Assessing the Potential for the Reactions of Epoxides with Amines on Secondary Organic Aerosol Particles

Santino J. Stropoli and Matthew J. Elrod*

Department of Chemistry and Biochemistry, Oberlin College, Oberlin, Ohio 44074, United States

Supporting Information

ABSTRACT: Nuclear magnetic resonance techniques were used to study the kinetics and products of the reaction of a variety of epoxides with various amines under varying pH conditions. In agreement with a previous finding, the amine–epoxide reactions were found to be water-catalyzed and not directly dependent on the pH of the reaction environment. At pH values higher than the pK_a of the particular amine, the amine–epoxide reactions were extremely efficient, outcompeting hydrolysis reactions even for



conditions where water was the solvent and the amine was a relatively low-concentration solute. This finding was rationalized by measurements that showed that the relative nucleophilic strength of amines relative to water was on the order of 1000, while the nucleophilic strength of protonated amines (which are predominant when $pH < pK_a$) was negligible. The epoxide carbon substitution environment was found to have a large effect on the measured rate constants (more substituted epoxides had slower rate constants), while the amine carbon substitution environment had a much more limited effect. While the amine—epoxide rate constants are large enough such that amine—epoxide reactions may be kinetically feasible for isoprene-derived epoxides and high amine secondary organic aerosol (SOA) concentrations, most atmospheric amines are expected to be present in protonated form on the largely acidic SOA found in the atmosphere and thus are expected to be largely unreactive toward epoxides.

INTRODUCTION

Secondary organic aerosol (SOA) has been implicated in human respiratory and cardiovascular disease,¹ visibility loss,² and climate modification.³ Recently, the formation of SOA from atmospheric amines has been identified as occurring via a number of chemical processes, such as salt formation,⁴ oxidation reactions,⁵ and aqueous-phase reactions.⁶ Atmospheric amines have both natural and anthropogenic emission sources, and field measurements indicate that aliphatic amines are most abundant.⁷ The major anthropogenic sources of amines are from agricultural activities and biomass burning. New carbon-capture technologies utilize aqueous solutions of amine compounds, such as monoethanol amine (MEA, HOCH₂CH₂NH₂), to effect reversible absorption of CO₂. Increasing use of such carbon-capture technologies will likely lead to increased atmospheric amine concentrations from the solvents such as MEA itself, as well as amine-based degradation products.8

Isoprene-derived SOA can make up a major proportion of atmospheric SOA in many continental locales.^{9,10} Extensive studies of SOA formation in the southeastern United States have identified epoxide intermediates as key species in the formation of isoprene-derived SOA.^{11–16} In this mechanism, SOA species are formed from the isomerization and nucleophilic addition reactions of common SOA nucleophiles (in particular, water and sulfate) with epoxides formed from gas-phase oxidation of isoprene and related species.^{17–19} In most cases, these reactions require acid catalysis to be kinetically facile. Because amines are known to be better nucleophiles than water,²⁰ it is quite possible that amineepoxide reactions are also efficient under atmospheric conditions. Indeed, a recent article suggested that amines and/or ammonia may react with and/or catalyze the reactions of isoprene-derived epoxides on SOA.²¹ Further, a previous article reported that amine—epoxide reactions appear to be water-catalyzed, rather than acid-catalyzed,²² which might allow amine—epoxide reactions to occur at a wider range of SOA pH than the previously identified isoprene-derived epoxide reactions with water and inorganic nucleophiles.

In this paper, we report pH-dependent measurements of the reaction kinetics of the aqueous-phase reactions of structurally varying epoxides with several amines, including potentially atmospherically relevant ones such as MEA, using nuclear magnetic resonance (NMR) as the analytic technique. We report fully isomer-specific NMR assignments of the various products that are observed, in addition to information on the kinetic stability of the products. These results are then used to ascertain the potential atmospheric relevance of these reactions in the formation of SOA.

EXPERIMENTAL SECTION

Bulk Aqueous Solution Preparation. Because of the basicity of amines, solutions compromised of only amine and water (such solutions will be referred to as the "ambient" pH systems) are characterized by pH values greater than 7 (in these cases, the pH is determined by the amine concentration and the

Received: August 12, 2015 Revised: September 18, 2015

 pK_a of the amine). To explore the effects of pH on the mechanistic pathways and on the kinetics of the reactions, as well as a range of atmospherically relevant aerosol pH values, strong acids and bases were sometimes also added to the solutions to adjust pH. The experimental solutions were prepared by adding small volumes of epoxide and larger volumes of amine to D₂O, and then, if a nonambient pH was desired, deuterated perchloric acid or sodium deuteroxide was additionally added (deuterated solvents were used because of NMR locking requirements). Experiments were performed using commercially available chemicals from Sigma-Aldrich (butylamine (99.5%), diethylamine (\geq 99.5%), *t*-butylamine (98%), ethanolamine (99+%), 4-amino-1-butanol (98%), glycine (≥99%), aniline (≥99%) 2,3-dimethyl-2,3-epoxybutane (99%), 2,3-epoxy-2-methylbutane (97%), cis-2,3-epoxybutane (97%), 1,2-epoxybutane (99+%), 1,2-epoxy-2-methylpropane (97%), perchloric acid-d solution (68 wt % in D_2O)), and sodium deuteroxide (40% in D2O) from Cambridge Isotope Laboratories, Inc.

