Muonium addition reactions in the gas phase: Quantum tunneling in Mu+C2H4 and Mu+C2D4

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The reaction kinetics for the addition of the muonium ($Mu = \mu^+ e^-$) atom to C_2H_4 and C_2D_4 have been measured over the temperature range 150–500 K at (N_2) moderator pressures near 1 atm. A factor of about 8 variation in moderator pressure was carried out for C_2H_4, with no significant change seen in the apparent rate constant k_{app}, which is therefore taken to be at the high pressure limit, yielding the bimolecular rate constant k_{Mu} for the addition step. This is also expected from the nature of the μSR technique employed, which, in favorable cases, gives $k_{app} = k_{Mu}$ at any pressure. Comparisons with the H atom data of Lightfoot and Pilling, and Sugawara *et al.* and the D atom data of Sugawara *et al.* reveal large isotope effects. Only at the highest temperatures, near 500 K, is k_{Mu}/k_H given by its classical value of 2.9, from the mean velocity dependence of the collision rate but at the lowest temperatures $k_{Mu}/k_H \gtrsim 30/1$ is seen, reflecting the pronounced tunneling of the much lighter Mu atom ($m_\mu = 1/9\, m_p$). The present Mu results should provide accurate tests of reaction theories on currently available *ab initio* surfaces.

I. INTRODUCTION

The study of H atom addition to unsaturated molecules has been central to free radical and combustion chemistry for many years.[1] The simplest such addition reaction to an olefin is H(D) atom addition to ethylene, forming the ethyl radical ($C_2H_5^*$). Thermal rate constants for this reaction have been measured between 200 and 600 K,[2–7] including detailed studies of deuterium kinetic isotope effects.[6] The most recent H-atom study is that of Lightfoot and Pilling,[7] whose data agree very well with the earlier results of Michael and co-workers[2–5] and Sugawara *et al.*[6] The reaction mechanism is now well established as

$$H + C_2H_4 \underset{k_d}{\overset{k_a}{\rightleftharpoons}} (C_2H_5)^* \overset{M}{\underset{k_s}{\to}} C_2H_5, \tag{1}$$
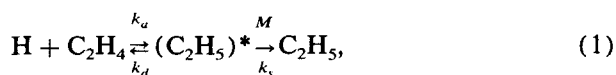
where a third body "M" is required to form a stable product. In general, the kinetics can be described by the three rate constants k_a, k_d, and k_s, for the processes of addition, (unimolecular) dissociation, and stabilization, respectively. These are related by the apparent bimolecular rate constant

$$k_{app} = \frac{k_a k_s M}{k_d + k_s M} \tag{2}$$

assuming the validity of the steady-state approximation for the concentration of $(C_2H_5)^*$. The stabilizing efficiency of the third body depends on temperature and the nature of M, but typically for molecular gases near room temperature the "high pressure" limit, where $k_{app} = k_a$, is reached at pressures $\gtrsim 100$ Torr.[2–7] At low enough pressures, k_{app} increases linearly with pressure M. The intermediate region, where $k_{app}/k_a < 1$, is described as the "falloff" region, and accurate measurements of the reaction kinetics in this region have long been important for comparing with RRKM predictions and related theories of unimolecular dissociation.[2,3,7–11] Here accurate measurements of k_{app} are important, particularly over a wide range of pressures leading up to the high pressure limit.[10,11] Such measurements are essential also for comparisons with transition state theory (TST)[6,7,12,13] and quasiclassical trajectory (QCT)[14,15] calculations of the collision dynamics, which relate further to the nature of the potential energy surface (PES) itself.[8,16–19]

In contrast to the situation prevailing in reaction dynamics studies of H-atom–diatomic-molecule collisions,[20–26] relatively little is known about the accuracy of theoretical methods for computing rate constants for reactions involving polyatomic molecules. Much of this uncertainty can in turn be traced to a lack of knowledge about the PES for polyatomics.[16–19] In this regard, a long-standing paradox in studies of H-atom addition reactions to ethylene, in which RRKM and TST did not agree,[12] was apparently resolved by the (new) *ab initio* surface of Schlegel,[18] in conjunction with a revised heat of formation for the ethyl radical.[12] However, these calculations were not able to account for the isotope effects seen in D-atom addition, a failure they have in common with earlier TST calculations comparing H- and D-atom addition to C_2H_4,[6,13] albeit on a different PES.[13] Also, discrepancies between the results of tunneling-corrected TST and QCT calculations on a similar well studied reaction, $H(D) + C_2H_2$, for which an *ab initio* surface also exists,[16] raise further questions about the viability of reaction theory on these polyatomic systems in general. Additional studies of the reaction kinetics, particularly those involving a wide range of isotopic mass, are required.

The present paper deals with the muonium ($Mu = \mu^+ e^-$) analog of reaction (1), in which the proton nucleus in the incident H atom is replaced by a positive muon. From a theoretical standpoint, this reaction is of interest because Mu is quite simply *the* lightest isotope of the H atom ($m_\mu \sim 1/9 m_p$), and hence can be effectively used to test the viability of theoretical calculations of reaction rates,

particularly quantum tunneling, at the most sensitive end of the mass scale.[22,25,26] Experimental interest relates to the nature of the μSR (muon spin rotation) technique employed.[23,24,26,27] In many experimental studies of addition reactions like reaction (1), it is often not clear as to just what pressure constitutes the high pressure limit, an uncertainty that, in turn, affects the interpretation of reported rate constants and their comparison with theory.[16] In the μSR technique, the evolution of the μ^+ spin in the muonium atom is perturbed by a reactive collision process, causing a dephasing in transverse field and hence a relaxation of the ensemble spin polarization. In this respect, μSR can be thought of in analogy with related H-atom maser studies,[28] providing, in principle, a *direct* measure of the value of k_a, which may be *independent* of pressure for reaction systems such as C_2H_4 involving several degrees of freedom in the transition state.[29]

