Determination of Arrhenius and Thermodynamic Parameters for the Aqueous Reaction of the Hydroxyl Radical with Lactic Acid

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Lactic acid is a major component of the TALSPEAK process planned for use in the separation of trivalent lanthanide and actinide elements. This acid acts both as a buffer and to protect the actinide complexant from radiolytic damage. However, there is little kinetic information on the reaction of water radiolysis species with lactic acid, particularly under the anticipated process conditions of aerated aqueous solution at pH ~ 3, where oxidizing reactions are expected to dominate. Here we have determined temperature-dependent reaction rate constants for the reactions of the hydroxyl radical with lactic acid and the lactate ion. For lactic acid this rate constant is given by the following equation: $\ln k_1 = (23.85 \pm 0.19) - (1120 \pm 54)/T$, corresponding to an activation energy of 9.31 ± 0.45 kJ mol^{-1} and a room temperature reaction rate constant of $(5.24 \pm 0.35) \times 10^8$ M^{-1} s^{-1} (24.0 °C). For the lactate ion, the temperature-dependent rate constant is given by $\ln k_2 = (24.83 \pm 0.14) - (1295 \pm 42)/T$, for an activation energy of 10.76 ± 0.35 kJ mol^{-1} and a room temperature value of $(7.77 \pm 0.50) \times 10^8$ M^{-1} s^{-1} (22.2 °C). These kinetic data have been combined with autotitration measurements to determine the temperature-dependent behavior of the lactic acid pK_a value, allowing thermodynamic parameters for the acid dissociation to be calculated as $\Delta H° = -10.75 \pm 1.77$ kJ mol^{-1}, $\Delta S° = -103.9 \pm 6.0$ J K^{-1} mol^{-1} and $\Delta G° = 20.24 \pm 2.52$ kJ mol^{-1} at low ionic strength.

Introduction

Understanding the radiolytic degradation behavior of organic molecules involved in new or existing schemes for the recycling of used nuclear fuels is of significant interest for sustaining a closed nuclear fuel cycle. The high radiation fields that exist in dissolved nuclear fuels, and even raffinates from processed fuel, produce a variety of transient and long-lived species which react with the reagents that facilitate these separations.[1,2] Depending on the extent of radiation damage, the addition of solvent regeneration steps may be required, as in the PUREX process.[3] However, if the reagents used in a proposed separations process are found to be vulnerable to radiolytic degradation this could be detrimental for the application of any such proposed separation process at an industrial scale.[4]

The TALSPEAK process[5] (Trivalent Actinide Lanthanide Separations by Phosphorus-reagent Extraction from Aqueous Komplexes) for the separation of the trivalent lanthanide and actinide elements is one process that has been receiving increased attention in recent years. The original process was developed at Oak Ridge National Laboratory in the 1960's and although the TALSPEAK process is at an advanced design stage, there is still little information available on the radiation resistance of the complexants used to accomplish the separation.[6−8] This process is a biphasic system that consists of an aqueous phase, in which the dissolved metal ions originally exist, in intimate contact with an organic phase to which the complexed lanthanide ions are extracted. The major component of the aqueous phase of TALSPEAK is a lactic acid (2-hydroxypropanoic acid) buffer. However, as elucidated in the recent review on the subject by Nilsson and Nash[4] the complete extent of the role of lactic acid and the lactate ion has yet to be fully understood.

The concentration of lactate buffer in previous reports on the TALSPEAK process has been varied over the range 0.2 to 1.5 M;[9] this is clearly in large excess of the concentration of the aqueous phase actinide complexant aminopolycarboxylic acid diethylene triamine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetic acid (DTPA) also used in the process. Previously, it has been demonstrated[8] that the presence of the lactic acid/lactate ion buffer suppressed the extent of the radiolytic degradation of the DTPA complexant. Under process conditions it is expected that the aqueous phase will be aerated, and at a pH ~ 3 (pK_a of lactic acid at 25 °C is *ca*. 3.60).[10−13] The dissolved oxygen present would be expected to remove most of the radiolytically generated hydrated electrons ($e^-_{(aq)}$) and hydrogen atoms ($H^\bullet$) leaving the formed hydroxyl radicals ($^\bullet OH$) as the major transient species responsible for any radiolytic degradation of the lactic acid, lactate ion, or DTPA.

