

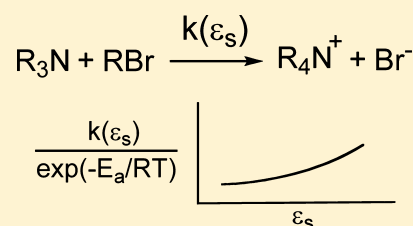
## Application of the Compensated Arrhenius Formalism To Explain the Dielectric Constant Dependence of Rates for Menschutkin Reactions

Matt Petrowsky, Daniel T. Glatzhofer, and Roger Frech\*

Department of Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma 73019, United States

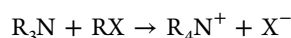
## Supporting Information

**ABSTRACT:** The dependence of the reaction rate on solvent dielectric constant is examined for the reaction of trihexylamine with 1-bromohexane in a series of 2-ketones over the temperature range 25–80 °C. The rate constant data are analyzed using the compensated Arrhenius formalism (CAF), where the rate constant assumes an Arrhenius-like equation that also contains a dielectric constant dependence in the exponential prefactor. The CAF activation energies are substantially higher than those obtained using the simple Arrhenius equation. A master curve of the data is observed by plotting the prefactors against the solvent dielectric constant. The master curve shows that the reaction rate has a weak dependence on dielectric constant for values approximately less than 10 and increases more rapidly for dielectric constant values greater than 10.

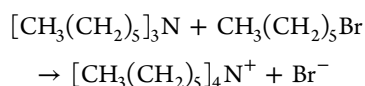


## 1. INTRODUCTION

The kinetics of Menschutkin reactions have been studied for over a century, and it is well-known that the rate of reaction is strongly dependent on the solvent in which the reaction occurs.<sup>1</sup> In a Menschutkin reaction, a tertiary amine reacts with an alkyl halide to form a tetraalkylammonium halide salt:

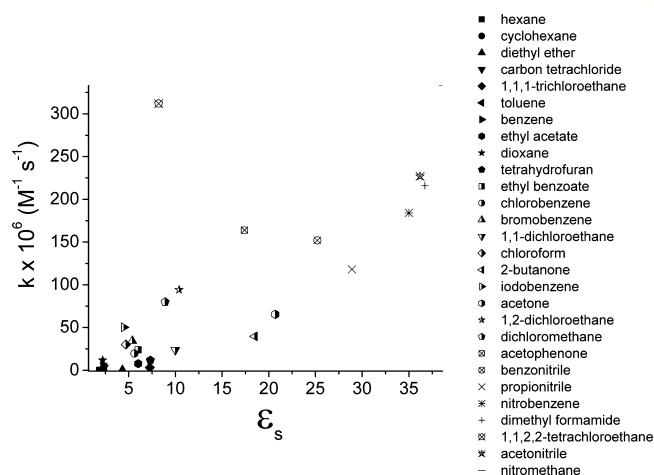


where R is an alkyl group and X is a halide. The specific Menschutkin reaction examined in this work is



Because the reactants are neutral and the products are ionic, it is expected that an increase in solvent permittivity should increase the reaction rate of these reactions.<sup>2</sup> Figure 1 consists of literature rate constants  $k$  (compiled in an excellent book by Connors<sup>1</sup>) at 25 °C for the Menschutkin reaction of triethylamine and ethyl iodide in a number of different solvents. Plotting the rate constant versus solvent dielectric constant  $\epsilon_s$  shows the general trend of increasing rate constant with solvent permittivity, but there is tremendous scatter in the data and it appears that the rate constant does not have a well-defined functional relationship with the dielectric constant.

