electron density at the benzyl position of $2B_2$ is considerably higher than that of $1A_2$ state. Significant mixing of the close-lying $2B_2$ (D_2) and $1A_2$ (D_1) might be responsible for a relatively high rate in the quenching of the *p*-chlorobenzyl fluorescence by CHD. From the analysis of the vibrational structure in the fluorescence excitation spectrum of *p*-fluorobenzyl in a supersonic jet, Fukushima and Obi[30] have demonstrated that the energy gap between $1A_2$ and $2B_2$ states is spread out by the introduction of fluorine atom at the para position of benzyl. Poor mixing of the two states might be therefore responsible for a low rate in the quenching of *p*-fluorobenzyl fluorescence by CHD. The predominant character of $1A_2$ is implied for the D_1 state of *p*-methoxybenzyl by a very low rate of 9.4×10^5 M^{-1} s^{-1} in the fluorescence quenching.

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Registry No. CHD, 628-41-1; *p*-cyanobenzyl radical, 4939-73-5; *p*-chlorobenzyl radical, 3327-51-3; *p*-fluorobenzyl radical, 2194-09-4; *p*-methoxybenzyl radical, 3494-45-9.

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Evaluation of the Arrhenius Parameters for the Thermal Isomerization of a Gaseous Ion. The Temperature Dependence of the Cyclohexylium Ion Unimolecular Rearrangement

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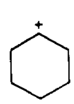
Abstract: Gas-phase isomerization of cyclohexylium ion (**1**), obtained via protonation of cyclohexene and of bicyclo[3.1.0]hexane and via hydride-ion abstraction from cyclohexane by $C_nH_5^+$ ($n = 1, 2$) and by s-$C_3H_7^+$ ions, has been investigated by a radiolytic technique in CH_4 and C_3H_8 in the pressure range from 106 to 1480 Torr. Temperature-dependence studies in the temperature interval from 310 to 353 K have provided the activation parameters of the *thermal* rearrangement of **1** into 1-methylcyclopentylium ion (**2**) in CH_4 at 750 Torr and in C_3H_8 at 1480 Torr. Least-squares analysis of the two mutually consistent sets of data leads to an activation energy of 7.4 ± 1 kcal mol^{-1} and to a preexponential factor of $10^{12\pm1.3}$ s^{-1}. These values represent the first estimates of the activation parameters of a unimolecular isomerization of a gaseous ion thermally equilibrated with the bath gas, i.e., under conditions which allow meaningful comparison with solution kinetics. The results support previous evidence for the existence of gaseous **1**, providing a quantitative evaluation of the energy barrier for its rearrangement into **2**. The more extensive formation of **2** from the protonation of bicyclo[3.1.0]hexane than that of cyclohexene is consistent with the long-postulated protonated-cyclopropane route in the branching rearrangement of cycloalkylium ions.

Cyclohexylium cation (**1**), well-characterized as an ionic intermediate in solution,[1] has long escaped detection in the gas phase, owing to its fast rearrangement into the 1-methylcyclopentyl isomer (**2**), occurring in a shorter time than required for analysis by structurally diagnostic mass spectrometric techniques, e.g., collisional activation (CA) spectrometry.[2] In previous papers[3,4] we have presented evidence for the existence of **1** in the gas phase, with a lifetime exceeding 10^{-8}–10^{-7} s, based on the results obtained with a radiolytic[5] and a nuclear-decay technique,[6] which allow structural and kinetic studies of gaseous ions in a wide pressure range. While demonstrating that **1** is indeed a legitimate ionic intermediate in the gas phase, characterized by a local minimum on the $C_6H_{11}^+$ energy surface,[7] our results confirmed its facile rearrangement into structure **2**, more stable by 11 kcal mol^{-1},[8] the activation energy of the process being roughly estimated as ≤10 kcal mol^{-1}.[4]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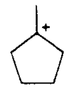
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We report now a more detailed investigation of the gas-phase isomerization of **1**, including an attempt at estimating its empirical activation parameters by temperature-dependence experiments in the pressure range from 106 to 1480 Torr.