To date there has been only one reported rate constant for the reaction of hydroxyl radical with lactic acid (4.3×10^8 M^{-1} s^{-1}, pH = 1)[14]

$$^\bullet OH + CH_3CH(OH)CO_2H \rightarrow \text{products} \qquad (1)$$

and two inconsistent values for the reaction of the lactate ion (1.2×10^9, pH = 9)[15] and (3×10^8 M^{-1} s^{-1}, pH = 11)[16]

$$^\bullet OH + CH_3CH(OH)CO_2^- \rightarrow \text{products} \qquad (2)$$

While there has not been any specific study of the hydroxyl radical reaction with the DTPA ligand under acidic conditions,

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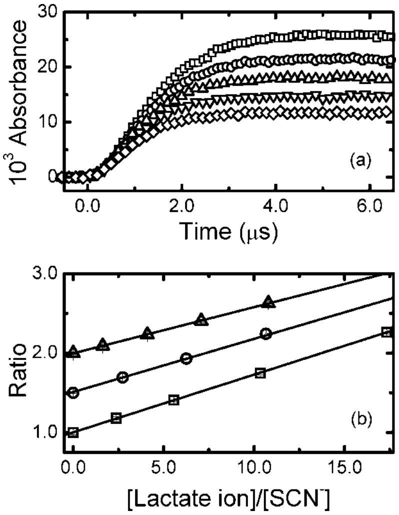

Figure 1. a) Measured $(SCN)_2^{-\bullet}$ absorbance for N_2O-saturated 118.6 μM KSCN with 0 (□), 325 (O), 742 (Δ), 1261 (▽) and 2175 (◇) μM added lactate at pH 6.14 and 22.2 °C. b) Transformed plots for lactate: (□) $T = 6.8$ °C, slope = 0.0727 ± 0.0003, $R^2 = 1.000$; (O) $T = 22.2$ °C, slope = 0.0691 ± 0.001, $R^2 = 0.999$ (vertical data offset by 0.5 units); and (Δ) $T = 41.0$ °C, slope = 0.0577 ± 0.0003, $R^2 = 1.000$ (vertical data offset by 1.0 units). Based on the measured activation energy for hydroxyl radical reaction with SCN- as 15.8 kJ mol^{-1}[1,20] and incorporating the appropriate concentration errors, these values correspond to reaction rate constants of $k = (5.94 \pm 0.33) \times 10^8$, $(7.77 \pm 0.50) \times 10^8$, and $(9.85 \pm 0.61) \times 10^8$ M^{-1} s^{-1}, respectively.

TABLE 1: Summary of Temperature-Dependent Hydroxyl Radical Rate Constants and Calculated Activation Energies Obtained in This Study

species	pH	temp, °C	$10^{-8}k_{meas}$, M^{-1} s^{-1}	E_a, kJ mol^{-1}
lactic acid	1.0	5.2	4.12 ± 0.32	
	1.0	15.4	4.67 ± 0.28	
	1.0	24.0	5.24 ± 0.35	
	1.0	30.0	5.74 ± 0.34	9.31 ± 0.45
lactate ion	6.14	6.8	5.94 ± 0.33	
	6.12	13.9	6.69 ± 0.38	
	6.14	22.2	7.77 ± 0.50	
	6.12	32.9	8.83 ± 0.56	
	6.11	41.0	9.85 ± 0.61	10.76 ± 0.34

its neutral pH value is around 5.2×10^9 M^{-1} s^{-1}.[17,18] Over the anticipated concentration range of lactic acid/lactate (total concentration of 0.2−1.5 M) and DTPA (~50 mM) to be used in TALSPEAK, a relative rates analysis shows that possibly only ~22% (0.2 M lactic acid/lactate, assumed to be 1:1 at this pH with $k_2 = 3 \times 10^8$ M^{-1} s^{-1}) to 68% (1.5 M lactic acid/lactate) of hydroxyl radical reaction occurs with the buffer.