Data like that shown in Figure 1 have led to the conclusion that the dielectric constant by itself cannot account for the solvent influence on reaction rate. Although this statement is true in general, we show here that the dielectric constant does explain the solvent influence when a family of solvents is considered. A solvent family consists of compounds that have the same functional group and differ only in the length of an alkyl chain attached to the functional group. For example, this work considers the family of 2-ketones consisting of 2-butanone, 2-pentanone, 2-heptanone, 2-octanone, and 2-



**Figure 1.** Rate constant versus solvent dielectric constant for the Menschutkin reaction of triethylamine and ethyl iodide in a number of different solvents at 25 °C. These data are taken from Table 8–5 in ref 1.

nonanone. The dipole moment changes very little going from member to member in a solvent family, and therefore the difference in dielectric constant between members at constant temperature is due to the difference in dipole density.<sup>3</sup>

The well-known dielectric constant dependence for Menschutkin reactions in conjunction with the commonly accepted idea that these reactions result from a thermally activated process, leads us to consider this class of reactions in terms of the compensated Arrhenius formalism (CAF). The CAF has been previously applied to mass and charge transport

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phenomena by assuming the temperature-dependent transport property has an Arrhenius-like form that also contains a static dielectric constant dependence in the exponential prefactor.<sup>4–7</sup> The analogous expression for the temperature-dependent rate constant  $k(T)$  of a chemical reaction is

$$k(T) = k_0(\epsilon_s(T)) \exp(-E_a/RT) \quad (1)$$

where  $E_a$  is the activation energy,  $T$  is temperature,  $R$  is the gas constant, and  $k_0(\epsilon_s(T))$  is the exponential prefactor. The prefactor is written to show that its temperature dependence is due only to the inherent temperature dependence of the static dielectric constant of the solvent, which follows from a key postulate of the CAF.<sup>4</sup> The activation energy is calculated through a scaling procedure that cancels the prefactor. In this procedure, each temperature-dependent rate constant  $k(T)$  at temperature  $T$  for a particular solvent is divided by a reference rate constant  $k_r(T_r)$  at temperature  $T_r$ . The reference rate constants are determined from an isothermal plot of  $k$  vs  $\epsilon_s$  that consists of data from each member of the solvent family at  $T_r$ . The reference rate constant  $k_r(T_r)$  is chosen to have the same value of  $\epsilon_s$  as  $k(T)$ . The scaling procedure has been described in detail elsewhere,<sup>4,6,8</sup> and the final result of this procedure is

$$\ln \left[ \frac{k(T)}{k_r(T_r)} \right] = -\frac{E_a}{RT} + \frac{E_a}{RT_r} \quad (2)$$

where the activation energy is obtained from either the slope or intercept of a plot of  $\ln[k(T)/k_r(T_r)]$  vs  $T^{-1}$ .

This work applies the CAF to temperature-dependent rate constants for the reaction of trihexylamine with 1-bromohexane in the aforementioned ketones over the temperature range 25–80 °C (the temperature range is reduced for some members). It will be shown that the CAF activation energy is substantially higher than that obtained from a simple Arrhenius plot of the data. Furthermore, the prefactors will be shown to follow a well-defined functional relationship with the solvent dielectric constant. Finally, we will explain why conventional reaction field approaches do not result in such well-defined correlation in the data.

## 2. EXPERIMENTAL METHODS

**2.1. Chemicals.** 2-Butanone (99%), 2-pentanone (99+%), 2-heptanone (99%), 2-octanone (98%), and 2-nonanone (98+%) were obtained from Alfa Aesar, and trihexylamine (96%), 1-bromohexane (98%), and tetrahexylammonium bromide (99%) were obtained from Aldrich. All chemicals were used as received. The chemicals were stored and all reactions were performed in a glovebox ( $\leq 5$  ppm  $\text{H}_2\text{O}$ ) under a nitrogen atmosphere.

