probably also acceptable given the low sensitivity of this data to reaction 1.

The rate and especially the products of benzyl radical dissociation are distressingly uncertain. Some benzyl may also be removed through radical attack, with unknown rate and products. The present results show that benzyl is certainly very stable, but they cannot define its decomposition pathways or their rates.

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Gas-Phase Addition of the Vinyi Cation to Hydrogen and Methane. A Nuclear Decay Study

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A nuclear technique based on the spontaneous decay of multitritiated precursors that allows the generation of free carbenium ions of exactly the same nature in different environments has been employed for generating the labeled vinyl cation ($C_2X_3^+$, X = H, T) from multitritiated ethylene and for investigating its reactivity toward hydrogen and methane at pressures ranging from 60 to 720 Torr. Kinetic data for the addition of $C_2X_3^+$ to H_2 and CH_4 and the ensuing product distributions are obtained by intercepting the ionic species with different gaseous nucleophiles, i.e., 1,4-dibromobutane, benzene, and methanol, and by isolating the corresponding neutral end products. The results are consistent with the intermediacy of the vinyl cation, formed by the β^{-} transition with a limited excess of vibrational energy, which inserts into the σ -bonds of H₂ and CH₄ yielding respectively $C_2H_5^+$ and $sC_3H_7^+$ ions. The experiments provide no evidence for the occurrence of alternative $C_3H_7^+$ structures, i.e., protonated cyclopropane, from the $C_2X_3^+$ attack on CH₄. At CH₄ pressures below 200 Torr, a fraction of the $C_3H_7^+$ adducts fragments directly into allyl cations and H₂. A definition of the $C_2X_3^+ + H_2$ (or CH₄) addition and fragmentation mechanisms is obtained by comparison of the present data with those arising from previous experimental studies based on different approaches (i.e., radiolysis, ICR, SIFT, HPMS, etc.) and with those of ab initio calculations.

Introduction

A singlet ground-state vinyl cation is the simplest member of the family of unsaturated carbenium ions in which the vacant p orbital of the ⁺C center is perpendicular to a strongly polarized π -bond orbital.¹ This electronic configuration confers to the vinyl cation the character of a singlet methylene with a CH_2^+ substituent and, therefore, the ability to insert into σ -type bonds.²

Experimental confirmation of this ability is provided by the significant reactivity of the gaseous vinyl cation toward σ -type molecules. Indeed, addition reactions between the vinyl cation and several simple σ -type molecules, including hydrogen (eq 1) and methane (eq 2), have been actively investigated by a variety

$$C_2H_3^+ + H_2 \rightarrow [C_2H_5^+] \rightarrow \text{products}$$
 (1)

$$C_2H_3^+ + CH_4 \rightarrow [C_3H_7^+] \rightarrow \text{products}$$
 (2)

of mass spectrometric approaches, such as the selected ion flow tube (SIFT) technique,³ photoionization,⁴ ion cyclotron resonance (ICR),⁴⁻⁶ and a tandem mass spectrometry.⁷ Special attention has recently been paid to the effect of internal energy upon the reactivity of the vinyl cation toward hydrogen and methane.⁴⁻⁷ As a result of such a sustained effort, a large body of experimental data is currently available concerning rate coefficients and ionic product distribution for these reactions. Unavoidably, the picture obtained by the exclusive application of even powerful mass spectrometric techniques is incomplete, owing especially to the recognized⁸ difficulties encountered by these techniques in the positive structural identification of ionic species. The picture is further blurred by the rapid fragmentation in the low-pressure ion source of the spectrometer of the adduct ions from insertion of $C_2H_3^+$ into H_2 or CH_4 , which prevents their direct isolation and characterization. In this case, isotopic labeling with ¹³C and

D is the only means to obtain indirect information on the course of the reactions.^{6,7}

A more complete mechanistic view of reactions 1 and 2 is desirable since it provides fundamental information on the carbenoid nature of $C_2H_3^+$, which is of interest, inter alia, to the study of the synthesis of large hydrocarbon molecules in interstellar molecular clouds⁹ and in the atmospheres of the outer planets.^{10,11}

This paper presents the results of a comparative study of the reactivity of $C_2H_3^+$ toward H_2 and CH_4 carried out in the gas phase in the pressure range 60-720 Torr, using ionic reactants from the β^- decay of T atoms in multitritiated ethylene.^{12,13}

The decay technique affords a convenient means to introduce free cations of defined structure and concentration into liquid and gaseous systems and to follow their reactions by radiotracer techniques.¹⁴⁻¹⁷ The wide pressure range accessible to the decay

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method allows highly effective collisional deactivation of any excited intermediates from the ion-molecule addition processes, thus minimizing their unimolecular fragmentation and secondary isomerization. Moreover, the structural assignments of the reaction intermediates rest on the positive evidence, provided by the actual isolation of the reaction products. This kinetic approach could hopefully bring to a sharper focus the mechanistic details of the $C_2H_3^+$ insertion into H_2 and CH_4 molecules and compare the relevant reactivity data with those observed in the corresponding low-pressure mass spectrometric experiments.

Experimental Section

Materials. The preparation of ethylene, containing at least two T atoms in the same molecule, used as a source of the decay vinyl cations has been described elsewhere.¹² H₂, CH₄, O₂, and N(C-H₃)₃ were obtained from Matheson Gas Products Inc.; their stated purity exceeded 99.3 mol %. C. Erba Co. and Fluka AG provided all the other chemicals used as reference compounds or as components of the nuclear-decay experiments.