The pH measurements were made with a stainless steel probe and were calibrated with pH 4.00 and 10.00 buffer solutions before each measurement. The stated precision of the probe was 0.3 pH units. Because the solutions were primarily composed of deuterated species, the use of a pH meter calibrated for normal isotope species will be in error. However, a previous study showed that pH and pD values differ by on the order of 0.3 pH units over the pH range of interest in this study.²³ Because this difference is on the order of the stated precision of the pH meter, the readings from the pH meter were not corrected for the effect of deuterated species.

To reduce the kinetic situation for the epoxide loss to that of a pseudo-first-order process, the amine was added in excess (amine/epoxide molar ratio = 10:1). The epoxides were added to the solutions last and stirred for 1-3 min to ensure solution homogeneity before being transferred to an NMR tube for analysis. Following preparation, product formation and kinetics were monitored and recorded using ¹H and ¹³C NMR spectroscopy.

NMR Technique. All NMR spectra were collected on a Varian 400 MHz instrument, using built-in autolock and gradient shim routines before collecting each spectrum. The ¹H chemical shifts were calibrated relative to HDO (4.79 ppm), and the relative amounts of reaction reactants and products were calculated by peak integration of unique protons for each species.

Aliquot NMR Analysis Method. To facilitate a separate study of water's potential catalytic role in the amine–epoxide reactions, a 10:1 molar ratio reaction mixture of *t*-butylamine and 1,2-epoxybutane (without D_2O) was stirred for 2–3 min and then stored in a vial at room temperature. Small-volume aliquots of this solution were periodically withdrawn from the vial, added to ~700 μ L of D2O, and the resulting mixtures were loaded in to NMR tubes and analyzed using ¹H NMR.

Computational Methods. Geometries (determined at the B3LYP/6-31G(d,p) level) and energies of the relevant species were calculated using a modified version of the G2MS compound method (MG2MS),²⁴ which is a variation on G2 theory.²⁵ The Polarizable Continuum Model (PCM) method²⁶ was used to account for the effects of aqueous solvation on the reactant and product properties. All calculations were performed with the Gaussian 03 computational suite.²⁷ Each stationary point was confirmed as a potential energy minimum

by inspection of the calculated frequencies. The overall energy expression for the MG2MS scheme is defined in eq 1:

$$E_{\text{G2MS}} = E_{\text{CCSD}(\text{T})/6-31\text{G}(\text{d})} + E_{\text{MP2}/6-311+\text{G}(2\text{df},2\text{p})} - E_{\text{MP2}/6-31\text{G}(\text{d})} + \text{HLC}$$
(1)

where HLC is an empirically defined correction term with HLC = $An_{\alpha} + Bn_{\beta}$ where n_{α} and n_{β} are the number of α - and β electrons, respectively, and the constants A and B are 6.06 and 0.19 mH, respectively (all species investigated were closed shell; therefore, $n_{\alpha} = n_{\beta}$.). Our previous MG2MS results for atmospherically relevant systems (including radicals and ions) indicate that the MG2MS-calculated thermodynamic properties are typically accurate to within 10 kJ mol⁻¹ for systems similar to those under study here.²⁸

RESULTS AND DISCUSSION

¹H NMR Spectral Assignments. The identification of products and the kinetics of all reactions were determined using the ¹H NMR technique. The epoxide reactants and the diol hydrolysis products have been previously studied, and their NMR spectra have been reported,²⁹ thus simplifying the identification of these potential species in the present study. The reactant amine NMR spectra were obtained separately by dissolving each amine in D2O and collecting the resulting spectrum. To the best of our knowledge, there are no previous ¹H NMR literature data for the amine–epoxide addition products that were observed. Therefore, these products were identified by analyzing the ¹H chemical shifts of the protons that were initially part of the reactant epoxide ring; these protons experience larger chemical shift differences upon nucleophilic addition and experience less spectral overlap than the other protons that exist in the epoxide reactants. Figure 1 shows a sample ¹HNMR spectrum of 1,2-epoxybutane, t-butylamine, and the primary amine addition product. The primary addition product was distinguished from the secondary addition product by observing difference in chemical shifts of the protons attached to the primary and secondary epoxide



Figure 1. ¹H NMR spectrum of the reaction between 1,2-epoxybutane and *t*-butylamine in D_2O at pH = 12.3.

bridge carbons. It is known from previous work that adjacent alcohol groups lead to chemical shifts between 0.7 and 1.0 ppm higher than the corresponding epoxide chemical shifts.²⁹ For a primary amine addition product, an alcohol group would be formed at the secondary carbon (which has one proton) and for a secondary amine addition product, an alcohol group would be formed at the primary carbon (which has two distinguishable protons). In addition to the epoxide reactant peaks at 3.0 (primary), 2.57 (primary), and 2.78 (secondary) ppm, Figure 1 shows several new peaks: a single multiplet at 3.6 ppm and two multiplets at chemical shift values of 2.95 and 2.74 ppm. Since there is only one new peak with a correct alcohol functionality chemical shift value (3.7 ppm) and there are two peaks at much lower chemical shift (2.95 and 2.74 ppm), the spectrum in Figure 1 indicates the sole presence of the primary amine addition product. On the basis of this spectrum, it appears the replacement of epoxide functionality with amine functionality leads to very small changes in chemical shift for adjacent protons. Similar analyses were made for other epoxide systems, and in every case only the primary addition product was observed. The details of the ¹H NMR spectral assignments for all of the reactants and products (and their chemical shifts for certain solution compositions) are given in the Supporting Information.

