

34%), 7-deoxynoganol (4, 43%), and bi(7-deoxynoganol-7-yl) (5, 9%). The unidentified minor product peaks with the exception of a peak at 7.2 min (5%) had the same retention times as the minor products from reduction in the presence of deoxyguanosine. The 7.2-min peak could not have been an adduct since an adduct would be considerably more polar than menogaril and would have eluted before menogaril. Its UV-vis spectrum also precluded it being an adduct.

The result described here indicates for the first time that an anthracycline quinone methide transient can covalently bind to a nucleophilic site in a nucleic acid. Studies of menogaril metabolism show low levels of recovery of drug and its known metabolites.¹⁶ Possibly, covalent binding to nucleophilic sites in proteins and/or nucleic acids through reductive activation is an explanation. The quinone methide from reductive activation of adriamycin or daunomycin bears an 11-hydroxy substituent and consequently is short lived and less likely to bind covalently to sites of lower nucleophilicity.^{13,15,17} In vivo modification of the 11-hydroxy group of these drugs prior to reductive activation might change the reactivity of their quinone methide states with nucleic acids.

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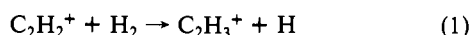
Chemical Reaction Mechanisms at Unusually Low Temperatures: The Gas-Phase Reaction of $C_2H_2^+ + H_2$

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We have recently developed a supersonic flow kinetic technique that allows reaction rate studies at extremely low collision energies.¹⁻⁵ We report the observation of gas-phase reactivity between the acetylene radical cation, $C_2H_2^+$, and molecular hydrogen at collision energies of less than 0.5 meV (translational temperatures near 2 K).



Reaction 1 has been well studied at temperatures above 80 K and is found to increase in rate with increasing temperature.⁶⁻¹⁰ The observed rate coefficient at 300 K is $1.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, and the reaction is not observed to occur at 80 K.^{6,7} The reaction cross section is observed to increase with collision energy between 0.05 and 0.8 eV.⁸ Vibrational excitation in the $C_2H_2^+$ also accelerates the rate at low energies.^{9,10} Appearance potential measurements for $C_2H_2^+$ and $C_2H_3^+$, from the photoionization of C_2H_4 , have suggested that the heat of formation of $C_2H_3^+$ lies in the range

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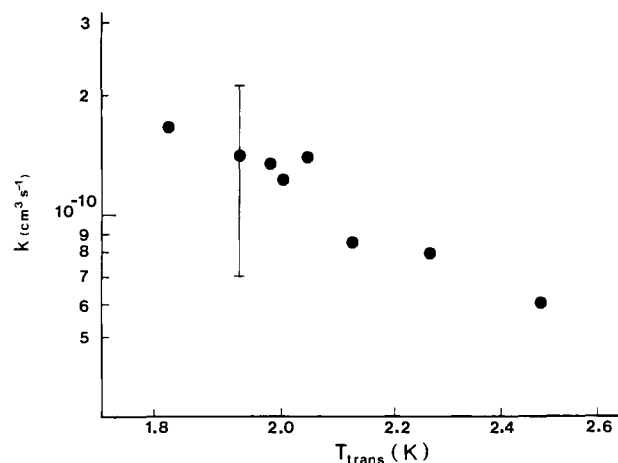


Figure 1. The observed translational temperature dependence of the experimentally measured rate coefficients for reaction 1. Temperatures are a neutral density weighted average of the perpendicular and parallel temperatures present in the jet over the range of an experiment.

$\Delta H^\circ_{f_0} = 267-269 \text{ kcal mol}^{-1}$.^{11,12} All of these results have led to an acceptance of an endothermicity for reaction 1 of 2.0 kcal mol^{-1} at 0 K.