Decay Experiments. Multitritiated ethylene (ca. 1-2 mCi), diluted with the corresponding unlabeled hydrocarbon to a specific activity of 363 Ci mol⁻¹, was introduced into carefully outgassed and evacuated Pyrex vessels containing measured amounts of hydrogen (60-200-600 Torr) or methane (60-200-720 Torr), together with the appropriate additives $(O_2, 4 \text{ Torr}; \text{ benzene}, 8-12)$ Torr; CH₃OH, 1.8-6.6 Torr; 1,4-dibromobutane, 1 Torr; and $N(CH_3)_3$, 0.3 Torr). The vessels were then sealed off and stored for 10-14 months in the dark at room temperature. The sealed ampules were then opened under air-tight conditions and their contents analyzed on a C. Erba Fractovap 4200 gas chromatograph equipped with a high-sensitivity hot-wire detector (Model 450), coupled in series with a Berthold proportional counter tube, kept a 180 °C. Two different sampling techniques were adopted: (1) small portions of the homogeneous gaseous content of the decay vessels, heated to ca. 100 °C, were withdrawn with a gas syringe and injected directly in order to analyze the gaseous tritiated products; (2) the vessels were cooled and thoroughly washed with ethyl acetate. Measured aliquots of the acetate extracts were analyzed by radio gas chromatography.

The tritiated products were identified by comparing their retention volumes with those of authentic samples on the following columns: (a) a 6-m-long stainless steel column packed with 20% bis(2-methoxyethyl)adipate on 60–80 mesh Chromosorb P-AW at 60 °C; (b) a 5-m-long stainless steel column containing 10% EDO-1 on 100-120 mesh Chromosorb P-AW at 30 °C; (c) a 2-m glass column packed with 0.1% SP 1000 on 80–100 mesh Carbopack C at 180 °C; (d) a 2-m stainless steel column packed with 5% SP 1200:1.75% Bentone 34 on 100–120 mesh Supelcoport at temperatures ranging from 80 to 100 °C; (e) a 5-m stainless steel column packed with 80–100 mesh Porapack PS at temperatures ranging from 60 to 100 °C.

Results

Hydrogen Systems. When tritiated ethylene is allowed to decay in gaseous hydrogen, in the presence of a gaseous nucleophile Nu, i.e. 1,4-dibromobutane, CH₃OH, or benzene, two major types of tritiated products are formed, namely those deriving from the attack of a vinyl cation on Nu (VinNu), i.e. respectively C_2H_3Br , CH₃CHO, and styrene, and those arising from the attack of an ethyl cation on Nu (EtNu), i.e. respectively C_2H_5Br , $C_2H_5OCH_3$, and ethylbenzene. Their relative distribution in each individual decay system is a function of the partial pressure of hydrogen, as shown in Figure 1. Reaction conditions were chosen to maintain [Nu] approximately constant, i.e. 1,4-dibromobutane, 1.0 Torr; CH₃OH, 3.9–6.6 Torr; benzene, 7.9–8.3 Torr, whereas



Figure 1. Relative distribution of radioactive EtNu and VinNu products (see text) from the $C_2X_3^+ + H_2$ decay samples as a function of the H_2 partial pressure (Nu = 1,4-dibromobutane (\bullet), benzene (\bullet), methanol (\circ)).



Figure 2. Relative distribution of radioactive EtNu and VinNu products (see text) from the $C_2X_3^+ + H_2$ decay samples as a function of the system composition (Nu = 1,4-dibromobutane (\bullet), benzene (\bullet), methanol (O)).

the partial pressure of H_2 was changed from 0 to 600 Torr. The absolute yields, defined as the ratio of the activity contained in the products to the total activity of the decay fragments formed within the system during the storage period, have been calculated from the initial activity of multitritiated ethylene, its isotopic composition and storage time, the decay rate of tritium, and activity of the products.

Owing to the propagation of errors, the absolute yield values calculated must be regarded as crude estimates. Nevertheless, tritiated VinNu and EtNu undoubtedly represent the major reaction products, their combined absolute yields ranging from 40 to over 90% in all the decay systems containing 0.3 Torr of N- $(CH_3)_3$. The balance is mainly provided by gaseous tritiated products, arising either directly from fragmentation processes, or deriving from hydrogen atom transfer between $C_2H_3^+$ or $C_2H_5^+$ and the nucleophile, leading to neutral labeled species (e.g., ethylene) indistinguishable from those initially present in the decay mixture. The ionic nature of the processes leading to the formation of VinNu and EtNu products is deduced from the fact that their yields, insensitive to the presence of an effective thermal radical scavenger, such as O_2 (4 Torr), are depressed by addition of gaseous N(CH₃)₃, which intercepts the ionic precursors of the neutral products.

Figure 1 shows that while VinNu products are the only ones formed in the systems containing no added hydrogen, they are invariably accompanied by the corresponding EtNu derivatives in the systems where H_2 is present. Their yield ratios ([EtNu]/[VinNu]) are linearly dependent upon the partial pressure of H_2 for each Nu employed. If a correlation is made between the [EtNu]/[VinNu] ratio and the [H_2] vs. [Nu] relative concentrations, a single linear relationship is obtained, which is

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Figure 3. Relative distribution of radioactive products from the $C_2X_3^+$ + CH₄ decay samples as a function of the CH₄ partial pressure (\bullet) *i*-PrNu; (\bullet) AllNu; (\circ) VinNu; (\blacksquare) *n*-PrNu).

valid for all the Nu used (Figure 2). No evidence for a significant deviation from linearity emerges from the plots of Figures 1 and 2, at least within the range of H_2 and Nu partial pressures investigated. This fact suggests that, under our experimental conditions, the EtNu and VinNu products are formed by two competitive independent processes, whose relative rate is rather insensitive to the nature of nucleophile Nu employed.

It is worth mentioning that no tritiated compounds, other than EtNu and VinNu (e.g., acetylene), have been recovered from the corresponding decay systems. Thus, compounds, such as propyl and butyl bromides, phenylacetylene, diphenylethylenes, diphenylethanes, methyl vinyl ether, ethylene glycol dimethyl ether, ethanol, $CH_3CH(OCH_3)_2$, could never be detected among the tritiated products from the corresponding decay systems, in spite of a specific search.