Hydrolysis Catalysis Issues. Most of the amine nucleophilic addition reactions were studied in aqueous solution. Since water can also react with epoxides via nucleophilic addition of water (hydrolysis), there is the potential for a nucleophile competition situation in the present systems. For the epoxides studied in the present work, the kinetics of the hydrolysis of epoxides has been previously reported and has been shown to undergo an acid-catalyzed mechanism at low pH.²⁹ In a general review of epoxide reactivity, Whalen reported that many epoxides undergo base-catalyzed hydrolysis at high pH, and at intermediate pH, the ring-opening reaction is neither acid- nor base-catalyzed.³⁰ Therefore, the most general rate law contains concentration dependences for epoxide, water, and a catalyst:

$$rate = k[epoxide][H_2O][catalyst]$$
(2)

Because the experiments are generally performed with excess water, and the catalyst concentration, by definition, does not change, the rate law can be expressed as a pseudo-first-order equation:

$$rate = k'[epoxide] \tag{3}$$

where k' is a pseudo-first-order rate constant that is proportional to the catalyst concentration. According to Whelan, at low pH, log(k') should be a negative linear function of pH (acid catalysis), while at high pH, log(k') should be a positive linear function of pH (base catalysis).

To confirm this catalysis situation for the present epoxides, a full pH-dependent determination of the hydrolysis rate constants for 1,2-epoxybutane was performed. Figure 2 shows how the logarithm of the pseudo-first-order rate constant k' varies with pH. These data agree with the framework suggested by Whelan, including an intermediate pH region where the pseudo-first-order rate constant does not depend on pH. One possible interpretation of this intermediate pH region data is that the hydrolysis reaction is uncatalyzed. However, Whelan suggests that the hydrolysis reaction undergoes general acid catalysis in this pH region, with water acting as a general acid (water acts as a proton donor to the epoxide oxygen atom).



Figure 2. pH dependence of the logarithm of the pseudo-first-order rate constant (log k', units: s⁻¹) for the 1,2-epoxybutane and D₂O reaction.

Since the water concentration itself depends extremely weakly on pH in this pH region, this mechanism is consistent with kinetics data shown in Figure 2.

Water as a Catalyst for Amine–Epoxide Systems. In a previous study, Azizi and Saidi synthesized various β -amino alcohols by reaction of epoxides in aqueous amine solutions and concluded that water was acting as a catalyst, since no reaction was observed between epoxides and amines in dry solvents.²² To confirm water's catalytic role in the amine– epoxide systems, *t*-butylamine and 1,2-epoxybutane were mixed together without any aqueous solvent present, and this mixture was monitored using the aliquot ¹HNMR technique described in the Experimental Section. No reaction was observed to occur over a 24 h time period. As proposed by Whelan for epoxide hydrolysis reactions for epoxides at intermediate pH, we propose that water is similarly acting as a general acid catalyst for the nucleophilic addition of amines to epoxides.

Kinetics of the Nucleophilic Addition Reaction of Amines with Epoxides. In the amine—epoxide systems, water behaves as both a catalyst and, potentially, as a competing nucleophile. Figure 3 shows the dependence of the logarithm of the pseudo-first-order rate constants as a function of pH at high pH for both the formation of the *t*-butylamine primary addition product (from nucleophilic addition of the amine to 1,2-epoxybutane) as well as the diol product (from nucleophilic addition of water to 1,2-epoxybutane).

As the pH increases by one unit, the corresponding logarithm of the pseudo-first-order rate constant for the diol formation increases by one unit (as expected for a first-order, base-catalyzed process), while the logarithm of the pseudo-firstorder rate constant for the amine addition product stays relatively constant. (The slight increase in the amine—epoxide reaction pseudo-first-order rate constants at high pH is most likely not due to the role of base catalysis but rather to an indirect effect of the changing solvent conditions (higher ionic strength, for example).) Thus, it appears that the rate of formation of the amine addition product is not characterized by base catalysis. As will be shown later, this process is similarly not influenced by any acid-catalyzed process either. Instead, it appears that the amine—epoxide reactions are characterized by



Figure 3. pH dependence of the logarithm of the pseudo-first-order rate constant (log k', units: s^{-1}) for water +1,2-epoxybutane reaction (red) and for the *t*-butylamine +1,2-epoxybutane reaction (black).

water acting as a general acid catalyst across the whole range of measured pH values.

Therefore, the rate law for the reaction for amine-epoxide reactions is assumed to follow the general form:

- -

- -

$$rate = k[epoxide][amine][H_2O]$$
(4)

However, because the catalyst water is held at a nearly fixed concentration (55 M), and the amine concentrations are held in at least 10-fold excess over the epoxide concentrations, this rate reduces a similar first-order form to that for hydrolysis

$$rate = k'' [epoxide]$$
(5)

$$k'' = [\operatorname{amine}][H_2O] \tag{6}$$

Because these rate equations do not contain any acid or base terms, it is reasonable to posit that the amine—epoxide reactions will not be pH-dependent. However, as will be discussed in the next section, unlike for acid- and base-catalyzed hydrolysis of epoxides, the concentration of the active nucleophile species itself, the unprotonated amine, is pH dependent, whereas the concentration of the hydrolysis reaction nucleophile, water, is not pH-dependent. This leads to a fundamentally different pH-dependent kinetics situation for amine—epoxide reactions as compared to epoxide hydrolysis.

pH Dependence of Amine-Epoxide Rate Constants. At moderate and low pH, the protonation equilibrium of amines becomes relevant:

$$R - NH_2 + H^+ \leftrightarrow R - NH_3^+ \tag{7}$$

As nucleophilic strength is related to the charge of the species (the more negatively charged the nucleophile, the stronger the nucleophile), it is expected that a protonated amine will be a significantly weaker nucleophile than an unprotonated amine. Using the pK_a for *t*-butylamine (10.68), a relatively strongly basic amine, and the pK_a for aniline (4.70), a relatively weakly basic amine,³¹ and assuming a 1 M total amine concentration, the fractions of unprotonated amine compared to total amine concentrations were calculated at experimentally utilized pH values and are plotted in Figure 4.





