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Generation of Xanthenium and 9-Phenylxanthenium Carbocations in Subcritical Water and Reactivity with Amylamine

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The ability of subcritical water to support ionic chemistry is evident from the successful generation of 9-R-xanthenium (R = H and C_6H_5) carbocations at temperatures up to 330 °C from their respective alcohol precursors using laser flash photolysis. The intrinsic carbocation decay in the solvent was found to follow simple Arrhenius behavior at all temperatures, from ambient up to 330 °C. In addition, we determined the bimolecular rate constants for the reactions of xanthenium cation and 9-phenylxanthenium cations with amylamine, a neutral nucleophile. The activation energies of the two reactions were 21.6 ± 1.2 kJ mol^{-1} and 18.2 ± 3.9 kJ mol^{-1}, respectively. More importantly, we found that the rate equations determined at high temperatures extrapolated extremely well to ambient conditions. Thus, we conclude that for ion/neutral isoCoulombic reactions, it would be reasonable to use low-temperature Arrhenius parameters to predict the rate constants in water at higher temperatures. Finally, we found that the effect of pressure on the bimolecular rate constants in the temperature range of 22−330 °C was negligible.

Introduction

An understanding of the reactivity of species in hot water is important for organic synthesis and for the oxidation of hazardous contaminants in aqueous waste streams. The reactivity of carbocations, as investigated here, is important for both of these applications.

In particular, subcritical water (near-critical water) has recently been suggested as a potentially important green solvent.[1−10] The physical properties of subcritical water are similar to those of polar organic solvents due to the decrease in the density and the dielectric constant. As shown in Table 1, the ion product of subcritical water is 3 orders of magnitude greater than that of ambient water, making it a strong source of hydronium and hydroxide ions. These ions can act as catalysts in acid- or base-catalyzed reactions.[1−10] Reactions that have been investigated include alkylations, nucleophilic substitutions, eliminations, hydrolysis, dehydration, and partial oxidations. The potential of using hot water to replace harmful organic solvents and hazardous mineral acids makes an understanding of the solvent effect on reactivity in this interesting medium extremely important.

In addition, supercritical water oxidation (SCWO) has been shown to be an efficient technology for treating hazardous waste, including chemical warfare agents.[11−13] At supercritical conditions (T_c = 374 °C; P_c = 218 atm) oxygen is completely miscible with water and most organic compounds are quite soluble. Thus, high destruction efficiencies can be achieved (>99.99%) at reaction temperatures less than 600 °C.[14,15] Another advantage of this technology is the absence of incomplete oxidation products such as CO, NO_x, and SO_x.[14] At high-temperature supercritical conditions, free-radical chemistry will dominate,[16−26] but ionic chemistry is important in the lower temperature heat-up and cool-down sections, as has been demonstrated by a variety of researchers.[27] Researchers have even studied ion solvation in SCW, both theoretically[28] and experimentally.[29]

TABLE 1: Physical Properties of Water at the Experimental Conditions

temp., °C	pressure, bar	density[39], g cm^{-3}	dielectric constant[40]	dissociation constant[41]
22	1	1.0000	79.73	10^{-14}
150	230	0.9293	44.77	$10^{-11.55}$
175	230	0.9060	39.96	$10^{-11.33}$
200	200	0.878	35.51	$10^{-11.19}$
200	220	0.8793	35.58	$10^{-11.18}$
200	230	0.8801	35.63	$10^{-11.17}$
200	240	0.881	35.68	$10^{-11.166}$
225	230	0.8513	31.70	$10^{-11.07}$
250	230	0.8192	28.09	$10^{-11.033}$
275	230	0.7827	24.71	$10^{-11.059}$
300	230	0.7401	21.47	$10^{-11.168}$
330	230	0.6758	17.55	$10^{-11.465}$

Clearly, the above studies demonstrate the importance of ionic chemistry in sub- and supercritical water. However, very few studies have been undertaken to examine the effect of the solvent on the rates of ionic reactions under SCW conditions. Bowman and Fulton[30] have presented some of the first studies of rates of ion reactivity in SCW with their account of the destruction of ammonium by nitrate at 400 °C. Ryan et al.[31] have studied excited-state proton-transfer reactions in subcritical and supercritical water. They concluded that the effect of solvent, near-critical water, on isoCoulombic reactions is different from that on ionogenic reactions. This is because charge is generated for an ionogenic reaction, as shown in eq 1 for water and ammonia (base) assisted proton-transfer reactions:

$$\text{2-NpOH}^{*} + \text{base} \rightleftharpoons \text{2-NpO}^{-*} + \text{Hbase}^{+} \qquad (1)$$

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In their study, 2-NpOH* was obtained upon excitation of 2-naphthol to the S_1 ($\pi-\pi^*$) state and 2-NpO^{-*} is the naphtholate anion in the S_1 state. For an isoCoulombic reaction, charge is neither created nor destroyed, as shown in eq 2, for the acetate and borate anion (base$^-$) assisted proton-transfer reactions:[31]

$$\text{2-NpOH}^* + \text{base}^- \rightleftharpoons \text{2-NpO}^{-*} + \text{Hbase} \qquad (2)$$

Their observation of different behavior for ionogenic and isoCoulombic reactions was attributed to the changes with temperature in the physical properties of water. This behavior was described using transition-state theory, based on the fact that the solvation energy of ions and dipolar molecules are more sensitive than neutral molecules to the changes in solvent properties such as dielectric constants and hydrogen bonding. It was also shown that low-temperature kinetic behavior can be extrapolated to higher temperatures for isoCoulombic reactions, whereas one cannot extrapolate low-temperature kinetic behavior to higher temperatures for ionogenic reactions.

