Gas-Phase Protonation of Allene and Propyne. Remarkably Selective Formation of 2-Propenyl Ions

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Abstract: The structure of $C_3H_5^+$ ions, obtained in the dilute gas state from the protonation of propyne and allene by radiolytically formed H_3^+ and $C_nH_5^+$ ($n = 1, 2$) ions, has been investigated in the pressure range from 150 to 760 torr. The $C_3H_5^+$ ions have been trapped with two gaseous nucleophiles, i.e., benzene and 1,4-dibromobutane, and their structure has been inferred from the nature of the neutral products isolated. The results, in particular those from the systems containing 1,4-dibromobutane, show that 2-propenyl ions are formed almost exclusively in the kinetically significant step of the protonation from both propyne and allene, a partial isomerization to the allyl structure being observed in the systems containing benzene. The results are compared with the evidence from structurally diagnostic mass spectrometric techniques and with the pertinent theoretical and solution-chemistry data.

Electrophilic additions to allenes[1] and alkynes[2] have been extensively investigated in condensed media. In particular, a recent study on the protonation of propyne and allene, the model C_3H_4 hydrocarbons, in aqueous sulfuric acid suggests predominant proton transfer to the terminal carbons.[3]

Extension of the study to the dilute gas state is of obvious mechanistic interest, allowing in principle direct evaluation of the intrinsic features of the protonation process, unperturbed by the effects of solvation and ion pairing which affect, to a variable extent, the different solvent systems.

Furthermore, $C_3H_5^+$ ions have been thoroughly investigated in the gas phase by mass spectrometry in order to establish their structure, stability, and reactivity.[4] Most of the available data derive from the collision-induced dissociation (CID) spectra of $C_3H_5^+$ ions from various precursors[5] or of the ionic adducts from their in situ derivatization.[6]

While the conclusions reached are somewhat affected by the inherent limitations of CID as a structural probe,[7] the occurrence of two distinct $C_3H_5^+$ isomers as long-lived gaseous cations appears to be established with reasonable confidence. The allyl ion is more stable by some 11 kcal mol^{-1},[4a,b] in agreement with the results of theoretical calculations,[8] and there is evidence that isomerization of the 2-propenyl ion into the allyl cation is characterized by a substantial barrier.[5c,8]

As to the specific site of protonation of propyne and allene, the available mass spectrometric data provide no clear-cut answer. In fact, both allyl and 2-propenyl ions are invariably formed from each of the C_3H_4 isomers, their proportions depending on the Brønsted acid employed.[5d,e] Thus, a high percentage of 2-propenyl ions (86% from propyne and 78% from allene) has been detected from the reaction of the relatively mild H_3O^+ acid, while more powerful reagents, such as CH_5^+ and $C_2H_5^+$, yield 65% allyl ions from allene and 30% from propyne.[5d]

Such a dependence on the exothermicity of the protonation process, together with the relatively inefficient collisional stabilization, and the large time lag between formation and structural assay of the ions suggest that the mass spectrometric results may be heavily affected by secondary isomerization. In fact, the observed isomeric composition may be considerably different from that obtained in the primary, kinetically significant protonation step, reflecting instead the isomerization of an unknown fraction of 2-propenyl ion into the more stable allylic structure.

Since the impact of gas-phase studies upon ionic chemistry in general depends essentially on their ability to provide simplified and unified models of the corresponding processes occurring in solution, the relevance of *kinetic* aspects of gas-phase reactions is paramount. Therefore, the experimental technique used should

be characterized by a highly effective collisional deactivation of any excited ions, ensuring a truly thermal energy distribution of reactants and products, and suppressing secondary isomerization. Moreover, the structural assignments should rest on positive evidence, as allowed by the actual isolation of the reaction products. Both the above requirements are largely met by recent refinements of "high-pressure" radiolytic techniques,[9] whose application to the gas-phase protonation of propyne and allene is reported in the present paper.

Experimental Section

Materials. The reagents and the compounds used as analytical standards were commercially available or were synthesized by unexcep-

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(2) (a) Schmid, G. H. "The Chemistry of the Carbon–Carbon Triple Bond"; Patai, S., Ed.; Wiley: New York, 1978. (b) Modena, G.; Rivetti, F.; Scorrano, G.; Tonellato, U. *J. Am. Chem. Soc.* **1977**, *99*, 3392. (c) Marcuzzi, F.; Melloni, G.; Modena, G. *J. Org. Chem.* **1979**, *44*, 3022. (d) Yates, K.; Go, T. A. *J. Org. Chem.* **1980**, 2385.

