

Agreement for the 6-methylene resonances of the galactose-glucose linkage is less good, although still useful, since these shifts show a strong conformational dependence which leads to cooperative shift changes when two rings are added to  $\alpha$ -glucose.

The improved resolving power and "fingerprint" character of experimental shift correlation maps can also be of use in the analysis of mixtures. Figure 8 shows the results of a chemical shift correlation experiment on a solution of approximately 20% by volume alfalfa clover honey (Kidd Bros. Produce Ltd., Burnaby, British Columbia) in  $D_2O$ . These shift correlations are summarized in Figure 9, together with the assignments made by using the data of Table I. As expected the major constituents of the mixture are identified as  $\alpha$ -glucose,  $\beta$ -glucose,  $\beta$ -fructopyranose,  $\alpha$ -fructofuranose, and  $\beta$ -fructofuranose.

### Discussion

The results described here represent the first tentative attempts at the chemical application of heteronuclear chemical shift correlation by two-dimensional NMR. The accuracy of the proton chemical shifts obtained by this technique is partly determined by the length of time available for data acquisition. In the experiments described the compromise chosen between sensitivity and accuracy was to aim for an estimated standard deviation on proton shifts of  $\pm 0.01$  ppm, which entails an experiment lasting approximately ten times as long as the acquisition of a normal proton-decoupled carbon-13 spectrum. In a few cases (noted in Table I) the accuracy obtainable was degraded by strong coupling effects or poorly resolved signals. Both accuracy and sensitivity of the 2D experiment compare very favorably with off-resonance decoupling<sup>12-18</sup> and heteronuclear INDOR<sup>33</sup> techniques for measuring correlated proton and carbon-13 shifts.<sup>34</sup>

Heteronuclear chemical shift correlation offers a number of

advantages over conventional NMR methods. The extra resolving power made available by detecting proton resonances indirectly via the carbon-13 signals allows the measurement of well-resolved proton signals in systems very much more complex than those amenable to study by conventional NMR. The improved resolving power should also aid the analysis of complex mixtures, since the number of signals resolvable in a 2D correlation experiment can be orders of magnitude more than those resolvable in a normal proton or carbon-13 spectrum. In assigning the spectra of unknowns or oligomers the availability of correlated proton shifts is perhaps the single most useful adjunct to a decoupled carbon-13 spectrum. The ability to follow both carbon-13 and proton shifts, which often offer complementary information, can be extremely useful in determining substitution patterns, solution conformations, etc.

The spectra presented here are typical of those obtained from aqueous solutions of carbohydrates; it seems reasonable to expect results of similar quality from many other types of systems. The sensitivity of the heteronuclear chemical shift correlation experiment and the utility of its results make it an attractive proposition for investigating systems whose complexity places them beyond the pale of conventional NMR methods. The principal barrier to its widespread use is the need for complex data processing software and good pulse programming facilities. Both of these problems are now diminishing in magnitude as spectrometer hardware improves, and several manufacturers now offer 2D NMR control programs for their instruments.

**Acknowledgment.** This work was supported by operating grants (A1905 to L.D.H.) from the National Research Council of Canada and by an Izaak Walton Killam Postdoctoral Fellowship to G. A.M. Components for the spectrometer used were purchased with funds provided by the Chemistry Department and by the President's Emergency Research Equipment Fund, both of the University of British Columbia. The expert assistance of Tom Markus in the construction of the spectrometer was warmly appreciated. We thank Dr. Geoffrey Bodenhausen for a preprint of his work.

(34) Since this manuscript was completed Dr. Alan Jones has informed us of his studies of aqueous sucrose using selective  $^{13}C$ - $^1H$  decoupling: his results (A. J. Jones, P. Hanish, and A. K. McPhail, to be published) are identical within experimental error with those reported here.

## Does the Cyclohexyl Cation Exist in the Dilute Gas State? Direct Evidence from a Radiolytic Study

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**Abstract:** The isomeric composition of the gaseous  $C_6H_{11}^+$  cations obtained via hydride ion abstraction from  $c$ - $C_6H_{12}$  has been investigated by allowing the charged species to react in the gas phase with water and analyzing the neutral products formed. The nature and the yields of the major products, cyclohexanol, cyclohexanone, and 1-methylcyclopentanol, and their dependence on the pressure and the composition of the gaseous system provide direct evidence for the existence of the cyclohexyl cation in the dilute gas state, with a lifetime in excess of  $10^{-7}$  s, and confirm its facile rearrangement to the more stable 1-methylcyclopentyl ion.