Figure 4. Fraction of unprotonated *t*-butylamine (black) and aniline (red) remaining in aqueous solution at various pH values.

These data predict that the *t*-butylamine nucleophilic addition to epoxides will be efficient for pH > 10, while the aniline nucleophilic addition reaction to epoxides will be efficient for pH > 4. Under the hypothesis that the addition of amines to epoxides is entirely dependent on the unprotonated amine concentration, the pseudo-first-order rate constants were measured at the pH values indicated in Figure 4. At higher pH values (for example, t-butylamine is 100% unprotonated at pH = 12.3), the primary amine addition product was the sole product observed. As pH was lowered, less amine product was formed, and the diol product from the competing hydrolysis reaction became observable. At lower pH values (for example, tbutylamine is more than 99% protonated at pH = 7.7), the amine addition product was no longer observable, and only the diol product was observed. Therefore, it is more accurate to define the pseudo-first-order rate constant for amine-epoxide reactions as

$$k'' = [unprotonated amine][H_2O]$$
(8)

To quantitatively establish this relationship, the data were analyzed in a traditional pseudo-first-order fashion, where k'' is plotted against the excess concentration (unprotonated amine in this case) to yield the overall rate constant k as the slope of the line. The particular analysis for the aniline-1,2-epoxybutane reaction is given in Figure 5 (the lowest pH data point for aniline from Figure 4 does not appear in Figure 5 due to the existence of an immeasurably small rate constant for this pH).

The overall rate constants k (for which the constant water concentration term is subsumed) for the formation of the primary amine addition products from 1,2-epoxybutane were determined to be 1.64 \pm 0.11 (1 σ) and 1.56 \pm 0.19 \times 10⁻⁴ M⁻¹ s⁻¹, respectively, for *t*-butylamine and aniline. Therefore, within the uncertainty of the measurements, there is no measurable difference in the rate of reaction of 1,2-epoxybutane with *t*-butylamine and aniline, which suggests that the amine structure does not sensitively affect the rate of the epoxide—amine reactions.

Amine Nucleophilic Strength Determination. At high pH values, all of the epoxide reactant is converted to the primary amine addition product, and no hydrolysis product is observed. Figure 2 suggests that over the pH = 8-12 range,



Figure 5. Pseudo-first-order determination of the overall rate constant for the reaction between aniline and 1,2-epoxybutane.

wherein the *t*-butylamine protonation equilibrium is important, the competing hydrolysis reaction may switch from a general acid-catalyzed mechanism at the lower pH to a faster basecatalyzed mechanism at the higher pH. However, since hydrolysis products are only observed at lower pH values, the appearance of hydrolysis products at the lower pH values must be due to a difference in nucleophile concentrations (unprotonated amine concentrations drop as the pH as lowered, while water concentrations stay constant) rather than to a change in mechanism. The relative nucleophilic strength of the amines as compared to water were calculated using reactant (X) and product (Y) mole fractions where

$$\frac{\text{amine nucleophilic strength}}{\text{water nucleophilic strength}} = \frac{(Y_{\text{amine product}}/X_{\text{unprotonated amine}})}{(Y_{\text{hydrolysis product}}/X_{\text{H}_{2}\text{O}})}$$
(9)

The $Y_{\text{amine product}}$ and $Y_{\text{hydrolysis product}}$ values were determined from NMR integrations, and $X_{\text{unprotonated amine}}$ and $X_{\text{H}_2\text{O}}$ values were determined from equilibrium calculations for the relevant pH values. Figure 6 shows the results of this analysis for aniline, where the slope corresponds to the relative nucleophilic strength of aniline as compared to water:

Because of the rigorous relationship between the formation of the amine product and the unprotonated amine concentration, the regression equation was forced through the origin. The measured nucleophilic strengths were found to be 3000 and 900 for *t*-butylamine and aniline, respectively. Even in comparison to the negatively charged inorganic ions nitrate and sulfate, which have nucleophilic strengths relative to water ranging from 5 to 70,¹⁷ respectively, it is clear that these amines are extremely strong nucleophiles.

Epoxide Structure–Reactivity Effects. To explore the effect of epoxide structure on the kinetics of the amine nucleophilic addition reaction, other epoxides were selected for study on the basis of differing carbon substitution on the epoxide ring. A previous study on the hydrolysis kinetics of epoxides indicated that as the extent of carbon substitution on the epoxide ring increased, the hydrolysis rate constants also increased.³² One of the textbook mechanisms for nucleophilic addition reactions of epoxides is a sequential ring-opening step followed by a nucleophilic attack step (commonly known as the S_N1 mechanism), while the other textbook mechanism is a concerted ring-opening and nucleophilic attack step (com-



Figure 6. Nucleophilic strength determination for aniline with 1,2-epoxybutane.

monly known as the $S_N 2$ mechanism).³³ These two mechanisms are depicted for the acid-catalyzed case in Figure 7.