II. EXPERIMENTAL

A. μSR and muonium addition reactions in gases

Positive muons are created ($\pi^+ \rightarrow \mu^+ \nu_\mu$) 100% longitudinally spin polarized, providing an easily recognizable experimental (μSR) signature.[24,26,27] During their thermalization in a moderating gas like N_2, positive muons undergo cyclic charge exchange,[30] producing muonium atoms that survive until observation times with polarization P_{Mu}. Some muons will also be observed in diamagnetic environments, with polarization P_D, and as muonated free radicals,[24,31,32] with polarization P_R. An example of the latter is the muonated ethyl radical formed in the Mu analog of reaction (1), and recently identified in the gas phase.[32] Finally, there may be a "lost" or "missing" fraction of polarization P_L such that $P_{Mu} + P_D + P_R + P_L = 1$. In the gas phase at low pressures this lost fraction is known to be primarily due to hyperfine mixing on a time scale of $1/\nu_0 = 0.22$ ns, where $\nu_0 = 4463$ MHz is the ($\mu^+ e^-$) magnetic hyperfine frequency.[30] At modest pressures, of order 1 atm, the time between collisions, even at 1 eV translational energy, is short compared to $1/\nu_0$ and hence the lost fraction $P_L \rightarrow 0$. This process will not concern us further here.

Regardless of its environment, the muon decays ($\mu^+ \rightarrow e^+ \nu_e \bar{\nu}_\mu$) with a mean life $\tau_\mu = 2.2$ μs, emitting a positron preferentially along its spin axis. In a transverse magnetic field, muons in the various environments noted above precess with characteristic Larmor frequencies. Of particular interest in the present experiment is the coherent precession of the $S = 1$ spin state of muonium in a weak field; $\nu_{Mu} = 1.39$ MHz/G $\times$ B. A positron counter fixed in the plane of precession will record a (time differential) histogram of the number of decay positrons measured as a function of the survival time of the corresponding muons. Thus, a μSR histogram is a decay curve modulated by a precession frequency, somewhat analogous to free induction (T_2) decay in magnetic resonance experiments. The corresponding μSR precession signal, often referred to as the "asymmetry" $A(t)$, has the form

$$A(t) = A_{Mu} e^{-\lambda_{Mu} t}(\cos \omega_{Mu} t + \phi_{Mu})$$
$$+ A_D (\cos \omega_D t + \phi_D) \qquad (3)$$

where A_{Mu}, λ_{Mu}, ω_{Mu}, and ϕ_{Mu} are the initial amplitude (asymmetry), relaxation rate, angular frequency ($\omega = 2\pi\nu$), and initial phase of muons in muonium, with corresponding definitions for those in diamagnetic environments. For μ^+ stopping in N_2 gas, most muons thermalize as muonium. A typical asymmetry plot is shown in Fig. 1 for N_2 at 1000 Torr, 200 K. The solid line is a chi-squared fit of Eq. (3) to the data, yielding the parameters of interest. In this paper we are primarily concerned with the measurement of λ_{Mu}, corresponding to the interaction of Mu atoms with ethylene molecules [reaction (1)]. In the weak ($\sim$8 G) fields used, the μSR signal is dominated by Mu precession; relaxation of the small diamagnetic amplitude (A_D) is not
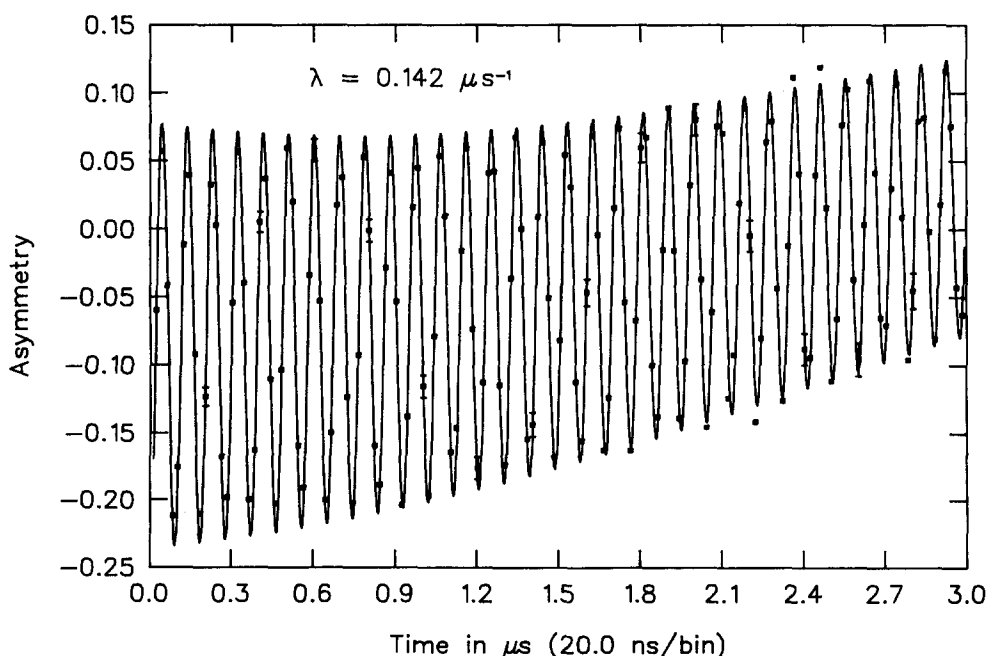
FIG. 1. The μSR asymmetry (signal) in pure N_2 at 1000 Torr pressure, 200 K, in a transverse magnetic field of 7.7 G. The signal is dominated by Mu precession. The solid line is a chi-squared fit of Eq. (3) to the data. Representative (1σ) error bars, due to counting statistics only, are indicated. The noted relaxation rate $\lambda = 0.142$ μs^{-1} is to be identified with λ_0 in Eq. (4).

measurable. It should be noted that the μSR technique demands that there be only *one* Mu atom in the system at a time, thus completely precluding the possibility that multiple Mu interactions could obscure the rate constant of interest, as has frequently been the case in the corresponding H-atom studies,[2-4] even when direct fluorescence techniques are involved.[6,7]

There are three basic processes occurring at random times that can contribute to the ensemble relaxation (λ_{Mu}) of the muon spin in muonium in a transverse field: (1) a chemical reaction placing the muon in a diamagnetic environment,[23,24,26] where the precession frequency is a hundredfold slower, so phase coherence is quickly lost; (2) a spin exchange reaction in which the ($\mu^+ - e^-$) hyperfine interaction is perturbed by electron spin flip processes,[33] thereby altering the time evolution of the muon spin via the ($\mu^+ e^-$) hyperfine interaction; and (3) an addition reaction forming a new paramagnetic (free radical) environment,[24,29,31,32] exemplified by the Mu analog of reaction (1), the subject of this paper.