The *solvated* cyclohexyl cation has long enjoyed a respectable position as a legitimate ionic intermediate in a variety of reactions occurring in solution, such as deamination, solvolytic processes, acid-induced isomerization, etc.<sup>1</sup> The situation, however, is entirely different for the *free* cyclohexyl cation in media of very low nucleophilicity or in the gas phase. Indeed, all attempts to generate  $c$ - $C_6H_{11}^+$  ions in superacid solutions invariably failed, the 1-methylcyclopentyl ion being the only species detectable by

NMR spectroscopy even at temperatures as low as  $-100$  °C.<sup>2-4</sup>

Understandably, this failure led to the suggestion that the free cyclohexyl cation is inherently unstable, rearranging instantly,<sup>4</sup> or even *before* its actual formation, i.e., in its "incipient" state,<sup>3</sup> into the 1-methylcyclopentyl ion, and this view was extended to the gas state.<sup>5</sup>





(2) Olah, G. A.; Bellinger, J. M.; Capas, C. A.; Lukas, J. *J. Am. Chem. Soc.* 1967, 89, 2692-4.

(3) Olah, G. A.; Lukas, J. *J. Am. Chem. Soc.* 1968, 90, 933-43.

(4) Arnett, E. M.; Petro, C. *J. Am. Chem. Soc.* 1978, 100, 5408-16.

(1) Olah, G. A.; Schleyer, P. v. R., Eds. "Carbonium Ions", Wiley-Interscience: New York, 1970; Vol. 2, Chapters 14 and 15.

Table I. Neutral Products from the Gas-Phase Reaction of Radiolytically Formed  $C_6H_{11}^+$  Ions with Water

system composition, <sup>a</sup> torr	relative yields of products, %				overall $G_{(+M)}$ <sup>b</sup>	ratio OH : Me OH
						
$C_3H_8$ 720, $c-C_6H_{12}$ 11.9, $H_2O$ 1.24	3	60	37		1.3	20
$C_3H_8$ 720, $c-C_6H_{12}$ 12.1, $H_2O$ 5.65	4	61	35		1.2	15
$C_3H_8$ 720, $c-C_6H_{12}$ 9.88, $H_2O$ 1.18, $NH_3$ 20.0		50	50		0.3	
$C_3H_8$ 720, $c-C_6H_{12}$ 1.85, $CH_3OH$ 1.94	<0.03	43	57		0.4	
$C_3H_8$ 100, $c-C_6H_{12}$ 1.82, $H_2O$ 0.47	14	60	26		1.4	4.3
$C_3H_8$ 40, $c-C_6H_{12}$ 0.52, $H_2O$ 0.10	23	54	23		1.1	2.4
$C_3H_8$ 46, $c-C_5H_9CH_3$ 0.60, $H_2O$ 0.15	100				0.6	
$H_2$ 720, $c-C_6H_{12}$ 1.13, $H_2O$ 1.24	11	47	42		c	4.3
$H_2$ 720, $c-C_6H_{12}$ 0.89, $H_2O$ 4.30	7	39	54		c	5.6
$H_2$ 720, $c-C_6H_{12}$ 0.93, $H_2O$ 1.07, $NH_3$ 17.0	1	55	44		c	55
$H_2$ 720, $c-C_5H_9CH_3$ 0.70, $H_2O$ 0.80	100				c	
$C_3H_8$ 720, $c-C_6H_{11}OH$ 2.24, $H_2O$ 2.03			39	61	0.9	
$C_3H_8$ 720, $c-C_6H_{11}OH$ 2.00, $H_2O$ 14.6			82	18	0.2	
$C_3H_8$ 720, $c-C_6H_{11}OH$ 1.37, $H_2O$ 2.37			55	45	0.3	
$C_3H_8$ 720, $c-C_6H_{11}OH$ 1.85			35	65	0.8	
$C_3H_8$ 720, $c-C_6H_{11}OH$ 2.01, $CH_3OH$ 2.15			50	50	0.6	
$H_2$ 720, $c-C_6H_{11}OH$ 0.89	3		97		c	

<sup>a</sup> All gaseous systems contain 1.5 mol %  $O_2$ . <sup>b</sup> For the accuracy of the data, see the text. <sup>c</sup> See the text.