It should be emphasized that meaningful evaluation of activation parameters comparable to those ordinarily measured in solution requires that the ions undergoing isomerization be thermally equilibrated with a bath gas of defined temperature, and that their rearrangement can be monitored by sufficiently fast techniques. These conditions can hardly be achieved by current mass spectrometric approaches, where the ionization process imparts excess internal energy to the charged species, whose collisional thermalization is generally inefficient at the low pressures attainable

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[6] Cacace, F.; Speranza, M. *Techniques for the Study of Ion Molecule Reactions*; Farrar, J. M., Saunders, W., Jr., Eds.; Wiley-Interscience: New York, 1988; Chapter VI.

[7] Our experimental findings are supported by later theoretical calculations. Cf.: Viruela-Martin, P. M.; Nebot, I.; Viruela-Martin, R.; Planelles, J. *J. Chem. Soc., Perkin Trans. 2* **1986**, 49.

[8] All thermochemical data are based (a) on the compilation of: Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695, except for the heat of formation of c-$C_6H_{11}^+$, 179 kcal mol^{-1}, taken from: (b) Lossing, F. P.; Holmes, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 6917.

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in the ion source. Furthermore, the structurally diagnostic mass spectrometric techniques required to monitor the rate of the isomerization process have typical sampling times of the order of 10^{-5} s, far too long in the case of fast rearrangements. A pertinent example is provided by the very cation of interest, gaseous c-$C_6H_{11}^+$, which could not be detected at all by CA mass spectrometry, undergoing complete rearrangement into **2** well before structural assay could take place.[2]

The β-decay technique is also hardly suitable to the specific application, since the daughter ions are formed from the decay with excess internal energy up to 30 kcal mol^{-1}, which is likely to promote their fast, nonthermal isomerization.[4]

A viable approach is provided by the radiolytic technique, whose principles, methods, and applications have amply been reviewed.[5] The design of a radiolytic study of the thermal kinetics of **1** → **2** isomerization can be outlined as follows. A bulk gas, M, containing traces of a suitable substrate, S, of a radical scavenger and of a gaseous nucleophile is subjected to γ irradiation. Ionization of M produces well-defined cations that react with S, yielding **1** according to ionic processes previously established by chemical ionization mass spectrometry. At sufficiently high pressures, e.g., up to several atmospheres, any excess internal energy imparted to **1** by its formation process is rapidly removed by collisional deactivation, very effective in the dense gas. Under such conditions, the thermalized ions **1** isomerize to **2** at a rate depending on the temperature of the gas. Both **1** and **2** are trapped by the nucleophile with unit collision efficiency and converted into distinguishable neutral products, whose determination, e.g., by GC or GC/MS, allows one to evaluate the extent of conversion of **1** into **2** occurring in the reaction time. The latter corresponds to the collision interval of **1** with the nucleophile, which depends on the concentration of the latter and can be estimated with sufficient accuracy from the current models of ion-neutral collisions. Introducing the measured extent of reaction and the estimated reaction time into a standard kinetic equation, one can evaluate the first-order rate constant of the thermal, unimolecular **1** → **2** isomerization at the temperature of the irradiation. Finally, a set of rate constants from irradiations carried out at different temperatures can be used to construct an Arrhenius plot and to deduce the activation parameters of the isomerization reaction.

Implementation of the above scheme requires a careful choice of the experimental variables, in particular of the nature and the pressure of the bulk gas, of the substrate, and of the nucleophile. Control experiments are required to ascertain whether essential requirements, e.g., efficient thermalization of ions **1** and rapid, unbiased trapping of **1** and **2** by the nucleophile, are met in the radiolytic systems. Furthermore, significant contributions of radical reactions to the formation of the neutral products of interest must be excluded by specific control experiments. A detailed discussion of these points will be taken up in the section after next.

Experimental Section

Materials. Methane and propane were research-grade samples from Matheson Gas Products Inc., having a stated purity in excess of 99.99 mol %. The other gases, as well as the chemicals used as reactants or analytical standards, were obtained from commercial sources or prepared according to unexceptional procedures, their purity being checked with the same techniques used in the analysis of the radiolytic products.

Irradiations and Analysis. The experimental procedures for the preparation of the gaseous samples and their γ irradiation in a variable-temperature 220 Gammacell (Nuclear Canada Ltd.) have repeatedly been described.[5] The products were analyzed by GC, using Perkin-Elmer Sigma 1 and Sigma 3, and Hewlett-Packard 5700A chromatographs, equipped with FID and PID detectors, on the following columns: (i) a 2-m long, 2-mm i.d. glass column, packed with Carbopack C, deactivated with 0.1% w/w SP 1000 silicone fluid, operated at 90 and 120 °C; (ii) a 2-m long, 2-mm i.d. glass column, packed with SP 1200 silicone fluid and Bentone 34, respectively 5% and 1.75% w/w, on 100–120 mesh Supelcoport, operated at 90–120 °C; and (iii) a 50-m long, 0.2-mm i.d. fused silica column, coated with a 0.5-μm layer of PONA stationary phase from Hewlett-Packard.

