbols when not shown). Error bars for *tert*-butyl benzene extend past axes and are not shown.

S9. Second-Order Rate Constants of Other Potentially Relevant Brominating Agents to the Bromination of Benzene

Calculations were performed assuming the non-zero value of the y-intercept (j) of $k_{\text{obs,net,benzene}}$ as a function of [Cl$^-$] (**Figure 1A**) could be attributed to only one brominating agent. Simplifying **eq 12** and using equilibrium constant expressions corresponding to **eq 3 and 4** (main text), upper limits of second-order rate constants for Br$_2$, Br$_2$O, and HOBr were determined (**Table S18**). The absence of a dependable literature value for pK_{a1} of H$_2$OBr$^+$ precludes upper limits to be calculated for reactions involving H$_2$OBr$^+$.

Table S18. Upper limits for second-order rate constants of additional brominating species in reactions with benzene at 20.0 ºC.

Brominating Agent	Equation[a]	Upper Limit of k (M^{-1} s^{-1})
Br$_2$	$k_{\text{Br}_2} = \dfrac{j K_3}{[\text{HOBr}][\text{Br}^-][\text{H}^+]}$	$(7 \pm 2) \times 10^{-4}$
HOBr	$k_{\text{HOBr}} = \dfrac{j}{[\text{HOBr}]}$	$(6 \pm 2) \times 10^{-3}$
Br$_2$O	$k_{\text{Br}_2\text{O}} = \dfrac{j}{K_4[\text{HOBr}]^2}$	1.6 ± 0.6

[a] [HOBr]$_{\text{avg}}$ = 6.16 × 10^{-4} M

The reactivity of brominating agents towards benzene is expected to follow the same trend as those for alkyl- and alkoxybenzenes (i.e., $k_{\text{BrCl}} < k_{\text{Br}_2} < k_{\text{Br}_2\text{O}} < k_{\text{HOBr}}$). The calculated upper limit of the rate constant for Br$_2$ best fits this expected trend (assuming that HOBr and Br$_2$O are not more inherently reactive than Br$_2$ toward benzene). We note that bromination reactions of benzene performed as a function of [Cl$^-$] were conducted in the presence of excess bromide (**Figure 1**, main text). As such, it is anticipated that the non-zero value of the y-intercept can be predominantly attributed to Br$_2$.

S10. Relevance of H$_2$OBr$^+$ to Bromination of Alkylbenzenes

Model fits comparing k_{obs} to k_{calc} as a function of pH were plotted with and without accounting for H$_2$OBr$^+$ in the determination of k_{calc} (**Figure S14**).
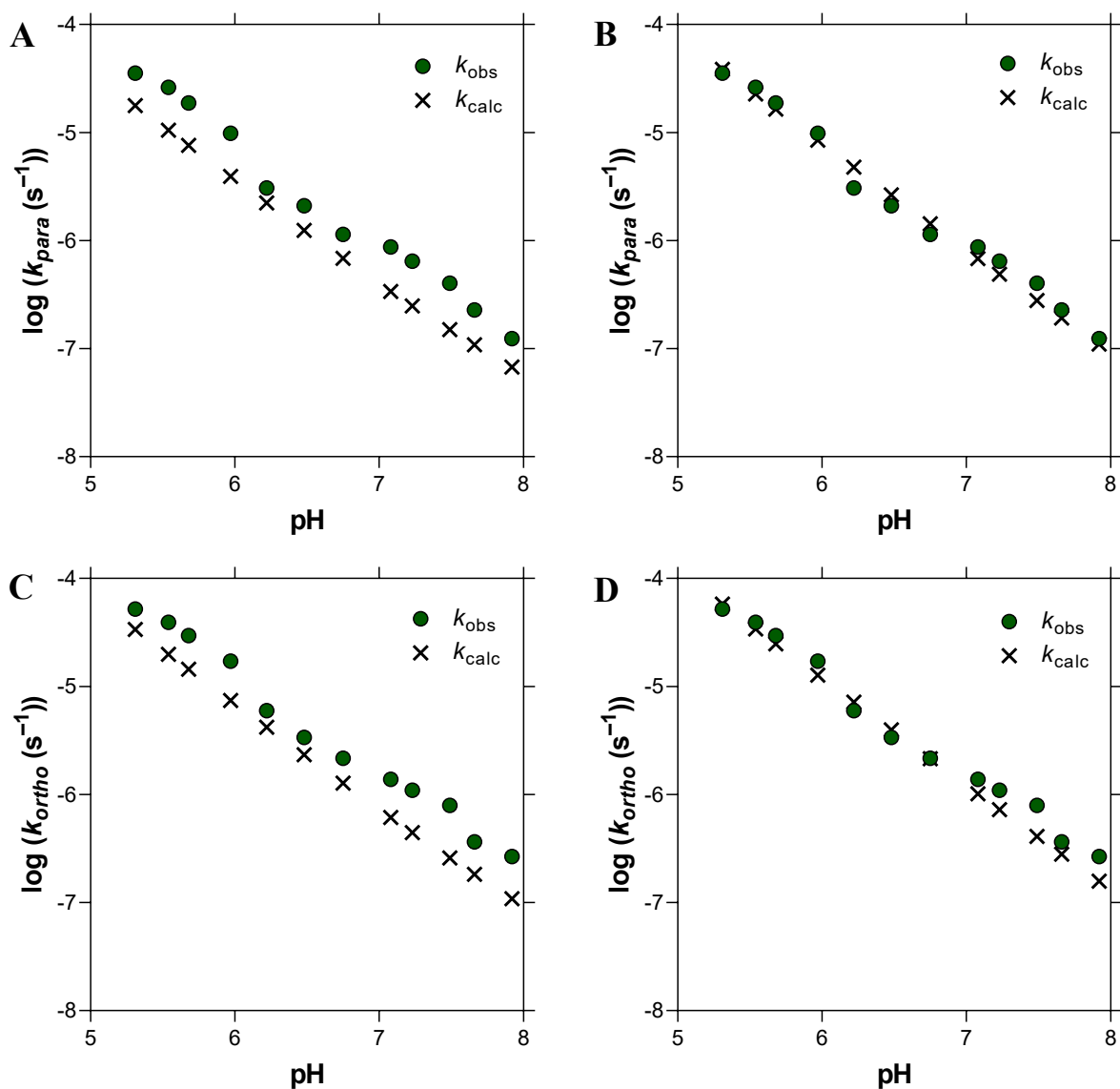
Figure S14. Regiospecific pseudo-first-order rate constants for bromination of ethylbenzene at the (**A, B**) *para* and (**C, D**) *ortho* positions as a function of pH. (**B**) and (**D**) account for the possible influence of H_2OBr^+ in the calculated bromination rates of ethylbenzene while (**A**) and (**C**) do not. The experimentally measured rate is denoted by k_{obs} and the calculated rate denotes the model fit of the form $k_{calc} = k_{BrCl}[BrCl] + k_{Br_2O}[Br_2O] + k_{H^+,HOBr}[H_2OBr^+]$ (noting that formation of Br_2 is negligible when free chlorine is added in excess relative to bromide). Reaction conditions were uniform for all frames: T = 20.00 °C, $[FAC]_o$ = 1.50 mM, $[Br^-]_o$ = 1.00 mM, phosphate (20 mM) as pH buffer, $[alkylbenzene]_o$ = 50 µM, [NaCl] = 5.00 mM, and $[NaNO_3]$ = 95 mM.