In the case of the S_N1 mechanism, the stability of the ringopened intermediate was used to rationalize structure– reactivity trends. For example, because it is known that tertiary carbocations are the most stable type of carbocation intermediate, the previously cited experimental result that epoxide hydrolysis is faster for more substituted epoxides was used to indicate the importance of the S_N1 character of tertiary epoxide reactions. Because of the instability of primary and secondary epoxides more likely react via an S_N2 -type mechanism. However, the epoxide hydrolysis kinetics literature indicates that these idealized mechanisms are likely too simple to explain actual kinetics trends and that some epoxides may react via a hybrid S_N1/S_N2 -type mechanism. 30,34,35 Table 1 contains the results of these experiments for the reactions of various epoxides with *t*-butylamine.

It is clear from these data that increasing carbon substitution on the epoxide ring leads to slower amine nucleophilic addition, with the case of the ditertiary substituted epoxide (2,3dimethyl-2,3-epoxybutane) being completely unreactive on the time scale (seven months) of the experiments. These results also suggest the likely importance of S_N2 character in the amine addition reactions; the more steric hindrance around the epoxide ring, the slower the amine addition reaction (the fact that primary nucleophilic addition is exclusively observed is also indicative of the likelihood of an S_N2-type mechanism). Note that because water is a catalyst in these reactions and because it was not possible to systematically vary water concentrations while keeping other important parameters constant, it was not possible to use a rate law determination to directly support the assertion of the dominance of S_N2 character in the mechanism of these reactions.

Potential Hydrolysis of Amine Addition Products. In previous work on organosulfates and organonitrates formed from epoxide reactions, it has been shown that some of these species are not stable against hydrolysis (nucleophilic substitution of nitrate or sulfate for water).^{17,19,36–38} Therefore, it is of interest to consider whether the amine addition products are stable against hydrolysis. Table 1 contains the computed



Figure 7. S_N1 (upper) and S_N2 (lower) nucleophilic addition mechanisms.





free energies of hydrolysis for the various amine addition products formed from reactions of 1,2-epoxybutane (the data used to compute these values are given in the Supporting Information). As was observed for the organosulfates and organonitrates,³⁸ these calculations generally indicate a higher thermodynamic propensity for hydrolysis for the most highly substituted amine products. However, as the computational method has an accuracy of only ~10 kJ mol⁻¹, these results are not unambiguous. Therefore, the amine addition products for the reaction of 1,2-epoxybutane with *t*-butylamine (under the

ambient basic conditions for these solutions) monitored for extended periods of time (three to five months) to experimentally assess their stability against hydrolysis. None of the amine addition products were observed to hydrolyze on these time scales. Therefore, the potential distribution of amine addition and hydrolysis (diol) products is expected to be determined solely by nucleophilic competition effects in the epoxide reactions themselves and not due to the hydrolysis of amine addition products to diols at later times. The potential hydrolysis of other systems and at lower pH values was not experimentally investigated.

Amine Structure–Reactivity Effects. To explore the effect of amine structure on the kinetics of the amine nucleophilic addition reaction, other amines were selected for study based on their differing carbon substitution characteristics. Table 2 contains the results of these experiments for the

Table 2. Amine +1,2-Epoxybutane Nucleophilic Addition Rate Constants

Amine	Amine pK _a	Product	k $(M^{-1}s^{-1})$
butylamine NH2	10.78	OH HN	5.94 x 10 ⁴
N H diethylamine	11.09	ОН	4.55 x 10 ⁻⁴
H ₂ N	10.68	н	1.64 x 10 ⁻⁴
NH ₂ aniline	4.70	NH OH	1.67 x 10 ⁻⁴
HO NH ₂ 4-amino-1-butanol (monoethanol amine; MEA)	9.50		2.16 x 10 ⁻⁴

reactions of 1,2-epoxybutane with various amines. While the effect of the amine structure on the nucleophilic addition rate constants is significantly less than the effect of the epoxide structure, it is clear that the more sterically hindered amines react somewhat more slowly.

Multifunctional Amine Structure–Reactivity Effects. To investigate whether multifunctional amines have different structure–reactivity properties than the monofunctional amines, the carbon dioxide capture fluid monoethanolamine (MEA) and the amino acid glycine were qualitatively investigated in their reactions with 1,2-epoxybutane (additionally, the nucleophilic addition rate constant was also measured for MEA and is reported in Table 2).

In the case of MEA, it is possible that the alcohol functional group could act as the nucleophile at low pH where the amino group's nucleophilic character has been deactivated by protonation. It is important to note that both of these functional groups are also in competition with solvent water as a nucleophile under the experimental conditions. A previous nucleophilic strength study of methanol and water in their nucleophilic addition reactions with methacrylic acid epoxide indicated that methanol was a slightly better nucleophile on a per-mole basis than was water.¹⁸ However, only primary amine addition products were observed at the high pH values where the unprotonated amine form was dominant, and only hydrolysis products were observed at the low pH values where the protonated amine form was dominant, thus indicating that the high-concentration solvent water was the better absolute nucleophile than the low-concentration alcohol group on MEA. Nonetheless, under lower water content conditions and low pH conditions, it is possible that MEA could use its alcohol group for nucleophilic addition reactions.

In the case of glycine, there are several ionization states possible as a function of pH. The amino group has a pK_a of 9.78, and the carboxylic group has a p K_a of 2.35.³¹ Therefore, at high pH values, the carboxylic acid group is deprotonated and the amino group is neutral, at intermediate pH values, both functional groups are charged (carboxylic acid group: deprotonated; amino acid group: protonated), and at low pH values, the carboxylic acid group is neutral and the amino group is protonated. Again, although the deprotonated carboxylic acid group might be expected to be a reasonably strong nucleophile as a negatively charged entity, no products were observed wherein glycine used its carboxylic group to perform nucleophilic addition on 1,2-epoxybutane. At high pH, only amine addition products were observed, at intermediate pH, both amine addition and hydrolysis products were observed, and at low pH, only hydrolysis products were observed. As for MEA, this result does not necessarily rule out that under lower water conditions and low pH conditions glycine could use its carboxylic acid group for nucleophilic addition reactions.