However, while it is clear that there could be a significant fraction of hydroxyl radical reaction with DTPA, with no direct study of the reaction rates or activation energies involved for the lactic acid/lactate system under these conditions, it is difficult to draw definitive conclusions about the practical extent of the overall degradation process. Therefore, to help develop an increased understanding of the radiolytically induced oxidative degradation behavior of lactic acid and the lactate ion, here we have determined the temperature dependent rate constants for hydroxyl radical reaction with both of these species in aqueous solution.

Experimental Section

All chemicals (Aldrich) used in this study were reagent grade or higher and used as received without any further purification.

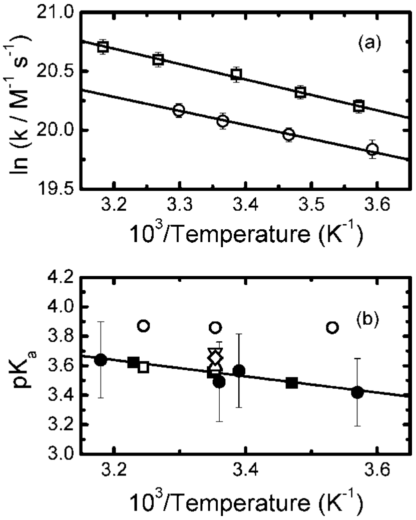

Figure 2. (a) Arrhenius plot for lactic acid (O) and lactate ion (□) at pH 1.0 and 6.14, respectively. Solid lines correspond to weighted linear fit, with slopes of −1119.9 ± 54.0 and −1294.7 ± 41.8, corresponding to activation energies of 9.31 ± 0.45 and 10.76 ± 0.35 kJ mol^{-1}. (b) van't Hoff plot for lactic acid pK_a temperature-dependence as determined by kinetic (●) and autotitration (■) methods. Open symbols are literature values, from data of Sarin and Munshi (□, $\mu = 0.2$ M),[10] Martin and Tartar (○, $\mu = 0.0$ M),[39] Cruywagen et al. (△, $\mu = 1.0$ M),[13] Gajda-Schrantz et al. (▽, $\mu = 0.1$ M),[12] and Gorzsas et al. (◇, $\mu = 0.15$ M).[11]

Solutions were made with ultrapure deionized water (≥18 MΩ) obtained from a Millipore Milli-Q system. Solutions prepared at pH~6 and ~3.6 were buffered with 10 mM sodium phosphate and sparged with high purity N_2O. Solutions prepared at pH 1 (0.1 M $HClO_4$) were sparged with high purity O_2, to ensure that any hydrated electrons or hydrogen atoms were removed from solution.

The measurements of hydroxyl radical reaction rate constants were performed using the linear accelerator (LINAC) electron pulse radiolysis system at the Radiation Laboratory, University of Notre Dame. The irradiation and transient absorption detection system has been described elsewhere.[19] Dosimetry[20] was performed on N_2O saturated solutions of KSCN (1.00×10^{-2} M) at $\lambda = 475$ nm ($G\epsilon = 5.2 \times 10^{-4}$ m^2 J^{-1}), with an average dose of 3−5 Gy per 2−3 ns pulse. During the course of the irradiation experiments, the solutions were bubbled with only the minimum amount of gas required to prevent air ingress.

Temperature control of the solutions was achieved by flowing the ambient temperature solutions through a short temperature controlled condenser prior to irradiation. The solution temperature was measured immediately post irradiation using a thermocouple placed directly in the flow.[21] Temperature stability of this system was ±0.3 °C.

Potentiometric titrations were carried out using a Mettler Toledo DL 50 Graphix titrator interfaced to a PC using LabX light software for data acquisition and a Ross combination pH electrode. The reference electrode filling solution was 3 M NaCl. Titrations were carried out at 15.1, 25 and 35 ± 0.1 °C in a water-jacketed vessel under a nitrogen atmosphere and at $I = 0.1$ M ($NaClO_4$). The titrant solution of sodium hydroxide was prepared from a concentrated solution (50% NaOH) and standardized against potassium hydrogen phthalate (dried at 100 °C). Gran's plots were carried out to ensure that the titrant solution was not contaminated by CO_2. Before and after each set of experiments, an electrode calibration titration was carried out to permit conversion of pH to $-\log[H^+]$. All solutions were