To determine if H_2OBr^+ was relevant to bromination of alkylbenzenes, k_{obs} values were plotted as a function
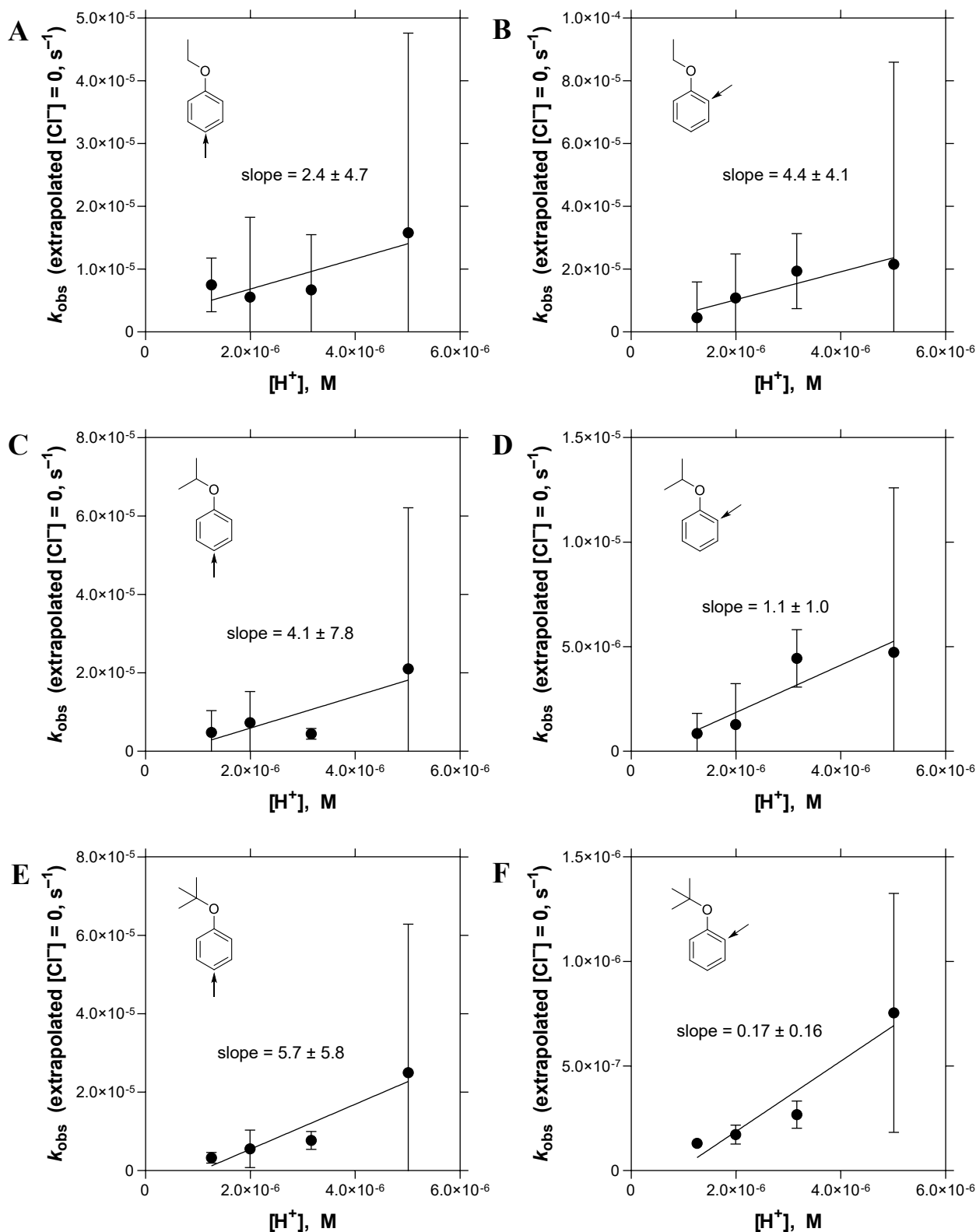
of $[Cl^-]$ at varying pH (**Figure S15**).

Figure S15. Alkylbenzene reactivity (extrapolated to [Cl⁻] = 0) as a function of [H⁺] for bromination of ethylbenzene at the (A) *para* and (B) *ortho* positions; isopropylbenzene at the (C) *para* and (D) *ortho* positions; and *tert*-butylbenzene at the (E) *para* and (F) *ortho* positions. Reaction conditions were uniform for all frames ([FAC]$_o$ = 1.50 mM, [Br⁻]$_o$ = 1.00 mM, [alkylbenzene]$_o$ = 50 μM, phosphate (40 mM) as pH buffer ranging from 5.30 – 5.90 and [NaNO₃] + [Cl⁻]$_o$ = 100 mM). [Cl⁻]$_o$ represents the contribution from NaCl only. [Cl⁻]$_{tot}$ (which is the contribution from all sources of Cl⁻, including NaCl, added FAC, and generation of Cl⁻ during oxidation of Br⁻ by FAC) varied from 5.60 – 40.43 mM. The y-intercept obtained from graphing k_{obs} versus [Cl⁻]$_{tot}$ is equal to k_{obs} (extrapolated to [Cl⁻] = 0). Slopes significantly different from zero (seen for all *ortho* products) demonstrate the reactivity of the bromine species H₂OBr⁺. Error bars denote 95% confidence intervals.