In the latter case, the source of relaxation is also the ($\mu^+ - e^-$) hyperfine interaction, due to a sudden change in the electron spin density at the muon. The essential point here is, if the lifetime τ_c of the intermediate $(C_2H_4Mu)^*$ complex formed is long compared to $1/\omega_R$, where ω_R is some characteristic angular frequency due to $\mu^+ - e^-$ hyperfine coupling in the muonated radical (which can be measured in high magnetic fields[31,32]), then the muon again loses phase coherence. Current experiments[32] have determined ω_R in muonated ethylene in the gas phase to be 2073 rad μs^{-1} and hence $1/\omega_R$ is expected to be of order 0.5 ns. In high fields ($\gtrsim 1$ kG), the μSR spectrum is characterized by only two muon frequencies, the difference of which gives ω_R,[24,31,32] but in *weak* magnetic fields, such as the ~ 8 G field in the present study, the additional hyperfine couplings

between the protons and electron spin, in concert with the μ^+ spin in the $(C_2H_4Mu)^*$ radical, generate a multitude of frequencies (792), with the result that no single frequency is coherent.[29,31] The result is spin relaxation, expected on average to be on the time scale of $1/\omega_R$. In favorable cases, what is measured experimentally in μSR is the equivalent of the high pressure limit, *regardless* of either the temperature or the moderator pressure and hence of the stabilization step in Eq. (1). A detailed theoretical development of this topic may be found in Ref. 29. Moreover, the spin–rotation interaction, which dominates in both nuclear magnetic resonance (NMR) and electron-spin resonance (ESR) studies of polyatomic molecules in the gas phase,[34] causes additional line broadening at low pressures. Current μSR experiments[32] indicate that these (T_2) relaxation rates could be $\sim 400 \mu s^{-1}$ at the ~ 1 atm (moderator) pressure in the present study, reinforcing the claim that the μSR relaxation rates reported herein will likely always be effectively in the high pressure limit.

Thus both dephasing[29] and intramolecular spin coupling following radical formation[32] lead to rapid depolarization of the muon spin, manifest by the relaxation rate λ_{Mu} in the first term of Eq. (3). An example spectrum is given in Fig. 2. Comparison with Fig. 1 reveals an obvious, marked increase in relaxation rate. Here λ_{Mu} is a pseudo-first-order rate constant defined by

$$\lambda_{Mu} = \lambda_0 + k_{Mu}[C_2D_4], \tag{4}$$

with λ_0 a background relaxation in the pure N_2 (Fig. 1), determined primarily by inhomogeneous "line broadening" resulting from the extended μ^+ stopping distribution, and $k_{Mu} = k_a$ is the high-pressure bimolecular rate constant of interest. Henceforth, the high-pressure rate constants will be referred to as k_{Mu} (k_H, k_D) for isotopic addition reactions to C_2H_4 or C_2D_4.
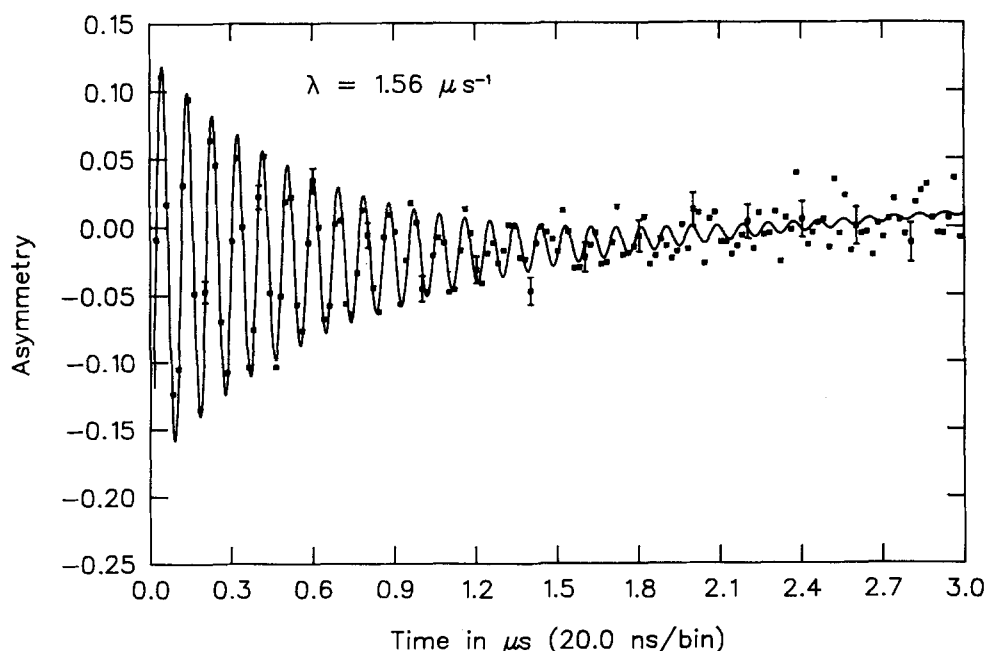

FIG. 2. As in Fig. 1, but in the presence of 1.0% added C_2D_4. The increased relaxation rate, $\lambda = 1.56 \mu s^{-1}$ due to the formation of MuC_2D_4, is noteworthy.