Thus, the understanding of ionic chemistry is important not only in SCW but also in subcritical water. Unfortunately, experimental evidence of the solvent effect on the rates of ionic reactions under hydrothermal conditions is very limited. In this report, the solvent effect on a simple well-characterized ion/neutral isoCoulombic reaction between a carbocation and a neutral nucleophile in subcritical water is reported. Our goal is to determine if the low-temperature data can be used to estimate rate constants under subcritical conditions. We used laser flash photolysis (LFP) to generate xanthenium and 9-phenylxanthenium carbocations in subcritical water and studied their reactivity with a neutral nucleophile, amylamine. The photochemical generation of xanthenium carbocations in aqueous solutions at ambient temperature from the respective xanthenol precursors and the photophysics of this process are well described in the literature.[32,33] Both of these carbocations show strong absorbance at 372 nm, and these peaks have been identified as the xanthenium carbocations based on comparison with spectrum obtained in sulfuric acid solution. These carbocations are relatively stable, with lifetimes between 44 μs and 0.043 s, depending on the substituent.[33] McClelland et al.[33] studied the reactivity of these carbocations at ambient conditions with nucleophiles, including primary amines and anions, in acetonitrile/water solutions. We chose to study these systems in subcritical water because these carbocations are relatively stable compared to other diarylmethyl and triarylmethyl carbocations.

Experimental Section

Materials. The chemicals, 9*H*-xanthen-9-ol (98%), 9-phenylxanthen-9-ol (98%), amylamine (99%), and acetonitrile (99.5+%) were purchased from Sigma-Aldrich Chemical Co. and were used as received. Water was filtered to 16 MΩ using a Millipore Reagent Water System at Notre Dame Radiation Laboratory. Oxygen-free helium purchased from Mittler Supply Inc., South Bend, IN, was used to degas the aqueous solutions.

Laser Flash Photolysis Apparatus and High-Pressure, High-Temperature Flow System. The laser flash photolysis apparatus has been described in detail elsewhere.[34] These experiments were performed using laser excitation perpendicular to a pulsed 1000 W xenon lamp monitoring source. A Quanta Ray DCR-1 Nd:YAG (266 nm; pulse width ~ 6 ns) laser system was used for the laser excitation. A Tektronix 7912 AD digitizer was used to digitize the transient absorption signals, and a VAX-11/780 computer was used to operate the LFP apparatus. Origin software (version 6, Microcal Software Inc.) was used to analyze the data and to determine the rate constants.

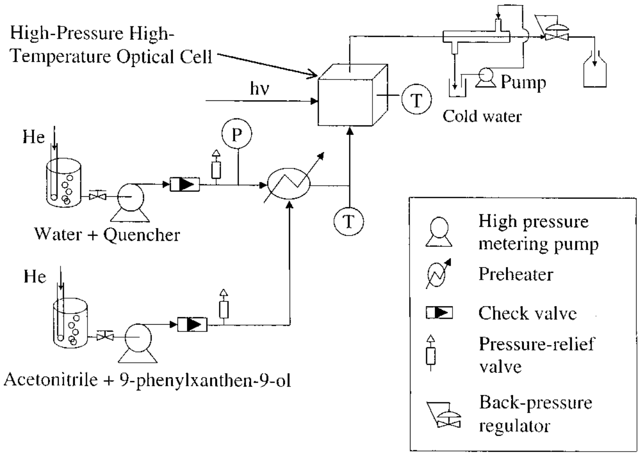


Figure 1. Schematic of the LFP apparatus and the high-pressure, high-temperature flow system.

A schematic of the high-pressure, high-temperature flow system used in this study is shown in Figure 1. The main features of the flow system include a high-pressure, high-temperature cell, an Eldex model AA-100-S metering pump, and a Tescom model 26-1723-24 back-pressure regulator. The details of the high-pressure, high-temperature cell have been given elsewhere.[35] The Eldex metering pump was used to pump the helium-saturated feed solution to the cell at the required flow rate. Coiled tubing made of 3 m long SS-316 tubing (0.635 cm o.d. by 0.386 i.d.) was used to dampen the pressure fluctuations generated by the pump, which were typically on the order of ±1.5 bar. The feed was preheated to the required temperature using Thermolyne heating tape, the temperature was measured with a K-type thermocouple (Omega Model KMTIN-062U-6), and the temperature was controlled using an Omega model CS-6001-K temperature controller. The cell was heated to the required temperature using four 150 W Watlow Firerod cartridge heaters. The temperature of the fluid in the cell was measured with a type K thermocouple (Omega model KTIN-116G-12). An Omega temperature controller, model MCS 6081-K, was used to control the temperature to ±1 °C. The cell was well insulated with Zircar-type ECO-1200A silica alumina insulation. A Tescom back-pressure regulator was used to maintain the pressure at the desired value to ±2.5 bar. A Heise pressure transducer, model 901A, was used to monitor the system pressure. A single-pass heat exchanger was used to cool the solution. A High-Pressure Equipment (HiP) safety valve, model 15-61AF1, was used to ensure the safe operation of the flow system, and HiP tubes and fittings, rated to 1000 bar, were used.

9-H-xanthen-9-ol System. 9-*H*-Xanthen-9-ol was found to be sufficiently soluble in water at ambient conditions, facilitating the preparation of a stock solution at the required concentration (2×10^{-4} M). In addition, amylamine is soluble in water at ambient conditions at the concentrations used in this study (up to 0.045 M). For the experiments studying the effect of amylamine concentration, the feed solution consisting of water, 9-*H*-xanthen-9-ol, and amylamine at required concentrations was prepared and fed to the cell using an Eldex AA-100S metering pump.