S11. Contributions of Individual Brominating Agent to Overall Bromination Rates

Influence of Bromide. The influence of bromide concentration on fraction of k_{calc} for the *para* and *ortho* bromination of isopropylbenzene and *tert*-butylbenzene is depicted in **Figure S16**. The influence of bromide concentration on fraction of k_{calc} for the *para* and *ortho* bromination of isopropoxybenzene, and *tert*-butoxybenzene is depicted in **Figures S17**.
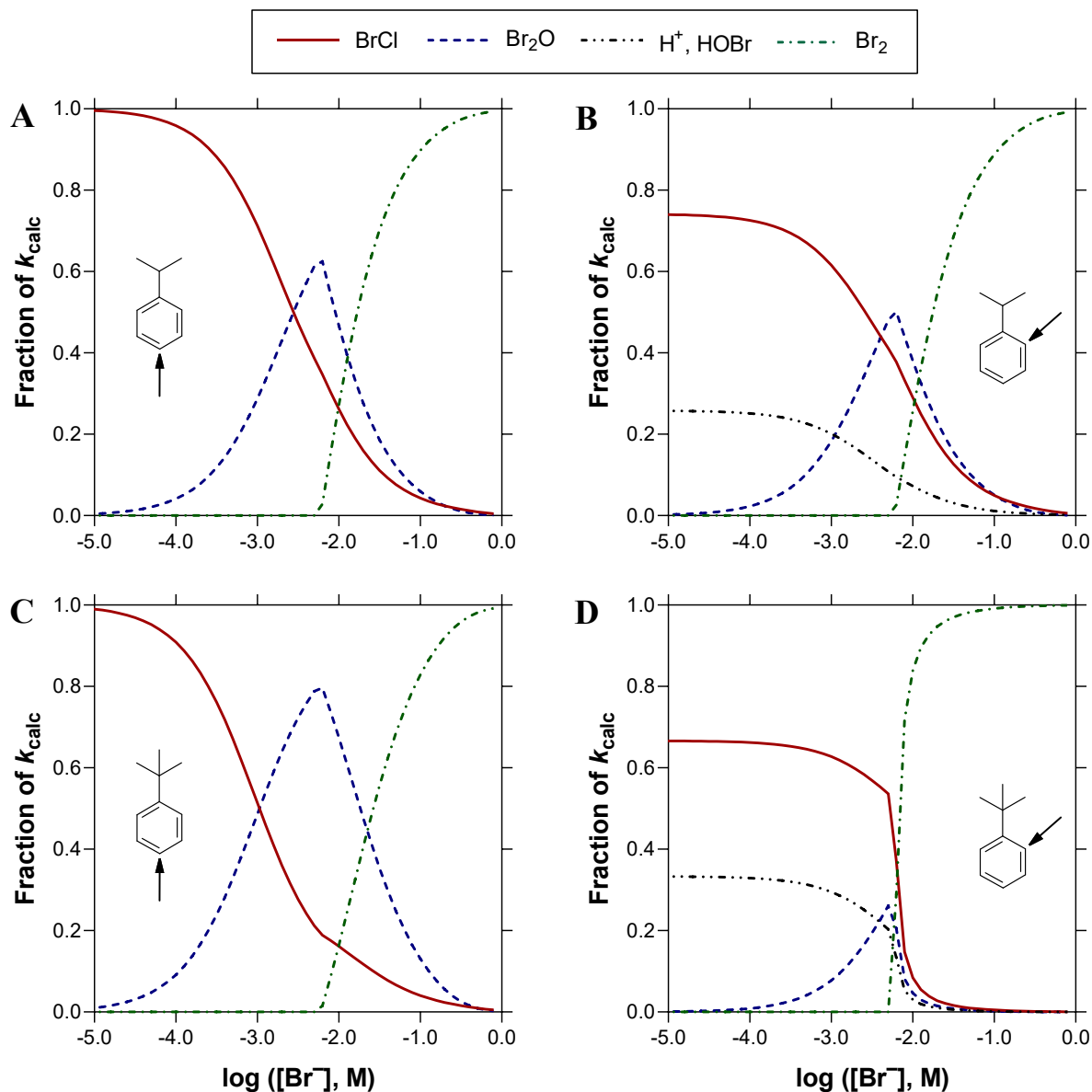
Figure S16. Contributions of brominating agents to alkylbenzene reactivity (as fraction of k_{calc} at 20 °C, where $k_{calc} = k_{BrCl}[BrCl] + k_{Br_2O}[Br_2O] + k_{H^+,HOBr}[H_2OBr^+] + k_{Br_2}[Br_2]$) as a function of $[Br^-]$ for bromination of isopropylbenzene at the (**A**) *para* and (**B**) *ortho* positions and *tert*-butylbenzene at the (**C**) *para* and (**D**) *ortho* positions. All k_{calc} values assume stoichiometric oxidation of Br^- by excess FAC. Conditions: $[FAC]_o = 6.00$ mM, $[NaCl] = 10.00$ mM, pH = 8.30, and T = 20.0 °C.
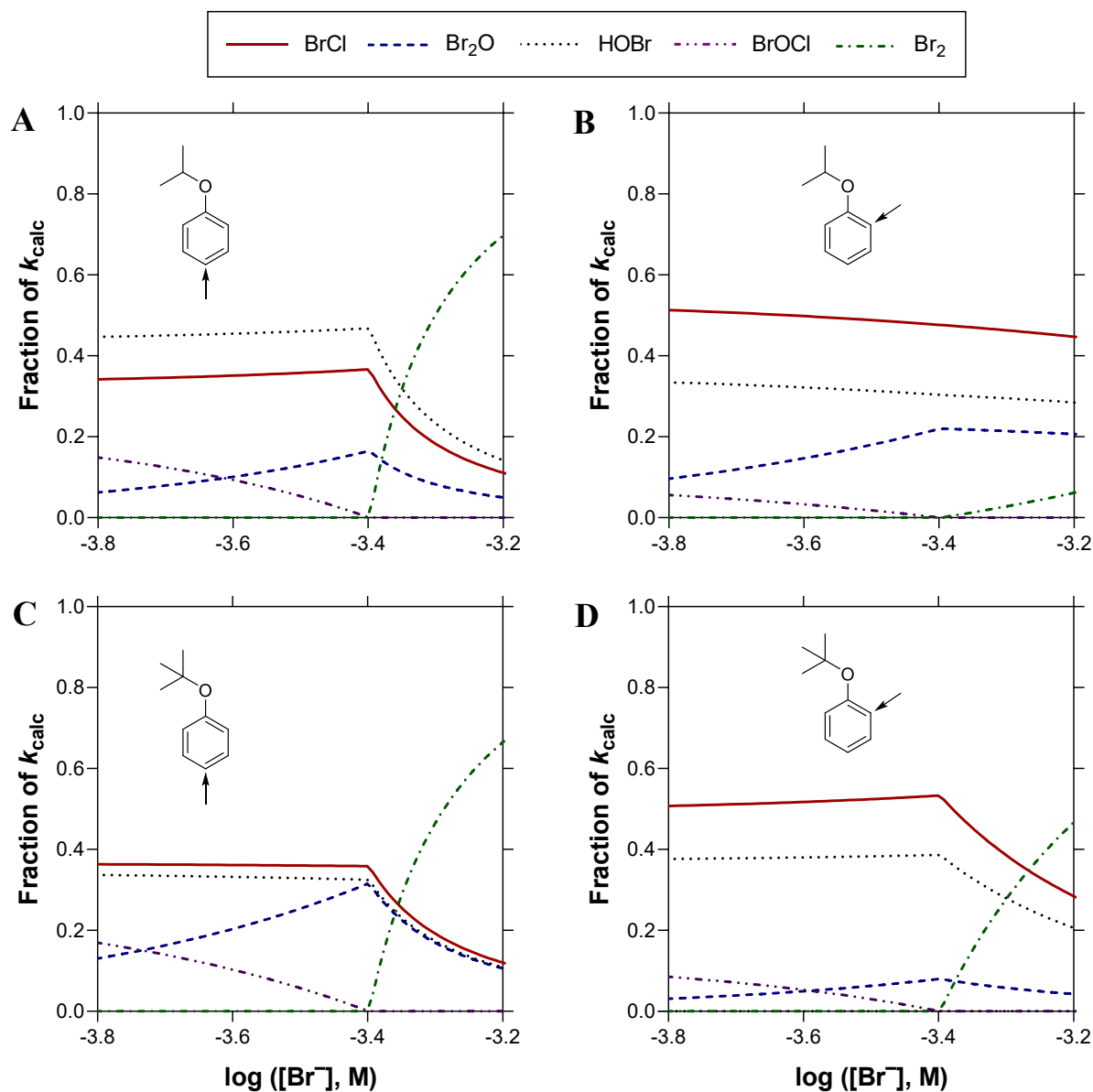
Figure S17. Contributions of brominating agents to alkoxybenzene reactivity (as fraction of k_{calc} at 20 °C, where $k_{calc} = k_{BrCl}[BrCl] + k_{Br_2O}[Br_2O] + k_{Br_2}[Br_2] + k_{HOBr}[HOBr] + k_{BrOCl}[BrOCl]$) as a function of $[Br^-]$ for bromination of isopropoxybenzene at the (**A**) *para* and (**B**) *ortho* positions and *tert*-butoxybenzene at the (**C**) *para* and (**D**) *ortho* positions. All k_{calc} values assume stoichiometric oxidation of Br^- by excess FAC. Conditions: $[FAC]_o = 0.40$ mM, $[NaCl] = 10.00$ mM, pH = 8.46, and T = 20.0 °C.