Therefore, it appears that these multifunctional amines can be thought of as possessing extremely strong amino nucleophilic strength for the pH ranges for which the amino group remains unprotonated, but that relatively low concentration alcohol and deprotonated carboxyl groups are not strong enough nucleophiles to compete with solvent water. In our previous work on the relative nucleophilic strengths of various reactants with methacrylic acid epoxide, we determined that methanol and acetic acid had similar nucleophilic strengths as compared to water.¹⁸ These previous results are consistent with the present finding that solvent water can outcompete alcohol and carboxyl groups in the nucleophilic addition reactions of the epoxides investigated in this work.

Atmospheric Implications. The mechanistic findings that the amine-epoxide nucleophilic addition reactions are watercatalyzed and that amines are extremely strong nucleophiles seems to suggest that these reactions may be more ubiquitous under atmospheric conditions than processes that are kinetically limited to acid-catalyzed conditions and utilize weaker nucleophiles (such as the acid-catalyzed epoxide reactions with water and sulfate that have previously been investigated as an explanation for the presence of isoprene-derived polyol and organosulfate species in SOA). While most of the amines studied in the present work are too volatile to partition significantly to atmospheric SOA, here we consider the potential reactivity of a hypothetical semivolatile amine that is present at 1 M SOA concentration. Using an average rate constant from Table 2 of 3×10^{-4} M⁻¹ s⁻¹ this amine would be expected to have a lifetime of ~ 1 h in its reaction with 1,2epoxybutane, which is quite fast enough to be an atmospherically significant SOA phase reaction. Since the rate constants were not found to be very sensitive to the structure of the

amine, actual semi- or nonvolatile amines present in the atmosphere would likely have epoxide reaction rate constants similar to the amines studied in this work. However, the most important atmospherically relevant epoxide, the isoprenederived species 2-methyl-2,3-epoxy-1,4-butanediol (IEPOX), resembles 2-methyl-2,3-epoxybutane in its carbon substitution environment. Table 1 indicates that this change in carbon substitution would be expected to decrease the amine nucleophilic addition rate constant by a factor of 200; therefore, a better estimate for the lifetime of an amine nucleophilic addition reaction with IEPOX is on the order of one week, which is on the order of the lifetime of an SOA particle. Therefore, it appears that amine—epoxide reactions are kinetically feasible on atmospheric SOA.

However, there is a more general situation that will likely circumvent the importance of amine reactions with epoxides on SOA. While very weakly basic amines like aniline can have significant unprotonated concentrations at acidic pH values (see Figure 4), most atmospherically relevant amines are aliphatic amines and thus stronger bases (like *t*-butylamine) and are not likely to have significant unprotonated concentrations below pH = 7. Therefore, most atmospheric amines are expected to exist in protonated form on the mostly acidic SOA^{39,40} thought to be prevalent in the atmosphere; in the protonated form, the amines are extremely weak nucleophiles and may not compete well with the other nucleophilic species commonly present on SOA (such as water and sulfate). Therefore, it seems unlikely that amine nucleophilic reactions with epoxides are important on acidic SOA.

CONCLUSION

In agreement with a previous finding, the amine-epoxide reactions were found to be water-catalyzed and not directly dependent on the pH of the reaction environment. At pH values higher than the pK_a of the particular amine, the amineepoxide reactions were extremely efficient, outcompeting hydrolysis reactions even for conditions where water was the solvent and the amine was a relatively low concentration solute. This finding was rationalized by measurements that showed that the relative nucleophilic strength of amines relative to water was on the order of 1000, while the nucleophilic strength of protonated amines (which are predominant when $pH < pK_a$) was negligible. The epoxide carbon substitution environment was found to have a large effect on the measured rate constants (more substituted epoxides had slower rate constants), while the amine carbon substitution environment had a much more limited effect. While the amine-epoxide rate constants are large enough such that amine-epoxide reactions may be kinetically feasible for isoprene-derived epoxides and high amine SOA concentrations, most atmospheric amines are expected to be present in protonated form on the largely acidic SOA found in the atmosphere and thus are expected to be largely unreactive toward epoxides.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.5b07852.

Full ¹H NMR spectral assignments of the reactants and products and computational chemistry results for geometries and energies. (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: mjelrod@oberlin.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation under Grant No. 1153861.

REFERENCES

(1) Pope, C. A., III; Dockery, D. W. Health Effects of Fine Particulate Air Pollution: Lines That Connect. *J. Air Waste Manage. Assoc.* **2006**, *56*, 709–742.

(2) Watson, J. G. Visibility: Science and Regulation. J. Air Waste Manage. Assoc. 2002, 52, 628-713.

(3) Hallquist, M.; Wenger, J. C.; Baltensperger, U.; Rudich, Y.; Simpson, D.; Claeys, M.; Dommen, J.; Donahue, N. M.; George, C.; Goldstein, A. H.; et al. The Formation, Properties and Impact of Secondary Organic Aerosol: Current and Emerging Issues. *Atmos. Chem. Phys.* **2009**, *9*, 5155–5236.