(3) Cramer, P.; Tidwell, T. T. *J. Org. Chem.* **1981**, *46*, 2683.

(4) (a) Lossing, F. P. *Can. J. Chem.* **1971**, *49*, 357. (b) Beck, D.; Osberghaus, O. *Z. Phys.* **1960**, *160*, 406. (c) Beck, D. *Discuss. Faraday Soc.* **1963**, *36*, 56. (d) Lossing, F. P. *Can. J. Chem.* **1972**, *50*, 3973. (e) Houriet, R.; Elwood, T. A.; Futrell, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 2320.

(5) (a) Cooks, R. G. In "Collision Spectroscopy"; Cooks, R. G., Ed.; Plenum: New York, 1978. (b) Nibbering, N. M. M.; Nishishita, T.; Van de Sande, C. C.; McLafferty, F. W. *J. Am. Chem. Soc.* **1974**, *96*, 5668. (c) Bowen, R. D.; Williams, D. H.; Schwarz, H.; Wesdemiotis, C. *J. Am. Chem. Soc.* **1979**, *101*, 4681. (d) Bowers, M. T.; Shuying, L.; Kemper, P.; Stradling, R.; Webb, H.; Aue, D. H.; Gilbert, J. R.; Jennings, K. R. *J. Am. Chem. Soc.* **1980**, *102*, 4830. (e) Aue, D. H.; Davidson, W. R.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 6700.

(6) Lay, J. O., Jr.; Gross, M. L. *J. Am. Chem. Soc.* **1983**, *105*, 3445.

(7) CID is essentially a "fingerprint" technique, allowing positive structural assignments only when "authentic" ions of unambiguously defined structure are available for comparison purposes, a feat hardly attainable in many cases. As an example, the structure of the $C_9H_{11}^+$ adduct(s) from the reaction of $C_3H_5^+$ ions with C_6H_6 has been inferred by comparison with model ions from the protonation of α-methylstyrene and allylbenzene. The absolute selectivity of the latter process is highly questionable, and a complex mixture of isomers, protonated at different sites, is likely to arise. Of course, one can argue that during the long delay ($\sim 10^{-5}$ s) before structural assay, these isomeric ions collapse to a single, most stable structure. Such a contention, however, would severely detract from the value of CID in kinetically oriented studies. For a discussion of other limitations of CID in the analysis of isomeric ionic mixtures, see: (a) Bass, L. M.; Bowers, M. T. *Org. Mass Spectrom.* **1982**, *17*, 229. Also see: (b) Proctor, C. J.; McLafferty, F. W. *Org. Mass Spectrom.* **1983**, *18*, 193. (c) *Ibid.* **1983**, *18*, 272.

(8) (a) Radom, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 6531. (b) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649. (c) Halgren, T. A.; Lipscomb, W. N. *Chem. Phys. Lett.* **1977**, *49*, 225. (d) Merlet, P.; Peyerimhoff, S. D.; Buenker, R. J.; Shih, S. *J. Am. Chem. Soc.* **1974**, *96*, 959.

(9) For a recent review, cf: Cacace, F. *Rad. Phys. Chem.* **1982**, *20*, 99.

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Table I. Alkylation Products from the Reaction of Gaseous $C_3H_5^+$ Ions with Benzene