Influence of Chloride. The influence of $[Cl^-]$ on fraction of k_{calc} values of alkylbenzenes is depicted in **Figure S18**.
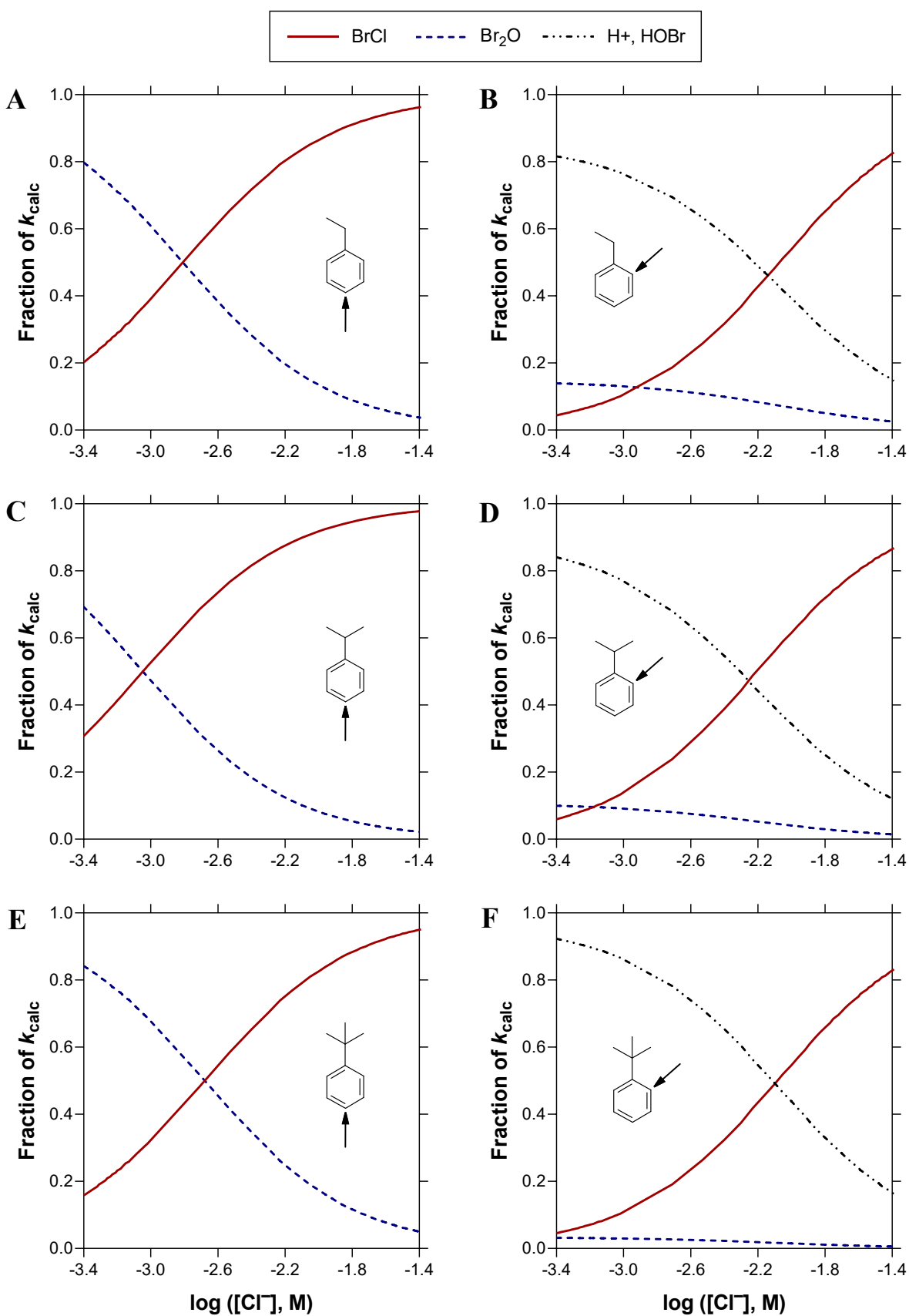
Figure S18. Contributions of brominating agents to alkylbenzene reactivity (as fraction of k_{calc} at 20 °C, where $k_{calc} = k_{BrCl}[BrCl] + k_{Br_2O}[Br_2O] + k_{H^+,HOBr}[H_2OBr^+]$) as a function of $[Cl^-]$ (log scale) for bromination of ethylbenzene at the (A) *para* and (B) *ortho* positions, isopropylbenzene at the (C) *para* and (D) *ortho* positions, and *tert*-butylbenzene at the (E) *para* and (F) *ortho* positions. Conditions: $[FAC]_o = 150$ μM, $[Br^-]_o = 130$ μM, pH = 8.30, and T = 20.0 °C. Graphed $[Cl^-]$ represents $[Cl^-]_{tot}$, which includes Cl^- from NaCl, FAC, and stoichiometric oxidation of Br^- by FAC.