The results of a careful mass spectrometric study<sup>6</sup> have recently supported the above conclusions, since collisional activation (CA) and kinetic energy release (T) spectra showed that the cyclohexyl cations from various sources, namely dissociative ionization of  $c-C_6H_{11}Br$ , protonation of  $c-C_6H_{10}$ , and acid-catalyzed dehydration of  $c-C_6H_{11}OH$ , apparently rearrange to the 1-methylcyclopentyl structure already in their "incipient" state, and under no circumstance can be detected as free  $c-C_6H_{11}^+$  ions. It was therefore concluded, summarizing the available results, that *there is no experimental evidence for the existence of the gaseous cyclohexyl cation*.<sup>6</sup> This statement appears entirely warranted on the grounds of the available evidence, that however can be hardly regarded as conclusive. In fact, it is generally recognized<sup>7</sup> that even the most sophisticated mass spectrometric tools for structural discrimination, such as CA techniques, suffer from serious limitations, in particular from the relatively long delay ( $\geq 10^{-5}$  s) before structural assay.

Under these conditions and in the absence of collisional stabilization, extensive or complete isomerization can occur before the ionic species can be assayed.<sup>8</sup> These considerations, and the relevance of the problem, have prompted us to exploit a different experimental technique, based on the radiolysis of carefully selected systems, successfully applied to the structural discrimination of charged species in the dilute gas state.<sup>9</sup>

### Experimental Section

**Materials.**  $H_2$  and  $C_3H_8$  were research grade gases from Matheson Gas Products Inc., with a stated purity exceeding 99.99 mol %.

Cyclohexane was obtained from Merck Co., while cyclohexanol, 1-methylcyclopentanol, methylcyclopentane, cyclohexene, cyclopentane-methanol, 3-methylcyclopentanol, *trans*-2-methylcyclopentanol, and cyclohexanone were research grade chemicals purchased from Aldrich Chemical Co., with a minimum stated purity of 99.5 mol %.

**Procedure.** The experimental techniques for the preparation and the irradiation of the gaseous systems have been described previously.<sup>8,9</sup> The samples were irradiated to a total dose of 5 MRad at a dose rate of 0.5 MRad  $h^{-1}$  in a 220 Gammacell from Nuclear Canada Ltd.

(5) Reference 18b in ref 4.

(6) Wesdemiotis, C.; Wolfschütz, R.; Schwarz, H. *Tetrahedron* **1979**, *36*, 275-8.

(7) Dimerski, P. P.; McLafferty, F. W. *J. Am. Chem. Soc.* **1976**, *98*, 6070-2.

(8) For instance, protonated cyclopropane can be identified by sampling the ionic population with ion-molecule reactions occurring at high pressure (cf. Attina, M.; Cacace, F.; Giacomello, P. *J. Am. Chem. Soc.* **1980**, *102*, 4768-72) but isomerizes completely to the  $s-C_3H_7^+$  ion before structural assay by CA.

(9) For a review, see Cacace, F. In "Kinetics of Ion-Molecule Reactions", Ausloos, P., Ed.; Plenum: New York, 1979; pp 199-221.

**Analysis of the Products.** The irradiated samples were analyzed by GLC, using a Sigma 1 gas chromatograph from Perkin-Elmer Co. and a FID detector on the following columns: (i) a 6-ft long glass column, packed with 0.2% Carbowax 1500 on 80-100 mesh Carbopack C, operated at 100 °C, (ii) a 6-ft long glass column packed with 0.1% SP-1000 on 80-100 mesh Carbopack C, operated at 110 °C, and (iii) a 20-ft long stainless steel column, packed with 10% SP-1000 on 80-100 mesh Supelcoport, operated at 110 °C. The yields of the products were deduced, using cyclopentanemethanol as an internal standard, from the areas of the corresponding elution peaks, corrected for the different response of the FID detector. The identity of the products was established by comparison of their retention volumes with those of authentic samples and confirmed by GLC-mass spectrometry, using a 5710 A gas chromatograph and a 5980 A mass spectrometer, connected to a 5934 A data system from Hewlett-Packard Co.