B. Experimental technique and results

The target vessel was placed between a pair of Helmholtz coils and consisted of two concentric cylinders separated from the outside world by a vacuum jacket. Both the inner (reaction) vessel and its jacket were equipped with thin (~0.1 mm) mylar windows to accommodate the incident muon beam. In an early series of experiments on ethylene, the coils were small (50 cm diameter), providing a magnetic field to ~80 G, homogeneous to ~0.5% over a stopping volume of ~1 ℓ. Some preliminary results from this work have been reported elsewhere.[35] A later and much more extensive series of experiments involving both C_2H_4 and C_2D_4, used much larger (1.5 m diameter) coils, homogeneous to ~0.1% over the same stopping volume and capable of magnetic fields in excess of ~300 G. In either case, the experimental procedure was straightforward and is briefly the following: a known pressure, typically ~1 Torr of reactant gas (C_2H_4), as determined in the most recent experiments by a Baratron capacitance manometer, was introduced into the previously evacuated inner target vessel (~15 ℓ capacity) to which N_2 moderator was then added up to the desired operating pressure near 1 atm. The temperature, as monitored by a moveable thermocouple, was varied in the range ~150–500 K by flowing either hot or cold compressed gas around the inner reaction cylinder. About four concentration points were taken at each temperature, from which a fit of Eq. (4) to the data yielded the desired value of k_{Mu} (T).

The data for k_{Mu} (T) are recorded in Tables I and II for Mu + C_2H_4 and Mu + C_2D_4, respectively, and compared also as Arrhenius plots in Fig. 3. The total N_2 stopping pressure was usually held near 1 atm, but for some measurements was varied in the range 200 to 1500 Torr. No significant change in the rate constant with total pressure was found, consistent with the previous assertion that the values report-

TABLE I. Kinetic data for Mu + C_2H_4 in N_2 moderator.

$T(K)$[a]	$P(Torr)$[b]	k_{Mu} (10^{-12} cm^3 molecule^{-1} s^{-1})[c]
167 ± 2	200	2.342 ± 0.092
174 ± 5	500	2.791 ± 0.080
174 ± 4	800	2.979 ± 0.073
207 ± 3	800	3.769 ± 0.185
234 ± 6	800	4.588 ± 0.165
261 ± 3	800	4.949 ± 0.135
294 ± 4	800	6.121 ± 0.207
294 ± 3	800	6.088 ± 0.181
294 ± 4	1500	5.519 ± 0.321
309 ± 10	800	6.670 ± 0.556
336 ± 5	800	7.666 ± 0.283
371 ± 2	800	8.816 ± 0.264
378 ± 7	800	9.289 ± 0.512
438 ± 6	800	11.760 ± 0.600
483 ± 11	1500	12.868 ± 0.634
484 ± 7	800	13.633 ± 0.889

[a] Temperature uncertainties include both the variation over the stopping distribution of the muon beam and the instability over the time needed to run each measurement.

[b] Total N_2 moderator pressure in Torr.

[c] Uncertainties due to counting statistics only, obtained as 1 standard deviation errors from the least squares fitting program MINUIT.

TABLE II. Kinetic data for Mu + C_2D_4 in N_2 moderator.

$T(K)$[a]	$P(Torr)$[b]	k_{Mu} (10^{-12} cm^3 molecule^{-1} s^{-1})[c]
154 ± 2	900	2.368 ± 0.062
189 ± 1	800	2.871 ± 0.062
200 ± 2	1000	3.100 ± 0.069
296 ± 1	800	5.747 ± 0.232
448 ± 1	800	14.188 ± 0.635
502 ± 1	800	15.754 ± 0.855

[a] See footnote a, Table I.
[b] See footnote b, Table I.
[c] See footnote c, Table I.

ed herein are indeed in the high-pressure limit ($k_{app} = k_{Mu}$). There is a small but noticeable secondary isotope effect favoring Mu + C_2D_4 (squares in Fig. 3) at the higher temperatures, but Mu + C_2H_4 (diamonds) at the lower temperatures, not seen in the corresponding H, D atom studies.[6] Note the level of reproducibility in the room-temperature C_2H_4 data (294 K) in Table I. Over data-taking periods on the TRIUMF cyclotron that spanned about 5 years,[35] the total deviation in measured rate constants is only 10%. Note also the entry at 167 K, which was obtained at a moderator pressure of 200 Torr. While seemingly lying below the trend in the data (Figs. 3 and 4), it is not viewed as significantly so. For example, the 1500 Torr point at 294 K is also somewhat low. Figure 4 compares Arrhenius plots for
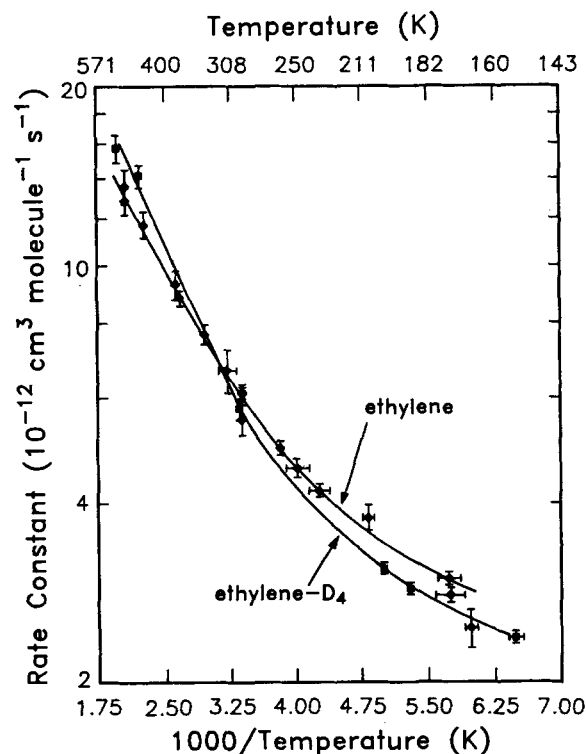

FIG. 3. Arrhenius plots for Mu + C_2H_4 (diamonds) and Mu + C_2D_4 (squares) from Tables I and II. The lines are drawn just to guide the eye. Note the small but significant secondary isotope effect, favoring Mu + C_2D_4 at the higher temperatures, but Mu + C_2H_4 at the lower temperatures. The lowest diamond point for C_2H_4 at 167 K was taken at a moderator pressure of 200 Torr; all others were taken over a range of pressures up to 1500 Torr, but most at ~800 Torr. See discussion in the text.