TABLE 2: Comparison of Lactic Acid pK_a Values Determined Using Kinetic and Autotitration Methods

measurement	pH	temp, °C	$10^{-8}k_{meas}$, M^{-1} s^{-1}	pK_a
kinetic	3.561	6.8	4.94 ± 0.45	3.42 ± 0.25
	3.654	22.2	6.26 ± 0.37	3.57 ± 0.23
	3.591	24.2	6.42 ± 0.66	3.49 ± 0.26
	3.561	41.6	8.40 ± 0.82	3.64 ± 0.27
autotitration		15.1		3.48 ± 0.02
		25.5		3.56 ± 0.01
		36.0		3.62 ± 0.02

prepared by weight to maximize concentration precision. Titrations were carried out in triplicate and analyzed using PSEQUAD.[22]

The quoted errors for our rate constant measurements are a combination of the measurement precision and concentration errors.

Results and Discussion

Kinetic Measurements. In the pH range 3−11, the electron pulse radiolysis of water produces free radicals and stable species in the stoichiometry:[23]

$$H_2O \xrightarrow{\text{radiation}} [0.28]{}^{\bullet}OH + [0.06]H^{\bullet} + [0.27]e^{-}_{(aq)} + [0.05]H_2 + [0.07]H_2O_2 + [0.27]H_3O^{+} \quad (3)$$

The numbers in brackets in the above equations represent the yield of each species (*G*-value) in μmol J^{-1}. Total radical concentrations generated by a pulse were typically around 2−4 μM. To isolate the reactions of only the oxidizing hydroxyl radical at near neutral pH conditions, all solutions were saturated with N_2O (∼24.5 mM) to quantitatively convert the formed hydrated electrons and hydrogen atoms to this radical:[23]

$$e^{-}_{(aq)} + N_2O + H_2O \rightarrow N_2 + OH^{-} + {}^{\bullet}OH \quad k_1 = 9.1 \times 10^{9}\ M^{-1}\ s^{-1} \quad (4)$$

$$H^{\bullet} + N_2O \rightarrow {}^{\bullet}OH + N_2 \quad k_2 = 2.1 \times 10^{6}\ M^{-1}\ s^{-1} \quad (5)$$

At neutral pH, this hydrogen atom reaction with dissolved N_2O is relatively slow, and thus will not be complete on our measurement timescales. In addition, some hydrogen atom reaction with the added SCN^- ($k = 2.3 \times 10^8\ M^{-1}\ s^{-1}$, $t_{1/2} \sim 90\ \mu s$)[24] and lactic acid ($k \sim 2 \times 10^7\ M^{-1}\ s^{-1}$, $t_{1/2} \sim 500\ \mu s$ for 1 mM acid)[23] will also occur. The reaction with thiocyanate will initially result in formation of $H(SCN)_2^{-\bullet}$,[25] which only slowly decays to $CN^{\bullet}$ at this pH, to ultimately produce more $(SCN)_2^{-\bullet}$ on the ms time scale. However, both slow side-reactions ensure that the N_2O pathway dominates, and that a fairly constant fraction (∼8−10%) of the initially produced hydrogen atoms will be converted to hydroxyl radicals under all our measurement conditions. However, this will not affect our kinetic analyses to any significant extent.

The reaction of only hydroxyl radicals with lactic acid (pH = 1) was ensured by presaturating the solutions with O_2, where quantitative conversion of the hydrated electron to the hydrogen atom:[23,26]

$$e^{-}_{(aq)} + H^{+} \rightarrow H^{\bullet} \quad k_3 = 2.3 \times 10^{10}\ M^{-1}\ s^{-1} \quad (6)$$

was followed by hydrogen atom reaction with the dissolved oxygen:[27]

$$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet} \quad k_3 = 1.2 \times 10^{10}\ M^{-1}\ s^{-1} \quad (7)$$