### Results

Table I summarizes the yields of the products from the condensation of radiolytically formed  $c-C_6H_{11}^+$  ions with water chosen as the trapping reagent. The *absolute*  $G_{(+M)}$  values are affected by a relatively large uncertainty, estimated around  $\pm 30\%$ , owing to the large errors in the experimental measurement of the absorbed dose. In particular, the data concerning the systems containing  $H_2$  as the bulk constituent are particularly unreliable, owing to dosimetric problems associated with the large difference between the density of the gas and that of the dosimetric solution, the enhancing effect of the vessel walls, etc. As a consequence, the *absolute*  $G$  values in these systems are scarcely meaningful, except for the depression of the yields caused by addition of  $NH_3$ , which is clearly detectable. On the other hand, the *internal* consistency of the data, namely the *relative* yields in a given system, which are most relevant to the purpose of the present study, is considerably better, with typical standard deviations well below 10%. The most significant features can be summarized as follows:

i. Trapping with water the ions obtained via hydride-ion abstraction from  $c-C_6H_{12}$  gives as major products cyclohexanol, 1-methylcyclopentanol, and cyclohexanone, via processes whose ionic character is ensured by the presence of a radical scavenger and demonstrated by the sharp decrease of the yields caused by addition of an ionic interceptor ( $NH_3$ ) to the gas.

ii. The nature of the Lewis acid used to generate the  $C_6H_{11}^+$  ions affects the relative yields of products, in particular the cyclohexanol:1-methylcyclopentanol ratio. The ratio *increases* in passing from  $H_3^+$  to  $i-C_3H_7^+$  and, for a given Lewis acid, *decreases* as the pressure is reduced.

iii. The ions generated via hydride-ion abstraction from methylcyclopentane give high yields of 1-methylcyclopentanol, with only traces, if any, of cyclohexanol, even at the lowest pressure investigated. The result is significant, showing that water is an

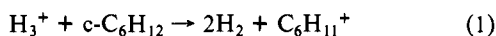
effective trapping agent for 1-methylcyclopentyl cations.

iv. Reactions of  $i\text{-C}_3\text{H}_7^+$  ions with cyclohexanol give isopropyl cyclohexyl ether and cyclohexanone as the major products, without appreciable formation of 1-methylcyclopentanol. Use of  $\text{H}_3^+$  as the Lewis acid gives high yields of cyclohexanone, with much smaller amounts of 1-methylcyclopentanol.

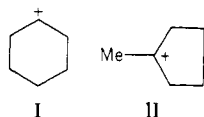
### Discussion

**The Ionic Reagents.**  $\text{H}_3^+$  and respectively  $i\text{-C}_3\text{H}_7^+$  ions are the only charged species present at appreciable concentrations in  $\text{H}_2$  and  $\text{C}_3\text{H}_8$  gas irradiated at the pressures and the dose rates prevailing in the present study. The reaction sequences responsible for the formation of the ions and their yields are well known from extensive mass spectrometric and radiolytic studies,<sup>10</sup> and need no further discussion here. It should be pointed out that any  $\text{H}_3^+$  and  $i\text{-C}_3\text{H}_7^+$  ions generated in an excited state from their exothermic formation processes must undergo a large number of unreactive collisions with the molecules of the bath gas ( $\text{H}_2$  or  $\text{C}_3\text{H}_8$ ) before reacting with the cycloalkane, contained at a low concentration in the system. Consequently, it is safe to assume that the charged reagents used to produce the cycloalkyl cations in  $\text{H}_2$  and  $\text{C}_3\text{H}_8$  are essentially  $\text{H}_3^+$  and respectively  $i\text{-C}_3\text{H}_7^+$  ions in their ground state.

**Formation of the  $\text{C}_6\text{H}_{11}^+$  Ions.** The process can be described with the following equations that apply respectively to the  $\text{H}_2$  and  $\text{C}_3\text{H}_8$  systems



Both processes are energetically allowed, irrespective of the structure of the cycloalkyl cation formed. In fact, reaction 1 can be estimated<sup>11</sup> to be exothermic by ca. 64 kcal mol<sup>-1</sup> and reaction 2 by 14 kcal mol<sup>-1</sup> if the ion formed has the cyclohexyl structure



I while formation of the more stable 1-methylcyclopentyl cation II would be a fortiori energetically possible. Hydride-ion abstraction from cyclohexane via reactions strictly analogous to processes 1 and 2 has been directly observed in the mass spectrometer,<sup>12</sup> and indeed cyclohexane has long been used as a hydride-ion donor to trap alkyl cations in gas-phase radiolytic and kinetic studies.<sup>13</sup>

**Structure and Isomerization of the  $\text{C}_6\text{H}_{11}^+$  Ions.** Inspection of Table I shows that the products containing a six-membered ring, i.e., cyclohexanol and cyclohexanone, predominate over 1-methylcyclopentanol, and this observation holds, with one exception, even when the comparison is restricted to the cyclohexanol:1-methylcyclopentanol pair, as in the last column of Table I. The result, and the dependence of the relative yields on the experimental variables, suggest that reactions 1 and 2 give pre-

