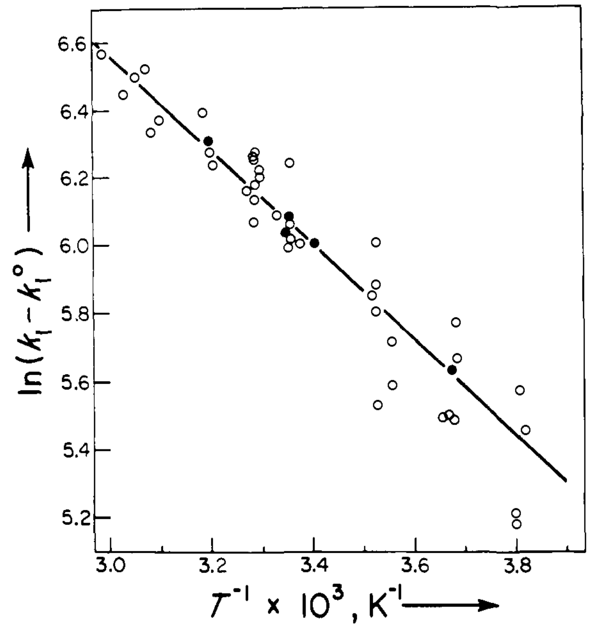

Figure 3. Adherence of DCA k_1 values to eq 17; closed symbols indicate coincidence of 2–5 independent measurements.

initial data sets had artificially high k_1''s and were discarded. Corresponding k_1's did not change with light exposure and were, therefore, used together with those given in Table I to obtain parameters for k_1 interpolations. It was assumed that k_1 consisted of a temperature and viscosity independent unimolecular decay part, k_1°, which is augmented by bimolecular quenching contributions. The k_1° value was determined by fitting[32] the k_1's to

$$k_1 = k_1^\circ + mT/\eta \qquad (16)$$

with use of T/η sources given in ref 15: $k_1^\circ = 1576 \pm 20$ s^{-1}, $m = (7.96 \pm 0.36) \times 10^{-3}$ P·K^{-1} s^{-1}. With $k_1^\circ = 1576$ s^{-1} fixed, the k_1's were then fitted[32] to

$$k_1 = k_1^\circ + b \exp(-E_q/RT) \qquad (17)$$

leading to $b = (4.75 \pm 0.96) \times 10^4$ s^{-1} and $E_q = 2.78 \pm 0.12$ kcal/mol, Figure 3. The interpolated k_1 values in Table I were obtained by using eq 17.

The 30-fold increase of k_1° relative to the corresponding constant in A is attributed to heavy-atom-enhanced spin–orbit coupling on both the radiative and nonradiative rate constants for the $T_1 \rightarrow S_0$ transition.[49] Our k_1° value, being somewhat lower than that previously reported, falls exactly on a line relating triplet decay rate constants for a series of halogen-substituted anthracenes to spin–orbit coupling factors.[49a] The explanation usually favored for the behavior reflected in the second term of eq 16 or 17 is that it represents quenching by impurities adventitiously present in the solute and/or the solvent.[14,50] Since our measurements were carried out by different investigators over a period of years employing different batches of materials and different purification techniques, we tend to discount this interpretation, unless the impurity is residual oxygen. Diffusion-controlled quenching by an impurity Q would be consistent with E_q because it is nearly identical with the activation energy for viscous flow in toluene,[15] and would account for b if [Q] were $\sim 5 \times 10^{-8}$ M. An alternative interpretation is provided by the self-quenching of ^{3}DCA* by ^{1}DCA. With use of [DCA] = 1.15×10^{-4} M, the value of b gives $A = 4.1 \times 10^8$ s^{-1} which is almost identical with $A_{sq} = 3.9 \times 10^8$ s^{-1}, the Arrhenius preexponential factor for self-quenching in A.[14] We anticipate testing this interesting possibility by determining the dependence of b on [DCA].

Registry No. Anthracene, 120-12-7; 9,10-dichloroanthracene, 605-48-1; *cis*-stilbene, 645-49-8; *trans*-stilbene, 103-30-0.

Supplementary Material Available: Table I-S, listing k_{obsd} and k_{en} values for A (1 page). Ordering information is given on any current masthead page.