**2.2. Instruments.** Resistances were measured with an Accumet Basic AB30 conductivity meter using an Accumet glass probe with  $0.1 \text{ cm}^{-1}$  cell constant. The capacitance was measured using a HP 4192A impedance analyzer that swept a frequency range from 1 kHz to 13 MHz. The sample holder was an Agilent 16452A liquid test fixture. The static dielectric constant  $\epsilon_s$  was calculated from the measured capacitance  $C$  through the equation  $\epsilon_s = \alpha \times C \times C_0^{-1}$ , where  $\alpha$  is a variable to account for stray capacitance and  $C_0$  is the atmospheric capacitance.<sup>9</sup> The reproducibility of the impedance analyzer has been previously estimated by measuring the capacitance of a 0.04 M TbaTf-1-octanol solution eight times. The uncertainty was 0.38%, where the uncertainty is defined as the capacitance standard deviation divided by the average capacitance. The

capacitance precision is expected to be even better for pure ketone liquids because they are nonconducting. A Huber ministat 125 was used to regulate the temperature of an oil bath from 25 to 80 °C. The bath was maintained at a constant temperature to within  $\pm 0.1$  °C of the set temperature.

**2.3. Procedure.** 1-Bromohexane–ketone (0.100 mol/kg) and trihexylamine–ketone (0.100 mol/kg) solutions were prepared for a particular ketone and then stirred magnetically. It should be noted that we intentionally chose the molality concentration scale instead of the more commonly used molarity scale because molalities are independent of temperature.<sup>10</sup> Exactly 5 g of each solution was placed into separate sealed vials and allowed to equilibrate in the oil bath at the given reaction temperature. These two solutions were then added together and stirred vigorously for approximately 1 min, giving 0.0500 mol/kg as the initial reactant concentrations. This initial reactant concentration was used for all reactions. The mixture was then added to a glass test tube, and the resistance probe was placed in the test tube, with great care being taken to ensure that the electrodes were completely immersed in the solution. The test tube was then immersed in the oil bath and the solution resistance was followed with time. The delay was approximately 1 min between reactant combination and the start of timing, whereas the elapsed time for these kinetics experiments ranged from 229 min (in 2-butanone at 45 °C) to 5828 min (in 2-octanone at 25 °C). An O-ring was placed over the probe so that a seal was formed with the test tube that helped prevent solvent evaporation. The measured resistances were converted to tetrahexylammonium bromide concentrations via a calibration curve. The calibration curve consisted of tetrahexylammonium bromide–ketone solutions at six different salt concentrations in the range from  $1.00 \times 10^{-5}$  to  $1.10 \times 10^{-4}$  mol/kg. The resistance was measured for each solution at the given reaction temperature, the tetrahexylammonium bromide concentration was plotted against the resistance, and these data were then fit to a power function of the form

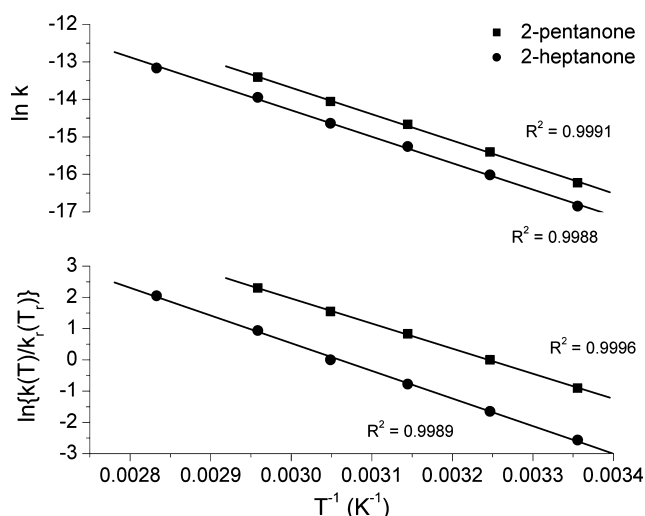
$$\text{concentration} = A(\text{resistance})^{-B}$$

where  $A$  and  $B$  are constants.