The reaction of lactic acid and the lactate ion with hydroxyl radicals did not generate any intermediate species with absorptions in the wavelength range 250−800 nm. Therefore, the reaction rate constant for hydroxyl radical with both lactic acid and the lactate ion was determined using SCN^- competition kinetics. This was done by monitoring the changes in the absorption due to the $(SCN)_2^{\bullet-}$ transient species at 475 nm (see Figure 1a for lactate ion) in the following competition reactions:[23]

$${}^{\bullet}OH + CH_3CH(OH)CO_2^{-} \rightarrow \text{products} \quad (2)$$

$${}^{\bullet}OH + SCN^{-}\ (+SCN^{-}) \rightarrow OH^{-} + (SCN)_2^{-\bullet} \quad (8)$$

As the products of the lactic acid/lactate reaction with hydroxyl radical do not absorb at 475 nm, this hydroxyl radical competition can be analyzed to give the following expression:

$$\frac{\mathrm{Abs}^{\circ}(SCN)_2^{-\bullet}}{\mathrm{Abs}(SCN)_2^{-\bullet}} = 1 + \frac{k_2[\text{lactate ion}]}{k_8[\text{SCN}]} \quad (9)$$

Here $\mathrm{Abs}^{\circ}(SCN)_2^{\bullet-}$ is the total yield of $(SCN)_2^{\bullet-}$ measured for a fixed concentration of only SCN^-, and $\mathrm{Abs}(SCN)_2^{\bullet-}$ is the reduced yield of this transient when the lactate ion is present in solution. Therefore by plotting the absorbance ratio $\mathrm{Abs}^{\circ}(SCN)_2^{\bullet-}/\mathrm{Abs}(SCN)_2^{\bullet-}$ against the concentration ratio [lactate ion]/[SCN^-] one should get a straight line with an intercept of 1.0, and a slope of k_2/k_8. On the basis of the rate constant for the reaction of ${}^{\bullet}OH$ with SCN^- being well established at room temperature as $1.05 \times 10^{10}\ M^{-1}\ s^{-1}$,[23] the rate constant k_2 (or k_1) is readily determined.[28]

A plot of the typical data obtained at 475 nm is shown in Figure 1 for the lactate ion at pH = 6.14 and a temperature of 22.2 °C. As expected, the $(SCN)_2^{\bullet-}$ absorption decreases with increasing lactate concentration. From the weighted linear fit of the transformed data, the calculated rate constant for this reaction was found to be $k_2 = (7.77 \pm 0.50) \times 10^8\ M^{-1}\ s^{-1}$. This measured rate constant is intermediate between the two previously reported values.[15,16] The analogous room temperature rate constant determined for the reaction of $OH^{\bullet}$ with lactic acid

TABLE 3: Calculated Thermodynamic Parameters for the Protonation of Lactic Acid from Kinetic and Autotitration Methods at 25°C

	Δ*G*°/kJ mol^{-1}	Δ*H*°/ kJ mol^{-1}	Δ*S*°/J K^{-1} mol^{-1}	μ	ref
kinetic	19.81 ± 4.50	−10.41 ± 3.17	−102.71 ± 10.7	<0.1	this work
autotitration	20.36 ± 1.05	−11.44 ± 0.74	−106.37 ± 2.49	0.1	this work
total	20.24 ± 2.52	−10.75 ± 1.77	−103.9 ± 6.0	<0.1	this work
lactic acid	20.37	−3.63	−80.5	0	10
glycolic acid	20.86	2.22	−66.11	0	32
acetic acid	27.14	−0.084	−91.63	0−0.1	32, 33
propanoic acid	27.82	−0.59	−95.40	0	32, 33
butanoic acid	27.51	−2.68	−101.25	0	32, 33

at 24.0 °C was found to be $k_1 = (5.24 \pm 0.35) \times 10^8$ M^{-1} s^{-1}, slightly faster than the only previous measurement (4.3×10^8 M^{-1} s^{-1}).[14]