Bicyclo[3.1.0]hexane, prepared from the reaction of cyclopentene with CH_2I_2 in the presence of a Zn/Cu alloy, was purified by preparative GC, using a 2-m long, 6-mm i.d. Apiezon L column, and subsequently analyzed on columns i and iii.

Mass Spectrometric Measurements. CI spectra were recorded with a Hewlett-Packard 5985A quadrupole mass spectrometer and a ZAB-2F magnetic instrument from VG Micromass Ltd.

Methods

Several radiolytic routes to **1** were investigated, based on the reactions of the stable ions from the γ irradiation of a suitable bulk gas, CH_4 or C_3H_8, with trace amounts of appropriate substrates. The $C_nH_5^+$ (n = 1, 2) and the s-$C_3H_7^+$ ions, obtained in high yields from the ionization of methane and propane, react efficiently with cyclohexane according to the following exothermic[8] processes, well-established by radiolytical and mass spectrometric studies.[9]

$$CH_5^+ + c\text{-}C_6H_{12} \rightarrow CH_4 + H_2 + \mathbf{1} \qquad \Delta H^\circ = -26 \text{ kcal mol}^{-1} \quad (1)$$

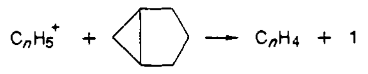
$$C_2H_5^+ + c\text{-}C_6H_{12} \rightarrow C_2H_6 + \mathbf{1} \qquad \Delta H^\circ = -28 \text{ kcal mol}^{-1} \quad (2)$$

$$s\text{-}C_3H_7^+ + c\text{-}C_6H_{12} \rightarrow C_3H_8 + \mathbf{1} \qquad \Delta H^\circ = -7.6 \text{ kcal mol}^{-1} \quad (3)$$

The following alternative routes, based on proton-transfer reactions, were also considered.

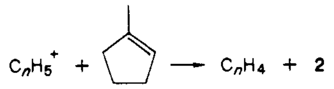
$$C_nH_5^+ + c\text{-}C_6H_{10} \rightarrow C_nH_4 + 1$$

$$\Delta H^\circ = -54\ (n=1) \text{ and } -24\ (n=2) \text{ kcal mol}^{-1} \quad (4)$$

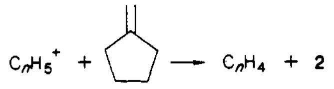


$$\Delta H^\circ = -64\ (n=1) \text{ and } -34\ (n=2) \text{ kcal mol}^{-1} \quad (5)$$

The following reactions have been exploited for the preparation of pure ions **2**, required to test the efficiency of the trapping reactions



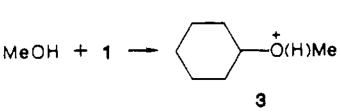
$$\Delta H^\circ = -65\ (n=1) \text{ and } -35\ (n=2) \text{ kcal mol}^{-1} \quad (6)$$



$$\Delta H^\circ = -69\ (n=1) \text{ and } -39\ (n=2) \text{ kcal mol}^{-1} \quad (7)$$

The choice of the trapping nucleophile is crucial in order to achieve an efficient and unbiased sampling of the population of gaseous $C_6H_{11}^+$ isomers. Water, 1,4-dibromobutane, *tert*-butyl fluoride, and methyl trimethylsilyl ether were found unsatisfactory for various reasons, including an inadequate trapping efficiency, a bias in favor of ions **1**, or the formation of neutral end products, undistinguishable from those of radical processes.