The reactant concentrations were calculated by subtracting the tetrahexylammonium bromide concentrations from 0.0500 mol/kg. Menschutkin reactions are well-known to follow second-order kinetics,<sup>11</sup> and plots of reciprocal reactant concentration versus time resulted in a linear relationship. The rate constant is equivalent to the slope of the line. These reactions were followed only up to 0.2% completion to avoid the effects of the reverse reaction. The probe was submerged in two different 5 mL aliquots of the particular ketone and wiped with a paper towel before immersing in the solution for the reaction run or calibration curve to prevent salt contamination that would adversely affect the resistance measurement. The procedure described above was applied to reproduce the literature result for the reaction of triethylamine and ethyl iodide in acetonitrile at 25 °C. The rate constant was calculated to be  $2.27 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ , which is identical to the literature value.<sup>12</sup>

## 3. RESULTS AND DISCUSSION

**3.1. Activation Energy.** The top half of Figure 2 shows simple Arrhenius plots of rate constant data over the temperature range 25–80 °C for the reaction of trihexylamine with 1-bromohexane in either 2-pentanone or 2-heptanone,

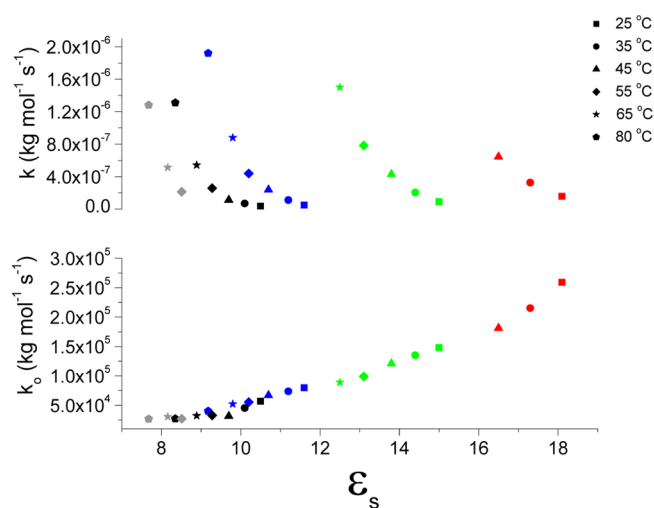


**Figure 2.** Top: simple Arrhenius plots of rate constant data over the temperature range 25–80 °C for the reaction of trihexylamine with 1-bromohexane in either 2-pentanone or 2-heptanone, respectively. Bottom: compensated Arrhenius plots of rate constant data for 2-pentanone ( $T_r = 35$  °C) and 2-heptanone ( $T_r = 55$  °C), respectively.

respectively. The bottom half of Figure 2 gives compensated Arrhenius plots of these data for 2-pentanone scaled to reference data at 35 °C and 2-heptanone scaled to reference data at 55 °C, respectively. Both simple Arrhenius and compensated Arrhenius plots are linear but result in different activation energies. The average CAF activation energy for the family of ketones is calculated to be  $70 \pm 1$  kJ/mol, and the average simple Arrhenius activation energy for 2-pentanone, 2-heptanone, and 2-octanone is  $59 \pm 1$  kJ/mol. The individual simple Arrhenius and compensated Arrhenius  $E_a$  values are summarized in the Supporting Information. The CAF  $E_a$  value is substantially higher than the simple Arrhenius value, which is a trend also observed in transport phenomena<sup>5,13</sup> and explained by accounting for the contribution of the polarization energy.<sup>14</sup>