(4) Ge, X.; Wexler, A. S.; Clegg, S. L. Atmospheric Amines – Part I. A Review. Atmos. Environ. 2011, 45, 524–546.

(5) Price, D. J.; Clark, C. H.; Tang, X.; Cocker, D. R.; Purvis-Roberts, K. L.; Silva, P. J. Proposed Chemical Mechanisms Leading to Secondary Organic Aerosol in the Reactions of Aliphatic Amines with Hydroxyl and Nitrate Radicals. *Atmos. Environ.* **2014**, *96*, 135–144.

(6) De Haan, D. O.; Tolbert, M. A.; Jimenez, J. L. Atmospheric Condensed-Phase Reactions of Glyoxal with Methylamine. *Geophys. Res. Lett.* **2009**, *36*, L11819.

(7) You, Y.; Kanawade, V. P.; de Gouw, J. A.; Guenther, A. B.; Madronich, S.; Sierra-Hernández, M. R.; Lawler, M.; Smith, J. N.; Takahama, S.; Ruggeri, G.; et al. Atmospheric Amines and Ammonia Measured with a Chemical Ionization Mass Spectrometer (CIMS). *Atmos. Chem. Phys.* **2014**, *14*, 12181–12194.

(8) Nielsen, C. J.; Herrmann, H.; Weller, C. Atmospheric Chemistry and Environmental Impact of the Use of Amines in Carbon Capture and Storage (CCS). *Chem. Soc. Rev.* **2012**, *41*, 6684–6704.

(9) Worton, D. R.; Surratt, J. D.; LaFranchi, B. W.; Chan, A. W. H.; Zhao, Y.; Weber, R. J.; Park, J.-H.; Gilman, J. B.; de Gouw, J.; Park, C.; et al. Observational Insights into Aerosol Formation from Isoprene. *Environ. Sci. Technol.* **2013**, *47*, 11403–11413.

(10) Hu, W. W.; Campuzano-Jost, P.; Palm, B. B.; Day, D. A.; Ortega, A. M.; Hayes, P. L.; Krechmer, J. E.; Chen, Q.; Kuwata, M.; Liu, Y. J.; et al. Characterization of a Real-Time Tracer for Isoprene Epoxydiols-Derived Secondary Organic Aerosol (IEPOX-SOA) from Aerosol Mass Spectrometer Measurements. *Atmos. Chem. Phys. Discuss.* **2015**, *15*, 11223–11276.

(11) Lin, Y.-H.; Zhang, H.; Pye, H. O. T.; Zhang, Z.; Marth, W. J.; Park, S.; Arashiro, M.; Cui, T.; Budisulistiorini, S. H.; Sexton, K. G.; et al. Epoxide as a Precursor to Secondary Organic Aerosol Formation from Isoprene Photooxidation in the Presence of Nitrogen Oxides. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110*, 6718–6723.

(12) Surratt, J. D.; Chan, A. W. H.; Eddingsaas, N. C.; Chan, M.; Loza, C. L.; Kwan, A. J.; Hersey, S. P.; Flagan, R. C.; Wennberg, P. O.; Seinfeld, J. H. Reactive Intermediates Revealed in Secondary Organic Aerosol Formation from Isoprene. *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107*, 6640–6645.

(13) Xu, L.; Guo, H.; Boyd, C. M.; Klein, M.; Bougiatioti, A.; Cerully, K. M.; Hite, J. R.; Isaacman-VanWertz, G.; Kreisberg, N. M.; Knote, C.; et al. Effects of Anthropogenic Emissions on Aerosol Formation from Isoprene and Monoterpenes in the Southeastern United States. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 37–42.

(14) Lin, Y. H.; Knipping, E. M.; Edgerton, E. S.; Shaw, S. L.; Surratt, J. D. Investigating the Influences of SO_2 and NH_3 Levels on Isoprene-Derived Secondary Organic Aerosol Formation Using Conditional Sampling Approaches. *Atmos. Chem. Phys.* **2013**, *13*, 8457–8470.

(15) Budisulistiorini, S. H.; Li, X.; Bairai, S. T.; Renfro, J.; Liu, Y.; Liu, Y. J.; McKinney, K. A.; Martin, S. T.; McNeill, V. F.; Pye, H. O. T.; et al. Examining the Effects of Anthropogenic Emissions on Isoprene-Derived Secondary Organic Aerosol Formation During the 2013 Southern Oxidant and Aerosol Study (SOAS) at the Look Rock, Tennessee Ground Site. *Atmos. Chem. Phys.* **2015**, *15*, 8871–8888.

(16) Budisulistiorini, S. H.; Canagaratna, M. R.; Croteau, P. L.; Marth, W. J.; Baumann, K.; Edgerton, E. S.; Shaw, S. L.; Knipping, E. M.; Worsnop, D. R.; Jayne, J. T.; et al. Real-Yime Continuous Characterization of Secondary Organic Aerosol Derived from Isoprene Epoxydiols in Downtown Atlanta, Georgia, Using the Aerodyne Aerosol Chemical Speciation Monitor. *Environ. Sci. Technol.* 2013, 47, 5686–5694.

(17) Mael, L. E.; Jacobs, M. I.; Elrod, M. J. Organosulfate and Nitrate Formation and Reactivity from Epoxides Derived from 2-Methyl-3-Buten-2-Ol. J. Phys. Chem. A 2015, 119, 4464–4472.

(18) Birdsall, A. W.; Miner, C. R.; Mael, L. E.; Elrod, M. J. Mechanistic Study of Secondary Organic Aerosol Components Formed from Nucleophilic Addition Reactions of Methacrylic Acid Epoxide. *Atmos. Chem. Phys.* **2014**, *14*, 12951–12964.