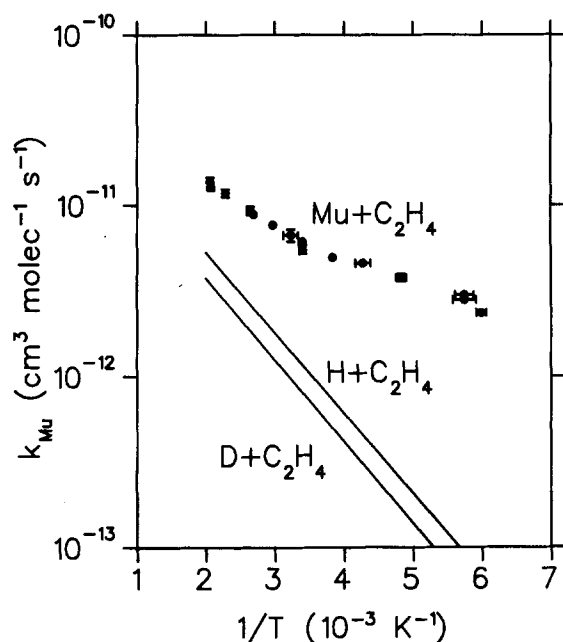FIG. 4. Arrhenius plots for Mu + C_2H_4 compared with the H and D atom data of Sugawara *et al.* (Ref. 6). The H atom data agree very well with both the earlier results of Lee *et al.* (Ref. 5) and the more recent ones of Lightfoot and Pilling (Ref. 7). The straight lines for the H, D atom data are from the Arrhenius parameters given in Ref. 6. See also Table III.

FIG. 5. As in Fig. 4, but comparing the Mu + C_2D_4 data with the H- and D-atom data of Sugawara *et al.* (Ref. 6).

the Mu + C_2H_4 data with the corresponding H- and D-atom data of Sugawara *et al.*[6] (solid lines), which have been measured over essentially the same temperature range. The solid lines were obtained from their published Arrhenius parameters.[6] As mentioned earlier, the H-atom data of Ref. 6 agree very well with the earlier results of Lee *et al.*,[5] as well as with the more recent data of Lightfoot and Pilling.[7] Figure 5 presents the same comparison for C_2D_4. The curvature seen in the low-temperature Mu data is dramatic in both cases. There is no corresponding effect seen in the H (D) atom results,[5-7] although there may be a hint of some curvature in the H + C_2H_4 data, commented upon in Ref. 7. The activation energies (E_a) obtained from the slopes over specific temperature ranges in Figs. 4 and 5 are given in Table III. The H and D atom values are independent of temperature,[5-7] but those for Mu clearly are not.

III. DISCUSSION

There have been two main focuses to date in comparing the experimental results of the reaction scheme in Eqs. (1) and (2) with theory: (1) the high pressure rate constants k_a have been compared with the predictions of TST[6,7,12-14] and QCT calculations;[14,15] and (2) the pressure dependence in the measured H atom rates for k_{app} has been compared with RRKM theory.[2,3,5,9,12] As is well known, the chemical activation process represented by Eq. (1) can be directly related to the corresponding unimolecular dissociation process for the (HE)* radical formed ($E = C_2H_4$ or C_2D_4 here) by

$$\frac{k_{app}}{k_a} = \frac{k_{uni}}{k_{uni}^{\infty}} = \int_{\epsilon_0}^{\infty} \frac{\omega f(\epsilon) d\epsilon}{\omega + k_d(\epsilon)}, \qquad (5)$$

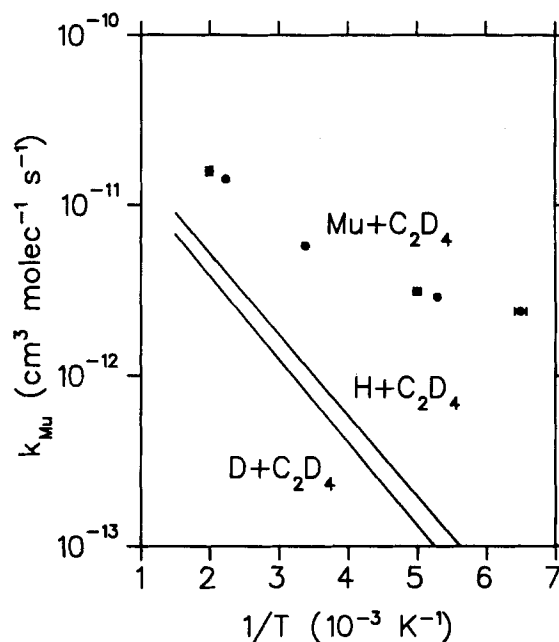where ω is the collision frequency of excited radicals with the third body species ($\omega = k_s M$), $f(\epsilon)$ represents the normalized density-of-states distribution function for the formation of excited radicals $\{f(\epsilon) \sim [HE]^*/[HE]\}$, and ϵ_0 is the critical (threshold) energy for dissociation. While the present μSR experiment is primarily concerned with the first point above, there are some features of the Mu analog of Eq. (1) that warrant further attention *vis a vis* the RRKM framework of Eq. (5). To date there have been no theoretical calculations for Mu + $C_2H_4(C_2D_4)$, although related studies on other molecules, notably C_2H_2, are in progress.[36]

A. Unimolecular dissociation

The arguments presented earlier, in terms of the lifetime of the intermediate complex τ_c being $> 1/\omega_R \sim 0.5$ ns, in order that the Mu addition rates reported herein are high-pressure limiting values at essentially any temperature or moderator pressure,[29] can be recast by stating that the average $\langle k_d(\epsilon) \rangle$ for Mu dissociation of the complex should be $\lesssim 2 \times 10^9$ s^{-1}. An (RRK) estimate of this can be made from Eq. (6), where the *ratio* of dissociation rate constants is represented by

$$\frac{k_d^{Mu}}{k_d^{H}} = 1/3 \left(\frac{(\epsilon^{Mu} - \epsilon_0^{Mu})/\epsilon^{Mu}}{(\epsilon^H - \epsilon_0^H)/\epsilon^H} \right)^{s^*}. \qquad (6)$$

Here the factor of 1/3 accounts for the fact that H dissociation from $(C_2H_4)^*$ is statistically more likely than Mu dissociation from $(C_2H_4Mu)^*$, and s^* represents the number of "active" vibrational degrees of freedom in the activated complex. To give reasonable agreement with a variety of different experiments, s^* is typically about one-third of the number of normal modes, over the temperature ranges of interest here (~ 150–500 K).[37,38] It is noted that H dissocia-

TABLE III. Arrhenius parameters[a] for Mu, H, D + C_2H_4, and C_2D_4.

