Muonium Reactions with Oxalic Acid and Oxalate Ions in Water: Huge Kinetic Isotope Effects When Compared with H

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The reactions of muonium atoms with the individual species HO_2CCO_2H, $HO_2CCO_2^-$, and $^-O_2CCO_2^-$ at ~295 K in water have absolute bimolecular rate constants of 5.6, 0.71, and 0.054×10^8 M^{-1} s^{-1}, respectively. No such 100-fold pH-dependence has hitherto been seen for muonium, although H and e_{aq}^- also show large pH effects in reactions with oxalic acid. Arrhenius plots for the muonium reactions at pH = 1, 3, and 8 show the unusually small activation energies of ≤17 kJ/mol for all three acid−base forms of oxalic acid. When the reaction rate of muonium is compared with published data on ordinary H atoms at pH = 1 (57% oxalic acid and 43% hydrogen oxalate ions), one obtains a kinetic isotope effect of 850 favoring muonium. For the dianion at pH ≥ 7, the muonium-to-H rate ratio is >300. These seem to be the largest primary kinetic isotope effects ever reported. The reaction is taken to be addition of muonium to one of the C=O groups, and the large isotope effect and small E_a suggest considerable contributions from quantum mechanical tunneling.

Introduction

This is a study of the pH-dependence of the reaction between oxalic acid and the muonium atom in water, muonium (Mu) being the light radioactive H isotope with a positive muon as nucleus.[1] Oxalic acid is of interest because in a survey of biochemicals it showed an unusually large pH-dependence and isotope effect in its reaction with Mu.[2]

H atom reactions in water have usually been measured at pH ≈ 1, because H is most easily produced in acid solution from hydrated electrons formed by radiolysis.[3−5] Mu atoms are produced with no such pH restrictions (except at pH ≥ 10, where Mu reacts with OH^- according to the reaction $Mu + OH^- \rightarrow MuOH + e_{aq}^-$), so their reactions have usually been studied at the natural pH of the solute. Mu generally shows no significant pH-dependence, and only a small one was found for the overall reaction rate of Mu with *p*-aminobenzoic acid (although the position at which Mu added to the benzene ring changed substantially).[6] Any pH-dependence in the acid region that does occur is almost certainly not a direct effect of H^+ on the reacting free atoms themselves (such as the formation of MuH^+), but on the relative reactivities of Mu with the neutral and deprotonated forms of the solutes.

Hydrogen atoms react only slowly ($k_H = 4 \times 10^5$ M^{-1} s^{-1}) with oxalic acid and at least an order of magnitude slower still with oxalate ions.[3] This reaction of H with oxalic acid has been shown to correspond to an "addition" reaction to a carbonyl group of one of the carboxylates, to give the H adduct free radical $HO_2C\dot{C}(OH)_2$.[4,5] There was no evidence for the occurrence of an H atom abstraction reaction to give H_2 at pH = 1.[7]

Mu usually reacts faster than H in addition reactions (due to its higher tunneling efficiency) and slower in abstraction reactions (due to the Mu adduct having a higher activation barrier).[8]

Experimental Section

These experiments were performed with beams of positive muons on the M9B channel at the TRIUMF cyclotron with the "sfumu" backward-muon counting equipment. The experiments utilized the muon-spin-rotation technique in transverse magnetic fields (μSR).[1,8,9] Absolute rate constants for muonium atoms reacting with an added solute in water were determined in the conventional way from the relaxation of the muon spin precession signal in fields of about 8 G. The count rates in each of at least two detectors were fitted separately to eq 1 to obtain the exponential relaxation constant λ of the muonium amplitude A_M,

$$N(t) = N_0 e^{-t/\tau_\mu}[1 + A_D \cos(\omega_D t + \phi_D) + A_M e^{-\lambda t} \cos(\omega_M t - \phi_M)] + Bg \quad (1)$$

where $N(t)$ and N_0 are the count rates at times t and $t = 0$, τ_μ is the mean muon lifetime (2.2 μs), A_D, ω_D, and ϕ_D are the amplitude, precession frequency, and initial phase of the diamagnetic component, A_M, ω_M, and ϕ_M are the corresponding parameters of the Mu component, and Bg is a background count rate.

The muonium bimolecular rate constant (k_M) comes from the relationship $k_M = (\lambda - \lambda_0)/[S]$, where λ_0 is the "background" value of λ in the water used at each particular pH when the solute concentration $[S] = 0$. Each pH was studied at three or four different concentrations of oxalate, with plots of λ versus [S] used to determine k_M. Typical examples are shown in Figure 1.