For bromination at both the *para* and *ortho* positions of alkylbenzenes, the contribution of BrCl to k_{calc} increased with increasing [Cl$^-$]. For formation of *para*-brominated alkylbenzenes at [Cl$^-$]$_o$ = 0.4 mM, Br$_2$O had a greater contribution than BrCl. The maximal Br$_2$O fraction of k_{calc} ranged from 69% to 84%. Br$_2$O contributed the most to overall bromination rates when [Cl$^-$] ≤ 1.95 mM, 0.93 mM, and 1.95 mM for bromination of ethyl, isopropyl, and *tert*-butylbenzene, respectively, at the *para* position under the stated conditions. For *ortho*-bromination of alkylbenzenes, H$_2$OBr$^+$ contributed the most to overall bromination rates when [Cl$^-$] ≤ 7.95 mM, 4.95 mM, and 7.95 mM for ethyl, isopropyl, and *tert*-butylbenzene, respectively, under the stated conditions. Due to the lesser reactivity of Br$_2$O toward the *ortho* positions of the alkylbenzenes, its fraction of k_{calc} never exceeded 10%.

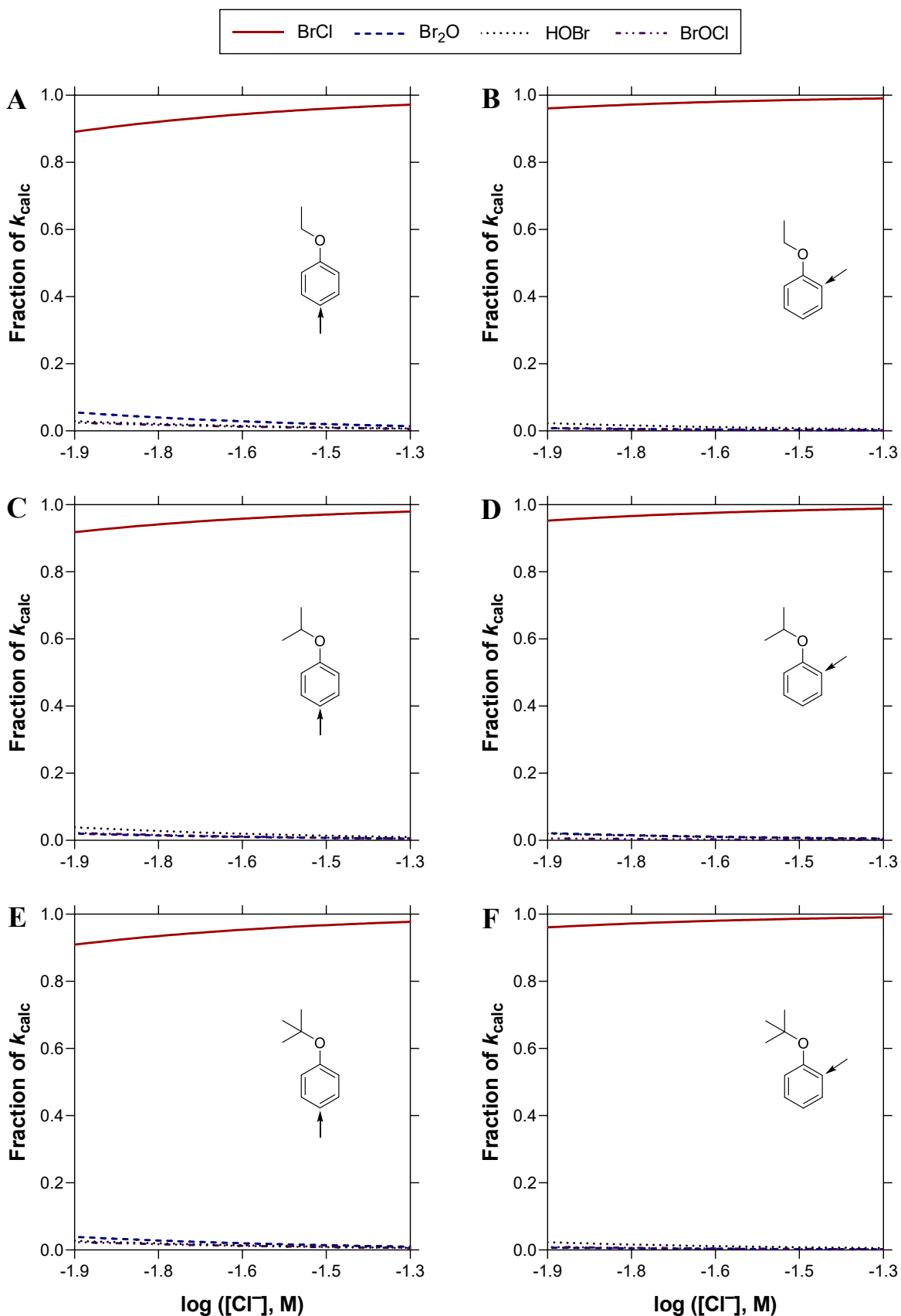The influence of [Cl$^-$] on fraction of k_{calc} values of alkoxybenzenes is depicted in **Figure S19**.