Muonium Addition Reactions to Aromatic Solutes

J. M. Stadlbauer,[†] B. W. Ng, R. Ganti,[‡] and D. C. Walker*

Contribution from the Chemistry Department, University of British Columbia, Vancouver, Canada V6T 1Y6. *Received August 30, 1983*

Abstract: Reaction rate constants of 0.3×10^{10}–1.1×10^{10} M^{-1} s^{-1} were determined for the reaction of muonium (μ^+e^-, Mu) with seven aromatic solutes in dilute aqueous solution at ~295 K. The reaction was deduced to be that of addition to the benzene ring to form cyclohexadienyl radicals. On comparison with the analogous H-atom reactions, the kinetic isotope effects were generally about 3, equal to the mean thermal velocity ratio of Mu/H. When analyzed through the Hammett equation there were serious discontinuities but a small positive ρ value was evident, not inconsistent with attack by a mildly electron-donating neutral atom forming only free radical intermediates.

A convenient and sensitive method of studying both hydrogen atom reactions and kinetic isotope effects is to study the reactions of muonium (Mu). This is the light atom ($^1/_9$ the mass of ^{1}H) which differs from hydrogen in having a positive muon rather than a proton as its nucleus. As the muon is unstable and spin polarized its chemical fate can be investigated by the muon spin rotation method (μSR) using nuclear physics counting techniques.[1-3] A variety of muonium reaction types in aqueous solution have been studied[3,4] including the following: addition, abstraction, substitution, electron spin exchange, redox, and acid–base reactions. For addition reactions, Mu has been observed to add cross C═C

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* Address correspondence to this author at the University of British Columbia.

[†] Present address: Department of Chemistry, Hood College, Frederick, MD 21701.

[‡] Present address: Department of Chemistry, University of Missouri—Kansas City, Kansas City, MO 64110.

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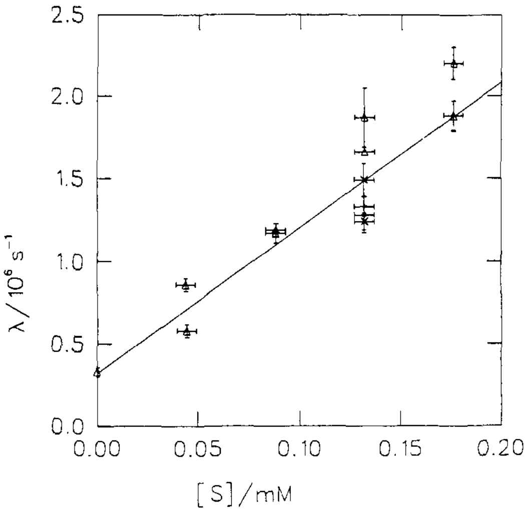

Figure 1. Representative λ vs. [S] data for aniline. The vertical error bars on each λ value represent the statistical errors, equal to the standard deviation arising from the MINUIT fit to each histogram.

double bonds in aliphatics at rates close to the diffusion-controlled limit of $\sim 2 \times 10^{10}$ M^{-1} s^{-1} [5] and across C≡N triple bonds of organic solutes some 300-fold slower.[6] Muonium-containing free radicals formed by addition have also been detected directly by μSR in several pure unsaturated compounds.[7] In the present study an attempt is made to evaluate the factors influencing the mechanism and rate the Mu reactions with substituted benzenes as solutes in dilute aqueous solution at room temperature.

Experimental Section

Muonium forms when an energetic muon comes to rest in an aqueous sample. Its spin undergoes Larmor precession at a characteristic frequency of 1.39 MHz G^{-1} in transverse magnetic fields. Upon decay, a positron is emitted preferentially along the spin vector so that oscillations appear on the ordinary muon lifetime histogram when the positrons are monitored in a given direction within the plane of precession. These oscillations provide an identification of the muonium chemical state, its yield, and a relaxation constant (λ). The latter is directly relatable to the bimolecular rate constant (k_M) when Mu reacts with a solute [S], through $k_M = (\lambda - \lambda_0)/[S]$, where λ_0 is a "background" component (solvent or apparatus artifact). Details of this μSR technique, together with the analysis and treatment of data, have been reviewed recently (see, for example, ref 1-3).

Dilute aqueous solutions of various aromatic solutes were placed in shallow plastic cells and held between the coils of a magnet at the end of the M20 beamline at TRIUMF (the Tri University Meson Facility at the University of B.C.). A field of 8 G was used for the kinetic studies, and spin-polarized "surface" muons with 4.1 MeV of energy were made to strike the aqueous solution through thin (0.05 mm) Mylar windows on the cell. Oxygen needs to be minimized in these solutions because it too reacts rapidly with Mu. For all the solutes studied here, except benzene, the solutions were bubbled with a flow of helium gas during the experiment, and prebubblers containing the same solution reduced the chance of solute loss by evaporation. For the benzene solutions it was necessary to use freeze-pump-thaw cycles together with glass cells and the more penetrating "backward" muon beam.[8] Solutions were made from triply distilled water and Reagent or Spectral Grade compounds.