Methanol, successfully used in an earlier study,[4] was found to be the most convenient trapping agent, reacting with the ions of interest according to the processes



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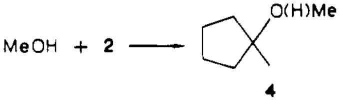
(8)



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(9)

yielding oxonium ions **3** and **4**, whose deprotonation eventually gives the corresponding ethers. The unwanted **3** → **4** isomerization

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(9) Occurrence of reactions 1 to 7 is confirmed by the CH_4 and C_3H_8/CI mass spectra of cyclohexane, cyclohexene, 1-methylcyclopentene, bicyclo[3.1.0]hexane, and methylenecyclopentane, as well as by published data; e.g., c-$C_6H_{11}^+$ accounts for ca. 80% of the total ionization in the CH_4/CI mass spectrum of cyclohexane. Cf.: Field, F. H.; Munson, M. S. B. *J. Am. Chem. Soc.* **1967**, *89*, 4272.

has been ruled out by specific experiments, involving methylation of cyclohexanol by radiolytically formed dimethylchloronium ions in MeCl at 750 Torr, according to the process

$$Me_2Cl^+ + c\text{-}C_6H_{11}OH \rightarrow MeCl + \mathbf{3} \qquad (10)$$

which was found to yield exclusively cyclohexyl methyl ether, although its exothermicity is comparable to that of process 8.[10]

Preliminary experiments demonstrated the feasibility of a radiolytic study based on the above outlined reactions. As an example, γ irradiation (310 K, 3×10^4 Gy) of CH_4 (750 Torr) containing O_2 (10 Torr) as a radical scavenger, c-C_6H_{12} (ca. 0.5 Torr), and MeOH (ca. 2 Torr) gives cyclohexyl methyl ether (**5**) and 1-methylcyclopentyl methyl ether (**6**) as the major products, with G_{+M} values of the order of 0.30 and 0.15, respectively, which correspond to a combined absolute yield of over 70%, if one takes into account the competition between MeOH and c-C_6H_{12} for the primary $C_nH_5^+$ ions.[11] Other radiolytic products are formed, albeit in lower yields, including cyclohexanol, cyclohexanone, and cyclohexene; however, **5** and **6** are the only ones which simultaneously satisfy the following criteria, regarded as necessary evidence of their ionic origin.

(i) The charged precursors of the product are directly detectable by CI mass spectrometry; e.g., ions whose *m/e* ratio corresponds to that of **1** and **2** are abundant in the CH_4/CI spectra of c-C_6H_{12}, and formation of adducts having the *m/e* ratio typical of **3** and **4** can be detected in the CI spectra of CH_4/c-C_6H_{12}/MeOH mixtures.

(ii) The yield of the product is unaffected by the presence of an efficient radical scavenger, e.g., O_2.

(iii) The yield of the product is depressed by addition of gaseous bases, B, e.g., NH_3 or NMe_3, capable of intercepting the $C_nH_5^+$ and the $C_6H_{11}^+$ ions. Moreover, the dependence of the yield on [B] quantitatively fits the trend predicted by the appropriate competition model. Finally, sufficiently high concentrations of B suppress the formation of the ionic products.

Extension of the study to higher temperatures has shown that an additional ionic product, 1-methylcyclopentene (**7**), becomes significant at 353 K in methane systems, its yields amounting to ca. 25% of that of **6**. Formation of **7** has also been detected at the highest temperature investigated (353 K) in C_3H_8 systems, albeit in lower yields than in CH_4.

On the grounds of the preceding considerations, the temperature and pressure dependence of the relative yields of **5**, **6**, and **7** in CH_4 and C_3H_8 have been the subject of a systematic investigation, whose results are illustrated in the next section.

Results

In order to identify the radiolytic systems most suitable for the planned temperature-dependence study, and the most appropriate experimental conditions of the latter, a large number of irradiations have been carried out at 310 K. Table I provides a partial illustration of such fixed-temperature experiments, giving the relative yields of **5** and **6**, representative of the extent of the **1** → **2** isomerization. The most salient features can be itemized as follows.

(i) Proton transfer to 1-methylcyclopentene and to methylenecyclopentane yields exclusively ions **2**, as shown by the failure to detect formation of **5**. This rules out the inverse **2** → **1** isomerization, despite the large exothermicity of the protonation step, and represents a necessary blank test.