9-Phenylxanthen-9-ol System. Unfortunately, 9-phenylxanthen-9-ol is not sufficiently soluble in water at ambient conditions. Thus, the 9-phenylxanthen-9-ol reactions were performed in an acetonitrile/water mixture. The flow system was modified accordingly to facilitate this requirement. Water

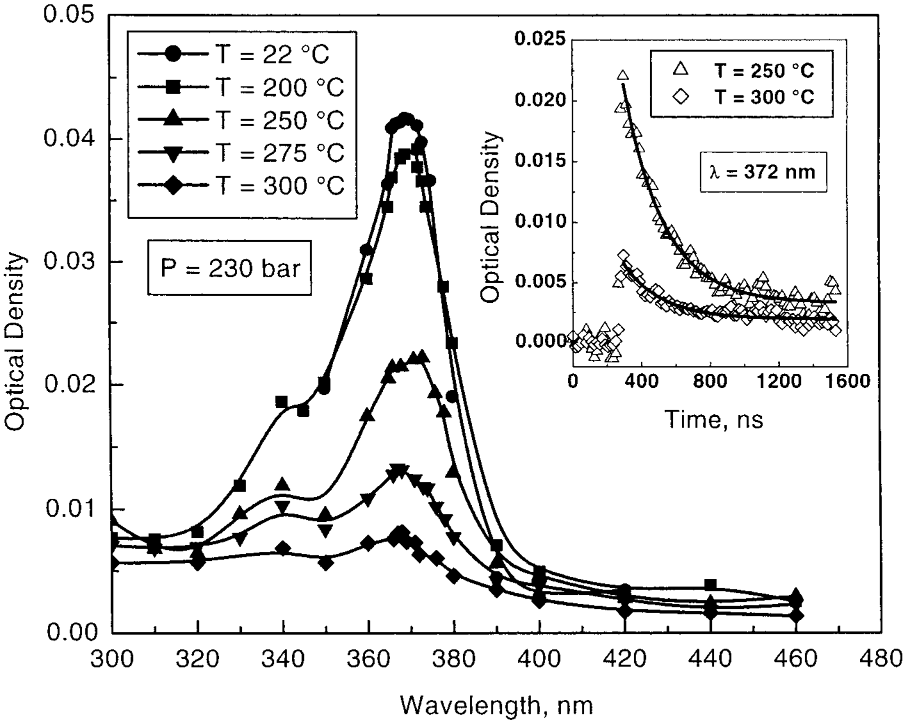


Figure 2. Transient absorption spectra following 266-nm laser excitation of 9-*H*-xanthen-9-ol in helium-saturated aqueous solution as a function of temperature at 230 bar. The inset shows a typical transient observed at 372 nm at two different temperatures; the solid line indicates the first-order fit.

and water−amylamine solution was fed to the cell using one Eldex AA-100-S metering pump. The carbocation precursor, 9-phenylxanthen-9-ol, was dissolved in acetonitrile and was fed to the cell using a second Eldex metering pump, A-30-S. The flow rates of the two pumps were maintained such that the final mixture contained 0.055 mol fraction acetonitrile. Moreover, the concentration of 9-phenylxanthen-9-ol was fixed at 3×10^{-4} M at ambient conditions. The acetonitrile solution was mixed with water in a high-pressure mixing tee, after both solutions had been preheated. Since typical residence times between the mixing tee and the optical cell are 4−5 s, we believe that a well-mixed homogeneous solution entered the cell. This was confirmed by reproducible absorption spectra. The 0.055 mol fraction acetonitrile in water solution should be single phase at reaction conditions of 100−330 °C, as supported by the solubility of polar and nonpolar organic compounds in water at similar conditions[4,9,36,37] and the phase equilibrium data for the methanol−water system.[38] To further ensure that the experiments were conducted in a single-phase system, the acetonitrile−water solution was observed through one of the sapphire windows prior to the laser excitation. It should be noted that 0.055 mol fraction acetonitrile in water is single-phase at ambient conditions, as well. Stock solutions were prepared before each experiment and were protected from light.

Results and Discussion

Below, we present the transient absorption spectra of xanthenium cation and 9-phenylxanthenium cation at temperatures to 330 °C, as well as the intrinsic rate constants for the decay of the carbocations in the presence of the solvent. In addition, we present the rate constants for the reaction of both carbocations with a nucleophile, amylamine. The stability of the two carbocation precursors, 9-*H*-xanthen-9-ol and 9-phenylxanthen-9-ol at the oxygen-free experimental conditions was tested using the high-pressure high-temperature flow system and they were found to be stable. The stability of these two carbocation precursors was confirmed by measuring the concentration of the solute in the effluent using UV−vis absorbance spectroscopy. The stability of the neutral nucleophile, amylamine, was tested in a batch reactor; the conversion of amylamine was found to be only 7.2% after 30 min at 325 °C and 250 bar. On the basis of this result, amylamine was considered to be stable in the high-pressure, high-temperature optical system since the residence time of the solution in this system is less than 3 min. Most of the experimental data were obtained at a pressure of 230 bar unless noted otherwise. This pressure is well above the pure water vapor/liquid equilibrium pressure at all of the temperatures investigated. As a result, all of the systems studied were liquid single-phase systems. The density,[39] dielectric constant,[40] and ion dissociation constant[41] of pure water at the experimental conditions are shown in Table 1. We did not make any attempt to estimate the properties of the 5.5 mol % acetonitrile in water solution, but the values in Table 1 for pure water can be used as a guide.