Experiments were conducted at temperatures ranging from 5 to 90 °C in highly purified deoxygenated water. Reagent-grade sodium oxalate was used as solute with the pH adjusted by the use of Analar-grade HCl and NaOH pellets. The actual pH was measured for each solution studied using a calibrated pH meter.

Results

The μSR technique gives an overall second-order reaction rate constant corresponding to the observed rate of disappearance of Mu atoms as a result of the presence of a solute. This

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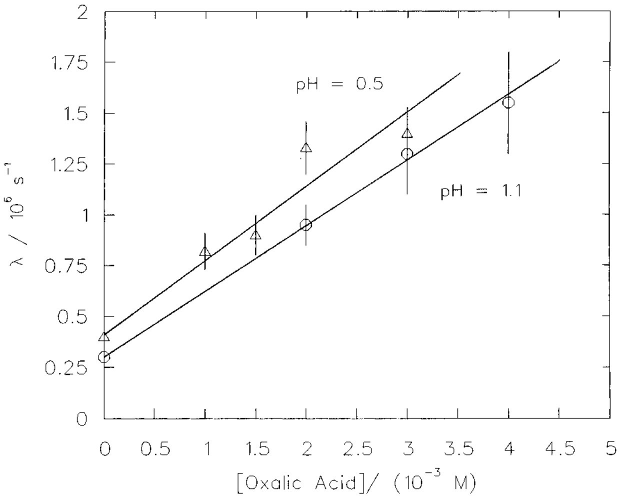

Figure 1. Typical plots of λ versus total concentration of oxalate species added (in acid solutions at ~295 K): at pH = 0.5 (triangles) and at pH = 1.1 (circles).

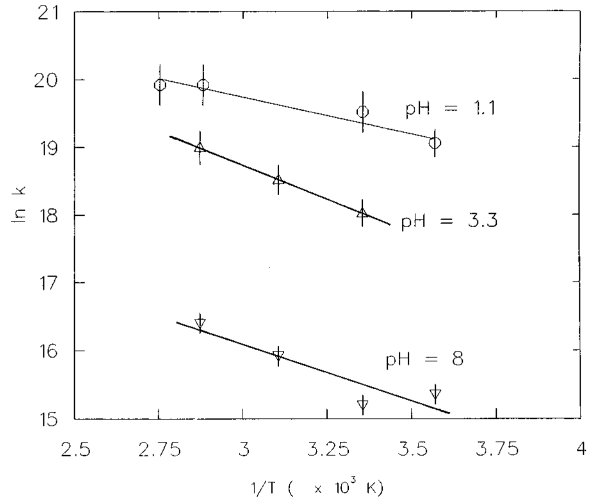

Figure 2. Arrhenius plot of k_{obs} against $1/T$ for the reaction of Mu atoms with oxalic acid/oxalate ions in water, at pH = 1.1 (circles), pH = 3.3 (triangles), and pH = 8 (inverted triangles).

TABLE 1: Values of k_{obs} Obtained for the Reaction of Mu with Oxalic Acid/Oxalate Ions at Four pH's, at ~295 K in Water

pH	k_{obs}/M^{-1} s^{-1}
0.52	$(4.8 \pm 0.4) \times 10^8$
1.1	$(3.4 \pm 0.3) \times 10^8$
3.3	$(6.8 \pm 0.7) \times 10^7$
8.0	$(5.4 \pm 0.6) \times 10^6$

"observed" rate constant will be designated k_{obs}, to distinguish it from the eventual calculated breakdown into k_M values for each of the three species in solution.

Table 1 shows the values of k_{obs} obtained at room temperature, ~295 K, for each of the four pH's studied.

The temperature-dependence of k_{obs} is reported in Figure 2 for temperatures between 5 and 90 °C for solutions at pH = 1.1, 3.3, and 8.0. These data are plotted as $\ln(k_{obs})$ versus $1/T$, in accordance with the Arrhenius equation ($k = Ae^{-E_a/RT}$). Values for the parameters E_a and A were obtained from the slope of the lines drawn in Figure 2. The results are given in Table 2.

The two acid dissociations of oxalic acid occur with $pK_{a_1} = 1.23$ and $pK_{a_2} = 4.19$.[10] These allow one to calculate the distribution of species in solution at any pH for oxalic acid ($H_2C_2O_4$), the hydrogen-oxalate anion ($HC_2O_4^-$), and the oxalate dianion ($C_2O_4^{2-}$). The four pH's used in this study were measured to be 0.52, 1.1, 3.3, and 8.0. The corresponding calculated fractional compositions (c) at these four pH's are given in Table 3.