	system composition, torr[a]			relative yields of products, %		apparent ratio $CH_3C^+=CH_2/$ $CH_2=CHCH_2^+$
H_2	C_3H_4	C_6H_6	base	$PhC(CH_2)CH_3$, $PhC(OH)(CH_3)_2$	$PhCH_2CH=CH_2$	
720	5.0 (allene)	0.40		74 ⎫	26 ⎫	2.8 ⎫
720	5.0 (allene)	0.46		69 ⎬ 70 ± 2	31 ⎬ 30 ± 2	2.2 ⎬
720	5.0 (allene)	0.61		69 ⎪	31 ⎪	2.2 ⎬ 2.4 ± 0.2
720	5.0 (allene)	0.55		70 ⎭	30 ⎭	2.3 ⎭
720	5.0 (allene)	0.56	3.0 (Me$_3$N)	61	39	1.6
720	5.0 (allene)	0.67	1.66 (pyridine)	58	42	1.4
720	5.0 (propyne)	0.57		79 ⎫	21 ⎫	3.8 ⎫
720	5.0 (propyne)	0.44		79 ⎪	21 ⎪	3.8 ⎪
720	5.0 (propyne)	0.50		73 ⎬ 75 ± 4	27 ⎬ 25 ± 4	2.7 ⎬ 3.0 ± 0.6
720	5.0 (propyne)	0.61		71 ⎪	29 ⎪	2.4 ⎪
720	5.0 (propyne)	0.58		71 ⎭	29 ⎭	2.4 ⎭
720	5.0 (propyne)	0.56	3.0 (Me$_3$N)	74	26	2.8
720	5.0 (propyne)	0.71	2.2 (pyridine)	71	29	2.4

[a] All systems contained O_2 (5 torr) as a thermal radical scavenger.

Table II. Brominated Products from the Reaction of Gaseous $C_3H_5^+$ Ions with 1,4-Dibromobutane

system composition, torr[a]				relative yields of products, %		apparent ratio $CH_3C^+=CH_2/$ $CH_2=CHCH_2^+$
X_2[b]	CH_4	C_3H_4	$1,4-C_4H_8Br_2$	$CH_2=CBrCH_3$	$CH_2=CHCH_2Br$	
760		5.0 (allene)	1.0	100	c	>30
150		5.0 (allene)	1.0	71	29	2.4
	760	5.0 (allene)	1.0	95	5	19
	150	5.0 (allene)	1.0	84	16	5.2
760		5.0 (propyne)	1.0	100	c	>30
150		5.0 (propyne)	1.0	75	25	3.0
	760	5.0 (propyne)	1.0	100	c	>30
	150	5.0 (propyne)	1.0	89	11	8.1

[a] All systems contained O_2 (5 torr) as a thermal radical scavenger.   [b] D_2 or H_2.   [c] Below detection limit (ca. 3%). Standard deviation of the data ca. 5%.

tional procedures. Their purity was checked by GLC, and purification by preparative GLC was carried out when required, using the same stationary phases chosen for the analysis of the reaction products.

Procedure. The samples for the γ irradiation were introduced into 300-mL Pyrex vessels, thoroughly outgassed, and dried, using a greaseless vacuum line. The irradiation was carried out in a 220 Gammacell (Nuclear Canada Ltd.) at a temperature of 37 °C and a dose rate of ca. 1 Mrd h^{-1}, to a total dose of approximately 4 Mrd.

Analysis. The nature and the yields of the products were determined by GLC, comparing their retention volumes with those of authentic specimens on at least two columns. Further confirmation was obtained by GLC/MS, using a Hewlett-Packard 5982A quadrupole mass spectrometer connected to a 5934A data system or a ZAB-2F magnetic spectrometer from Micromass Ltd.

The GLC analyses were carried out with a Sigma 1, or a Sigma 3B instrument from Perkin-Elmer Co., equipped with a FID unit, on the following columns: (i) a 100-m-long, 0.25-mm i.d. stainless steel capillary column, coated with LB 550 X stationary phase, operated isothermally (60 °C) for 25 min and then programmed at 5 °C min^{-1} to 150 °C; (ii) a 50-m-long, 0.25-mm i.d. stainless steel capillary column, coated with squalane and operated isothermally (30 °C) for 12 min and then programmed to 90 °C at 15 °C min^{-1}; (iii) a 3-m-long, 3.2-mm i.d. stainless steel column, packed with 5% SP-1200 + 1.75% Bentone 34 on 100–120-mesh Supelcoport support, operated at 140 °C; (iv) a 50-m-long, 0.2-mm i.d. fused-silica capillary column, coated with Carbowax 20 M deactivated dimethyl silicone fluid, operated at 80 °C; and (v) a 1.90-m-long, 2-mm i.d. glass column, packed with 0.1% SP-1000 on 80–100-mesh Carbopack C, operated at 185 °C.