Methane Systems. Both VinNu and the corresponding propyland allyl-Nu (C₃Nu) are recovered in variable proportions in the decay systems, containing CH₄ at partial pressures from 60 to 720 Torr, together with approximately constant concentrations of Nu (Nu = 1,4-dibromobutane, 1.1 Torr; CH₃OH, 1.8-3.7 Torr; benzene, 10.1-11.9 Torr). The nature of VinNu and C₃Nu tritiated products, when Nu = benzene, and their relative distribution as a function of the CH₄ partial pressure are illustrated in Figure 3. No *n*-PrOMe is formed in the Nu = CH_3OH systems, while appreciable yields (8-20%) of tritiated propylene were recovered. A plot, similar to that of Figure 3, is obtained for these systems if the *i*-PrNu curve represents the combined yields of *i*-PrOMe (28-68%) and propylene. Tritiated propylene is the major product (61-81%) in the Nu = 1,4-dibromobutane systems, accompanied by i-PrBr (15-39%), allyl bromide (0-9%), and by barely detectable amounts of vinyl bromide. Again, no n-PrBr was formed. In analogy with the benzene and CH₃OH systems, the combined yields of *i*-PrBr and propylene from the 1,4-dibromobutane samples increase with the CH_4 pressure (from 91 to 100%), whereas the allyl bromide yield decreases from 9% to zero.

It should be also noted that only the above-mentioned VinNu and C₃Nu tritiated products are formed in the corresponding CH₄ decay systems. Tritiated acetylene, allene, and other tritiated compounds, such as 1- and 2-bromopropene and cyclopropyl bromide, α - and β -methylstyrene and cyclopropylbenzene, 1- and 2-methoxypropene, cyclopropyl methyl ether, *n*-propyl methyl ether, acetone, propyl alcohols, etc., could never be recovered among the tritiated products from the corresponding decay systems.

The overall absolute yield of the tritiated products from the decay systems amounts to 40–90%, the remainder being accounted for by gaseous fragmentation and hydrogen-transfer products.

A graphic presentation of the combined C_3Nu yields (\sum -[C_3Nu]) vs. the VinNu yield as a function of the partial pressure of methane is given in Figure 4, for Nu = benzene or methanol.



Figure 4. Relative distribution of radioactive C_3Nu and VinNu products (see text) from the $C_2X_3^+ + CH_4$ decay samples as a function of the CH_4 partial pressure (Nu = benzene ($\mathbf{0}$), methanol ($\mathbf{0}$)).



Figure 5. Relative distribution of radioactive C_3Nu and VinNu products (see text) form the $C_2X_3^+ + CH_4$ decay samples as a function of the system composition (Nu = benzene (\mathbf{O}), methanol (\mathbf{O})).

In analogy with the H₂ systems (Figure 1), a linear dependence is observed for both nucleophiles, which is similarly consistent with two independent reaction channels for the formation of VinNu and C₃Nu products. The relative extent of these two reaction paths is insensitive to the nature of the Nu employed as demonstrated by the approximately linear correlation between the \sum -[C₃Nu]/[VinNu] ratio and the [CH₄]/[Nu] ratio irrespective of the nature of Nu (Figure 5).

Discussion

The Reagents. The formation of labeled vinyl cation from the decay of multitritiated ethylene has been discussed in detail elsewhere (eq 3).^{12,13} The daughter $C_2X_3^+$ ion is formed in a high

$$C_2 X_4 \xrightarrow{\beta^-} C_2 X_3^+ + {}^3\text{He} + \beta^- + \bar{\nu}$$
(3)

yield,¹³ in a vibrationally excited state, owing to the relaxation of its original geometry, reminiscent of the parent ethylene, to the linear structure of the ground-state vinyl cation. The excess internal energy of the nuclear decay formed (nucleogenic) $C_2X_3^+$, whose upper limit can be set around 50 kcal mol⁻¹,^{18,19} can affect the reactivity of the decay $C_2X_3^+$ ions toward H₂ and CH₄, while collisional deactivation is likely to thermalize the products from

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$C_2X_3^+ + H_2$ or CH_4 Reaction

reactions 1 and 2 well before their trapping by the nucleophile Nu, contained in trace amounts in the excess H_2 and CH_4 .

The reactions chosen to sample the population of the ionic species from the decay samples are listed in Table I. They involve nucleophilic acceptors, Nu = benzene, methanol, and 1,4-dibromobutane, whose choice responds to definite requisites. Methanol and benzene are respectively pure n- and π -type nucleophiles, which efficiently react with the ions formed in the decay systems by exothermic ion-molecule reactions, characterized by moderately negative ΔH° values, which should prevent or minimize isomerization of their products. 1,4-Dibromobutane is a pure n-nucleophile, characterized by the additional advantage of yielding directly stable and structurally diagnostic neutral products, acting as a Br⁻ donor to gaseous cations with formation of the tetramethylenebromonium ion.24-26

Vinyl Cation Attack on Hydrogen. The single exothermic reaction channel 1 is opened to a ground-state tritiated vinyl cation

$$C_{2}X_{3}^{+} + H_{2} \frac{k_{1}}{k_{-1}} \left[C_{2}X_{3}H_{2}^{+}\right]^{+} \frac{k_{-1}}{k_{1}} C_{2}X_{2}H^{+} + HX \quad (1)$$

$$+ M \downarrow k_{2} \qquad k_{-1} \downarrow \not k_{1}$$

$$\left[C_{2}X_{3}H_{2}^{+}\right]^{0} \qquad \text{etc.}$$

in its attack on hydrogen. While the overall reaction enthalpy of the quasi-resonant hydrogen-exchange process is obviously ca. zero, the addition step of sequence 1 is estimated to be ca. 47 kcal mol^{-1} exothermic.²⁷⁻²⁹ Other conceivable reaction paths, such as the charge-exchange or hydrogen-atom transfer reaction between $C_2X_3^+$ and H_2 are highly endothermic ($\Delta H^{\circ} \ge +90$ kcal mol⁻¹), and therefore inaccessible even to nucleogenic $C_2X_3^+$ ions.