TABLE 2: Observed Arrhenius Parameters (E_a, A) from the Plots of Figure 2 for the Reactions of Mu with Oxalic Acid/Oxalate Ions in Water at pH = 1.1, 3.3, and 8.0 over the Temperature range 5−90 °C

pH	E_a/kJ mol^{-1}	A/M^{-1} s^{-1}
1.1	~7	5.5×10^9
3.3	16.7(± 2)	6×10^{10}
8.0	15.4(± 2)	3×10^9

TABLE 3: Distribution of the species from the Acid−Base Dissociations of Oxalic Acid/Oxalate Ions in Water at ~295 K: c-Values Are the Calculated Fractional Compositions of the Three Species, Based on the Published Values of the K_a's (See Text); c_1 that of $H_2C_2O_4$, c_2 that of $HC_2O_4^-$, and c_3 that of $C_2O_4^{2-}$

pH	c_1	c_2	c_3
0.52	0.83	0.17	<0.01
1.1	0.57	0.43	<0.01
3.3	0.008	0.89	0.10
8.0	0	<0.01	>0.99

TABLE 4: Actual Individual Absolute Bimolecular Rate Constants Deduced for the Reaction of Mu with Oxalic Acid and Its Two Anions, in Water at ~295 K

reaction	k_M/M^{-1} s^{-1}
Mu + $H_2C_2O_4$	$k_M^1 = 5.6 \times 10^8$
Mu + $HC_2O_4^-$	$k_M^2 = 7.1 \times 10^7$
Mu + $C_2O_4^{2-}$	$k_M^3 = 5.4 \times 10^6$

Discussion

(i) Individual Rate Constants. A strong pH-dependence on the observed rate of reaction of Mu is found: k_{obs} decreases from 4.8×10^8 M^{-1} s^{-1} at pH = 0.52 to 5.4×10^6 M^{-1} s^{-1} at pH = 8. Since the degree of dissociation changes with pH, these values of k_{obs} are the weighted averages of the individual rate coefficients with each oxalate species in solution at a particular pH.

There are three distinct reactions to consider:

(i) Mu + $H_2C_2O_4 \rightarrow$ Mu adduct, with rate constant k_M^1

(ii) Mu + $HC_2O_4^- \rightarrow$ Mu adduct, with rate constant k_M^2

(iii) Mu + $C_2O_4^{2-} \rightarrow$ Mu adduct, with rate constant k_M^3

where each Mu product is very probably a Mu radical formed by Mu adding into the C=O of a carboxylate group, resulting in a C-centered Mu radical with Mu attached to an O atom as in $HO_2C\dot{C}(OMu)OH$ (by analogy with H[4,5]). At any pH, k_{obs} will be the sum of the three components in eq 2,

$$k_{obs} = c_1 k_M^1 + c_2 k_M^2 + c_3 k_M^3 \qquad (2)$$

where c_1, c_2, and c_3 are the fractional compositions of the three species as calculated from the K_a's, and given in Table 3, for each pH. Fitting all four pH's together gives the values for the individual k_M's reported in Table 4.

These are absolute, bimolecular, rate constants for the reaction of Mu with the three individual oxalic acid species, HO_2CCO_2H, $HO_2CCO_2^-$, and $^-O_2CCO_2^-$. k_M is seen to decrease by a factor of 8 for loss of the first proton and by a factor of 13 for the second. This undoubtedly stems, at least in part, from the progressive delocalization of the π-electron density in the anions, thereby making them less susceptible to addition reactions. It is also consistent with Mu's nucleophilicity.[6] The magnitude of this pH effect is unprecedented for Mu reactions;[1,2,6,8,9] but

TABLE 5: Comparisons of k_{obs} for Mu with Published Data on ^{1}H and Hydrated Electrons (e_{aq}^-) and the Observed Kinetic Isotope Effects (Mu/H) at pH = 1 and ≥7

observed *k*'s	pH ≈ 1	pH ≈ 3	pH ≥ 7
k_{obs} (Mu)	3.4×10^8	6.8×10^7	5.4×10^6
k_{obs} (H)[a]	4×10^5		$\leq 4 \times 10^4$
k_{obs} (e_{aq}^-)[b]	2.5×10^{10}	3×10^9	3×10^7
k_{obs} (Mu)/k_{obs} (H)	850		>300
k_{obs} (e_{aq}^-)/k_{obs} (Mu)	73	44	5.5

[a] From refs 3 and 4. [b] From ref 12.

it is comparable to that found for H atoms and e_{aq}^- in the case of oxalic acid (see later, Table 5), so it is a peculiarity of oxalic acid rather than of Mu.

(ii) Arrhenius Parameters. Figure 2 shows the dependence of ln(k_{obs}) on $1/T$ at pH = 1.1, 3.3, and 8.0. At pH = 3.3 and 8.0 the plots are reasonably linear, but at pH = 1.1 there is a monotonic indication of a concave-downward curvature.