Results

Benzene Systems. The composition of the ionic products from the alkylation of benzene with $C_3H_5^+$ ions obtained from propyne and allene following protonation with H_3^+ ions is given in Table I, together with the composition of the irradiated systems. The ionic nature of the processes leading to the formation of the products is deduced from the insensitivity of their yields to the presence of a large concentration of O_2, an effective thermal radical scavenger, and by the depression of their yields caused by addition of gaseous bases, which intercept the ionic precursors of the neutral products.

As an example, the combined $G_{(+M)}$ values of allylbenzene, α-methylstyrene, and 2-phenyl-2-propanol, the major ionic products from the irradiation of allene, gradually decrease from 1.1, corresponding to an *absolute* yield of ca. 35% in the absence of bases, to 0.8, 0.6, and 0.3 in systems containing respectively 1.0, 2.0, and 10.0 torr of NH_3.

The *relative* yields of α-methylstyrene and 2-phenyl-2-propanol (both containing a branched C_3 side chain and both presumably arising from the reaction of 2-propenyl ions) are given together, since their individual yields change rather erratically, depending on the concentration of water in the irradiated systems.[10] It should be noted, in this connection, that addition to the system of sufficiently strong bases, such as Me$_3$N and pyridine, suppresses the formation of 2-phenyl-2-propanol, only allylbenzene and α-methylstyrene being formed, if in reduced yields.

It is also worth mentioning that no other C_9H_{10} isomers, nor their oxygenated derivatives, could be detected among the products. Indeed, formation of *cis-* and *trans-β*-methylstyrene, cyclopropylbenzene, and indane has been positively excluded.

1,4-Dibromobutane Systems. The composition of the irradiated systems and the relative yields of the products are summarized in Table II. A few additional runs have been carried out, by irradiating a gaseous system containing D_2 (760 torr), allene (5 torr), O_2 (5 torr), and water vapor (1 torr). Analysis of the products revealed formation of acetone, with a $G_{(+M)}$ value of ca. 1.0, while only traces of allyl alcohol could be detected.

Discussion

Protonation of Propyne and Allene. Radiolysis of H_2 (D_2) and CH_4 gases at atmospheric pressure is known to yield respectively

(10) Despite extreme efforts to dry the reagent gases and the irradiation vessels, only in a few runs were allylbenzene and α-methylstyrene not accompanied by 2-phenyl-2-propanol. Traces of water are apparently released from the glass walls under γ-irradiation or are formed from O_2, used as a scavenger. The effects of such minute amounts of H_2O are usually entirely negligible, except in those systems where extremely stable ions of low inherent acidity, such as Me$_3$C$^+$ or Me$_2$PhC$^+$, are formed.
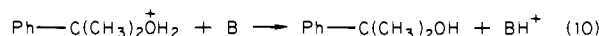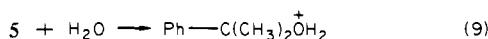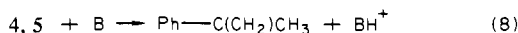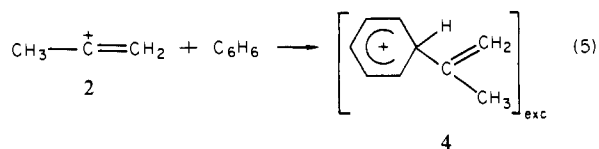
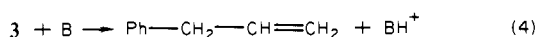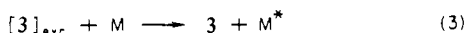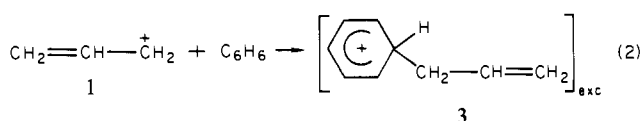2500 *J. Am. Chem. Soc., Vol. 106, No. 9, 1984*

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H_3^+ (D_3^+) and $C_nH_5^+$ (n = 1, 2) ions, according to well-established reaction sequences.[11] The ions formed are thermalyzed by many unreactive collisions with their neutral parent molecules before reacting with the C_3H_4 hydrocarbons according to the exothermic process

$$AH^+ + C_3H_4 \rightarrow A + C_3H_5^+ \qquad (1)$$
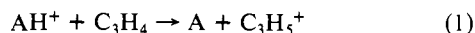
From the available thermochemical data, the $\Delta H°$ value of (1) can be calculated to be -81 kcal mol^{-1} (A = H_2),[12] -53 kcal mol^{-1} (A = CH_4),[13] and -21 kcal mol^{-1} (A = C_2H_4).[14]