T range	Mu		H[b]		D[b]	
	A	E_a	A	E_a	A	E_a
C_2H_4						
295–485	41.2 ± 4.0	1.11 ± 0.12	46 ± 3	2.15 ± 0.03	34 ± 2	2.19 ± 0.02
175–235	10.9 ± 3.7	0.45 ± 0.08				
C_2D_4						
295–500	66.7 ± 6.4	1.44 ± 0.16	46 ± 3	2.17 ± 0.04	36 ± 3	2.23 ± 0.04
150–200	7.6 ± 1.3	0.36 ± 0.06				

[a] In the definition $k(T) = Ae^{-E_a/RT}$, A given in units of 10^{-12} cm^3 molecule^{-1} s^{-1} and E_a in kcal mol^{-1}.
[b] Taken from Table I, Ref. 6. These values are independent of temperature over the whole range studied, from ~200–500 K. Errors are believed to be $\pm 1\sigma$. These parameters give rise to the solid lines in Figs. 4 and 5. See also published data in Refs. 5–7.

tion from $(C_2H_4Mu)^*$ is unlikely, since it is considerably more endothermic than Mu dissociation. The energy threshold ϵ_0^H is estimated by various authors[2,3,9,12,18] to be (39 ± 1) kcal mol^{-1}, consistent with measured heats of formation for C_2H_5.[12,39] Correcting for differences in zero-point energy (as, e.g., in Ref. 23), ϵ_0^{Mu} is estimated to be $\simeq (33 \pm 1)$ kcal mol^{-1}, and taking a value of 3 kcal mol^{-1} for the excess energy $(\epsilon - \epsilon_0)$ at the highest temperature measured, estimated from Ref. 14, yields essentially unity for the ratio k_d^{Mu}/k_d^H from Eq. (6). From the RRKM calculations of Refs. 3 and 12, it follows that k_d^{Mu} is about 2×10^8 s^{-1}, well within the stated limit. It is recalled that the spin relaxation time in the complex is likely to be much faster than $1/\omega_R$, due to intramolecular (spin rotation) relaxation mechanisms.

While the above estimate of the lifetime $\tau_c = k_d^{-1} \simeq 0.5$ ns may be taken as justification for the belief that the loss of muon polarization in Mu addition kinetics to C_2H_4 should be independent of pressure and temperature,[29] this clearly depends on the value of ϵ and particularly on the exponent (s^*) in Eq. (7). Rigorous (RRKM) calculations of Mu dissociation from $(C_2H_4Mu)^*$ are certainly required to support this claim. Such calculations for muonated radicals would be of general interest as well, since we are currently engaged in a broad study of Mu addition reactions to unsaturated bond systems.[32,36] In those studies, as in the present one, varying the moderator pressure over a wide range, up to 40 atm in the case of C_2H_2, revealed no significant change in k_{Mu}, confirming that this is at least in a conventional high-pressure limit.

B. The high pressure rate constants for Mu(H) atom addition

In the high pressure limit of Eq. (5), where $\omega \gg k(\epsilon)$, then $k_{app} = k_a = k_{Mu}$ and can be understood in terms of direct reaction theories, based on either TST or QCT calculations. From comparing the data in the Arrhenius plots for H, D, and Mu addition in Figs. 4 and 5, the ratios $k_{Mu}/k_H/k_D$ are ~4.0/1.4/1.0 at the highest temperatures measured, whereas at the lowest (Mu) temperatures, where the pronounced curvature seen only in the Mu results is ap-

parent, the ratio k_H/k_D remains at its classical value of 1.4, but the k_{Mu}/k_H ratio approaches 50/1. Only at the highest temperatures, near 500 K, is k_{Mu}/k_H given essentially by its classical value of 2.9 ($k_a \propto \bar{v}_{rel} \propto 1/\sqrt{mass}$).

The temperature-dependent slopes and hence E_a's seen in the case of Mu reactivity in Figs. 4 and 5 can be understood in terms of the Tolman definition of the activation energy, $E_a(T) = \langle E^* \rangle - \langle E \rangle$, where $\langle E^* \rangle$ is the average energy of those molecules that lead to products, while $\langle E \rangle$ represents the average energy of all molecules. Classically $\langle E^* \rangle$ is expected to increase faster than $\langle E \rangle$ with increasing T, thus leading to larger E_a's at higher temperatures.[26,40] This effect is not seen, though, in either the H- or D-atom-addition data,[5–7] represented by the Arrhenius plots in Figs. 4 and 5, or in a variety of other H-atom-addition reactions to both alkenes and alkynes.[41] In all these studies, there is essentially *no* curvature seen in the H-atom Arrhenius plots, with $E_a(T)$ concomitantly independent of temperature. The dramatic curvature seen *only* in the case of Mu addition to both C_2H_4 and C_2D_4 at *low* temperatures in Figs. 4 and 5, respectively, as well as in other related data,[36] is clear evidence of pronounced quantum tunneling. This feature can again be interpreted in terms of the Tolman definition above. Because of its remarkably light mass $(m_\mu \sim 1/9 m_p)$, quantum tunneling is greatly facilitated for Mu in comparison with H(D), so $\langle E^* \rangle$ is relatively smaller for Mu than for H(D) at a given temperature, and particularly at lower temperatures; thus $E_a(Mu)$ is correspondingly reduced. This anticipated result can be seen from the Arrhenius fits at both high (~300–500 K) and low (~200–150 K) temperatures in Table III; $E_a(Mu) \ll E_a(H) = E_a(D)$. The dramatic changes seen at the low temperatures in the Mu data is noteworthy, as is the constancy in the H- and D-atom values. The secondary isotope effect noted earlier in comparing the Mu + C_2H_4 and C_2D_4 data is also reflected in the Arrhenius parameters in Table III; addition to C_2D_4 is somewhat faster at higher temperatures, but slower at lower temperatures.