The $C_2X_3H_2^+$ adduct of eq 1, excited by the exothermicity of its formation process, may undergo back-dissociation to a vinyl cation and hydrogen molecule (k_{-1}) as observed under ICR conditions.⁶ In the present high-pressure experiments, the back-dissociation of C₂X₃H₂⁺ is efficiently hampered by competing collisional deactivation of the excited adduct by the bulk gas molecules $(k_2, M = H_2)$. All $C_2 X_3 H_2^+$ adducts escaping backdissociation, as well as any residual vinyl cations, react efficiently with the gaseous nucleophiles Nu yielding eventually the corresponding labeled neutrals, i.e. EtNu and VinNu (reactions 4, 6, 12, 14, 20, and 22 of Table I). The linear [EtNu]/[VinNu] vs. $P(H_2)$ correlations of Figure 1 point to the efficient collisional deactivation of the excited $C_2X_3H_2^+$ adducts in these systems. According to the energetics of the relevant reactions of Table I, proton transfer from $C_2X_3^+$ (or $C_2X_3H_2^+$) to Nu is energetically allowed (reactions 5, 7, 13, 15, 21, and 23). However, these processes do not seem to be significant in the present experiments, as suggested by the lack of appreciable amounts of acetylene among the products. Product analysis cannot provide a similar direct evidence against proton transfer from $C_2X_3H_2^+$ to Nu (reactions 7, 15, and 23). In fact, in most cases, only labeled ethylene would be formed, which cannot be discriminated from the tritiated ethylene initially present in the decay mixture.³⁰

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However, on the grounds of the similar reactivity displayed by $C_2X_3H_2^+$ toward largely different nucleophiles (Figure 2), and in agreement with the predominant Lewis-acid character noted for related cationic species in their attack on the same Nu,^{24,25} proton transfer processes 7, 15, and 23 can be expected to be relatively limited and to affect, in any case, all systems studied to a comparable extent.

In this view, the product distributions of Figure 1 can be considered as representative of the major ionic processes occurring in the corresponding H_2 decay systems. Their dependence upon H_2 and Nu concentrations is in agreement with the reaction pattern 28. Accordingly, a quantitative estimate of the $k_{\rm D}({\rm H_2})$

$$C_{2}X_{3}^{+} - \begin{bmatrix} C_{2}X_{3}H_{2}^{+} \end{bmatrix} \xrightarrow{A_{NU}(Et)} [C_{2}X_{3}H_{2}Nu^{+}] \xrightarrow{neutralizn} [C_{2}X_{3}H_{2}Nu^{+}] \xrightarrow{neutralizn} C_{2}X_{3}H_{2}Nu (EtNu) (28a) \\ +Nu \\ +Nu \\ A_{Nu}(Vin) \end{bmatrix} [C_{2}X_{3}Nu^{+}] \xrightarrow{neutralizn} C_{2}X_{3}Nu (VinNu) (28b)$$

rate constant arises from the slope of the linear relation of Figure 2, if the trapping steps of $C_2X_3^+$ and $C_2X_3H_2^+$ by Nu (k_{Nu} (Vin) and $k_{Nu}(Et)$ and the neutralization processes of the corresponding adducts to a base present in the system $(0.3 \text{ Torr of } N(CH_3)_3)$ are assumed to be fast, their rate coefficients approaching the calculated ADO and AQO limits (k_{Nu} (Vin), k_{Nu} (Et) (× 10⁹ cm³ molecule⁻¹ s⁻¹) = 4.7, 4.5 (Nu = $1,4-C_4H_8Br_2$); 1.7, 1.6 (Nu = C_6H_6 ; 5.4, 5.3 (Nu = CH₃OH)).

 $k_{\rm D}({\rm H_2}) = (2.8 \pm 0.5) \times 10^{-11} \,{\rm cm^3} \,{\rm molecule^{-1}} \,{\rm s^{-1}}$ is obtained for the addition reaction 1 from the linear correlation of Figure 2 and is slightly lower than the value previously measured by the ICR technique $(k_{ICR}(H_2) = 6.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}).^6$ In view of the different nature of the vinyl cations generated by the two methods and of the largely different experimental conditions adopted, the agreement between $k_{\rm D}({\rm H_2})$ and $k_{\rm ICR}({\rm H_2})$ appears considerable. Both these experimental values are, however, several orders of magnitude lower than the calculated collision rate for eq 1 $(k_{coll}(H_2) = (1.5-1.8) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}).^4$ This difference can be ascribed to the significant activation barrier involved in the addition process 1. The calculated value for this barrier is ca. 9 kcal mol^{-1} ,² which is in reasonable agreement with the 6-16 kcal mol⁻¹ activation energy range, experimentally obtained for reaction 1 from metastable transition studies.^{28,29}

The essential agreement between the $C_2X_3H_2^+$ adduct formation rate constant $k_{\rm D}({\rm H}_2)$ from the decay experiments and the exchange rate constant $k_{ICR}(H_2)$ between $C_2H_3^+$ and D_2 , measured by ICR methods,⁶ is consistent with the complete back-dissociation of the excited $C_2H_5^+$ adducts from sequence 1 at $P(H_2)$ around 10⁻⁵ Torr, whereas, as the $P(H_2)$ pressure exceeds 60 Torr, back-dissociation of $C_2H_5^+$ is efficiently prevented by collisional stabilization. An additional piece of evidence on this point is provided by the relative low value $(2 \times 10^{-29} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1})$ obtained at 300 K for the third-order rate constant $k_{SIFT}(H_2)$ of the addition of $C_2H_3^+$ to H₂ under SIFT conditions ($P_{\text{He}} \simeq 0.4$ Torr). Assuming a k_{-1} $\simeq 10^9 \, \text{s}^{-1}$ value for the C₂H₅⁺ back-dissociation (eq 1) and a value $k_2 \simeq 7.7 \times 10^{-10} \, \text{cm}^3$ molecule⁻¹ s⁻¹ for its quenching rate coefficient (taken equal to the Langevin collision limit between $C_2H_5^+$ and He), we can estimate a second-order rate constant k_1 = 2.6×10^{-11} cm³ molecule⁻¹ s⁻¹ from the SIFT experiments, which compares well with the corresponding $k_{\rm D}({\rm H_2})$ and $k_{\rm ICR}({\rm H_2})$ values obtained from decay and ICR data.