Trapping $C_3H_5^+$ Ions with Benzene. Benzene has been the first nucleophile tried, since its reaction with allyl ions has been thoroughly investigated by tandem ICR spectrometry,[4e] and it has been used most recently for in situ derivatization of $C_3H_5^+$ ions before CID analysis.[6] Accordingly, the $C_3H_5^+$ ions from the protonation of propyne and allene, thermalyzed by a large number of unreactive collisions, were allowed to react with C_6H_6, introduced at low concentrations into the radiolytic system. Formation of the neutral end products is expected to occur according to the reaction scheme outlined in Chart I.

Chart I. Reactions Promoted by the Attack of $C_3H_5^+$ Ions on Benzene

$$[3]_{exc} + M \longrightarrow 3 + M^* \qquad (3)$$

$$3 + B \longrightarrow Ph-CH_2-CH=CH_2 + BH^+ \qquad (4)$$

$$[4]_{exc} \begin{cases} \xrightarrow[-M^*]{+M} 4 \qquad (6) \\ \xrightarrow{isomerization} e.g., 3. Ph-\overset{+}{C}(CH_3)_2, etc \qquad (7) \\ \qquad\qquad\qquad 5 \end{cases}$$

$$4, 5 + B \longrightarrow Ph-C(CH_2)CH_3 + BH^+ \qquad (8)$$

$$5 + H_2O \longrightarrow Ph-C(CH_3)_2\overset{+}{O}H_2 \qquad (9)$$

$$Ph-C(CH_3)_2\overset{+}{O}H_2 + B \longrightarrow Ph-C(CH_3)_2OH + BH^+ \qquad (10)$$
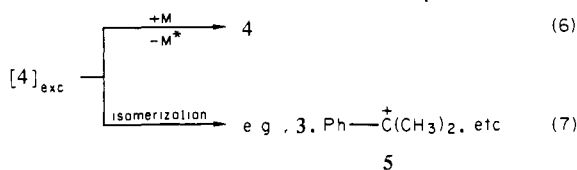
The results have been rather disappointing. In fact, inspection of Table I shows that the apparent ratio of allyl to 2-propenyl cations from the same C_3H_4 hydrocarbon undergoes significant variations, depending, in particular, on the presence of a gaseous base in the system.

This suggests that isomerization can occur within the charged adduct(s) formed by the 2-propenyl cation with benzene, either before or after formation of the arenium ion **4**.

Strong evidence for occurrence of isomerization is provided by the formation of 2-phenyl-2-propanol, that requires intramolecular conversion of the arenium ion **4** into the tertiary cation **5**. Occurrence of isomerization **4 → 5** is supported by the CID spectrum

of the ionic adduct(s) formed by $C_3H_5^+$ with C_6D_6, showing H/D exchange between the ring and the side-chain carbons.[6]

The tertiary cation **5** is presumably very stable toward deprotonation, unless strong bases are deliberately added to the gas, on account of the very high PA (210.4 kcal mol^{-1}) of its conjugate base, α-methylstyrene.[15] Consequently, **5** must be long lived in the radiolytic systems, and its fate, common to other unreactive tertiary cations such as Me_3C^+,[16] is to be trapped eventually by traces of water, unavoidably present in the system, yielding 2-phenyl-2-propanol via the sequence (9)–(10). This view is supported by the effects of Me_3N and pyridine, having respectively a PA of 228.6[17] and 224.6 kcal mol^{-1},[18] which completely inhibit formation of 2-phenyl-2-propanol. No 3-phenyl-1-propanol, 1-phenyl-2-propanol, or other oxygenated products from the hydration of **3** could be detected, presumably due to the lower PA of allylbenzene, which makes (4) a relatively fast process.

In conclusion, the complex nature of the reaction sequence leading to isolable products, and especially the likely isomerization of charged intermediates *even in systems at atmospheric pressure*, spell a word of caution on use of benzene as a nucleophile to sample the population of the $C_3H_5^+$ ions.