The importance of quantum tunneling in Mu atom addition kinetics in the ethylenes means that the barrier to reaction must be decidedly "early," where the translational energy is largely determined by the light Mu atom mass,[22–26] in agreement with PES calculations for other isotopic H-atom

addition reactions on C_2H_4.[12,13,17,18] The present Mu data though, likely provide the most convincing experimental verification of this. It is interesting to note in this regard that the E_a (Mu) = 1.1 kcal mol^{-1}, found from the high temperature regime for Mu + C_2H_4 in Fig. 4 (Table III), is very similar to that seen in the Mu + F_2 reaction over the same temperature range.[26] Both reactions are exothermic and both exhibit dramatic Arrhenius curvature at low temperatures, indicative of pronounced tunneling on early-barrier PES's. Similarly in both, over the whole temperature range studied, E_a (Mu) is a factor of 2–5 smaller than E_a (H) for the corresponding H atom reactions. In marked contrast to these features is a comparison of the reaction rates of Mu and H atoms with $H_2(D_2)$.[22,23] The Mu + H_2 reaction is highly endothermic, with a late (mass weighted) barrier, resulting in $k_{Mu} \ll k_H$. The study of Mu reaction kinetics clearly provides a highly sensitive probe of both the magnitude and the location of the (vibrationally adiabatic) barrier on a given PES.

To date, most theoretical studies of the reaction rates for the (high pressure) addition step k_a (k_H) of Eq. (1) have relied on TST.[6,12,13,16] Comparisons of TST and QCT calculations on model surfaces have been carried out for the H + C_2H_4 reaction that demonstrate essential agreement in both approaches.[14] There are no corresponding calculations as yet for Mu + C_2H_4, although those for Mu + C_2H_2 are in progress.[36] It can be noted that well-known deficiencies in the essentially classical QCT calculations (neglect of both quantum tunneling and vibrational adiabaticity at the TS, effects which tend to cancel in the overall result[42]), will be much more severely tested by a comparison of QCT and TST calculations for Mu + C_2H_4 than for H + C_2H_4.[14] There have been several ab initio surfaces calculated for C_2H_5, including those of Nagase et al.[13] and Schlegel[18] that have been utilized in TST calculations of the bimolecular H atom addition rates.[6,7,12,13] In all these surfaces the barrier to reaction is in the entrance channel. This location of the barrier has two important consequences: (1) zero-point energy effects on the height of the potential barrier are likely to be relatively unimportant, unlike the situation prevailing with late barrier (endothermic) reactions;[9,22,23,26,43] and (2) translational energy is much more effective than vibrational (zero-point) energy in promoting reactivity,[22–26] again in contrast to the situation prevailing in the case of a late barrier.[22,23] As noted above, it is this second point that is largely responsible for the sensitivity of the reaction dynamics in Mu + C_2H_4 (and Mu + F_2) to quantum tunneling.

In TST, the ratio of rate constants for an atom–molecule (A + BC) reaction for the isotopic species A and A' on the same molecule BC can be written[23,26,44] as

$$\frac{k}{k'} = \frac{\Gamma_t}{\Gamma_t'} \left(\frac{q_A'}{q_A} \right)_{trans} \frac{q^{\ddagger}}{(q^{\ddagger})'} e^{-\Delta E^{VA}/k_B T}$$

$$= \frac{\Gamma_t}{\Gamma_t'} \left(\frac{\mu^*(A')}{\mu^*(A)} \right)^{1/2}$$

$$\times \prod_{i=1}^{3N-7} \frac{U_i^{\ddagger}(A) \cdot \sinh[U_i^{\ddagger}(A')/2]}{U_i^{\ddagger}(A') \cdot \sinh[U_i^{\ddagger}(A)/2]}, \quad (7)$$

where Γ_t is a transmission (tunneling) coefficient, N is the number of bound vibrational degrees of freedom in the TS, each of frequency $v_i^{\ddagger}$, q_A and $q^{\ddagger}$ are the translational and total partition function of the incident light atom and TS, respectively, ΔE^{VA} is the difference in vibrationally adiabatic (VA) barriers, and $U_i^{\ddagger} = h v_i^{\ddagger}/k_B T$. Here μ^* denotes the effective (reduced) mass of the system on its barrier crossing trajectory. For an early barrier, as in the case under discussion $[\mu^*(A')/\mu^*(A)]^{1/2} = [\mu(A')/\mu(A)]^{1/2} \approx \sqrt{9}$ for the ratio k_{Mu}/k_H (and $\sqrt{2}$ for k_H/k_D); i.e., it depends only on the reduced masses of the reactants and is then the same factor that appears in collision theory.[14,15,20,24,44] However, for a late barrier, this factor lies closer to the reduced mass of the products and as such contains dynamical information, in contrast to collision theory.[22,23,44]

Sugawara et al.[6] have reported the vibrational (zero point) frequencies of the $C_2H_5^{\ddagger}$ and $C_2H_4D^{\ddagger}$ radicals from the ab initio PES calculated by Nagase et al.[13] Substituting these frequencies into Eq. (7) to give the ratio k_H/k_D, we find, e.g., at 300 K (k_H/k_D)$_{TST}$ = 1.20; and at 100 K, 0.60, assuming $\Gamma_t = 1$ in both cases. These values compare well with those reported by Nagase et al. at the same temperatures, 1.17 and 0.59, respectively.[13] Since the barrier is early, the transition state can be described as "loose," which means that the largest isotope effects are to be found in the (two) additional relatively low energy bending vibrations ($v_b \sim 400$ cm^{-1}). As noted earlier, however, the experimental results for C_2H_4 (Fig. 4, Refs. 5–7), show k_H/k_D = 1.4 essentially independent of temperature, as expected from the reduced mass dependence in Eq. (7) for an early barrier. If one now demands agreements with the TST calculations, the need for a small tunneling correction Γ_t favoring the lighter H atom at lower temperatures is suggested.[7] Sugawara et al.[6] had earlier considered this aspect by utilizing a Wigner correction in a wide range of isotopic substitution of both the incident atom and target ethylene. However, poor agreement with the data was again obtained. Similar calculations have been carried out by Hase and Schlegel[12] and Hase and Swamy.[14] While these latter calculations tend to give a good "fit" to the experimental Arrhenius plot for H + C_2H_4, they do not account for the range of deuterium isotope effects seen.[6] This suggests that both surfaces, those of Nagase et al.[13] and Schlegel,[18] may be in error, particularly in the region near the barrier.