Figure S19. Contributions of brominating agents to alkoxybenzene reactivity (as fraction of k_{calc} at 20 °C, where $k_{calc} = k_{BrCl}[\text{BrCl}] + k_{Br_2O}[\text{Br}_2\text{O}] + k_{HOBr}[\text{HOBr}] + k_{BrOCl}[\text{BrOCl}]$) as a function of $[\text{Cl}^-]$ (log scale) for bromination of ethoxybenzene at the (**A**) *para* and (**B**) *ortho* positions, isopropoxybenzene at the (**C**) *para* and (**D**) *ortho* positions, and *tert*-butoxybenzene at the (**E**) *para* and (**F**) *ortho* positions. Conditions: $[\text{FAC}]_o = 400$ μM, $[\text{Br}^-]_o = 350$ μM, pH = 7.0, T = 20.0 °C. Graphed $[\text{Cl}^-]$ represents $[\text{Cl}^-]_{tot}$, which includes Cl^- from NaCl, FAC, and stoichiometric oxidation of Br^- by FAC.

BrCl was the predominant contributor to bromination of alkoxybenzenes; the fraction of k_{calc} for all other species was $\leq$ 5% at all [Cl$^-$]. For *para* bromination of alkoxybenzenes, the contribution of BrCl was greater than 95% at [Cl$^-$] > 20 mM; for *ortho* bromination of alkoxybenzenes, the contribution of BrCl was greater than 95% at all examined chloride concentrations.

Influence of FAC. Because [FAC]$_o$ had no influence on bromination rates of alkylbenzenes, fraction of k_{calc} values were not calculated for alkylbenzenes as a function of [FAC]$_o$. The influence of [FAC]$_o$ on the fraction of k_{calc} for alkoxybenzenes is illustrated in **Figure S20**.
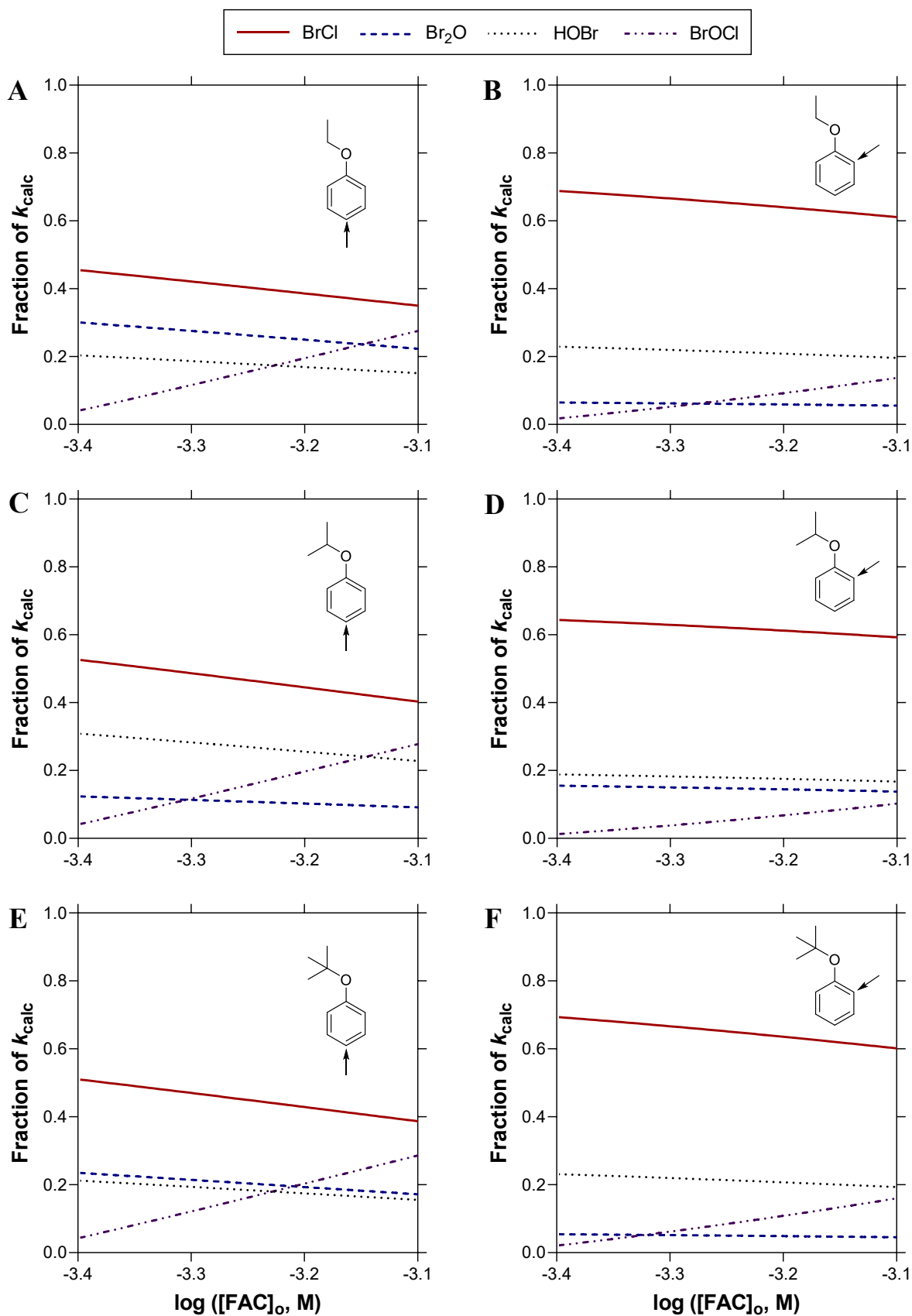
Figure S20. Contributions of brominating agents to alkoxybenzene reactivity (as fraction of k_{calc} at 20 °C, where $k_{calc} = k_{BrCl}[BrCl] + k_{Br_2O}[Br_2O] + k_{HOBr}[HOBr] + k_{BrOCl}[BrOCl]$) as a function of $[FAC]_o$ (log scale) for bromination of ethoxybenzene at the (**A**) *para* and (**B**) *ortho* positions, isopropoxybenzene at the (**C**) *para* and (**D**) *ortho* positions, and *tert*-butoxybenzene at the (**E**) *para* and (**F**) *ortho* positions. All k_{calc} values assume stoichiometric oxidation of Br^- by excess FAC. Conditions: $[NaCl] = 10$ mM, $[Br^-]_o = 350$ μM, pH = 8.2, and T = 20.0 °C.