(ii) Protonation of cyclohexene and of bicyclo[3.1.0]hexane by $C_nH_5^+$ in CH_4 causes extensive formation of **2**, much more pronounced from the latter substrate. This is mechanistically interesting, since the difference can hardly be traced to the slightly higher exothermicity of (6) than of (5). The faster isomerization to **2** of the ion from the protonation of the substrate which contains a preexistent cyclopropane moiety may reflect the long-postulated role of protonated-cyclopropane intermediates in the branching rearrangement of carbocations.[1]

Table I. Relative Yields of Cyclohexyl and 1-Methylcyclopentyl Methyl Ether from Various Radiolytic Systems at 310 K

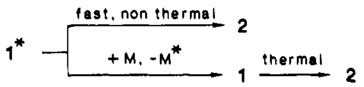
bulk	system composition (Torr)[a]				rel yields (%)[b]	
gas	substrate		MeOH	NMe_3	**5**	**6**
CH_4						
106	cyclohexane	0.59	1.91		41	59
750		0.55	1.86		68	32
750		0.63	2.13	3.0	75	25
750		0.48	6.02		76	24
750		7.00	2.23		65	35
750		8.30	21.00		76	24
1370		0.50	2.00		77	23
1425		0.50	2.00		77	23
1470		8.31	21.10		76	24
750	cyclohexene	0.53	2.40		58	42
750		0.69	2.55	3.0	60	40
750		7.00	2.00	3.0	52	48
106		0.38	1.80		45	55
750	bicyclo[3.1.0]hexane	0.52	1.87		16	84
750		7.00	2.00		10	90
750		0.54	1.91	3.0	22	78
106		0.59	1.38		9	91
750	1-methyl-1-cyclopentene	0.54	1.51			100
106	methylenecyclopentane	0.52	1.80			100
C_3H_8						
750	cyclohexane	7.74	2.14		80	20
1480		7.27	2.23		96	4

[a] Radiation dose $1-3 \times 10^4$ Gy. All systems contained O_2 (10 Torr) as a radical scavenger. [b] Standard deviation of the relative yields 5%.

(iii) The ions obtained by hydride-ion abstraction from c-C_6H_{12} (eq 1 and 2) in CH_4 at 106 Torr undergo extensive isomerization (ca. 40%), which can be reduced, as expected, by raising the CH_4 pressure to 750 Torr and by introducing into the gas increasing concentrations of MeOH, which causes a corresponding decrease of the trapping time. Remarkably, however, the isomerization rate is unaffected by further increasing $p(CH_4)$ up to 1470 Torr and p(MeOH) up to 21 Torr, attaining a constant value, ca. 25%, that cannot be further reduced.

(iv) Isomerization of the ions obtained via hydride-ion abstraction from c-C_6H_{12} by s-$C_3H_7^+$, much less extensive than in the CH_4 systems, displays nevertheless the same qualitative trend, dropping from 20% in C_3H_8 at 750 Torr to only 4% in C_3H_8 at 1480 Torr. The small residual isomerization cannot be further reduced by increasing p(MeOH) up to 23 Torr and is independent of temperature up to 353 K.

The above experimental features are accomodated by a model envisaging two different isomerization processes



(11a)

(11b)

The first one is a fast, nonthermal rearrangement occurring before collisional deactivation of **1***, formed in an excited state from reactions 1 to 5. The rate of (11a) depends on the exothermicity of the formation process and on the pressure of the bath gas, being largely independent of the temperature, at least in the limited range of interest. The collisionally deactivated ions undergo a slower, thermal isomerization process 11b, whose rate depends on the temperature and whose extent, at a given temperature, depends on the lifetime of free **1** before its trapping by MeOH.

The above scheme accounts satisfactorily for the features of the fixed-temperature experiments and has provided the criteria for the design of the temperature-dependence study. The latter should obviously exploit the least exothermic process for the formation of **1**, in a bath gas at the highest attainable pressure, containing a constant concentration of MeOH, in order to ensure the same reaction time for the isomerization process at the different

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(10) Based on $H_f°$ ($MeCl_2^+$) = 172 kcal mol^{-1}. Cf.: Mathews, P. J.; Stone, J. A. *Can. J. Chem.* **1988**, *66*, 1239. The exothermicity of process 10 should differ from that of process 8 by ca. 8 kcal mol^{-1}.

(11) G_{+M} values express the number of molecules M formed per 100 eV absorbed by the gas. The G_{+M} value of $C_nH_5^+$ ions from methane in ca. 2.8. Cf.: Ausloos, P.; Lias, S. G.; Gorden, R., Jr. *J. Chem. Phys.* **1963**, *39*, 3341.

