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A Simple, Effective Boron-Halide Ethoxylation Catalyst

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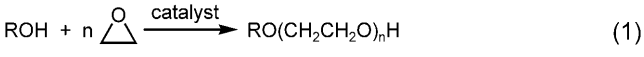
Abstract: Boron esters $B(OR)_3$, readily derived from boric acid and alcohols, combine with iodide or bromide to catalyze the ethoxylation of alcohols and phenols, giving good rates and narrow product distributions. The combined action of a weak electrophile [$B(OR)_3$] and a weak nucleophile (halide) allows for the ethoxylation of base-sensitive alcohols. Experiment suggests a new mechanism for this commercially important reaction proceeding through key β-haloalkoxy intermediates.

Keywords: boron; halides; ethoxylation; ethylene oxide; ring-opening polymerization

In the presence of various catalysts, alcohols and phenols insert multiple equivalents of ethylene oxide (EO) to give alkyl ethoxylates, the monoethers of poly(ethylene glycol) [Eq.(1)]. A wide variety of ethoxylates are used in commercial applications as non-ionic surfactants and detergents, coatings additives, solvents, emulsifiers and dispersants, and drug conjugates. The scale of this chemistry is large, with an annual global consumption of 1.7 million tonnes of EO.[1] The length of the poly(EO) chain varies considerably depending on the application. Surfactant and detergent ethoxylates are low molecular weight oligomers typically comprised of 5–20 EO monomers.[2] At the other extreme, functionalized ethoxylates used as drug conjugates employ chains averaging several hundred EO monomers (MW = ~5–40 kDa).[3] While EO-based oligomers and polymers dominate these applications, substituted epoxides, especially propylene oxide, are similarly employed.



(1)

Ethoxylation catalysts include strong Lewis acids and bases. Lewis acids, such as BF_3, are very active but generally avoided because they also generate 1,4-dioxane.[1a,2] Indeed, in the absence of alcohols BF_3 is an effective catalyst for the conversion of EO to 1,4-dioxane[4] and the yield of this undesired by-product can exceed that of the intended ethoxylate. For this reason strong base catalysts are more generally used for the commercial production of ethoxylates. The simplest and most common catalysts are the alkali or alkaline earth metal alkoxides of the alcohol substrate. Many variations and modifications of these catalysts have been reported, and the field has been recently reviewed.[2] Although they are used extensively in commercial applications the base catalysts have limitations. The molecular weight distributions obtained with simple base catalysts (alkoxide, hydroxide) are broad and there is a need for catalysts that give narrow distributions.[1a,2,5] This is especially true for low molecular weight, oligomeric ethoxylates used as surfactants, where a broad distribution containing high concentrations of unreacted alcohol diminishes the surface-active properties (surface tension, etc.). Alcohol substrates bearing functional groups reactive toward alkoxide are unsuitable with these catalysts, and thus the scope of the materials that can be prepared by this chemistry is limited. This point is important for the consideration of appropriate monofunctionalized ethoxylates useful as drug conjugates which must be prepared by multistep syntheses.[3]

Inspired by patents describing catalyst recipes employing boron reagents [$NaBH_4$ or $B(OH)_3$ plus NaOH] and sodium iodide for the ethoxylation of fluorinated alcohols,[6] it has been found that boron esters $B(OR)_3$ combined with bromide or iodide are excellent catalysts for alcohol ethoxylation. Evidence is provided supporting a novel mechanism for this commercially important reaction. The borate ester-halide ethoxylation does not involve either strong acid or strong base, but rather the combined action of a weak nucleophile and a weak electrophile. As a result, this new catalyst permits the ethoxylation of base-sensitive alcohols to give materials that cannot

be prepared with traditional alkali metal alkoxide catalysts. Moreover, the ethoxylate products have narrow molecular weight distributions, resulting in further advantage over traditional alkoxide catalysts.