An earlier barrier, for example, or equivalently a looser TS ($v_b \sim 100$ cm^{-1}), would considerably favor the H atom reaction, as convincingly demonstrated herein by its Mu analog. The somewhat tighter TS of $v_b \sim 400$ cm^{-1}, however, seems necessary to give agreement with the pressure (and M) dependence for H atom addition leading up to the high pressure limit.[2,3,12] On the other hand, the use of a Wigner tunneling correction is notoriously inaccurate at low temperatures, where reaction-path curvature can play an important role.[43,45] Moreover, some variational treatment of the transition state[25,43] may yield significant improvement in the isotope effect. In either case, the Mu data can be expected to play an important role in accurately establishing the topography of the PES's involved.

By assuming a simple harmonic (zero-point) mass dependence for the difference between $v_H^\ddagger$ and $v_{Mu}^\ddagger$ at the TS, the ratio k_{Mu}/k_H can also be calculated by TST at different temperatures from the published frequencies for $v_H^\ddagger$ in Ref. 6. The results are given in Table IV for temperatures of 500 and 165 K for both C_2H_4 and C_2D_4. At 500 K, e.g., $(k_{Mu}/k_H)_{TST} = 1.7$ in C_2H_4 vs the experimental ratio of 2.8, whereas at 165 K, $(k_{Mu}/k_H)_{TST} = 0.080$ vs the experimental ratio of ~ 30 (Fig. 4). Similar discrepancies are seen for C_2D_4. These comparisons further support the conclusion already reached that the Mu reaction (at low temperatures) is completely dominated by quantum tunneling ($\Gamma_{Mu} \gg 1$). Applying a Wigner correction for tunneling at 165 K gives Γ_{Mu}/Γ_H of only $\sim 5/1$, but this is even less likely to be meaningful in the case of muonium than it is for hydrogen. It remains to be seen if accurate theoretical calculations on available PESs[13,18] will be able to account for the pronounced quantum tunneling seen in the Mu reactions. If one can argue that Γ_{Mu} is the same in both $Mu + C_2H_4$ and $Mu + C_2D_4$, then the TST calculation should be able to account for the *ratio* of $k_{Mu}(C_2H_4)/k'_{Mu}(C_2D_4)$. This is shown in the last column of Table IV. While the experimental trend towards a somewhat enhanced Mu addition rate to C_2H_4 at the lower temperatures (Fig. 3) is seen in the calculation, the calculated ratios are in fact too high, suggesting that there may be relatively more tunneling in $Mu + C_2D_4$ than in $Mu + C_2H_4$. This is also suggested by the differences in E_a (Mu) at low temperatures in Table III. If true, this result implies that variational effects at the TS may indeed be important, giving rise to an earlier barrier and hence an enhanced tunneling probability for $Mu + C_2D_4$. Rigorous theoretical calculations of these reaction systems are now urgently required.

IV. CONCLUSIONS

The present report of the rate constants for the $Mu + C_2H_4$ and $Mu + C_2D_4$ reactions represents the first detailed study of the kinetics of Mu atom addition reactions in the gas phase.[36] While there appears to be a small but significant secondary isotope effect (Fig. 3), in contrast to similar results found in the analogous H and D atom studies,[6] a large primary isotope effect is seen, particularly at the lowest temperatures ($\lesssim 200$ K), where the ratio k_{Mu}/k_H approaches 30/1 (Fig. 4) or even 50/1 (Fig. 5) and

E_a (Mu) is only a fraction of its H(D) atom counterpart (Table III). In marked contrast, the ratio $k_H/k_D = 1.4$ is essentially independent of temperature, as are the corresponding activation energies.[5-7] The present Mu results (and those recently reported for $Mu + F_2$ at similar temperatures[26]) represent the largest isotopic enhancements in rate yet seen in gas-phase muonium chemistry. Quantum tunneling dominates the Mu kinetics. It is now of considerable interest to have a comparison of the predictions of (3D) quantum and QCT, as well as (variational) TST calculations of the $Mu + C_2H_4(C_2D_4)$ reaction rates on currently available *ab initio* surfaces,[13,17,18] in order to provide further tests of both the reaction theory for polyatomics and the surfaces themselves. The lack of agreement noted herein between measured and calculated H and D atom isotope effects[6] and those calculated by TST on these surfaces already indicates that they may be somewhat in error.

TABLE IV. Transition state theory calculations[a] of Mu and H addition reactions to C_2H_4 (k_{Mu}/k_H) and C_2D_4 (k'_{Mu}/k'_H).

T(K)	k_{Mu}/k_H (C_2H_4)		k'_{Mu}/k'_H (C_2D_4)		k_{Mu}/k'_{Mu}[c]	
	TST	Expt.	TST	Expt.	TST	Expt.
500	1.7	2.8	1.6	3.4	1.0	0.85
165	0.080	$\sim 30^b$	0.052	$\sim 40^b$	1.5	1.1

[a] Assuming a simple harmonic $\sqrt{mass}$ dependence of the vibrational frequencies at the transition state given by Sugawara *et al.* (Ref. 6). No tunneling correction.
[b] H atom data (Ref. 6) linearly extrapolated from 205 K.
[c] Calculated from the ratio of the first two columns, assuming that $k_H(C_2H_4) = k'_H(C_2D_4)$, as seen in the data of Ref. 6.

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