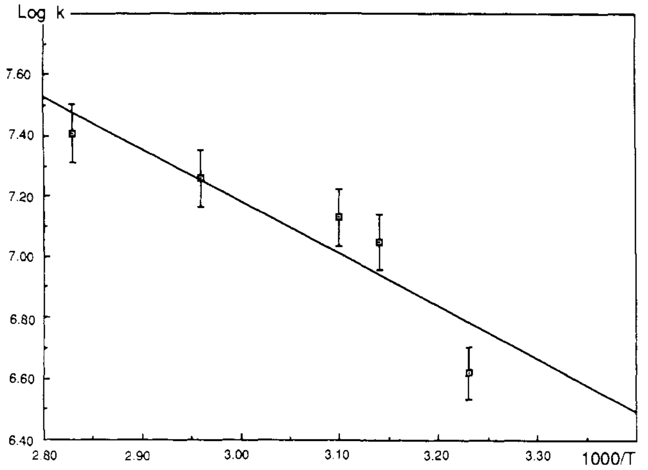

Figure 1. Arrhenius plot for the **1** → **2** isomerization in propane at 1480 Torr. In this one, and in the following figure, the vertical bars refer to the reproducibility of data from different irradiations carried out under identical conditions.

temperatures. Consequently, the pressure-dependence study, covering the range from 310 to 353 K, has been based on reaction 3, carried out in C_3H_8 at 1480 Torr, at a fixed MeOH concentration (2.00 Torr) corresponding to a collisional interval of ca. 1.1×10^{-8} s, calculated according to the ADO model, or the Su/Chesnavich theory.[12]

The first-order rate constant of the **1** → **2** unimolecular rearrangement has been calculated at each temperature via the ordinary first-order rate equation, deducing the extent of isomerization at time *t* directly from the experimentally measured ratio of the combined yields of **6** and **7** to that of **5**. It should be noted that formation of **7** is appreciable only at 353 K, and that the minor contribution from the nonthermal process 11a, which according to control experiments amounts to ca. 4% in C_3H_8 at 1480 Torr, must be subtracted from the yield of **6**. The reaction time, i.e., the time allowed to thermal isomerization of ions **1**, knowledge of which is necessary for the calculation of the rate constants, has been taken equal to the collision interval of **1** with MeOH, under the assumption that the trapping reaction occurs with unit collision efficiency.

The Arrhenius plot for the **1** → **2** isomerization in C_3H_8 at 1480 Torr, illustrated in Figure 1, is characterized by a relatively poor linearity, deriving, at least in part, from the large experimental errors in the measurement of low yields of **6**. Regression analysis of the data leads to the equation

$$\log k = 12.4 \pm 1.3 - \frac{(7.9 \pm 1) \times 10^3}{2.30RT}$$

with a correlation coefficient of 0.91. In order to test the validity of the assumptions made, the study has been extended to CH_4 systems at 750 Torr, where ions **1** were obtained from reactions 1 and 2, all other conditions being the same as in C_3H_8. The rate constants at the different temperatures have been estimated as in the case of C_3H_8 and corrected in the same way for the contribution of the fast, nonthermal isomerization 11a, which is much higher than in C_3H_8, amounting to ca. 21%, owing to the lower pressure of CH_4 and the higher exothermicity of reactions 1 and 2. The linearity of the Arrhenius plot from the experiments in CH_4 at 750 Torr (Figure 2) is satisfactory and its regression analysis leads to the following equation:

$$\log k = 12.2 \pm 0.4 - \frac{(7.2 \pm 0.6) \times 10^3}{2.30RT}$$

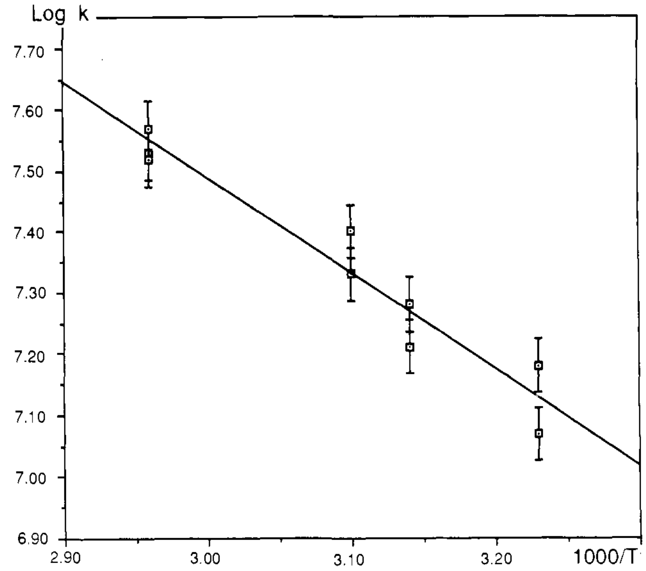

Figure 2. Arrhenius plot for the **1** → **2** isomerization in methane at 750 Torr.

with a correlation coefficient of 0.97.