These measurements for both the lactate ion and lactic acid were repeated over the temperature range 6.5−41.0 °C, the individual rate constants are listed in Table 1. To obtain these values using the SCN$^-$ competition kinetics method, the temperature dependence of reaction (8) was required. To date, there have been two separate determinations for the hydroxyl radical reaction with thiocyanate: Chin and Wine[29] used laser flash photolysis to directly measure the formation of $(SCN)_2^{-\bullet}$ at low thiocyanate concentrations, obtaining an activation energy of 15.8 kJ mol^{-1} over the temperature range 277−321 K, while Elliot and Simsons[30] studied this reaction by HCO_2^- competition kinetics to obtain 10.6 kJ mol^{-1} over the range 292−352 K. We have chosen the former value of 15.8 kJ mol^{-1} to use in this study, as it was a more direct measurement, and has been subsequently confirmed by Ervens et al.[31] On the basis of this standard value, the temperature-dependence of the hydroxyl radical reaction with lactic acid, reaction 1, can be well described by the equation

$$\ln k_1 = (23.85 \pm 0.19) - (1120 \pm 54)/T \quad R^2 = 0.995 \tag{10}$$

This corresponds to an activation energy of 9.31 ± 0.45 kJ mol^{-1} (see Figure 2a). The equivalent equation for the lactate ion, reaction (2), is given by:

$$\ln k_2 = (24.83 \pm 0.14) - (1295 \pm 42)/T \quad R^2 = 0.997 \tag{11}$$

giving an activation energy of 10.76 ± 0.35 kJ mol^{-1}.

Similar activation energies for the two reactions suggest a common mechanism, which from thermodynamic considerations would be expected to predominately be a hydrogen atom abstraction to form the tertiary carbon-centered radical. A survey of the literature for analogous compounds showed that the hydroxyl reaction rate constant for propanone (acetone) was slightly slower, with reported values over the range $k = (0.8 - 1.4) \times 10^8$ M^{-1} s^{-1}.[23] However, this could be expected, as mechanistic work carried out by Stefan and Bolton[32] on the degradation pathway of acetone has identified that H-atom abstraction from one of the terminal methyl groups to form a primary carbon-centered radical predominately occurs in contrast to the expected tertiary carbon-centered radical expected for lactic acid/lactate ion.[23] The hydroxyl radical oxidation of propylene glycol ($k = 1.7 \times 10^9$ M^{-1} s^{-1}),[14] 2-hydroxypropionamide (1.3×10^9 M^{-1} s^{-1})[33] and 1,3-butanediol ($k = 2.2 \times 10^9$ M^{-1} s^{-1})[14] are all faster than determined here for either lactate ion/lactic acid, however, these molecules also have additional sites for hydroxyl radical reaction. No activation energies were determined for any of these compounds.

Arrhenius parameters have been determined for two analogous compounds: 2-propanol and butanone. 2-propanol has a room temperature recommended[23] rate constant of 1.9×10^9 M^{-1} s^{-1}, (although literature values have been reported in the range of $(1.6-2.4) \times 10^9$ M^{-1} s^{-1}).[34−36] These values are some 30−50% faster than our k_1 or k_2 values. The corresponding activation energy determination of 5 kJ mol^{-1} was based on $^\bullet OH + SCN^-$ being 10.6 kJ mol^{-1}.[30] However, a closer examination showed some inconsistencies with these data, with the measured rate constant at 59 °C being exactly the same as at 79 °C. Reanalyzing these data for only temperatures up to 59 °C, and correcting this SCN$^-$ activation energy to the value used in this study (15.8 kJ mol^{-1}) gives a 2-propanol value of 10 kJ mol^{-1}, in very good agreement with our measured lactic acid/lactate ion data. For butanone,[14,34,37,38] the average room temperature rate constant determined from several studies is 8.1×10^8 M^{-1} s^{-1}, with a corresponding activation energy of 9.98 ± 1.66 kJ mol^{-1}, again in excellent agreement with the lactic acid/lactate ion values of this study.

The measured k_1 and k_2 rate constants of this study confirm the original prediction that hydroxyl radical reactions with DPTA in the TALSPEAK process will occur to a significant extent, even at the highest lactic acid concentrations.