Transient Absorption Spectra. The transient absorption spectrum obtained upon 266-nm laser excitation of 9-*H*-xanthen-9-ol in helium saturated water as a function of temperature is shown in Figure 2. At 22 °C, the spectrum compares well with the spectrum reported in the literature, which identifies the strong absorbance at 372 nm as the cation.[33] This peak did not shift significantly with increasing temperature. Upon excitation, heterolytic cleavage of the C−OH bond leads to the formation of the cation, whereas homolytic cleavage leads to the formation of the free radical, xanthenyl radical. The radical absorbs around 345 nm both at ambient conditions and at elevated temperatures, as shown in the Figure 2. It decays with second-order kinetics at all temperatures, as is characteristic of radical−radical recombination. The cation decays by first-order kinetics with a rate constant, k_o. Typical decay traces observed at 372 nm at 250 and 300 °C are shown as an inset in Figure 2. The first-

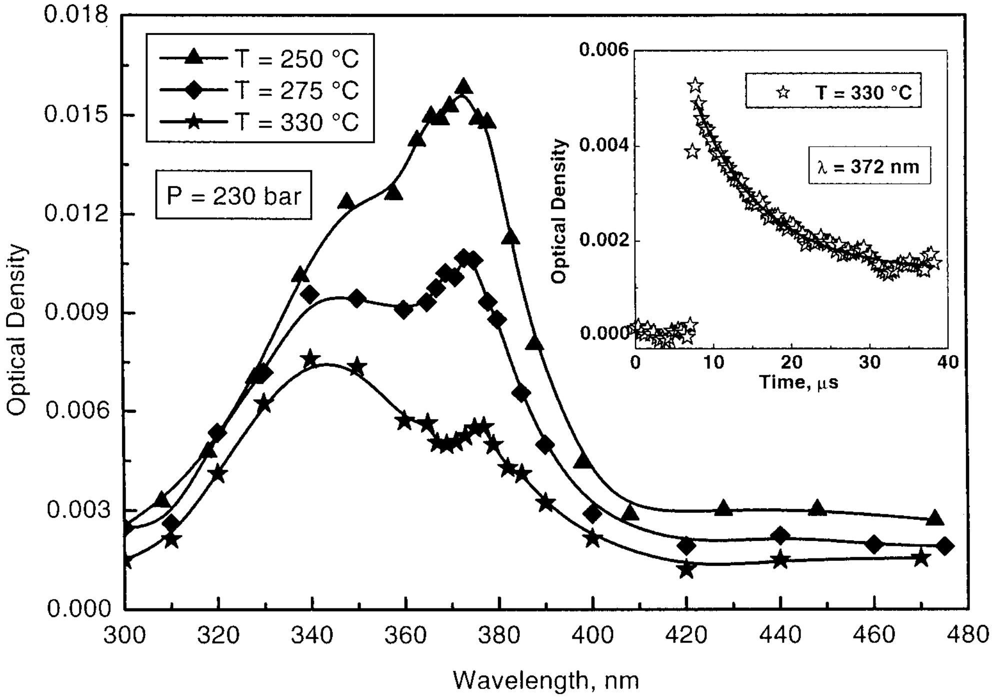


Figure 3. Transient absorption spectra following 266-nm laser excitation of 9-phenylxanthen-9-ol in helium saturated acetonitrile−water solution as a function of temperature at 230 bar. The inset shows a typical transient observed at 372 nm at 330 °C; the solid line indicates the first-order fit.

order fit to the data points is indicated with the solid line. The xanthenium cation was detected up to a temperature of 300 °C.

As shown in Figure 2, the absorbance at 372 nm decreased with an increase in the temperature. This decrease in the absorbance may be due to several factors. First, over this temperature range, the dielectric constant of the water decreases from 80 to 21. Decreasing dielectric constant would favor formation of the radical rather than the cation, and this appears to be the case since the relative intensity of the radical peak does appear to increase with increasing temperature.[33,42] This trend is observed by taking the ratio of the absolute absorbances at the peak maxima (approximately 340 and 372 nm) or by proper deconvolution of the two peaks. However, the extinction coefficients of both the xanthenium cation and the radical may be decreasing with increasing temperature. The determination of the yield of these two species would provide insight into the observed decrease in the absorbance; however, we did not estimate the yield of the cation at any conditions.

At each temperature, the rate constant for the solvent decay, k_o, was estimated. The lifetime ($1/k_o$) of the xanthenium cation decreased from 43 μs to 152 ns as the temperature was increased from 22 to 300 °C. At temperatures greater than 300 °C, the dielectric constant of water and the lifetime of the xanthenium cation decreased further, leading to a very weak signal for the xanthenium cation. As the stability of the 9-phenylxanthenium cation at ambient conditions has been shown to be much greater than the xanthenium cation,[33] we were able to study the reactivity of this cation at somewhat higher temperatures.

The transient absorption spectrum obtained upon 266-nm laser excitation of 9-phenylxanthen-9-ol in helium-saturated acetonitrile/water solution as a function of temperature is shown in Figure 3. As described above for 9-*H*-xanthen-9-ol, the laser excitation led to the homolytic and heterolytic cleavage of the C−OH bond, leading to the formation of the 9-phenylxanthenium radical (∼340 nm) and 9-phenylxanthenium cation (∼372 nm), respectively. The decay trace obtained at 372 nm at a temperature of 330 °C and 230 bar is shown as the inset. The solid line corresponds to the first-order fit, confirming that the intermediate observed is the carbocation. In this case, we were able to observe the formation of the 9-phenylxanthenium carbocation up to 330 °C, but experienced the same problems of weak signal at higher temperatures.