The satisfactory agreement between the two sets of data is somewhat reassuring, if not on the correctness, at least on the internal consistency of the model adopted. Combining the above equations, one obtains an empirical activation energy $E^{\ddagger} = 7.4 \pm 1.0$ kcal mol^{-1} and a preexponential factor $A = 10^{12.3\pm1.3}$ s^{-1}.

Discussion

Previous evidence for the existence of **1** as a gaseous intermediate characterized by a local minimum on the $C_6H_{11}^+$ energy surface[3,4] is confirmed by the present results, which provide a quantitative, albeit approximate estimate of its lifetime and of the depth of the corresponding energy well. In addition, the relatively high value of the rate constant for the thermal rearrangement, exceeding 10^7 s^{-1} at 310 K, explains why detection of gaseous **1** could only be achieved by radiolytic and decay techniques, while defying CA spectrometry[2] and EBFlow-reactor technique.[13] In fact, the two latter approaches allow structural characterization or trapping of the ions only after a delay of at least 10^{-5} s, far too long, in the light of the present results, to prevent **1** → **2** isomerization from reaching completion, even neglecting the difficulty of obtaining a thermally equilibrated population of c-$C_6H_{11}^+$ ions by electron-impact ionization in low-pressure sources.

It is of interest to compare the results from this work with those of earlier experimental and theoretical studies of the cyclohexylium ions.

The only available experimental estimate of the barrier to gas-phase **1** → **2** isomerization ($\leq$10 kcal mol^{-1} according to our RRKM elaboration of the data from the β-decay work[4]) is consistent with the present results. Passing to condensed-phase studies, it has been shown that the activation energy for the inverse **2** → **1** rearrangement is ca. 17 kcal mol^{-1}.[1b,14] Taking into account the stability difference between **1** and **2**,[15] an activation energy ranging from 7 to 10 kcal mol^{-1} can be derived, remarkably close to the present gas-phase results.

As to computational approaches, recent MINDO/3 calculations indicate that **1** corresponds to a local minimum on the $C_6H_{11}^+$ energy surface, and that alternative pathways exist for the rearrangement, the activation energy of which (estimated around 10–15 kcal mol^{-1}) is somewhat higher than the gas-phase and condensed-phase experimental values.[7] According to the MIN-

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[12] The values have been calculated according to the ADO model. See: Su, T.; Bowers, M. T. *J. Chem. Phys.* **1973**, *58*, 3027. Application of the theory of Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, *76*, 5182, leads to slightly smaller collision intervals. The difference (<10%) is trivial in comparison with the much larger uncertainties affecting the estimated preexponential factor.

[13] Marinelli, W. J.; Morton, T. H. *J. Am. Chem. Soc.* **1978**, *100*, 3536.

[14] Brouwer, D. M. In *Chemistry and Chemical Engineering of Catalytic Processes*; Prins, R., Schuit, G. C. A., Eds.; Sitthoff, Noordhoff, Alphen and der Rijn: The Netherlands, 1980; p 137.

[15] The stability difference in the gas phase amounts to 7 kcal mol^{-1} (ref 8a), a value of 6–10 kcal mol^{-1} being estimated in solution: see ref 7.

DO/3 study, later extended to methylcyclohexylium ion,[16] the energetically favored isomerization pathway corresponds to the protonated cyclopropane route, long suggested by Brouwer[17] and Saunders.[18] In this connection, our finding that rearrangement of gaseous $C_6H_{11}^+$ ions from the protonation of bicyclo[3.1.0]hexane is much faster than that from the protonation of cyclohexene, despite the equal exothermicity of the two processes, provides fresh evidence for the mechanistic role of protonated cyclopropane in the **1** → **2** isomerization.