Results with 1-octanol are illustrative. First, the neutral ester B(O-*n*-Oct)$_3$ alone fails to ethoxylate 1-octanol under all conditions examined, including temperatures as high as 140 °C. This result is not surprising given the weak Lewis acidity of this class of compounds.[7] Even the aluminum analogues are poor ethoxylation catalysts, requiring promoters such as H_2SO_4 to achieve adequate activity.[8] However, when B(O-*n*-Oct)$_3$ is combined with iodide (as soluble Bu_4NI) an active ethoxylation catalyst is obtained. As shown in Table 1, EO consumption is complete and the ethoxylate *n*-OctO(CH$_2$CH$_2$O)$_n$H is obtained within 15 h at 110–120 °C and boron/iodide loadings of 2–4 mol%. The reaction parameters have not yet been optimized and these results should be considered to be preliminary, for instance, the optimum concentrations of boron ester and iodide have not been determined.

These results may be compared with those obtained with the simple alkoxide catalyst NaO-*n*-Oct. At the same concentration and reaction conditions the alkoxide gives rates nearly 10-times faster than that obtained with B(O-*n*-Oct)$_3$/Bu_4NI. A comparison of the product distributions obtained with the two catalysts is shown in Figure 1. Each distribution in the examples shown averages *ca.* 4.7 mol of EO per mol of *n*-octanol. The NaO-*n*-Oct derived distribution is broad, with a polydispersity of 1.16. As a result, the *n*-octanol conversion in this example is 90% and the product contains 10% unreacted starting material. The oligomer distribution obtained with B(O-*n*-Oct)$_3$/Bu_4NI is significantly more narrow with a polydispersity of 1.08, resulting in >97% *n*-octanol conversion.

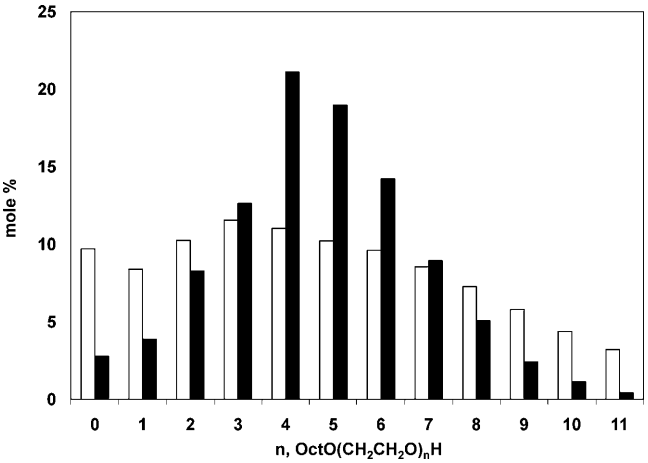


Figure 1. Comparison of the *n*-OctO(CH$_2$CH$_2$O)$_n$H distributions obtained with NaO-*n*-Oct (open rectangles) and B(O-*n*-Oct)$_3$/Bu_4NI (filled rectangles) catalysts.

The anionic ester NaB(O-*n*-Oct)$_4$ also catalyzes alcohol ethoxylation with initial rates comparable to B(O-*n*-Oct)$_3$/I^- at equal boron concentration. However, with NaB(O-*n*-Oct)$_4$ the EO uptake slows significantly after about 3 equivalents of EO are consumed and driving the ethoxylation to high EO consumption requires higher temperatures or increased catalyst concentration. In addition, the ethoxylate distribution is broad and resembles that obtained with NaO-*n*-Oct. Further evidence suggests that NaB(O-*n*-Oct)$_4$ is actually an inhibited form of the simple alkoxide NaOR generated by the equilibrium shown in [Eq. (2)]. Thus, the ethoxylation behavior (rate, product distribution) obtained with NaB(O-*n*-Oct)$_4$ is, unsurprisingly, indistinguishable from that derived by combining equimolar amounts of NaO-*n*-Oct and B(O-*n*-Oct)$_3$.[10] Addition of excess B(O-*n*-Oct)$_3$ (2.5:1 ratio) results in a further rate reduction and is additional evidence that NaOR is the actual catalytic species.