From Figure 3, one could conclude that an increase in the temperature leads to a decrease in the absorbance at 372 nm, consistent with the 9-*H*-xanthen-9-ol system, whereas the relative absorbance (A_{340}/A_{372}) at 340 nm increases with temperature. This observation can be better explained by comparing the relative yields of the carbocation and the radical produced upon LFP of 9-phenylxanthen-9-ol in various liquid solvents at ambient conditions. The relative yield of carbocation increased from 0.05 to 1.0, where as the relative yield of the radical decreased from 1.0 to a negligible value, as the solvent was changed from acetonitrile to 1/1 H_2O/MeOH, increasing the hydrogen-bonding ability and dielectric constant of the solvent.[32] Therefore, from these results, one can conclude that the decrease in the absorbance at 372 nm (yield of the carbocation) with an increase in temperature is due to the changes in the nature of water. As the effective dielectric constant and hydrogen-bonding ability of water decreases with temperature,[36,43] the ability of subcritical water to support ionic chemistry diminishes.

At each temperature, the rate constant for the solvent decay, k_o, was estimated. The lifetime of the 9-phenylxanthenium cation ($1/k_o$) decreased from 0.043 s to 8.6 μs with an increase in temperature from 22 to 330 °C. The effect of temperature on k_o for both the systems at 230 bar is shown in Figure 4. In both cases, an increase in temperature led to an increase in the rate constant, and the kinetics followed an Arrhenius relation. From the high-temperature data (i.e., temperatures above 100 °C), Arrhenius parameters were estimated and are reported in Table 2. The activation energy for decay of the xanthenium cation in water was found to be 29.4 ± 0.7 kJ mol^{-1}, whereas for the decay of the 9-phenylxanthenium cation in water was 39.5 ± 2.6 kJ mol^{-1}. These values compare reasonably well with the

TABLE 2: Arrhenius Parameters for k_o and k_{bi} at 230 bar and a Comparison between Experimental and Predicted Rate Constants for the Reactions between Xanthenium and 9-Phenylxanthenium Cations with Amylamine at 22 °C

		9-*H*-xanthen-9-ol system	9-phenylxanthen-9-ol system
k_o	preexpon. factor, s^{-1}	$(3.37 \pm 0.67) \times 10^9$	$(3.08 \pm 1.75) \times 10^8$
	act. energy, kJ mol^{-1}	29.4 ± 0.7	39.5 ± 2.6
	$k_o^{predicted}$ @ 22 °C, s^{-1}	2.08×10^4	30.9
	$k_o^{experimental}$ @ 22 °C, s^{-1}	2.16×10^4	23[33]
k_{bi}	preexpon. factor, $M^{-1}\,s^{-1}$	$(1.67 \pm 0.62) \times 10^{11}$	$(5.39 \pm 3.25) \times 10^8$
	act. energy, kJ mol^{-1}	21.6 ± 1.2	18.2 ± 3.9
	$k_{bi}^{predicted}$ @ 22 °C, $M^{-1}\,s^{-1}$	2.53×10^7	3.19×10^5
	$k_{bi}^{experimental}$ @ 22 °C, $M^{-1}\,s^{-1}$	2.44×10^7	3.58×10^5

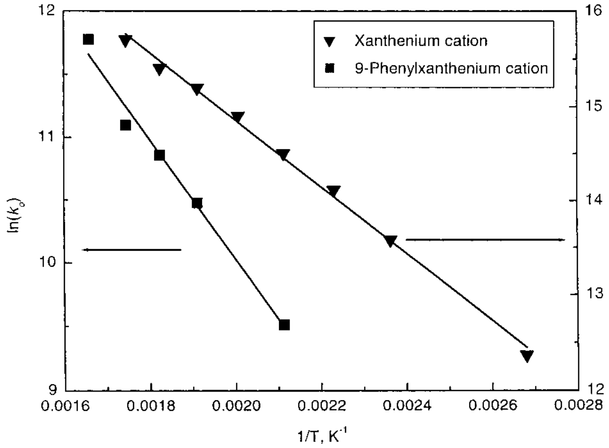
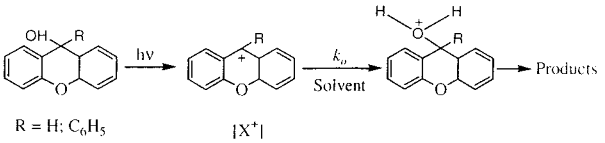


Figure 4. Effect of temperature on the solvent decay rate constants, k_o, for xanthenium and 9-phenylxanthenium carbocations at 230 bar. Arrhenius parameters were obtained from the solid lines shown.

values reported for the decay of oxy carbocations in water (5.86−31.8 kJ mol^{-1}, depending on the carbocation).[44,45] These Arrhenius parameters were then used to estimate k_o at 22 °C. As can be seen in Table 2, the estimated and experimental values compare quite favorably. Thus, we conclude that rate constants for the intrinsic decay of these carbocations obtained at low temperatures could be safely extrapolated to estimate rate constants in higher temperature subcritical water.

Reactivity with Amylamine. In the presence of a nucleophile, such as amylamine, the carbocation can either react with the amine or can undergo solvent decay according to eqs 3 and 4. The rate of disappearance of the cation is given by eq 5.