In view of the above considerations, it follows that a nucleogenic $C_2X_3^+$ ion undergoes an average of several tens unreactive collisions with H₂ prior to yielding a persistent σ -bonded C₂X₃H₂⁺ adduct. This is so, in spite of the large excess of internal energy of nucleogenic vinyl cation (≤ 50 kcal mol⁻¹),^{18,19} which is sufficient to cross the barrier $(11 \pm 5 \text{ kcal mol}^{-1})^{28,29}$ associated with the formation of $C_2X_3H_2^+$. The answer lies in the preliminary occurrence of an electrostatic adduct between $C_2X_3^+$ and H_2

⁽³⁰⁾ The recovery of tritiated benzene in the $Nu = C_6H_6$ decay systems cannot be taken as evidence for the occurrence of proton transfer 5 and 7 (Table I), since it may be formed by protonation of \hat{C}_6H_6 by ionic fragments accompanying nuclear decay in tritiated ethylene.

$$C_{2}X_{3}^{+} - \begin{pmatrix} k_{D}(CH_{4}) \\ +CH_{4} \\$$

characterized by a rather shallow potential energy well (~ 4 kcal mol⁻¹),³¹ prior to the formation of the σ -bonded C₂X₃H₂⁺ intermediate (eq 1'). The efficiency of the reaction depends on the

$$C_2 X_3^+ + H_2 \underbrace{\stackrel{k_+}{\leftarrow}}_{k_-} [C_2 X_3^+ \cdot H_2] \underbrace{\stackrel{k_p}{\leftarrow}}_{k_-} [C_2 X_3 H_2^+] \qquad (1')$$

relative values of k_{-} , k_{p} , and k_{-p} , the k_{+} being represented by the encounter rate $(k_{coll}(H_2))$. These, in turn, reflect the relative height of the relevant activation barriers and the difference in the corresponding entropies of activation or preexponential A factors. The forward reaction k_p is, in effect, a unimolecular isomerization with comparately "tight" transition state (low A factor). The back-dissociation of the electrostatic adduct k_{-} is normally a fragmentation process with an exceptionally "loose" transition state involving essentially free rotations of the product moieties (high A factor). Thus, although excess energy of $C_2X_3^+$ allows crossing over all the activation barriers of eq 1', entropy factors favor k_{\perp} over k_p and, therefore, the overall efficiency of process 1' results rather low. Once formed, however, most of the σ -bonded C₂X₃H₂⁺ intermediates dissipate their internal energy by unreactive H₂ collisions preventing their back-dissociation. In their lifetime (ca. 10^{-9} s), C₂X₃H₂⁺ ethyl cations undergo complete hydrogen-atom scrambling, which is known to involve negligible, if any, activation energy.32-34

Vinyl Cation Attack on Methane. The nature of the tritiated products, recovered in the CH_4 decay systems, and their relative distribution as a function of the CH_4 concentration (Figure 3) indicate sequence 2 as the major reaction path for $C_2X_3^+$ attack on CH_4 . The overall standard enthalpy change of (2) is -23 kcal

$$C_{2}X_{3}^{+} + CH_{4} \xrightarrow{R_{1}} [C_{3}X_{3}H_{4}^{+}]^{*} \xrightarrow{R_{3}} + H_{2} (2)$$

+ $M'_{4}k_{2}$
 $[C_{3}X_{3}H_{4}^{+}]^{0}$

mol⁻¹, the k_1 step being 59 kcal mol⁻¹ exothermic, and the k_3 step 36 kcal mol⁻¹ endothermic. Other conceivable reaction pathways on the $C_2X_3^+ + CH_4$ potential surface, such as charge exchange, hydrogen-atom transfers, and multiple fragmentation of $C_3X_3H_4^+$, are highly endothermic. Occurrence of several such processes conceivably accessible to nucleogenic $C_2X_3^+$ ions having a large excess of internal energy appears nevertheless unlikely on the grounds of product analysis.

According to sequence 2, the $C_3X_3H_4^+$ adduct, excited by the exothermicity of its formation process ($\Delta H^\circ = -59$ kcal mol⁻¹), may undergo fragmentation to allyl cation and a H₂ molecule, unless deactivated by collision with the bulk gas molecules (M' = CH₄). In each decay sample, vinyl, propyl, and allyl cations are formed, whose relative proportions strongly depend upon the corresponding experimental conditions (Figure 3). All these cations eventually react with the nucleophiles Nu present in the gaseous mixture (eq 4, 8, 10, 12, 16, 18, 20, 24, and 26 of Table I) yielding the corresponding tritiated products, i.e. VinNu and C₃Nu (PrNu + AllNu + C₃H₆). While the thermochemical data of Table I show that proton-transfer processes from vinyl (eq 5, 13, and 21), propyl (eq 9, 17, and 25), and allyl cations (eq 11, 19, and 27) to Nu are all energetically allowed, their extent must be negligible in the present decay experiments, as shown by the lack of tritiated acetylene or allene among the labeled products.^{24,30} On the other hand, the recovery of detectable amounts of tritiated propylene shows that a significant fraction of propyl ions act as Bronsted acids, especially toward CH₃OH and 1,4-C₄H₈Br₂ (eq 9, 17, and 25 of Table I). In view of the above considerations and in analogy with the H₂ decay systems, the formation of the tritiated products, and their dependence upon the experimental conditions in the C₂X₄/CH₄ decay systems (Figure 4), are consistent with the reaction pattern 29.