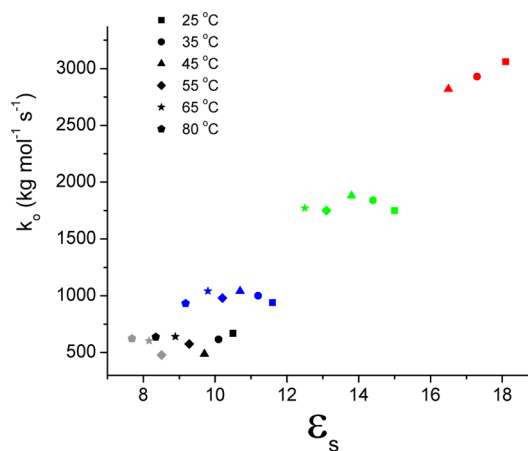
**3.2. Exponential Prefactor.** The CAF assumes that the dielectric constant dependence is contained in the prefactor, and therefore the influence of solvent polarity on rate is observed by plotting the prefactor versus  $\epsilon_s$ . The prefactors are calculated from eq 1 by dividing the rate constants at each temperature by the Boltzmann factor  $\exp(-E_a/RT)$ , where the average CAF activation energy is used for  $E_a$ . The top half of Figure 3 shows that plotting the rate constant against the dielectric constant gives five separate curves with each curve depicting the temperature dependent data for a particular ketone member. The rate constant increases exponentially with temperature, which is a trend that is commonly observed.<sup>15</sup> A single master curve results by dividing the rate constant data by  $\exp(-E_a/RT)$ , and then plotting this quantity against  $\epsilon_s$  (bottom of Figure 3). The formation of a master curve supports the core postulate of the CAF by demonstrating that the prefactor exhibits a distinct functional dependence on the dielectric constant. These prefactor data show that the dielectric constant has only a small influence on the rate for  $\epsilon_s$  values less than approximately 10. However, for larger values of the dielectric constant the reaction rate increases to a much greater extent as  $\epsilon_s$  increases. We have observed similar master curves for temperature-dependent transport data.<sup>3,5–7,16,17</sup>

It is important to emphasize that a master curve is only observed for  $E_a$  values in a narrow range from about 66 to 72



**Figure 3.** Top: rate constant versus dielectric constant at six different temperatures for the reaction of trihexylamine with 1-bromohexane in 2-butanone (red), 2-pentanone (green), 2-heptanone (blue), 2-octanone (black), or 2-nonanone (gray). Bottom: rate constant data from the top divided by  $\exp(-E_a/RT)$  using  $E_a = 70$  kJ/mol, and then plotted against the dielectric constant.

kJ/mol. The average CAF activation energy falls roughly in the center of this range, whereas the activation energies obtained from simple Arrhenius plots of the data are much lower in value. Figure 4 underscores the necessity of using compensated



**Figure 4.** Prefactor versus dielectric constant, where the prefactors were calculated from the rate constant data in Figure 3 using the simple Arrhenius  $E_a$  value for 2-heptanone and 2-octanone (59 kJ/mol). The ketone members are represented by the same color as shown in Figure 3

Arrhenius  $E_a$  values to calculate the prefactor by showing prefactor data that are calculated using the simple Arrhenius activation energy obtained for 2-heptanone and 2-octanone (59 kJ/mol). The data in Figure 4 are scattered and fail to show a simple correlation with the dielectric constant.

**3.3. Origin of  $\epsilon_s$  Dependence.** The influence of the dielectric constant on reaction rate has been attributed to the effect of the reaction field.<sup>1,2</sup> Each molecule in a polar liquid is a dipole, and any given dipole experiences a net field from the surrounding dipoles called the reaction field. The resulting polarization energy affects the energy of the transition state. Although we do agree that the dielectric constant dependence

of the reaction rate is due to the presence of the reaction field, we disagree with the origin of the dielectric constant dependence in a conventional analysis of rate constant data. Kinetic data are often explained using a simplified model of the polarization energy given as<sup>18,19</sup>

$$W = -\frac{\mu^2}{r^3} \left( \frac{\epsilon_s - 1}{2\epsilon_s + 1} \right) \quad (3)$$