$$NaB(OR)_4 \rightleftharpoons B(OR)_3 + NaOR \quad (2)$$

Ethoxylation with the B(OR)$_3$-based catalyst has been extended to other alcohols and phenols, and a few representative examples are provided in Table 1. The product distributions in all cases are narrow, reflecting the results obtained with 1-octanol previously presented. As a result, high alcohol conversions are obtained at low EO consumption in almost all cases (*vide infra*). The ethoxylation is not limited to iodide, bromide works equally well but chloride does not yield an active catalyst. The reaction is not limited to quaternary ammonium counterions, but those that are

Table 1. Representative alcohol ethoxylations.[a]

Entry	Substrate	T [°C]	Alcohol Conversion [%]	Avg n[b]
1	1-octanol[c]	120	97	4.7
2	1-octanol	120	>99	7
3	1-propanol	110	>99	6
4	$CF_2HCF_2CH_2OH$	110	98	4
5	*p*-$CH_3OC_6H_4OH$	90	98	3.5
6	C_6H_5OH[d]	110	>99	6
7	ICH_2CH_2OH	100	99	6
8	ICH_2CH_2OH[e]	100	>99	12
9	$BrCH_2CH_2OH$[f]	100	96	8
10	$ClCH_2CH_2OH$	100	>99	12
11	$AcOCH_2CH_2OH$	110	94[g]	9

[a] All experiments: 4 mol% B(OR)$_3$, 4 mol% Bu_4NI, 16 h unless noted.
[b] Average n in RO(CH$_2$CH$_2$O)$_n$H.
[c] 2.1 mol% B(OR)$_3$ and Bu_4NI.
[d] LiI (4.0 mol%) cocatalyst.
[e] 1.0 mol% B(OR)$_3$, 2.5 mol% Bu_4NI.
[f] Bu_4NBr (4.0 mol%).
[g] Conversion limited by I^- exchange; see text.

poorly soluble in the alcohol – Na^+, K^+, Li^+ – show an induction period as judged by the EO uptake rate. These salts are soluble in the ethoxylate product and the induction period is likely due to the increasing solubility of the salt in the reaction mixture as the ethoxylate concentration begins to build. The tetraalkylammonium salts are soluble in the alcohol substrates and the induction period is not observed with those bromides or iodides.

Trace amounts of the halogenated ethoxylates $XCH_2CH_2O(CH_2CH_2O)_nH$, the formal product of ethoxylation of the halohydrins XCH_2CH_2OH, are observed. The formation of these ethoxylates is unusual because halohydrins are well known to undergo rapid elimination in the presence of base to give epoxides. Alkoxide catalysts, therefore, cannot be used to ethoxylate these base-sensitive substrates. It is likely for this reason that the ethoxylates of XCH_2CH_2OH have not been previously reported. In fact, ethoxylation of 2-halohydrins proceeds smoothly using the $B(OR)_3/X^-$ catalyst (Table 1, entries 6–10). Ethoxylation of $BrCH_2CH_2OH$ requires the use of bromide as co-catalyst to avoid halide exchange and product containing a mixture of bromo and iodo ethoxylates. This was not a problem with the chloro derivative and $ClCH_2CH_2O(CH_2CH_2O)_nH$ is obtained in good purity with iodide. 2-Acetoxyethanol is ethoxylated but displacement of acetate by iodide is competitive. Because acetate does not promote ethoxylation the iodide-acetate exchange leads to catalyst loss and thereby limits monomer conversion.