The contributions of HOBr and Br_2O did not change substantially as a function of $[FAC]_o$. The contributions were approximately 20% for HOBr and $6 - 30\%$ for Br_2O, depending on substitution position. Generally, the fraction of k_{calc} associated with Br_2O was greater for *para* than for *ortho* bromination of the alkoxybenzenes. The contribution of BrOCl increased with increasing $[FAC]_o$ to maximums of $10 - 29\%$. BrCl was the primary contributor to bromination rates with maximums of $45 - 69\%$ that decreased slightly as $[FAC]_o$ increased.

Influence of pH. The influence of pH on fraction of k_{calc} for the *para* and *ortho* bromination of alkylbenzenes is depicted in **Figure S21**.
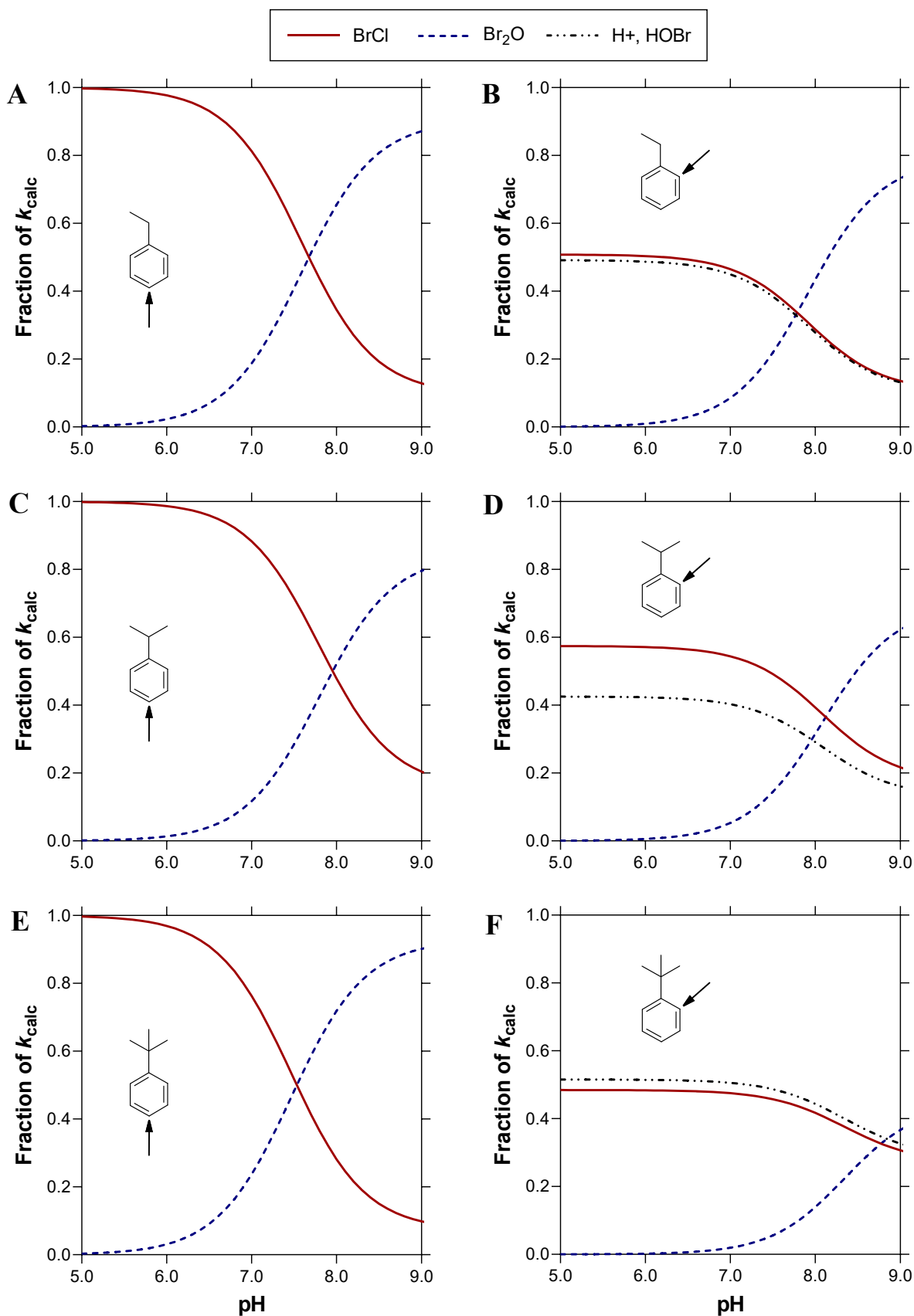
Figure S21. Contributions of brominating agents to alkylbenzene reactivity (as fraction of k_{calc} at 20 °C, where $k_{calc} = k_{BrCl}[BrCl] + k_{Br_2O}[Br_2O] + k_{H^+,HOBr}[H_2OBr^+]$) as a function of pH for bromination of ethylbenzene at the (**A**) *para* and (**B**) *ortho* positions, isopropylbenzene at the (**C**) *para* and (**D**) *ortho* positions, and *tert*-butylbenzene at the (**E**) *para* and (**F**) *ortho* positions. Conditions: $[FAC]_o = 2.50$ mM, $[Cl^-]_{tot} = 7.50$ mM, and $[Br^-] = 2.00$ mM, T = 20.0 °C. $[Cl^-]_{tot}$ includes Cl^- from added NaCl, added FAC, and Cl^- formed during stoichiometric oxidation of Br^- by FAC.

For all compounds and substitution positions, there was a point at which BrCl and Br_2O intersect (at pH values between 7.50 and 8.80); at higher pH, the contribution of BrCl fell below that of Br_2O. The concentrations of BrCl and H_2OBr^+ increased as pH decreased (**eqs 2** and **6**). The contribution of BrCl to the fraction of k_{calc} was similar to the contribution of H_2OBr^+ at any given pH for *ortho* bromination of the alkylbenzenes.