Lactic Acid pK_a Values. Implicit in our kinetic measurements of these temperature-dependent hydroxyl radical rate constants for each species was the assumption that the pK_a of lactic acid remained fairly close to previously reported room temperature values of *ca.* 3.60.[10−13] Previous literature values for the temperature-dependence of this pK_a value are shown as the open symbols in Figure 2b, and significant scatter is observed. To test our assumption, we performed additional kinetic experiments at an intermediate pH, where both lactic acid and lactate would be present. On the basis of the two reactions simultaneously occurring

$$^\bullet OH + CH_3CH(OH)CO_2H \rightarrow \text{products} \tag{1}$$

$$^\bullet OH + CH_3CH(OH)CO_2^- \rightarrow \text{products} \tag{2}$$

the equilibrium

$$CH_3CH(OH)CO_2H = H^+ + CH_3CH(OH)CO_2^- \quad K_{12} \tag{12}$$

and mass balance, one can readily derive the following formula for the overall hydroxyl radical reaction at any temperature:

$$pK_{a12} = pH + \log\left(\frac{k_1 - k_{meas}}{k_{meas} - k_2}\right) \tag{13}$$

where k_{meas} is the experimental rate constant determined at this intermediate pH. Using this, measurements were performed at four different temperatures at pH ∼ 3.6 (see Table 2 for specific values) and the p$K_{a\ 12}$ values calculated. These data are shown in Figure 2b in comparison to three autotitration determinations under similar conditions. Very good agreement is observed for the two different techniques. Using the van't Hoff relation (eq 14), one can determine the enthalpy and entropy of the protonation reaction:

$$\ln K = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R} \tag{14}$$

Here ln K is the natural logarithm of the K_a value for the deprotonation reaction.

As previously demonstrated, the results of this study show that there is little variance in the lactic acid pK_a with temperature, a common phenomena for carboxylic acids.[10−13,39] However, the pK_a's reported here are a little lower than those reported by Martin and Tartar[39] in the first extensive study of this system. Despite this our reported temperature dependent pK_a determinations are more consistent with those obtained in more recent studies.[10−13] As our measured pK_a's differ slightly from previous reports it should be expected that the calculated thermodynamic parameters are higher than those already in the literature from similar studies.

The slope and y intercept of the linear plot of ln K vs $1/T$ were used to calculate the enthalpy (ΔH°) and the entropy (ΔS°) for the protonation reaction, respectively. The calculated thermodynamic parameters for the deprotonation of lactic acid are given in Table 3 in comparison to literature values for other simple organic acids.[40,41] Under low ionic strength conditions (0−0.1 M) our value of $\Delta S° = -103.9 \pm 6.0$ J K^{-1} mol^{-1} is seen to be in good agreement with the other reported values. However, our calculated value for $\Delta H° = -10.75 \pm 1.77$ kJ mol^{-1} is considerably higher than the previous value for lactic acid (-3.6 kJ mol^{-1}) and also for the listed analogous acids ($+0.41$ to -6.6 kJ mol^{-1}). The considerable scatter in these reported values prevents us making any further quantitative comparison, but clearly additional experimentation is required to resolve this difference.

Conclusion

Temperature-dependent rate constants for hydroxyl radical reaction with lactic acid have been determined, and found to be well-described by the following equation:

$$\ln k_1 = (23.85 \pm 0.19) - (1120 \pm 54)/T \quad R^2 = 0.995 \tag{10}$$

This corresponds to an activation energy of 9.31 ± 0.45 kJ mol^{-1}. The corresponding equation for the lactate ion is

$$\ln k_2 = (24.83 \pm 0.14) - (1295 \pm 42)/T \quad R^2 = 0.997 \tag{11}$$

with a slightly higher activation energy of 10.76 ± 0.35 kJ mol^{-1}. These data have been combined with kinetic and autotitration data at pH ~ 3.6 to evaluate the thermodynamic parameters for the lactic acid pK_a to be $\Delta H° = -10.75 \pm 1.77$ kJ mol^{-1}, $\Delta S° = -103.9 \pm 6.0$ J K^{-1} mol^{-1} and $\Delta G° = 20.24 \pm 2.52$ kJ mol^{-1}. These data show that while the lactic acid buffer will reduce oxidative damage from hydroxyl radical reactions in the TALSPEAK formulation, its relatively slow reaction rate constant will not prevent the actinide complexant ligands from being degraded during the process.

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