The extremely poor Lewis acidity of $B(OR)_3$ and the successful ethoxylation of base-sensitive XCH_2CH_2OH suggests that $B(OR)_3$/halide-catalyzed ethoxylation proceeds *via* a mechanism unlike those typically described for strong acid or base catalysts. To probe the mechanism a deuterium-labelling experiment was conducted with $BrCD_2CD_2OH$ (98 atom% d_4) as ethoxylation substrate and $B(OCH_2CH_2Br)_3$/KBr catalyst [2.3 mol% $B(OR)_3$, 2.1 mol% Br^-, 91.1% total deuterium enrichment]. At low EO consumption (3 mol EO/mol ROH) LC-MS analysis shows the expected ethoxylate distribution. The mass spectra of the individual oligomers are especially informative; that for the oligomer containing 3 EO monomers is representative (Figure 2a). The spectrum shows multiple -CD_2CD_2- fragments are incorporated into this oligomer and that for the composition $Br[(CH_2CH_2O)_x(CD_2CD_2O)_{4-x}]H$ every possible value of x (=0, 1, 2, 3, 4) is observed. Note-

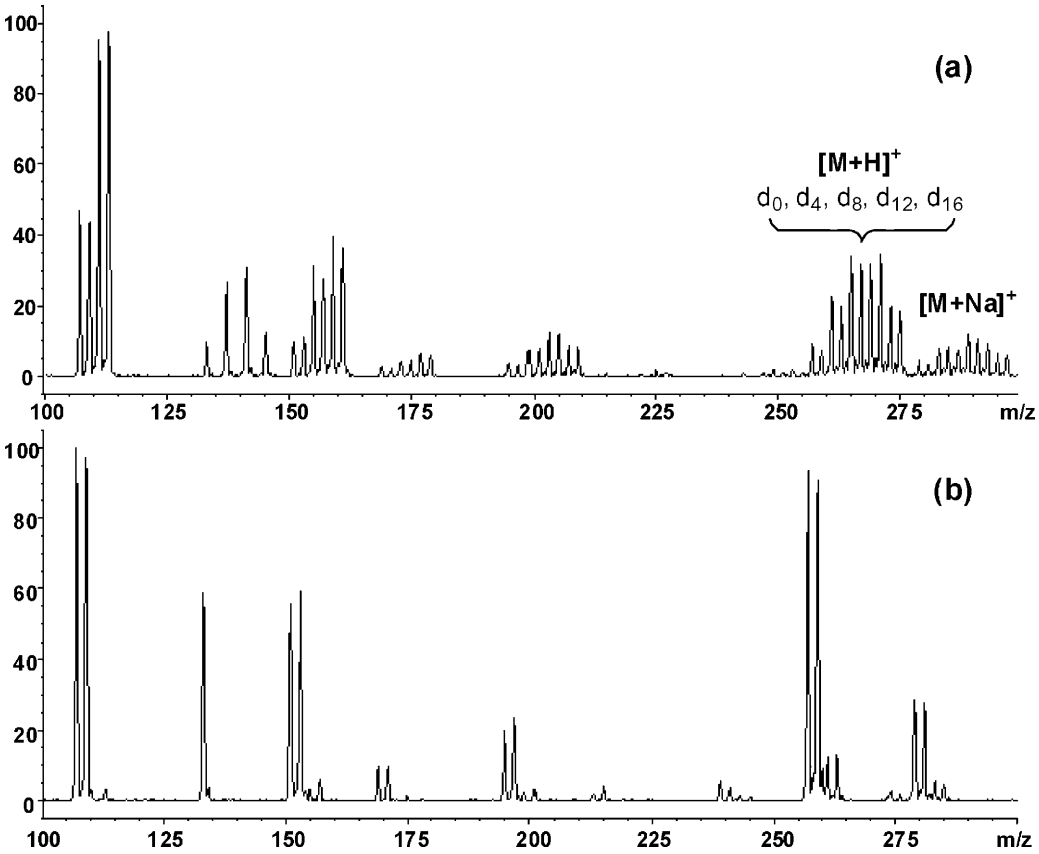


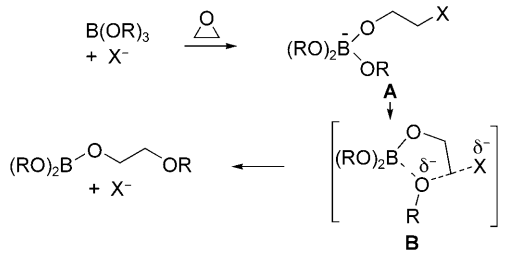
Figure 2. Mass spectra of $Br(CH_2CH_2O)_x(CD_2CD_2O)_{4-x}H$ (x=0–4) oligomer obtained at (a) low and (b) high ethylene oxide uptake. Selected fragments (amu): $BrCH_2CH_2$ (d_0, 107/109; d_4, 111/113); $CH_2CH_2O(EO)_2H$ (d_0, 133; d_4, 137; d_8, 141; d_{12}, 145); $BrCH_2CH_2OCH_2CH_2$ (d_0, 151/153; d_4, 155/157; d_8, 159/161).

worthy are the pairs of peaks due to the fragment ions $[^{79/81}BrCD_2CD_2]^+$ (111, 113 amu) and $[^{79/81}BrCH_2CH_2]^+$ (107, 109 amu), where the relative intensities show *ca.* 30% proton incorporation into the 2-bromoethyl end group as compared to the 91% deuterium content initially charged. GC-MS analysis did not provide evidence of deuterium enrichment in the unreacted EO.