Conclusion

The present work points to the possibility of deriving the activation parameters for the *thermal*, unimolecular isomerization of a gaseous cation from a systematic temperature-dependence study, carried out with the now well-established radiolytic technique in different gases in a wide pressure range, and utilizing different reactions for the preparation of the ion of interest.

The usefulness of such an approach can be desumed from the contrast between the plethora of data on the kinetics of *bimolecular* ionic reactions from low-pressure mass spectrometric studies[19] and high-pressure β-decay[6] and radiolytic[5] investigations, and the preciously little which is known on the kinetics of *unimolecular* rearrangements of *thermal* gaseous ions. In this connection, it should be noted that only under conditions ensuring a thermal energy distribution do gas-phase processes lend themselves to standard kinetic treatments and to meaningful kinetic comparison with ionic reactions in solution.

Although the absolute accuracy of the results, in particular of the preexponential factor, depends to some extent on the accuracy of the current theories of ion-neutral collisions used to calculate the trapping time, to our knowledge this study provides the first estimate of the activation parameters for the unimolecular, thermal rearrangement of a gaseous ion, which, incidentally, marks a significant advance over previous radiolytic studies, where only activation-energy *differences* and *ratios* of preexponential factors of *bimolecular* reactions could be evaluated.[20,21]

As to the specific problem addressed, which represents a long-standing question of gas-phase ion chemistry, this work corroborates previous evidence for the existence of free cyclohexylium ion, providing a quantitative estimate of the barrier to its rearrangement and fresh mechanistic support to the protonated-cyclopropane route.

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Registry No. 1, 22499-63-4; **2**, 17106-22-8; C_1H_5, 15135-49-6; C_2H_5, 14936-94-8; *s*-C_3H_7, 19252-53-0; cyclohexene, 110-83-8; bicyclo[3.1.0]hexane, 285-58-5; 1-methylcyclopentene, 693-89-0; methylenecyclopentane, 1528-30-9.

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(18) Saunders, M.; Hagen, E. L. *J. Am. Chem. Soc.* **1968**, *90*, 2436. See also *Acc. Chem. Res.* **1973**, *6*, 53.

(19) See, for instance, *Ionic Process in the Gas Phase*; Almoster-Ferreira, M. A., Ed.; D. Reidel: Dordrecht, The Netherlands, 1982, and references therein.

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Gas-Phase Reactions of Charged Electrophiles with Styrene and Phenylacetylene

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Abstract: The reactions of styrene and phenylacetylene toward charged electrophiles have been studied in the gas phase by a radiolytic technique, supported by chemical ionization mass spectrometry. The two substrates undergo a methylation reaction by Me_2F^+ both at the ring and at the side chain, at variance with the side-chain electrophilic attack prevailing in condensed phase. The nitrating $(MeONO_2)H^+$ ion selectively nitrates the ortho position of styrene, an unprecedented ring nitration on this substrate. The formation of neutral isomeric products is determined by the efficiency of deprotonation of their ionic precursors and is sensitive inter alia to the presence of oxygen nucleophiles. The overall reactivity pattern is rationalized in terms of preferential electrostatic interactions between the reactants in a preliminary collision complex, whereby an incoming ROH molecule can simulate a "solvating" environment, shifting the reactivity in the direction observed in solution.

The reaction of styrenes with electrophilic reagents in solution occurs primarily at the double bond.[1] The phenyl ring thus behaves as "spectator" and, when systematically substituted, is exploited as a means to probe the development of charge on the α-carbon in the transition state.[2]

Acid catalysts promote well-known dimerization reactions and polymerization sequences involving the double bond.[1] Direct electrophilic attack on the aromatic nucleus occurs successfully only when the double bond is deactivated by the presence of electron-withdrawing groups.[3] In such way, it was found that the aromatic ring of styrene is actually *activated* toward electrophilic nitration by the vinyl substituent, although in general its reactivity is obscured by the overwhelming competition of side-chain attack.

The gas-phase protonation of styrene appears to display a close similarity to the behavior of this substrate in solution, in that the

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(1) (a) *Friedel–Crafts and Related Reactions*; Olah, G. A., Ed. Interscience: New York, 1963–1965; Vol. I–IV. (b) Roberts, R. M.; Khalaf, A. A. *Friedel–Crafts Alkylation Chemistry*; M. Dekker: New York, 1984.

(2) For a recent example, see: Ruasse, M. R.; Argile, A.; Dubois, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 4846.

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