At pH = 1.1 there are two species present in comparable amounts, $H_2C_2O_4$ (57%) and $HC_2O_4^-$ (43%). It is improbable that the separate reactions involving these two species (i and ii) have the same E_a and/or A values, so a simple Arrhenius plot should not be linear. In addition, K_{a_1} and K_{a_2} will have different T-dependences, so the composition also changes with temperature, and this leads to further nonlinearity. All one can conclude is that the pH = 1.1 data in Figure 2 shows a slope that is shallower than that of the two higher pH's, and thus its E_a value is smaller. For the computer-drawn line shown, E_a is a mere 7 kJ/mol.

At pH = 8, however, the dianion is the only species present, so the E_a = 15.4 kJ/mol obtained from the slope at pH = 8 represents only reaction iii. A similar situation occurs at pH = 3.3, where 89% of the species present are hydrogen-oxalate anions, and most of the rest are the dianions with virtually the same E_a. So, even if the acid dissociation constants alter significantly with temperature, it remains very probable that reactions ii and iii have E_a's between 15 and 17 kJ/mol.

The important points to be gleaned from the Arrhenius parameters (Table 2) are the following: (a) All of the E_a's are small: comparable to, or less than, those of diffusion-controlled reactions of Mu in water (~16 kJ/mol due to the viscous energy barrier to diffusion in water[8,11]). (b) These k_M's are 2−4 orders of magnitude slower than the limits imposed by diffusion alone, so their small E_a's suggest the reactions are not simple one-step activation-controlled reactions (where $E_a \approx 30-40$ kJ/mol are typical[8,11]). (c) These facts may suggest a composite effect, such as that resulting from the occurrence of a relatively long-lived Mu−oxalato complex as intermediate. In analyzing the appropriate kinetics, using either pre-equilibrium or steady-state treatments of the complex, the observed Arrhenius parameters would be composite values of three individual steps (see for example pp 115−120 of ref 8). (d) Equally, the low E_a values suggest that the reaction has a large tunneling component.

(iii) Comparison with H (Kinetic Isotope Effects). Table 5 shows the comparison of our observed values for Mu (k_{obs}(Mu)) with the published data at pH = 1 and 7 for ordinary ^{1}H atoms (k_{obs}(H)). At pH ≈ 1 there would be a mixture of reactions i and ii in accordance with Table 3, whereas at pH ≥ 7 the species present were only the oxalate dianions, $C_2O_4^{2-}$. Since k_H has not been subdivided into its ionic components, only "observed" k's can be discussed.

Comparisons of Mu with ^{1}H reactions are direct measures of *primary* kinetic isotope effects, involving as they do, the reactions of the isotopic atoms themselves. The "observed" ratios, given as lighter-over-heavier, are shown in the fourth row of Table 5 for oxalic acid and oxalate. For pH ≈ 1, where reactions i and ii both occur, Mu wins by a factor of ~850. At pH ≥ 7, where only reaction iii occurs, Mu wins by a factor > 300.

No prior examples seem to exist for the Mu rate to exceed that of H by more than ~10^2,[1,8,9] for the same reaction mechanism. So these may be the largest primary kinetic isotope effects ever reported, because the isotopic mass ratio of Mu/H of 1/9 (1/27 for Mu versus ^{3}H) so greatly exceeds the isotopic mass ratios of all other atoms.

(iv) Comparison of Mu with e_{aq}^- and ^{1}H. Table 5 also shows the observed hydrated electron reaction rates toward oxalic acid and the two oxalate ions.[12] Again, there is some uncertainty about the exact pH and hence about the distribution of reactive species, but the basic message is clear: e_{aq}^- reacts much faster than Mu with $H_2C_2O_4$ and $HC_2O_4^-$, as shown in the last row of Table 5. It even reacts ~5 times faster than Mu with $C_2O_4^{2-}$ dianions, despite the electrostatic repulsion between $C_2O_4^{2-}$ and e_{aq}^-.

This places Mu between ^{1}H and e_{aq}^- in their reactivities toward oxalic acid and its anions. This is not the first time we have noted that Mu lies squarely between H and e_{aq}^- in its fundamental reactivity, because, in the acid-test of how Mu reacts in the competition between N_2O and 2-propanol, Mu lay directly between them.[13]

Oxalic acid and its anions thus afford extra evidence for this basic picture of Mu. Its reactions at room temperature are governed by Mu's intermediate quantum mechanical character: it reacts faster than H but slower than e_{aq}^- for reaction paths in which tunneling plays a significant role.

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