Results

Values of k_M were evaluated from plots of λ vs. [S]. A typical plot is shown as Figure 1, where some ten individual λ measurements contribute to the value of k_M. A feeling for the relative magnitude of the statistical errors (shown as error bars) on each λ value compared with the probable error in the evaluated k_M (variation of slope of line) can be gleaned from this plot. For the seven solutes studied, the ranges of [S] and λ are given in Table I, together with the k_M values obtained by least-squares fitting. Realistic errors in k_M are about ±25%.

Table I. Muonium Rate Constants (k_M) Evaluated for the Reaction of Muonium with Aromatic Solutes in Aqueous Solution at ~295 K, from the Measured Values of λ over a Range of [S]

solute	[S]/mM range	$\lambda/10^6$ s^{-1} range	no. of λ	$k_M/10^9$ M^{-1} s^{-1}
nitrobenzene	0.08-0.24	1.16-3.0	6	11
aniline	0.04-0.18	0.72-2.2	10	8.8
cyanobenzene	0.12-0.20	1.23-1.82	6	7.2
benzoic acid	0.10-0.59	0.91-6 ± 2	6	7.0
benzaldehyde	0.21-2.0	1.90-9.3	9	5.1
benzene	0.22-0.44	0.90-1.65	3	3.3
[phenol, previously (ref 17)				7 ± 2]

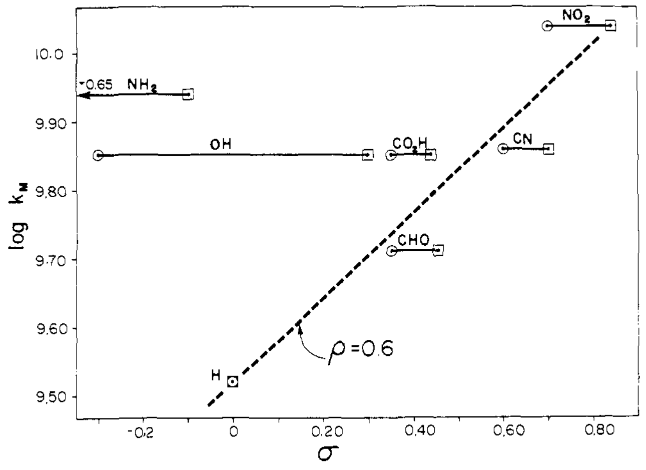

Figure 2. Plot of log k_M vs. σ in accordance with the Hammett equation. The meta and para σ values were taken from ref 10 showing the range of σ_m(o) and σ_p(□) reported. The dashed line has a slope (equal to ρ) of +0.6.

Discussion

Table I shows that the values obtained for k_M with these solutes range from 0.3×10^{10} M^{-1} s^{-1} for unsubstituted benzene to 1.1×10^{10} M^{-1} s^{-1} for nitrobenzene. Such values fall short by factors of 2 to 6 from the diffusion-controlled limit of $\sim 2 \times 10^{10}$ M^{-1} s^{-1} for Mu reactions with solutes of this size in water—as established for efficient redox and spin-exchange reactions.[3,9] They coincide, however, with the range found for Mu addition to vinyl monomers.[5] Apparently the intrinsic reaction rate, k_i in eq 1,

$$k_M = (k_d^{-1} + k_i^{-1})^{-1} \qquad (1)$$

makes the larger contribution to k_M, perhaps due to loss of aromatic resonance energy, with diffusion (k_d) being of secondary importance. These values of k_M for "addition" reactions are some two orders of magnitude faster than those generally found for "abstraction" or "substitution" reactions for muonium.