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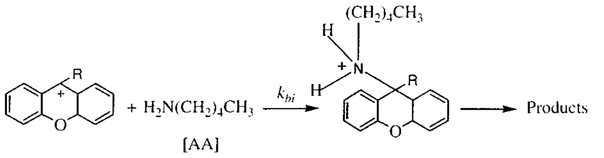

(4)

$$-\frac{d[X^+]}{dt} = k_o[X^+] + k_{bi}[X^+][AA] \qquad (5)$$

In the presence of huge excess of the amine, the rate of disappearance can be treated as a pseudo-first-order reaction, leading to the following relationship:

$$k_{obs} = k_o + k_{bi}[AA] \qquad (6)$$

As a result, the bimolecular rate constant, k_{bi}, at any particular temperature and pressure can be obtained by plotting the pseudo-first-order observed rate constant, k_{obs}, as a function of amylamine concentration.

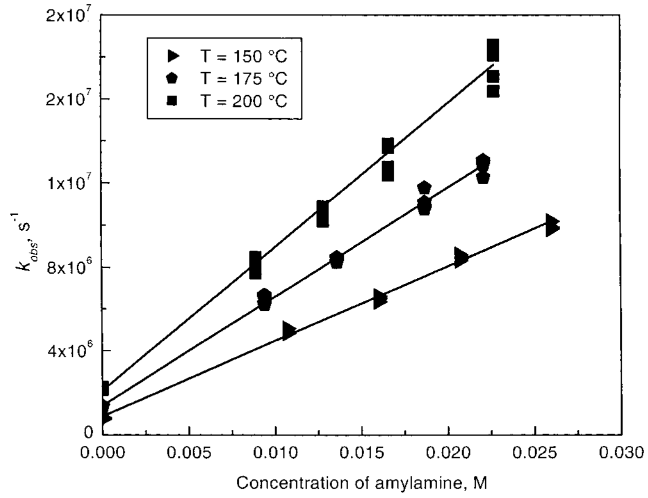

Figure 5. Effect of amylamine concentration on the observed rate constant for the reaction between xanthenium cation and amylamine in water as a function of temperature at 230 bar.

The effect of amylamine concentration and temperature on the observed rate constant for the reaction between xanthenium cation and amylamine at 230 bar and three different temperatures is shown in Figure 5. As expected, the observed rate constant increases with an increase in the amylamine concentration and with an increase in the temperature. The multiple symbols at each amylamine concentration indicate replicate measurements of the observed rate constant. Linear fits of the data, shown as the solid lines in Figure 5, provide good representations of the kinetics. The bimolecular rate constant at each temperature was obtained from the slopes of these lines, according to eq 6. The equivalent plot of the effect of amylamine concentration on the observed rate constant for the reaction between 9-phenylxanthenium cation and amylamine at 230 bar and three temperatures is shown in Figure 6. The bimolecular rate constant for this reaction was estimated at each temperature according to eq 6, and the linear fits are shown as the solid lines. The rate of the reaction of amylamine with 9-phenylxanthenium cation is about 2 orders of magnitude slower than the reaction with the unhindered xanthenium carbocation, and this trend is expected on the basis of both electronic and steric effects.

The final results, of the effect of temperature on the bimolecular rate constants for both reactions, are shown in Figure 7. Both reactions follow Arrhenius behavior, and the activation energies and preexponential factors determined from the high-temperature data are given in Table 2. The activation energy for the reaction between xanthenium cation and amylamine was found to be 21.6 ± 1.2 kJ mol^{-1}, whereas for the reaction between 9-phenylxanthenium cation and amylamine it was 18.2 ± 3.9 kJ mol^{-1}. These values compare reasonably

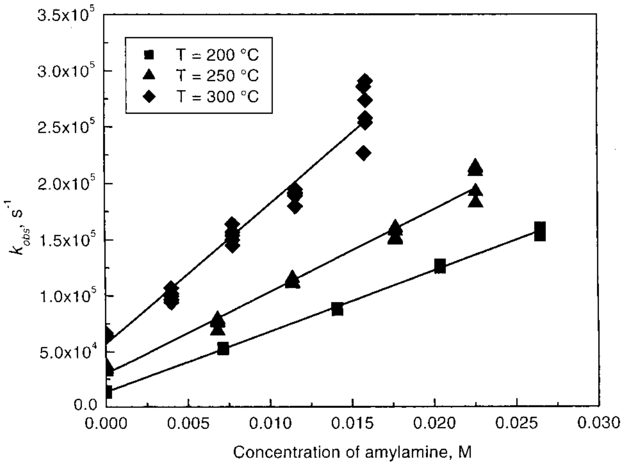

Figure 6. Effect of amylamine concentration on the observed rate constant for the reaction between 9-phenylxanthenium cation and amylamine in 0.945/0.055 water−acetonitrile solution as a function of temperature at 230 bar.