After ethoxylating this sample to higher average molecular weight (6–7 mol EO/mol ROH) the mass spectra show significant changes, again best exemplified by that for the $n=3$ ethoxylate, Figure 2b. This species now shows almost no deuterium incorporation, with only $x=0$ and traces of $x=1$ observed. The bromoethyl end group in this oligomer is now nearly deuterium-free. The mass spectra further show that deuterium is found exclusively in the high molecular weight end of the oligomer distribution.

The deuterium labelling results clearly indicate that halide-carbon bond making and breaking are intimately involved in the reaction mechanism. Otherwise, deuterium would only be found as $BrCD_2CD_2O$ end groups, the degree of deuterium incorporation would be independent of molecular weight, and multiple CD_2CD_2O units per oligomer would not be observed. Especially, halide-carbon bond making and breaking is required to explain the increasing degree of deuterium-free $BrCH_2CH_2O$ end groups with increasing molecular weight (i.e., EO conversion).

A mechanism that accounts for these observations is shown in Scheme 1. The first step involves combined action of halide and $B(OR)_3$ on EO to yield borate anion intermediate **A**. Although the details of this ring opening are not yet known, it likely proceeds by nucleophilic attack of halide on EO. Formation of of **A** is assisted by electrophilic activation at oxygen by $B(OR)_3$ or, alternatively, the transient alkoxide is trapped with $B(OR)_3$. This proposal is similar to the mechanism proposed for the ring-opening of 2,3-epoxy alcohols with halides and other nucleophiles in the presence of stoichiometric $B(OCH_3)_3$.[11] While the insertion of epoxides into B–X bonds is known,[12] it is unlikely that B–X species are generated in alcohol solvent.



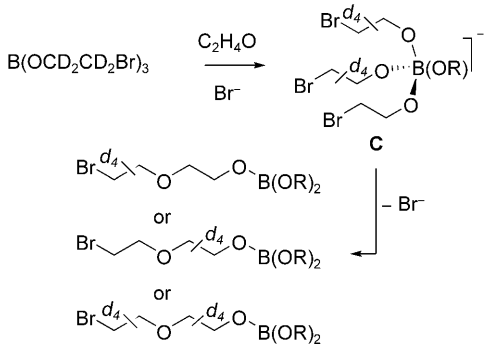
Scheme 1. Proposed mechanism for $B(OR)_3$/halide-catalyzed ethoxylation of alcohols and phenols.