In particular, the linear correlation of Figure 5 provides a direct estimate of the rate constant $k_D(CH_4)$ for the addition reaction between $C_2X_3^+$ and CH_4 (eq 2), if trapping of vinyl, propyl, and allyl cations by Nu and neutralization of the ensuing adducts are assumed to be relatively fast. The value obtained for $k_{\rm D}(\rm CH_4)$ is equal to $(5.5 \pm 1.0) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ and is slightly higher than the rate coefficients, measured for the same sequence 2 by conventional low-pressure kinetic methods, i.e. ICR ($P(CH_4)$) 10^{-5} Torr, $k_{\rm ICR}$ (CH₄) = $(2.2 \pm 0.2) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹), ^{5,6} SIFT (P(He) 0.4 Torr; $k_{SIFT}(CH_4) = 1.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1}$ s^{-1}),³ and "high-pressure" mass spectrometry (P(CH₄) 0.3 Torr; $k_{\text{HPMS}}(\text{CH}_4) = (0.87 \pm 0.12) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}).^{35}$ The $k_{\rm D}({\rm CH_4})$ value obtained from the present decay experiments closely approaches the corresponding Langevin collision limit $(k_{\text{coll}}(\text{CH}_4) = 1.2 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}),^{27} \text{ thus suggesting}$ that addition of $C_2X_3^+$ to CH_4 may involve negligible activation barriers, if any. Under the decay conditions, the ensuing $C_3H_7^+$ species are efficiently quenched by unreactive collisions with CH₄, as demonstrated by the very limited yields of AllNu, recovered at relatively high CH₄ partial pressure ($P(CH_4) \ge 200$ Torr; see Figure 3).

Two possible fragmentation pathways are accessible to sufficiently excited $C_3H_7^+$ intermediates. The kinetically most favored fragmentation path leads to an allyl cation and a H_2 molecule $(\Delta H^\circ = +36 \text{ kcal mol}^{-1})$,³⁶ with an activation energy of 41.5 kcal mol⁻¹, estimated from metastable transition studies.^{28,29} The activation barrier of the alternative fragmentation channel, yielding the 2-propenyl cation and H_2 ($\Delta H^\circ = +47 \text{ kcal mol}^{-1}$) can be estimated, if one assumes an activation energy of at least 11 ± 5 kcal mol⁻¹ for the reverse reaction, namely the addition of a 2-propenyl cation to H_2 .³⁷ On these grounds, the activation barrier for the latter fragmentation pathway is expected to exceed 58 ± 5 kcal mol⁻¹. The recognized poor reactivity of both 2-propenyl and allyl cations toward H_2 in the gas phase at relatively high

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TABLE I: Trapping Reactions and Their Energetics

		ΔH° , a kcal mol ⁻¹	neutral products
(4)	$\overline{C_2 X_3^+ + C_6 H_6 \rightarrow C_8 H_6 X_3^+}$	-65 ^b	styrene
(5)	$C_2X_3^+ + C_6H_6 \rightarrow C_6H_6X^+ + C_2X_2$	-28	acetylene, benzene
(6)	$C_2X_3H_2^+ + C_6H_6 \rightarrow C_8H_8X_3^+$	-43 ^b	ethylbenzene
(7)	$C_2X_3H_2^+ + C_6H_6 \rightarrow C_6H_6X^+ + C_2X_2H_2$	-18	ethylene, benzene
(8)	$C_3X_3H_4^+ + C_6H_6 \rightarrow C_9X_3H_{10}^+$	$-24^{b,c}$	propylbenzene
(9)	$C_3X_3H_4^+ + C_6H_6 \rightarrow C_6H_6X^+ + C_3X_2H_4$	-2	propylene, benzene
(10)	$C_{3}X_{3}H_{2}^{+} + C_{6}H_{6} \rightarrow C_{9}X_{3}H_{8}^{+}$	-40 ^{b,d}	allylbenzene
(11)	$C_{3}X_{3}H_{2}^{+} + C_{6}H_{6} \rightarrow C_{6}H_{6}X^{+} + C_{3}X_{2}H_{2}$	+5	allene, benzene
(12)	$C_2X_3^+ + CH_3OH \rightarrow C_2X_3O(H)CH_3^+$	-74 ^e	methyl vinyl ether
(13)	$C_2X_3^+ + CH_3OH \rightarrow CH_3OHX^+ + C_2X_2$	-29	acetylene
(14)	$C_2X_3H_2^+ + CH_3OH \rightarrow C_2X_3H_2O(H)CH_3^+$	-47	methyl ethyl ether
(15)	$C_2X_3H_2^+ + CH_3OH \rightarrow CH_3OHX^+ + C_2X_2H_2$	-19	ethylene
(16)	$C_3X_3H_4^+ + CH_3OH \rightarrow C_3X_3H_4O(H)CH_3^+$	-33°	methyl propyl ether
(17)	$C_3X_3H_4^+ + CH_3OH \rightarrow CH_3OHX^+ + C_3X_2H_4$	-2	propylene
(18)	$C_3X_3H_2^+ + CH_3OH \rightarrow C_3X_3H_2O(H)CH_3^+$	-45	allyl methyl ether
(19)	$C_3X_3H_2^+ + CH_3OH \rightarrow CH_3OHX^+ + C_2X_2H_2$	+4	allene
(20)	$C_2X_3^+ + 1,4-C_4H_8Br_2 \rightarrow C_2X_3Br + C_4H_8Br^+$	-40	vinyl bromide
(21)	$C_2X_3^+ + 1,4-C_4H_8Br_2 \rightarrow C_4H_8XBr_2^+ + C_2X_2$	<-278	acetylene
(22)	$C_2X_3H_2^+ + 1,4-C_4H_8Br_2 \rightarrow C_2X_3H_2Br + C_4H_8Br^{+f}$	-23	ethyl bromide
(23)	$C_2X_3H_2^+ + 1,4-C_4H_8Br_2 \rightarrow C_4H_8XBr_2^+ + C_2X_2H_2$	<-178	ethylene
(24)	$C_{3}X_{3}H_{4}^{+} + 1,4-C_{4}H_{8}Br_{2} \rightarrow C_{3}X_{3}H_{4}Br + C_{4}H_{8}Br^{+/}$	-6	propyl bromide
(25)	$C_3X_3H_4^+ + 1,4-C_4H_8Br_2 \rightarrow C_4H_8XBr_2^+ + C_3X_2H_4$	<0	propylene
(26)	$C_{3}X_{3}H_{2}^{+} + 1,4 - C_{4}H_{8}Br_{2} \rightarrow C_{3}X_{3}H_{2}Br + C_{4}H_{8}Br^{+/}$	-7	allyl bromide
(27)	$C_3X_3H_2^+ + 1,4-C_4H_8Br_2 \rightarrow C_4H_8XBr_2^+ + C_3X_2H_2$	≤0	allene