The influence of pH on fraction of k_{calc} for the bromination of alkoxybenzenes is shown in **Figure S22**.
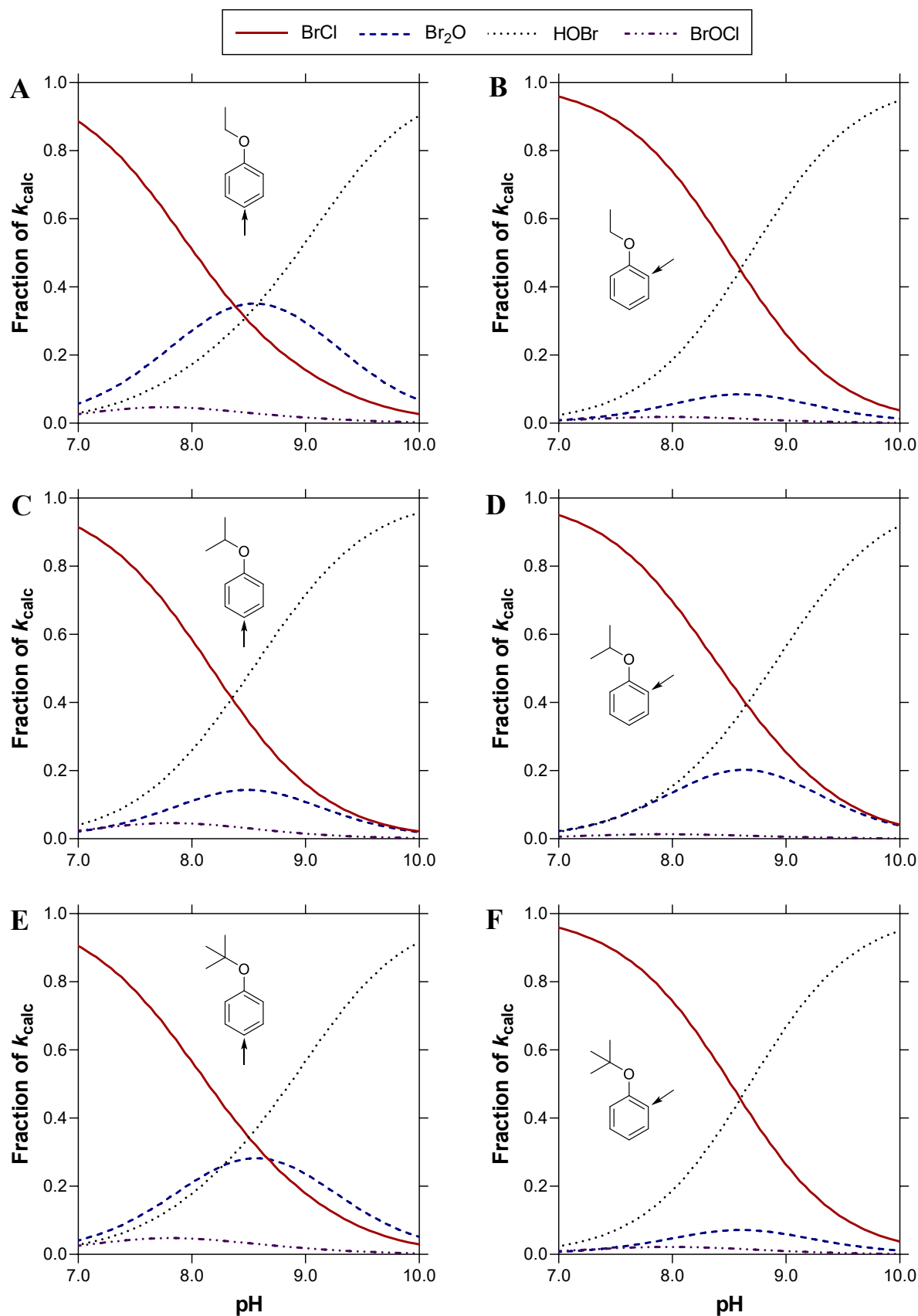
Figure S22. Contributions of brominating agents to alkoxybenzene reactivity (as fraction of k_{calc} at 20 °C, where $k_{calc} = k_{BrCl}[BrCl] + k_{Br_2O}[Br_2O] + k_{HOBr}[HOBr] + k_{BrOCl}[BrOCl]$) as a function of pH for bromination of ethoxybenzene at the (**A**) *para* and (**B**) *ortho* positions, isopropoxybenzene at the (**C**) *para* and (**D**) *ortho* positions, and *tert*-butoxybenzene at the (**E**) *para* and (**F**) *ortho* positions. All k_{calc} values assume stoichiometric oxidation of Br⁻ by excess FAC. Conditions: [FAC]$_o$ = 400 µM, [NaCl] = 10 mM, [Br⁻]$_o$ = 350 µM, and T = 20.0 °C.

For all alkoxybenzenes at both substitution positions, the contribution of HOBr increased to >90% with increasing pH; the contribution of BrCl was greater than 95% at the lowest examined pH (6.50) and decreased to less than 5% with increasing pH up to 9.91. The contribution of HOBr and BrCl intersected at pH 8.34 – 8.51 and 8.60 – 8.64 for *para* and *ortho* substituted alkoxybenzenes, respectively. The contribution of Br_2O increased to a maximum of 7 – 35% at pH 8.47 – 8.64, then decreased to less than 5% at higher pH values.

S12. References

(1)   Lau, S. S.; Dias, R. P.; Martin-Culet, K. R.; Race, N. A.; Schammel, M. H.; Reber, K. P.; Roberts, A. L.; Sivey, J. D. 1,3,5-Trimethoxybenzene (TMB) as a New Quencher for Preserving Redox-Labile Disinfection Byproducts and for Quantifying Free Chlorine and Free Bromine. *Environ. Sci. Water Res. Technol.* **2018**, *4* (7), 926–941. https://doi.org/10.1039/c8ew00062j.

(2)   Dias, R. P.; Schammel, M. H.; Reber, K. P.; Sivey, J. D. Applications of 1,3,5-Trimethoxybenzene as a Derivatizing Agent for Quantifying Free Chlorine, Free Bromine, Bromamines, and Bromide in Aqueous Systems. *Anal. Methods* **2019**, *11* (43), 5521–5532. https://doi.org/10.1039/c9ay01443h.

(3)   Taft Jr., R. W. Separation of Polar, Steric, and Resonance Effects in Reactivity. In *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; John Wiley & Sons, Inc.: New York, 1956; pp 556–675.