Trapping $C_3H_5^+$ Ions with 1,4-Dibromobutane. The results obtained with benzene prompted the search for more suitable nucleophiles. Ideally, the reagent should trap the $C_3H_5^+$ ions yielding *directly* stable and structurally diagnostic neutral products, according to an *exothermic* ion–molecule reaction, characterized however by a moderate enthalpy change to prevent isomerization of highly excited products.

Trapping $C_3H_5^+$ ions with water yields acetone, with negligible amounts of allyl alcohol. However, interpretation of the results is ambiguous since an alternative pathway, namely direct reaction of H_3O^+ ions with C_3H_4 hydrocarbons, can lead to the same products as hydration of $C_3H_5^+$ ions.

The best results were obtained by using 1,4-dibromobutane, which reacts as a Br$^-$ donor giving *directly* neutral and distinguishable bromides. The reactions are moderately exothermic,[19]
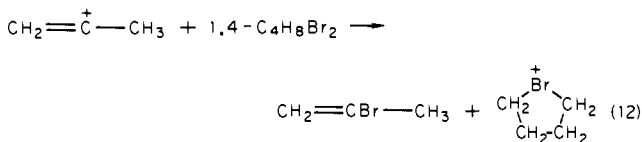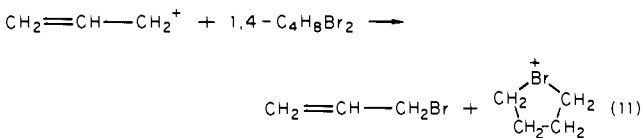
e.g., $\Delta H°_{11} = -7$ kcal mol^{-1}. The facile occurrence of bromide-transfer processes similar to (11) and (12) has been first demonstrated by ICR spectrometry,[19a] and 1,4-dibromobutane has been used already as a nucleophile to characterize gaseous halonium ions.[20]

The results summarized in Table II show that, irrespective of the Brønsted acid used, the $C_3H_5^+$ ions from protonation of *both* allene and propyne give almost exclusively 2-bromopropene when trapped with 1,4-dibromobutane in gaseous systems at atmospheric pressure.

(11) (a) Ausloos, P.; Lias, S. G. *J. Chem. Phys.* **1964**, *40*, 3599 and references therein. (b) Field, F. H.; Munson, M. S. B. *J. Am. Chem. Soc.* **1965**, *87*, 3289.

(12) Based on a value of 182 kcal mol^{-1} for the PA of allene and propyne, cf. ref 5d, and of 101 kcal mol^{-1} for the PA of H_2, cf.: Po, P. L.; Radus, T. P.; Porter, R. F. *J. Phys. Chem.* **1978**, *82*, 520.

(13) Based on a value of 129.4 kcal mol^{-1} for the PA of CH_4, cf.: Hemsworth, R. S.; Rundle, H. W.; Bohme, D. K.; Schiff, H. I.; Dunkin, D. B.; Fehsenfeld, F. C. *J. Chem. Phys.* **1973**, *59*, 61.

(14) Based on a value of 161 kcal mol^{-1} for the PA of C_2H_4, cf.: Sullivan, S. A.; Sandford, H.; Beauchamp, J. L.; Ashe, A. J.; III *J. Am. Chem. Soc.* **1978**, *100*, 3737.

(15) Taft, R. W. In "Proton Transfer Reactions"; Caldin, E., Gold, V. Eds.; Chapman and Hall: London, 1975.

(16) Attinà, M.; Cacace, F.; Giacomello, P.; Speranza, M. *J. Am. Chem. Soc.* **1980**, *102*, 6896.

(17) Aue, D. H.; Webb, H. M.; Bowers, M. J. *J. Am. Chem. Soc.* **1976**, *98*, 2081.

(18) Lav, Y. K.; Saluja, P. P. S.; Kebarle, P.; Alder, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 7328.

(19) Based on $\Delta H_f°$ = 182.5 kcal mol^{-1} for the tetramethylene bromonium ion a $\Delta H_f°$ value of -25 kcal mol^{-1} for 1,4-$C_4H_8Br_2$ (cf.: (a) Staley, R. H.; Wieting, R. D.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 5964), a $\Delta H_f°$ value of 226 kcal mol^{-1} for the allyl cation (cf. ref 4a,d), and a $\Delta H_f°$ value of 11.8 kcal mol^{-1} for allyl bromide, from Stull et al. ((b) Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. "The Chemical Thermodynamics of Organic Compounds"; Wiley: New York, 1969).