where  $W$  is the polarization energy (i.e., the contribution of the free energy due to the transfer of a dipole from a medium with  $\epsilon_s = 1$  to a medium of dielectric constant  $\epsilon_s$ ),  $\mu$  is the molecular dipole moment, and  $r$  is the molecular radius. Kinetics data have been interpreted by plotting the free energy of activation or rate constant against the quantity  $(\epsilon_s - 1)/(2\epsilon_s + 1)$  in eq 3, but it is well-known that these types of plots often show poor correlation in the data.<sup>1</sup> However, it has been shown that an extension of the above model to a collection of  $N_A$  polarizable molecules results in the following expression for the polarization energy:<sup>20</sup>

$$W = -\frac{4\pi N_d N_A}{3} \left( \frac{\epsilon_s - 1}{2\epsilon_s + \epsilon_\infty} \right) \left( \frac{\epsilon_\infty + 2}{3} \right) \mu^2 \quad (4)$$

where  $\epsilon_\infty$  is the high frequency value of the real part of the dielectric constant,  $N_A$  is Avogadro's constant, and  $N_d$  is the dipole density. The dipole density is expressed as  $N_d = dM^{-1}N_A$ , where  $d$  is density and  $M$  is the molecular weight of the liquid. It should be emphasized that because the molecular radius is a fixed distance, the volume dependence given in the denominator of eq 3 has no temperature dependence whereas the dipole density in eq 4 is a temperature-dependent system property. We contend that the dielectric constant dependence of the rate constant is poorly described by the quantity  $(\epsilon_s - 1)/(2\epsilon_s + 1)$ , and in fact this quantity changes very little for the ketone data analyzed here. Table 1 provides data demonstrating that this quantity changes only slightly over the temperature range 25–80 °C as well as isothermally from member to member in the ketone family. These results indicate that the temperature dependence of the polarization energy given by eq 4 is due to the dipole density because  $\epsilon_\infty$  and  $\mu$  have negligible temperature dependence. The origin of the  $\epsilon_s$  dependence in the rate constant prefactor is explained analogously to that for transport properties. We have previously shown that the temperature dependence of a transport property  $A$  can be represented with an Arrhenius-like expression of the form  $A = A_0 \exp(-E_a/RT)$ , where  $A_0 \propto \exp(-W/RT)$ .<sup>14</sup> Because the temperature dependence of the polarization energy  $W$  is given by  $N_d$  as described above, the temperature dependence of the prefactor can be expressed as  $A_0 \propto \exp(BN_d/T)$ , where  $B$  is a temperature-independent constant. Onsager has demonstrated that  $N_d T^{-1}$  represents the temperature dependence of  $\epsilon_s$  for aprotic, polar liquids through the equation<sup>21</sup>

$$\epsilon_s = \frac{2\pi N_d \mu^2}{9kT} (\epsilon_\infty + 2)^2 \quad (5)$$

Therefore, the temperature dependence of the prefactor is given as  $A_0 \propto \exp(C\epsilon_s)$ , where  $C$  is a temperature-independent constant. By analogy to transport data, we postulate that the dielectric constant dependence of the rate constant prefactor is represented by  $k_0 \propto \exp(D\epsilon_s)$ , where  $D$  is constant. Consequently, the factor  $\exp(-W/RT) \propto \exp(D\epsilon_s)$  leads to

**Table 1. Temperature-Dependent Values of  $\epsilon_s$  and  $(\epsilon_s - 1)/(2\epsilon_s + 1)$  for Pure 2-Butanone, 2-Pentanone, 2-Heptanone, 2-Octanone, and 2-Nonanone**

temperature (°C)	$\epsilon_s$	$(\epsilon_s - 1)/(2\epsilon_s + 1)$
2-Butanone		
25	18.1	0.460
35	17.3	0.458
45	16.5	0.456
2-Pentanone		
25	15.0	0.452
35	14.4	0.450
45	13.8	0.447
55	13.1	0.445
65	12.5	0.442
2-Heptanone		
25	11.6	0.438
35	11.2	0.436
45	10.7	0.433
55	10.2	0.430
65	9.80	0.427
80	9.18	0.422
2-Octanone		
25	10.5	0.432
35	10.1	0.429
45	9.70	0.426
55	9.28	0.423
65	8.89	0.420
80	8.35	0.415
2-Nonanone		
55	8.51	0.417
65	8.16	0.413
80	7.68	0.408

the dielectric constant dependence of the rate constant instead of the quantity  $(\epsilon_s - 1)/(2\epsilon_s + 1)$ .