Anion **A** is positioned to undergo intramolecular displacement of halide by alkoxide as in **B**, resulting in net insertion of EO into the B–OR bond and regeneration of the catalyst (neutral ester plus halide). Repetition of this process leads to chain growth. There is a literature precedent for the proposed intramolecular displacement of halide *via* **B**. Letsinger et al. proposed an identical pathway to account for the hydrolysis and alcoholysis of 2-chloroethanol, catalyzed by arylborate esters.[13] Transition states with similar structures have been proposed to account for related modes of epoxide activation mediated by borates.[14]

This mechanism accounts for the deuterium labelling results. As exemplified in Scheme 2, activation of non-labelled EO with bromide and a labelled ester yields intermediates such as borate anion **C** bearing d_0- and d_4-bromoethyl groups. For the example shown, intramolecular displacement of bromide by alkoxide leads to any of the three isotopomers shown. Further isotope scrambling occurs *via* exchange of alcohol with ester, a very rapid reaction with borate esters.[10b] Repetition of these processes results in an oligomer distribution with the observed isotope incorporation.

The viability of intramolecular displacement *via* **B** was further substantiated by investigating the reaction of $NaB(OCH_3)_4$[15] with $HOCH_2CH_2Br$ and $EtOCH_2CH_2Br$, where alkoxide exchange at boron is possible only with $HOCH_2CH_2Br$. Treatment of $NaB(OCH_3)_4$ with $HOCH_2CH_2Br$ in CH_3OH cleanly yields $HOCH_2CH_2OCH_3$ within hours at room temperature (GC, GC-MS). In contrast, $NaB(OCH_3)_4$ and $CH_3CH_2OCH_2CH_2Br$ do not yield $CH_3CH_3OCH_2CH_2OCH_3$ after 24 h. $NaOCH_3$, on the other hand, reacts on mixing with $HOCH_2CH_2Br$ to give EO and traces of $HOCH_2CH_2OCH_3$, and also with $CH_3CH_2OCH_2CH_2Br$ to give $CH_3CH_2OCH_2CH_2OCH_3$ and small amounts of the elimination product $CH_3CH_2OCH{=}CH_2$.

In conclusion, a new catalyst and mechanism for the ethoxylation of alcohols and phenols has been de-



Scheme 2. Isotope scrambling.

scribed. The catalyst combines the action of a weak nucleophile (halide) and a weak electrophile [$B(OR)_3$] to activate ethylene oxide and proceeds through a key β-haloalkoxy ester intermediate. The esters $B(OR)_3$ are obtained in a single step from inexpensive boric acid and alcohol following well-known chemistry, with water the only by-product. It may be possible that this species and the mechanism described herein are operative in the commercial processes based on $NaBH_4$ or $B(OH)_3$ and NaI, although owing to the basic reagents (borohydride and hydroxide, respectively) employed with the commercial catalysts it is very likely that $NaB(OR)_4$ is generated as well (and, therefore, NaOR), thus confounding a simple, direct comparison of the work described herein with the commercial system. The $B(OR)_3$/halide catalyst also ethoxylates base-sensitive alcohols such as β-halohydrins, affording a new route to heterobifunctional EO oligomers. Finally, the oligomer distributions are narrow, allowing for the synthesis of short chain, surfactant-range products containing trace unreacted alcohol substrate. These results are preliminary and further investigation is required for optimization, to better understand the kinetics of this chemistry, and to broaden the findings to other substrates.

Experimental Section

The boric esters $B(OR)_3$ were prepared by esterification of $B(OH)_3$ or B_2O_3 with ROH and concomitant water removal.[15] $NaB(O\text{-}n\text{-}Oct)_4$ was prepared by transesterification of $NaB(OCH_3)_4$[16] with 1-octanol.[17]

Alcohol Ethoxylation – General Considerations

Ethoxylation reactions were performed in a 30-mL stainless steel reactor using a solution of catalyst (1–4 mol%) in the neat alcohol ROH (0.01–0.02 mol). The reactor was chilled with ice, evacuated, and then a premeasured amount (4–12 equiv.) of EO was condensed into the reactor. The reactor was sealed and brought to reaction temperature, typically in the range 90–120 °C; initial pressures ranged from 7–10 bar. Reaction times varied, but were usually allowed to proceed overnight (16 h) whereupon complete EO consumption was achieved (0 bar pressure). The products were analyzed by a variety of techniques including GC, GC-MS, HPLC with phenyl isocyanate derivatization, HPLC-MS, and ^1H NMR.

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