Our experiment is outlined below. Briefly, a 1-3% mixture of C_2H_2 in H_2 at 0.5-1.4 atm is formed into a free jet by expansion through a 0.03- or 0.05-cm orifice into a vacuum chamber. Downstream, a pulsed dye laser is used to selectively ionize C_2H_2 via resonant multiphoton ionization through the $G^1\Pi_u, v=0$ state of C_2H_2 . This ionization technique allows selective production of $C_2H_2^+$ (or $C_2D_2^+$ in separate experiments using C_2D_2) in the ground vibrational state with 100% state purity.¹³ The photoions remain in translational equilibrium with the surrounding neutrals. Velocity and temperature slip under our expansion conditions are negligible.⁵ The properties of both the reactor and the expansion assure that all collisions occur at the extremely low energies characteristic of a free jet flow. Temporal monitoring of the chemical composition of the cold ion packet via mass spectrometry allows determination of an absolute reaction rate coefficient.

The experimentally observed rate coefficient is actually an average over two distribution functions, the relative ion-neutral collision energy and the neutral rotational state distribution function.¹⁴ These degrees of freedom are not in equilibrium in the jet, therefore,

$$k_{\text{expt}} = \sum_{j=0}^{\infty} f_{\text{rot}}(j) \int_0^{\infty} k(\epsilon, j) f_{\text{trans}}(\epsilon) d\epsilon \quad (2)$$

The f_i are the appropriate distribution functions, $k(\epsilon, j)$ are the microcanonical rate coefficients, and ϵ is the relative collision energy, while j is the rotational quantum number for the diatomic reactant. It is well-known that H_2 does not efficiently rotationally relax within a free jet, and the resulting rotational temperature is between 150-200 K under our expansion conditions.¹⁵ Even at these temperatures, 98% of the H_2 population resides in rotational levels with j less than or equal to 2. At the same time, the translational distribution can be well represented by an average temperature in the range 1.8-2.5 K. These translational temperatures are averages over the parallel and perpendicular degrees of freedom in the jet. They are calculated by using the thermal conduction model of Klots¹⁶ and the observed H_2 rotational tem-

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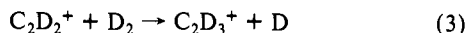
(14) Only low-lying rotational levels of the ion are initially prepared. Since the cross section for exothermic rotational-to-translational energy transfer collisions should be very large, we assume that the rotational temperature of the ions is negligible and the distribution is collapsed to the rotationless ground state.

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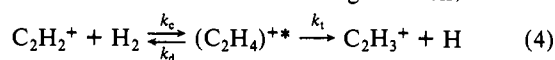
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peratures reported by Gallagher and Fenn¹⁵ as well as by Hüber-Walchli and Nibeler.¹⁷

Figure 1 shows the dependence of k_{expt} for reaction 1 on the translational temperature present in the jet. The measured rates are approximately one order of magnitude greater than those at 300 K and show a significant negative temperature dependence. Since the neutral H_2 does not have a permanent dipole moment, the temperature dependence suggests that the reaction mechanism proceeds through a long-lived collision complex. Competition between reactive branching and complex dissociation can then lead to negative temperature dependence in the net reaction rate coefficient. The deuterated analogue to reaction (1) exhibits an



observed rate that is about 3 times slower than reaction 1. From the vibrational frequencies of all reactants and products,¹⁸ we calculate that reaction 3 should be 1.4 kcal mol⁻¹ less exothermic than reaction 1. Although the observed kinetic isotope effect may originate from the zero point energy effects, it could also be a manifestation of reactive branching involving H/D tunneling through a barrier. A simple reinterpretation of the data of Adams and Smith on the endothermicity of the reaction would then lead to a barrier height of at least 1.6 kcal mol⁻¹.⁷ Reactant collisions would initially form a $(\text{C}_2\text{H}_4)^{+*}$ complex, which would then branch between dissociative and reactive tunneling channels.



The total energy of the $(\text{C}_2\text{H}_4)^{+*}$ complex is determined by the relative collision energy and the rotational energy of the H_2 . Assuming rapid energy randomization, k_t and k_d are only functions of the total energy of the collision complex. The rotationally excited H_2 molecules cannot drive the reaction over the barrier. As the translational temperature is decreased in our experiments, the rotational temperature drops in proportion, yet the observed rate coefficient is found to rapidly increase. This strongly implies that the observed reaction in the jet is not being driven by excited rotational states. Reactive tunneling of a hydrogen atom from a low energy collision complex could be the dominant mechanism at low temperatures.