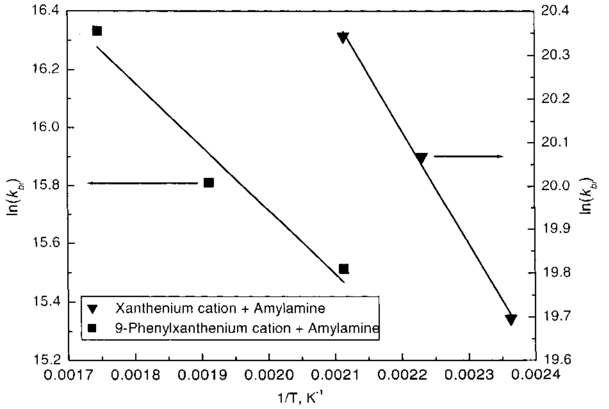

Figure 7. Arrhenius plot of the bimolecular rate constant for the reaction between 9-R-xanthenium cation and amylamine at 230 bar.

well with the activation energy for the reaction shown in eq 2, 11.6 kJ mol^{-1}.[31] These Arrhenius parameters were used to estimate the bimolecular rate constants for these two reactions at 22 °C. As can be seen in Table 2, the extrapolated bimolecular rate constants (2.53×10^7 and 3.19×10^5 M^{-1} s^{-1}) match our measurements of the rate constants at room temperature and pressure (2.44×10^7 and 3.58×10^5 M^{-1} s^{-1}) quite well. From this comparison, we conclude that kinetic parameters determined from low-temperature bimolecular rate constants could be used to estimate the rate constants of these ion/neutral isoCoulombic reactions in water at higher temperatures. This result is in agreement with the earlier suggestion that low-temperature Arrhenius parameters can be used to predict high-temperature behavior for isoCoulombic reactions.[31]

Finally, we investigated the effect of pressure on the bimolecular rate constant for the reaction between xanthenium cation and amylamine at 200 °C, and these results are given in Table 3. The pressure was varied over the modest range from 200 to 240 bar. The absence of any discernible pressure effect on this reaction at 200 °C is not surprising since water is still relatively incompressible at this temperature and the change in dielectric constant is minimal.

TABLE 3: Effect of Pressure on the Bimolecular Rate Constant for the Reaction between Xanthenium Cation and Amylamine at 200 °C

temp., °C	pressure, bar	k_o, s^{-1}	k_{bi}, M^{-1} s^{-1}
200	202	$(1.93 \pm 0.15) \times 10^6$	$(7.06 \pm 0.12) \times 10^8$
200	219	$(2.01 \pm 0.27) \times 10^6$	$(7.04 \pm 0.19) \times 10^8$
200	230	$(2.09 \pm 0.21) \times 10^6$	$(6.85 \pm 0.14) \times 10^8$
200	240	$(2.04 \pm 0.19) \times 10^6$	$(6.98 \pm 0.13) \times 10^8$

Conclusions

Laser flash photolysis was used to generate 9-R-xanthenium cations (R = H and C_6H_5) in subcritical water to demonstrate the importance of ionic chemistry at these conditions. The carbocations were generated at temperatures up to 330 °C, but at higher temperatures the decrease in the dielectric constant of water resulted in weak cation signals with short lifetimes. Nonetheless, we determined that the temperature effect on the intrinsic solvent decay followed Arrhenius behavior and could be safely extrapolated all the way from ambient conditions to 300 °C. In addition, we determined the bimolecular rate constants for the reactions of xanthenium and 9-phenylxanthenium cations with amylamine at temperatures between 100 and 300 °C. These ion/neutral isoCoulombic reactions followed Arrhenius behavior according to k_{bi} (M^{-1} s^{-1}) $= 1.67 \pm 0.62 \times 10^{11} \exp[(-21.6 \pm 1.2 \text{ kJ mol}^{-1})/RT]$ and $5.39 \pm 3.25 \times 10^8 \exp[(-18.2 \pm 3.9 \text{ kJ mol}^{-1})/RT]$ for the 9-*H*-xanthen-9-ol and 9-phenylxanthen-9-ol systems, respectively. Moreover, these rate expressions predict the rate constants at ambient conditions extremely well. Thus, we conclude that for this kind of ion/neutral isoCoulombic reaction it would be reasonable to use low-temperature Arrhenius parameters to predict the rate constants in water at higher temperatures. Finally, we determined that there is no measurable pressure effect on the rate constants since water is still relatively incompressible at temperatures below 300 °C.

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References and Notes

(1) Chandler, K.; Deng, F. H.; Dillow, A. K.; Liotta, C. L.; Eckert, C. A. *Ind. Eng. Chem. Res.* **1997**, *36*, 5175−5179.

(2) Lesutis, H. P.; Glaser, R.; Liotta, C. L.; Eckert, C. A. *Chem. Commun.* **1999**, 2063−2064.

(3) Kuhlmann, B.; Arnett, E. M.; Siskin, M. *J. Org. Chem.* **1994**, *59*, 5377−5380.

(4) Kuhlmann, B.; Arnett, E. M.; Siskin, M. *J. Org. Chem.* **1994**, *59*, 3098−3101.

(5) Eckert, C. A.; Bush, D.; Brown, J. S.; Liotta, C. L. *Ind. Eng. Chem. Res.* **2000**, *39*, 4615−4621.

(6) Eckert, C. A.; Chandler, K. *J. Supercrit. Fluids* **1998**, *13*, 187−195.

(7) Brown, J. S.; Glaser, R.; Liotta, C. L.; Eckert, C. A. *Chem. Commun.* **2000**, 1295−1296.

(8) Chandler, K.; Liotta, C. L.; Eckert, C. A.; Schiraldi, D. *AICHE J.* **1998**, *44*, 2080−2087.

(9) Chandler, K.; Eason, B.; Liotta, C. L.; Eckert, C. A. *Ind. Eng. Chem. Res.* **1998**, *37*, 3515−3518.

(10) Holliday, R. L.; Jong, B. Y. M.; Kolis, J. W. *J. Supercrit. Fluids* **1998**, *12*, 255−260.

(11) Hazlebeck, D. A.; Downey, K. W.; Jensen, D. D.; Spritzer, M. H. In *Proc. Annual Meeting − Air and Waste Management Association*, Denver, CO, 1993.