The effect of the substituents on k_M can be discussed with regard to the Hammett linear free energy relationship, eq 2. In this k

$$\log (k/k_0) = \sigma\rho \qquad (2)$$

and k_0 are taken as the k_M values with and without a substituent, σ is the Hammett substituent factor, and ρ is the reaction constant parameter indicating the susceptibility of the reaction to electronic substituent effects. Figure 2 shows the plot of log k_M vs. σ, using the range quoted for σ_m and σ_p.[10] It is clear that no simple

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Table II. Kinetic Isotope Effects (k_M/k_H): Comparison of Mu and H Reactions with Solutes in Aqueous Solution at ~295 K

solute	$k_M/10^9$ M^{-1} s^{-1}	$k_H{}^a/10^9$ M^{-1} s^{-1}	$k_M/k_H{}^b$
nitrobenzene	11	3.3	3.3
aniline	8.8	2.9	3.0
cyanobenzene	7.2	0.7	10
benzoic acid	7.0	1	7
phenol	7	2	3.5
benzaldehyde	5.1	1.5	3.4
benzene	3.3	1.1	3.0

[a] k_H data taken from ref 18. [b] Accumulated errors are difficult to assess but probably range from 20 to 50%.

correlation over the full σ range exists.

If one ignores the substituents with negative σ values (NH_2 and OH) then the remainder show a resonably linear correlation, as indicated by the dashed line in Figure 2, with a ρ factor of +0.6. Perhaps alternative, competitive, reaction paths are available to aniline and phenol: indeed, it has been postulated that H atoms "abstract" from these molecules.[11] On the other hand, if one ignored benzene and nitrobenzene instead (the latter on the grounds that H adds to the NO_2 group),[12] then a shallow negatively sloped line would result. Either way, the ρ factor is very small: not inconsistent with H ($\rho = -0.45$)[13] and in sharp contrast with the strongly electron donating character of hydrated electrons (where $\rho = 4.8$).[14] A small ρ is to be expected for such fast reactions, in accordance with the reactivity–selectivity principle,[15] and it also suggests that the transition states of the reactions have very little polar character. This is consistent with addition by a neutral atom giving free radicals as intermediates in the reaction. It coroborates a previous finding, based on the Brønsted–Bjerrium treatment of ionic atmospheres,[16] that Mu behaves strictly as a neutral atom, showing no tendency to long-range electron or proton (muon) transfer in its reactions in water.

Kinetic isotope effects involving Mu compared to H are multifarious.[3] For the reactions of this study one has the values presented in the last column of Table II. Five out of seven of them are ca. 3. The ratio of 3 happens to equal the ratio of mean thermal velocities of Mu relative to H from the mass ratio, as in eq 3. This would correspond to the relative encounter frequency

$$\bar{v}_M/\bar{v}_H = (m_H/m_M)^{1/2} \tag{3}$$

(and thus to the preexponential factor in a collision theory interpretation of the Arrhenius equation) if the solvent had no control over diffusion. But, as it is, the kinetic isotope effect has always been found to be unity in the diffusion-controlled limit, suggesting that these atoms behave as Stokes–Einstein particles (where $D \alpha 1/R$) in which diffusion is dominated by the solvent rather than the solute.[3,9] This means that the radius of the atom counts but not its mass. An indication of the effective size of H has emerged from recent calculations.[19] As "abstraction" reactions of Mu and H (toward CH_3OH, for instance) have large inverse isotope effects ($k_H \gg k_M$) due, presumably, to the zero-point energy effect in the activated complexes, perhaps one has in the case of "addition" to the aromatic solutes a fortuitous intermediate stage–with an intrinsic preexponential factor based on velocities. It seems to be neither dominated by the solvent, as in the diffusion-controlled limit, nor dominated by activation in slow reactions where quantum effects take over (tunneling, favoring Mu, or zero-point energy in the transition state, favoring H).

Conclusions

This study has indicated the value of μSR in elucidating H-atom reactions and kinetic isotope effects. Both H and Mu are of particular interest in chemistry because of their low mass and small size. They are likely to be the first to break the stanglehold (in water, at least) of the Stokes–Einstein restriction on mobility, on the one hand, and the first to show greatly changed probabilities of reaction due to quantum mechanical effects, on the other. It remains to be seen whether the somewhat unsatisfactory concordance with the Hammett equation in Figure 2 arises simply from the variations of reaction types which are possible for Mu and H. However, it is clear that the exceptionally low mass of Mu, which may be a disadvantage in abstraction and substitution reactions, certainly is not in addition, even with respect to the π delocalization of the benzene ring.

Acknowledgment. The continuing collaborations with Prof. Y. C. Jean, Prof. Y. Ito, and Y. Miyake are greatly appreciated and so was the advice of Prof. R. Stewart and the financial support from the Natural Sciences and Engineering Research Council of Canada.

Registry No. Muonium, 12587-65-4; nitrobenzene, 98-95-3; aniline, 62-53-3; cyanobenzene, 100-47-0; benzoic acid, 65-85-0; phenol, 108-95-2; benzaldehyde, 100-52-7; benzene, 71-43-2.

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