From phase space calculations,¹⁹ we estimate that the lifetime for a 2 K collision with H_2 in $j = 1$ is about 5000 times shorter than that for $j = 0$. If our above mechanism is correct, the observed low reaction efficiency and the calculated lifetimes suggest that only collisions with $\text{H}_2(j=0)$ lead to complexes where tunneling can effectively compete with complex dissociation to reactants. This point is supported by the observed low-temperature behavior of the rate. A collision involving $\text{H}_2(j=1)$ brings 122 cm⁻¹ of rotational energy into the complex. A small change in the collision energy (± 0.5 cm⁻¹) would have an insignificant effect on the lifetime of the collision complex. Therefore, the rate coefficient will remain relatively constant, and no temperature dependence from $k(\epsilon, j=1)$ would be observed. Since the relative population of $j = 1$ is approximately 3 times that of $j = 0$ due to spin statistics, the observed temperature dependence in itself suggests that only $j = 0$ collisions result in reaction. Using the experimental rotational distributions of Gallagher and Fenn,¹⁵ we can then determine $k(T, j=0)$ from k_{obsd} . This calculation suggests a rate coefficient of $(6.2 \pm 3) \times 10^{-10}$ cm³ s⁻¹ for reaction 1 involving pure para- H_2 at 2 K and a true kinetic isotope effect of 6. The fact that the reaction occurs at 2 K allows us to establish a new upper limit to the heat of formation of C_2H_3^+ of $\Delta H_{f,0}^\circ \leq 265.9$ kcal mol⁻¹. This result is also supported by dissociative photoionization studies of C_2H_6 and $\text{C}_2\text{H}_3\text{Cl}$.^{20,21} The barrier (either energetic or dynamic) to the reaction must impede the C_2H_3^+ channel in the photoionization of C_2H_4 . From these ex-

periments, we believe that 265 (± 1) kcal mol⁻¹ is the correct value for the C_2H_3^+ heat of formation at 0 K. This value would then make reaction 3 0.5 kcal mol⁻¹ endoergic and may explain the kinetic isotope effect, independent of a barrier on the surface. This heat of formation also requires the C-H bond energy of ethylene to be in excess of 104.9 kcal mol⁻¹.²²

The observation of reaction 1 near 2 K is important to the C_2H_n chemistry observed in interstellar gas clouds.²³ The major production channel for C_2H^+ is photoionization of C_2H . This ion reacts rapidly with H_2 to produce C_2H_2^+ . Previously, it was thought that the major loss channel of C_2H_2^+ was dissociative electron-ion recombination to produce CH or C_2H . This study suggests that in dense clouds the major loss channel may not be recombination, but reaction with H_2 to form C_2H_3^+ , depending on the thermal conditions and the density of the cloud. This ion does not react with H_2 and will most likely recombine with electrons to produce neutral acetylene and possibly other radicals.

Tunneling is rarely a dominant mechanism in gas-phase chemistry, where collision times are usually extremely short. Dunn's group has suggested that tunneling plays an important role in the low-temperature reaction between NH_3^+ and H_2 .^{24,25} Their results, combined with the results reported in this communication, suggest that some reactions involving the transfer of H or H^+ may show dramatic increases in rate at low temperatures. This effect can have important consequences regarding the chemistry and isotopic balance in low-temperature environments such as the interstellar medium.

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High-Resolution NMR in Cholesteric Medium: Visualization of Enantiomers

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The technique of NMR associated with liquid crystal solvents has been widely used for the past 20 years to study the structure and ordering of solute molecules. Most of the work has been realized in nematic phases. The reason is that nematics orientated themselves very rapidly and homogeneously in the magnetic fields commonly employed in NMR spectroscopy. On the other hand, much less work has been published which concerns experiments with cholesteric liquid crystal solvents. The latter are known as nematics twisted under the influence of chiral centers, and they give rise to a director field of the helical structure.^{1,2} The response of a cholesteric phase to an external homogeneous magnetic field depends on the sign of its molecular anisotropic magnetic susceptibility. Collings et al.³ have shown that when $\Delta\chi$ is positive,

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