#### 4. CONCLUSIONS

We have shown here that the dielectric constant dependence on the reaction rate of a Menshutkin reaction is accounted for by writing the rate constant as an Arrhenius-like expression that also includes a dielectric constant dependence in the exponential prefactor. The dielectric constant dependence is observed by plotting the prefactors versus  $\epsilon_s$  for a family of ketones. It is expected that a master curve of the data will result for other solvent families, although the CAF may not work as well for protic families as the data presented here. Hydrogen bonding interactions may affect the rate in one family member differently than another family member, and it has been observed that rate constants for Menshutkin reactions in 1-alcohols do not always follow a consistent trend with alkyl chain length.<sup>1,11</sup> It should be noted that the CAF does describe transport phenomena well in protic systems, which emphasizes the difference between time-dependent reaction rates and equilibrium mass/charge transport properties. The large activation energies and correspondingly small rate constants for the kinetic data presented here indicate that these reactions are obviously not diffusion-controlled. Therefore, the CAF does not work for kinetic data simply because it also describes diffusion well in polar liquids. In fact, the CAF activation energies presented here for a chemical reaction are much larger than those obtained from diffusion coefficient data for a wide variety of polar liquids.<sup>3</sup> The CAF explains both kinetic and



transport phenomena well because in both cases it is the effect of the polarization energy due to the reaction field of the permanent dipoles that must be accounted for via the dielectric constant to have a complete description of the temperature dependence of these data.

The CAF also offers implications for other kinetic problems that have not been definitively resolved. For example, simple Arrhenius plots of rate constant data are observed to be nonlinear for some systems.<sup>22</sup> It has been argued that curvature in an Arrhenius plot results either from temperature-dependent enthalpies/entropies of activation or because the reaction does not occur in a single step but instead consists of multiple elementary reactions.<sup>15</sup> However, we have previously shown that the CAF scaling procedure compensates for the temperature dependence in the prefactor for transport data so that a curved Arrhenius plot becomes linear.<sup>4,17</sup> It is possible that this scaling procedure would work in a similar fashion for non-Arrhenius kinetic data resulting from a single step reaction. Some reactions with no solvent effect (gas phase) exhibit non-Arrhenius behavior, which is attributed to the multistep nature of the reaction.<sup>23,24</sup> There is disagreement in the literature over whether Menschutkin reactions occur as a single step or whether there are multiple steps with an ion pair intermediate.<sup>11,25</sup> The formation of a charge-protected product can greatly aid in the mechanistic identification of a reaction. The product of the reaction studied here, tetrahexylammonium bromide, provides a good example. The four hexyl groups surrounding the nitrogen atom of the tetrahexylammonium cation most likely prevents any discrete, ionic coordination from occurring with the bromide anion. Spectroscopic data have indicated that this is the case for many tetrabutylammonium-containing systems.<sup>17,26–30</sup> Therefore, it is highly unlikely that an ion pair intermediate exists in the Menschutkin reaction studied in this work.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Temperature-dependent rate constant and dielectric constant data are given for the reaction of trihexylamine with 1-bromohexane in 2-butanone, 2-pentanone, 2-heptanone, 2-octanone, or 2-nonanone. CAF and simple Arrhenius activation energies are also given for these data. Furthermore, a representative plot is shown for both a calibration curve and a second-order rate plot. This information is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*R. Frech: e-mail, [rrech@ou.edu](mailto:rrech@ou.edu).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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