 ${}^{a}H^{o}_{f}$ values of neutral species from ref 20. Proton affinities (PA) of neutrals and H^{o}_{f} values for ionic species taken from ref 21–23. Reaction energetics obtained by assuming ground-state ions. ^bA tentative estimate of this reaction enthalpy can be arrived at by assuming that the PA of styrene at the ring position bearing the vinyl group is the same as that of benzene (PA = 181.3 kcal mol⁻¹). $^{\circ}C_{3}X_{3}H_{4}^{+}$ taken as the s-propyl ion. ${}^{d}C_{3}X_{3}H_{2}^{+}$ taken as the allyl cation. ${}^{e}H^{o}_{f}$ of oxygen-protonated methyl vinyl ether, calculated by using a PA for methyl vinyl ether equal to that of MeOEt (PA = 196 kcal mol⁻¹). ${}^{f}C_{4}H_{8}Br^{+}$ taken a tetramethylenebromonium ion. $\Delta H^{o}_{f}(C_{4}H_{8}Br^{+}) = 182.5$ kcal mol⁻¹; $\Delta H^{o}_{f}(1,4-C_{4}H_{8}Br_{2}) = 25$ kcal mol⁻¹; cf. ref 24-26. ${}^{g}PA(1,4-C_{4}H_{8}Br_{2})$ is estimated to exceed 180 kcal mol⁻¹.

H₂ pressures (150-760 Torr) provides an independent support to $C_3H_7^+$ fragmentation channels, with energy barriers appreciably exceeding their endothermicity.24

In this view, the experimental observation of the predominant formation of s-PrNu and AllNu in the CH₄ decay systems is justified. The isopropyl cation is the thermodynamically most stable species from the addition of $C_2X_3^+$ to CH_4 . Alternative isomeric structures, such as the n-propyl cation, are expected to isomerize to isopropyl or to protonated cyclopropane ions in a time estimated to be much shorter $(<10^{-10} \text{ s})^{38-40}$ than that of a reactive encounter with a Nu molecule in our systems. The protonated cyclopropane ion is not a stable structure significantly involved in the $C_2X_3^+$ addition to CH_4 , as demonstrated by the negligible yields of tritiated n-PrNu and cyclopropane.⁴¹ It is, therefore, concluded that the $C_3H_7^+$ complexes, generated from the addition of a nucleogenic vinyl cation to CH₄ and quenched by unreactive collisions with the bulk gas molecules, eventually collapse to the $s-C_3H_7^+$ structure, without the need of postulating the intermediacy of a protonated cyclopropane structure.

Those $C_3H_7^+$ adducts with sufficient energy excess to undergo fragmentation yield directly $C_3H_5^+$ fragments with the allyl cation structure. Any conceivable formation of the 2-propenyl ion isomer is, in fact, excluded on the grounds that its isomerization to allyl cation is characterized by a activation barrier largely exceeding 11 kcal mol^{-1,42,43} and, therefore, in contrast with the experimental

results, significant amounts of 2-Nu-propene should be produced under the decay conditions.24

Reaction Mechanism. The distinct affinity of $C_2X_3^+$ for H_2 and CH₄ and the nature of the ensuing ionic intermediates are consistent with the carbene-like character of the vinyl cation. According to molecular orbital calculations,² the insertion of $C_2H_3^+$ into a σ H-H bond is considered to proceed in two distinct consecutive steps. The first step (a in sequence 30) is the electrophilic



phase of the insertion reaction, wherein a two-electron three-center bond is formed between the H_2 molecule and the empty p_x orbital of vinyl cation. The second step (b in sequence 30) is the nucleophilic phase of the reaction, since the antibonding orbital of H_2 combines with the occupied π orbital of the vinyl cation to form the second C-H bond at the expense of the σ bond of H₂. The calculated value for the activation energy of the two-phase mechanism 30 is 9 kcal mol⁻¹ at a C-H distance of 2.3 Å. However, the relative contributions of phases a and b to the creation of the activation energy are still rather obscure.

In view of the significant anologies in the electrophilic addition of positive ions⁴⁵ and singlet carbenes⁴⁶ to H_2 and CH_4 , insertion of a vinyl cation into the C-H bond of methane is expected to

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⁽⁴³⁾ It is interesting to note that Lampe predicts an activation barrier E^*_1 for the fragmentation of $C_3H_7^+$, formed from addition of $C_2H_3^+$ to CH_4 , to For the fragmentation of C_3H_7 , for the from a dimension of C_2H_3 , is occur, to $C_3H_5^+$, and to H_2 , which is *lower* than that (E^*_2) for the back-dissociation to $C_2H_3^+$ and CH_4 (ref 7). However, when the $C_3H_7^+$ adduct is formed by addition of CH_3^+ to C_2H_4 , he finds $E^*_1 > E^*_2$ (ref 44). This apparent discrepancy may arise from a diverse isomeric $C_3H_7^+$ distribution obtained from the two addition processes, which may fragment according to different pathways with formation of different $C_3H_5^+$ isomers or neutral fragments.