(12) Harradine, D. M.; Buelow, S. J.; Dellorco, P. C.; Dyer, R. B.; Foy, B. R.; Robinson, J. M.; Sanchez, J. A.; Spontarelli, T.; Wander, J. D. *Hazard. Waste Hazard. Mater.* **1993**, *10*, 233−246.

(13) Barner, H. E.; Huang, C. Y.; Johnson, T.; Jacobs, G.; Martch, M. A.; Killilea, W. R. *J. Hazard. Mater.* **1992**, *31*, 1−17.

(14) Modell, M. In *Standard Handbook of Hazardous Waste Treatment and Disposal*; Freeman, H. M., Ed.; McGraw-Hill: New York, 1989.

(15) Tester, J. W.; Holgate, H. R.; Armellini, F. J.; Webley, P. A.; Killilea, W. R.; Hong, G. T.; Barner, H. E. In *Emerging Technologies in Hazardous Waste Management III*; Tedder, D. W., Pohland, F. G., Eds.; American Chemical Society: Washington, DC, 1992; Vol. ACS Symposium Series 518.

(16) Dagaut, P.; Demarcillac, B. D.; Tan, Y.; Cathonnet, M.; Boettner, J. C. *J. Chim. Phys.-Chim. Biol.* **1995**, *92*, 1124−1141.

(17) Dagaut, P.; Cathonnet, M.; Boettner, J. C. *J. Supercrit. Fluids* **1996**, *9*, 33−42.

(18) Brock, E. E.; Oshima, Y.; Savage, P. E.; Barker, J. R. *J. Phys. Chem.* **1996**, *100*, 15834−15842.

(19) Brock, E. E.; Savage, P. E.; Barker, J. R. *Chem. Eng. Sci.* **1998**, *53*, 857−867.

(20) Brock, E. E.; Savage, P. E. *AICHE J.* **1995**, *41*, 1874−1888.

(21) Savage, P. E.; Yu, J. L.; Stylski, N.; Brock, E. E. *J. Supercrit. Fluids* **1998**, *12*, 141−153.

(22) Savage, P. E.; Rovira, J.; Stylski, N.; Martino, C. J. *J. Supercrit. Fluids* **2000**, *17*, 155−170.

(23) Holgate, H. R.; Tester, J. W. *Combust. Sci. Technol.* **1993**, *88*, 369−397.

(24) Holgate, H. R.; Tester, J. W. *J. Phys. Chem.* **1994**, *98*, 810−822.

(25) Gopalan, S.; Savage, P. E. In *Innovations in Supercritical Fluids − Science and Technology*; Hutchenson, K. W., Foster, N. R., Eds.; American Chemical Society: Washington, DC, 1995; Vol. ACS Symposium Series 608; pp 217−231.

(26) Gopalan, S.; Savage, P. E. *AICHE J.* **1995**, *41*, 1864−1873.

(27) Clark, D. N. *Final Report to the U. S. Army Biomedical Research and Development Laboratory*; 1989.

(28) Balbuena, P. B.; Johnston, K. P.; Rossky, P. J. *J. Phys. Chem.* **1995**, *99*, 1554−1565.

(29) Pfund, D. M.; Darab, J. G.; Fulton, J. L.; Ma, Y. *J. Phys. Chem.* **1994**, *98*, 13102.

(30) Bowman, L. E.; Fulton, J. L. In *12th International Conference on the Properties of Water and Steam*, Orlando, FL, 1994.

(31) Ryan, E. T.; Xiang, T.; Johnston, K. P.; Fox, M. A. *J. Phys. Chem.* **1996**, *100*, 9395−9402.

(32) Minto, R. E.; Das, P. K. *J. Am. Chem. Soc.* **1989**, *111*, 8858−8866.

(33) McClelland, R. A.; Banait, N.; Steenken, S. *J. Am. Chem. Soc.* **1989**, *111*, 2929−2935.

(34) Roberts, C. B.; Chateauneuf, J. E.; Brennecke, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 8455−8463.

(35) Kremer, M. J.; Connery, K. A.; DiPippo, M. M.; Feng, J. B.; Chateauneuf, J. E.; Brennecke, J. F. *J. Phys. Chem. A* **1999**, *103*, 6591−6598.

(36) Bennett, G. E.; Johnston, K. P. *J. Phys. Chem.* **1994**, *98*, 441−447.

(37) Furutaka, S.; Ikawa, S. *J. Chem. Phys.* **2000**, *113*, 1942−1949.

(38) Ohe, S. *Vapor−Liquid Equilibrium Data at High Pressure*; Elsevier: New York, 1990.

(39) Haar, L.; Gallagher, J. S.; Kell, G. S. *NBS/NRC Steam Tables; Thermodynamic and Transport Properties and Computer Programs for Vapor and Liquid States of Water in SI Units*; Hemisphere Publishing Corportation: New York, 1984.

(40) Uematsu, M.; Franck, E. U. *J. Phys. Chem. Ref. Data* **1980**, *9*, 1291−1306.

(41) Marshall, W. L.; Franck, E. U. *J. Phys. Chem. Ref. Data* **1981**, *10*, 295−304.

(42) Das, P. K. *Chem. Rev.* **1993**, *93*, 119−144.

(43) Lu, J.; Brown, J. S.; Liotta, C. L.; Eckert, C. A. *Chem. Commun.* **2001**, 665−666.

(44) Steenken, S.; Buschek, J.; McClelland, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 2808−2813.

(45) McClelland, R. A.; Steenken, S. *J. Am. Chem. Soc.* **1988**, *110*, 5860−5866.