(19) Darer, A. I.; Cole-Filipiak, N. C.; O'Connor, A. E.; Elrod, M. J. Formation and Stability of Atmospherically Relevant Isoprene-Derived Organosulfates and Organonitrates. *Environ. Sci. Technol.* **2011**, *45*, 1895–1902.

(20) Carey, F. A.; Giuliano, R. M. Organic Chemistry; McGraw-Hill: New York, 2013.

(21) Nguyen, T. B.; Coggon, M. M.; Bates, K. H.; Zhang, X.; Schwantes, R. H.; Schilling, K. A.; Loza, C. L.; Flagan, R. C.; Wennberg, P. O.; Seinfeld, J. H. Organic Aerosol Formation from the Reactive Uptake of Isoprene Epoxydiols (IEPOX) onto Non-Acidified Inorganic Seeds. *Atmos. Chem. Phys.* **2014**, *14*, 3497–3510.

(22) Azizi, N.; Saidi, M. R. Highly Chemoselective Addition of Amines to Epoxides in Water. *Org. Lett.* **2005**, *7*, 3649–3651.

(23) Krężel, A.; Bal, W. A Formula for Correlating Pka Values Determined in D₂O and H₂O. J. Inorg. Biochem. 2004, 98, 161–166.

(24) Froese, R. D. J.; Humbel, S.; Svensson, M.; Morokuma, K. IMOMO (G2MS): A New High-Level G2-Like Method for Large Molecules and Its Applications to Diels-Alder Reactions. *J. Phys. Chem. A* **1997**, *101*, 227–233.

(25) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. Assessment of Gaussian-2 and Density Functional Theories for the Computation of Enthalpies of Formation. *J. Chem. Phys.* **1997**, *106*, 1063–1079.

(26) Tomasi, J.; Mennucci, B.; Cammi, R. Quantum Mechanical Continuum Solvation Models. *Chem. Rev.* 2005, *105*, 2999–3093.

(27) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M. et al. *Gaussian 03*; Gaussian, Inc: Wallingford, CT, 2003.

(28) Cappa, C. D.; Elrod, M. J. A Computational Investigation of the Electron Affinity of CO₃ and the Thermodynamic Feasibility of $CO_3^{-}(H_2O)_N$ + ROOH Reactions. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2986–2994.

(29) Minerath, E. C.; Elrod, M. J. Assessing the Potential for Diol and Hydroxy Sulfate Ester Formation from the Reaction of Epoxides in Tropospheric Aerosols. *Environ. Sci. Technol.* **2009**, *43*, 1386–1392.

(30) Whalen, D. L. Mechanisms of Hydrolysis and Rearrangements of Epoxides. *Adv. Phys. Org. Chem.* **2005**, *40*, 247–298.

(31) Toxicology Data Network. http://toxnet.nlm.nih.gov/cgi-bin/ sis/htmlgen?HSDB. (Accessed September 18, 2015).

(32) Cole-Filipiak, N. C.; O'Connor, A. E.; Elrod, M. J. Kinetics of the Hydrolysis of Atmospherically Relevant Isoprene-Derived Hydroxy Epoxides. *Environ. Sci. Technol.* **2010**, *44*, 6718–6723.

(33) Loudon, G. M. Organic Chemistry; Addison-Wesley: Reading, MA, 1984.

(34) Piletic, I. R.; Edney, E. O.; Bartolotti, L. J. A Computational Study of Acid Catalyzed Aerosol Reactions of Atmospherically Relevant Epoxides. *Phys. Chem. Chem. Phys.* **2013**, *15*, 18065–18076.

(35) Eddingsaas, N. C.; VanderVelde, D. G.; Wennberg, P. O. Kinetics and Products of the Acid-Catalyzed Ring-Opening of Atmospherically Relevant Butyl Epoxy Alcohols. *J. Phys. Chem. A* **2010**, *114*, 8106–8113.

(36) Jacobs, M. I.; Burke, W. J.; Elrod, M. J. Kinetics of the Reactions of Isoprene-Derived Hydroxynitrates: Gas Phase Epoxide Formation and Solution Phase Hydrolysis. *Atmos. Chem. Phys.* **2014**, *14*, 8933–8946.

(37) Bleier, D. B.; Elrod, M. J. Kinetics and Thermodynamics of Atmospherically Relevant Aqueous Phase Reactions of A-Pinene Oxide. J. Phys. Chem. A 2013, 117, 4223–4232.

(38) Hu, K. S.; Darer, A. I.; Elrod, M. J. Thermodynamics and Kinetics of the Hydrolysis of Atmospherically Relevant Organonitrates and Organosulfates. *Atmos. Chem. Phys.* **2011**, *11*, 8307–8320.

(39) Hennigan, C. J.; Izumi, J.; Sullivan, A. P.; Weber, R. J.; Nenes, A. A Critical Evaluation of Proxy Methods Used to Estimate the Acidity of Atmospheric Particles. *Atmos. Chem. Phys.* **2015**, *15*, 2775–2790.

(40) Guo, H.; Xu, L.; Bougiatioti, A.; Cerully, K. M.; Capps, S. L.; Hite, J. R.; Carlton, A. G.; Lee, S. H.; Bergin, M. H.; Ng, N. L.; et al. Fine-Particle Water and pH in the Southeastern United States. *Atmos. Chem. Phys.* **2015**, *15*, 5211–5228.