(20) Angelini, G.; Speranza, M. *J. Am. Chem. Soc.* **1981**, *103*, 3800.

Lowering the pressure to 150 torr causes an increase of the relative yields of allyl bromide, more pronounced when the protonation is carried out with the more energetic H_3^+ acid. Under comparable conditions, the proportions of allyl bromide are appreciably higher from allene than from propyne.

The results are consistent with a simple reactivity pattern, where isomerization of the excited $C_3H_5^+$ ions from (1) competes with collisional stabilization, before trapping by dibromobutane can occur ($\approx 10^{-6}$ s). Lowering the pressure, and consequently the efficiency of collisional stabilization, increases the fraction of $C_3H_5^+$ ions which undergoes **1** → **2** isomerization, which of course is more pronounced for the ions formed via the more exothermic proton transfer from H_3^+.

No isomeric bromides were detected, in particular 1-bromopropene and cyclopropyl bromide, whose isolation would suggest formation of 1-propenyl and cyclopropyl cations from the protonation of the C_3H_4 hydrocarbons.

Conclusions

The results of the present study, in particular those obtained by using 1,4-dibromobutane as a trapping reagent, show with the degree of confidence allowed by the actual isolation of the reaction products that *2-propenyl ions are formed almost exclusively in the kinetically significant step of the gas-phase protonation of allene and propyne.*

The observed selectivity must be traced to purely *kinetic* factors, since allyl ion **1** is known to be appreciably more stable than the isomeric 2-propenyl ion **2**, as confirmed by the trend of our low-pressure experiments.

A reasonable explanation has been offered,[5e] on the basis of the view that protonation at the central carbon is quite unfavorable, yielding a "twisted" allyl ion, while concerted protonation and CH_2 rotation to give **1** are characterized by a high barrier.

The existence of a significant activation energy in the isomerization **1** → **2** is confirmed, in agreement with previous mass spectrometric and theoretical conclusions,[5,6] as well as the lack of stability of 1-propenyl and cyclopropyl ions, whose derivatives never have been detected, even under conditions ensuring a very effective collisional stabilization.

The results obtained in gaseous systems at atmospheric pressure are fully consistent with those reported for the protonation of allene and propyne by mineral acids in aqueous solution.[3]

Finally, the discrepancy between the results obtained by using respectively benzene and 1,4-dibromobutane as the nucleophilic reagent deserves a brief comment. The higher proportions of the allyl derivative from C_6H_6 can be traced to higher probability of isomerization of the 2-propenyl moiety in the longer reaction sequence leading to α-methylstyrene.

In particular, the PA of propyne and allene appears to be nearly the same as that of benzene, within the scatter[21] of the available thermochemical data.

Proton transfer from allyl ions to benzene does occur,[4a] but it is relatively insignificant in comparison to alkylation, even under typical mass spectrometric conditions. It is quite conceivable that proton transfer to benzene is more efficient from the less stable 2-propenyl ion, and the competition of the protonation channel with process 5 would impair the accuracy of isomeric sampling by benzene.

Benzene may even *catalyze* isomerization of 2-propenyl into allyl ions, according to the sequence occurring in an early ionic adduct
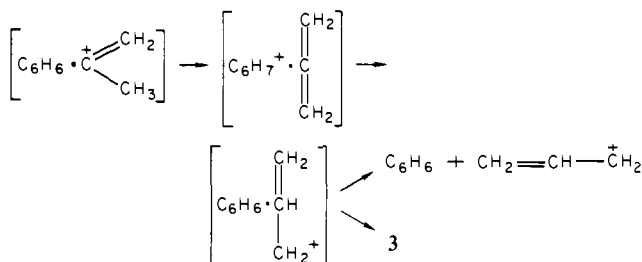
Significantly, the isotopic exchange with C_6D_6 is much larger for 2-propenyl than for the allyl cation under mass spectrometric conditions.[6] The results of the present work underline the importance of examining gas-phase ionic reactions by independent methods, such as radiolysis at nearly atmospheric pressure and CID spectrometry. In both approaches, there is a need for a careful choice of the nucleophile used to sample the population of isomeric ions.

(21) Walder, R.; Franklin, J. L. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *36*, 85.