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Figure 6. Most favored transition state structure for the $C_3H_7^+ \rightarrow allyl^+ + H_2$ fragmentation reaction (see ref 47).

involve a two-phase mechanism similar to sequence 30. Accordingly, the significant reactivity difference displayed by the unsubstituted vinyl cation and 2-propenyl ion toward CH₄²⁴ may provide a hint into the origin of the activation barriers in these insertion processes. From previous studies,²⁴ 2-propenyl ions are found to be rather unreactive toward CH₄. Taking into account the present results, this indicates that substitution of the H₁ atom of the vinyl cation with an electron-releasing methyl group substantially decreases the reactivity of the unsaturated ion toward H_2 and CH_4 . This can be expected, if one assumes that the electrophilic phase a of the insertion process is the major factor in determining its activation energy. Should, instead, the nucleophilic phase b predominantly contribute to the activation energy of the insertion process, a reverse effect would be expected, owing to the presence of a methyl group substituent at the π unsaturation of the ionic electrophile. Therefore, it can be concluded, on the grounds of the present results, that the predominant contribution to the activation barriers, for the vinyl-cation insertion into the σ -bonds of H₂ and CH₄ is associated with the electrophilic phase of the process. This conclusion is further supported by the qualitative correspondence between the reactivity of H_2 and of CH_4 toward $C_2H_3^+$ and their proton affinities ($PA(H_2) = 101$) kcal mol⁻¹; $PA(CH_4) = 128 \text{ kcal mol}^{-1}$).²²

While the 1,1 addition-elimination mechanism involved in the vinyl-cation attack on H_2 seems well established,^{28,29} the mechanism of addition-elimination reaction to yield allyl cation from the $C_2H_3^+$ insertion into CH_4 is still rather uncertain. Metastable transition studies indicate that allyl cations are formed by symmetry-forbidden 1,2-H₂ elimination from *n*-propyl ions or, alternatively, by symmetry-forbidden 1,3-H₂ elimination from spropyl ions.^{27,28} Ab initio molecular orbital calculations exclude the latter mechanism on the grounds of the exceedingly high activation energy involved (ca. 147 kcal mol⁻¹).⁴⁷ An additional hypothetical mechanism, which involves a symmetry-allowed 1,1-H₂ elimination from corner-protonated cyclopropane, has been conceived.⁴⁷ The present results agree with related metastable transition data in suggesting that this mechanism is unlikely, since it involves a calculated activation energy of ca. 73 kcal mol⁻¹, well above the activation energy (65 \pm 2 kcal mol⁻¹) for the backdissociation of $C_3H_7^+$ to $C_2H_3^+$ and CH_4 . In this view, after the electrophilic attack of $C_2H_3^+$ on the σ C-H bond of methane has

taken place, an open-chain σ -bonded $C_3H_7^+$ complex is likely to be formed which, given a sufficient amount of internal energy from its formation step, may rearrange to the structure shown in Figure 6 and collapse directly to allyl cation and a H_2 molecule. Under conditions favoring collisional deactivation ($P(CH_4) \ge 200$ torr) of the $C_3H_7^+$ complex from the vinyl cation insertion into CH₄, the *s*-propyl ion structure becomes predominant and the transition state of Figure 6 for 1,2 elimination to allyl ion and H_2 becomes unaccessible.

Conclusion

The present results provide convincing evidence for a nucleogenic vinyl cation which is able to insert into the σ bonds of H₂ and CH₄ to give the corresponding carbenium ions, C₂H₅⁺ and C₃H₇⁺. The specific features of the nuclear-decay technique adopted, i.e. the relatively high pressure of the reaction systems and the possibility to structurally discriminate the neutral end products, allow formation of these persistent addition complexes and determination of their structure, as well as of that of the accompanying fragmentation species (e.g. C₃H₅⁺). Comparative analysis of the kinetic data concerning the insertion reactions 1 and 2, obtained under different experimental conditions by different investigation methodologies (nuclear decay, radiolysis, ICR, SIFT, HPMS, etc.), points to the need of using different complementary investigation approaches to obtain a satisfactory kinetic and mechanistic definition of an ion-molecule reaction.

Gas-phase insertion of $C_2H_3^+$ into a H_2 molecule is a process characterized by an activation energy $(11 \pm 5 \text{ kcal mol}^{-1})$ whereas that involved in the analogous insertion into a C-H bond of methane is negligible. The nature of such a difference is attributed to a different response of the σ bond of the substrate in the electrophilic phase of the insertion process. At H₂ pressures below 60 Torr, the σ -bonded C₂H₅⁺ adduct is able to back-dissociate to $C_2H_3^+$ and H_2 in a time comparable to the collision interval operative under such conditions (ca. 10⁻⁹ s). This finding provides a satisfactory explanation of the persistent failure to detect and characterize the gaseous $C_2H_5^+$ adduct with other experimental techniques, in particular with mass spectrometric methods. A similar situation is met for $C_3H_7^+$ ions formed from $C_2H_3^+$ addition to CH₄. Here, a s-propyl ion is found to be the most favored structure, while occurrence of persistent protonated-cyclopropane species is excluded. When sufficiently excited (low-pressure experiments), s-propyl ions may interconvert readily with distorted *n*-propyl structures able to give directly allyl cations and H_2 via a 1,2- H_2 elimination reaction, whose activation energy (41.5 kcal mol⁻¹) compares well with that of ab initio calculations (ca. 45 kcal mol^{-1}).

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Registry No. C_2T_4 , 683-80-7; C_2HT_3 , 106471-61-8; $C_2H_3^+$, 14604-48-9; $C_2T_3^+$, 106471-62-9; $sC_3H_7^+$, 19252-53-0; $C_2H_5^+$, 14936-94-8; H_2 , 1333-74-0; methane, 74-82-8; 1,4-dibromobutane, 110-52-1; benzene, 71-43-2; methanol, 67-56-1; allyl cation, 1724-44-3.

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