(10) Concerning the formation of  $\text{H}_3^+$  and its applications in CI mass spectrometry, cf.: (a) Aquilanti, V.; Galli, A.; Giardini-Guidoni, A.; Volpi, G. *J. Chem. Phys.* **1968**, *48*, 4310-13 and references therein. On the radiolysis of propane and its high-pressure mass spectrometry, see: (b) Ausloos, P.; Lias, S. G. *J. Chem. Phys.* **1962**, *36*, 3163-8. (c) Lias, S. G.; Ausloos, P. *Ibid.* **1962**, *37*, 877-83. (d) Ausloos, P. In "Ion-Molecule Reactions", Franklin, J. L., Ed.; Plenum Press: New York, 1970. (e) Freeman, G. R. *Radiat. Res. Rev.* **1968**, *1*, 1 and references therein. (f) Munson, M. S. B.; Franklin, J. L.; Field, F. H. *J. Chem. Phys.* **1964**, *68*, 3039-45. (g) Bone, L. I.; Futrell, J. H. *Ibid.* **1967**, *46*, 4084-89. (h) Derwish, G. A. W.; Galli, A.; Giardini-Guidoni, A.; Volpi, G. *Ibid.* **1964**, *41*, 2998-3003. (i) Lias, S. G.; Rebbert, R. E.; Ausloos, P. *J. Am. Chem. Soc.* **1970**, *92*, 6430-7.

(11) Calculations based on  $H_f^\circ$  values for ionic species taken from: (a) Ausloos, P.; Jackson, J. A.-A.; Lias, S. G. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *33*, 269-83 and references therein. The thermochemical data for neutral species are taken from: (b) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970. The PA data for  $\text{H}_2$  is a value selected from: (c) Walder, R.; Franklin, J. L. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *36*, 85-112.

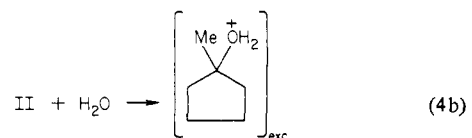
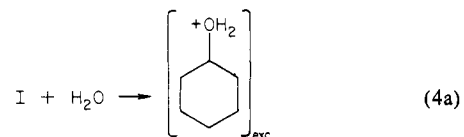
(12) For instance,  $\text{C}_6\text{H}_{11}^+$  is the most abundant ion in the  $\text{CH}_4$  CI spectrum of  $\text{c-C}_6\text{H}_{12}$ , cf. Field, F. H.; Munson, M. S. B. *J. Am. Chem. Soc.* **1967**, *89*, 4272-80.

(13) Ausloos, P.; Lias, S. G. *Discuss. Faraday Soc.* **1965**, *39*, 36-44.

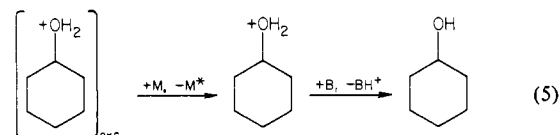
dominantly cyclohexyl ions I excited by the exothermicity of their formation process. These ions undergo partial rearrangement to the 1-methylcyclopentyl structure II, which is known<sup>4</sup> to be more stable by 6-10 kcal mol<sup>-1</sup>



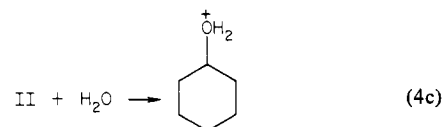
followed by condensation with water



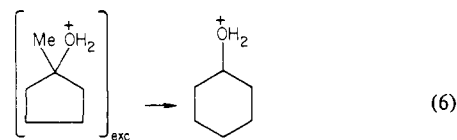
The condensation step is an exothermic process, characterized<sup>14</sup> by a standard enthalpy change of approximately -16 kcal mol<sup>-1</sup> for process 4a. The excited condensation products, following collisional stabilization, eventually undergo proton transfer to a gaseous base contained in the system, e.g.



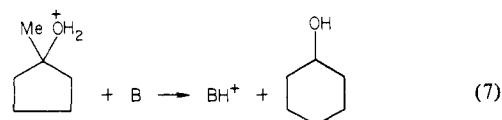
The extent of isomerization, i.e., the branching ratio (3b)/(3a), is *higher* for the  $\text{C}_6\text{H}_{11}^+$  ions from (1) than from (2), and *increases* as the pressure of the gas is lowered. These results support the view that formation of II involves isomerization of *excited* cyclohexyl ions I. In fact, such a process would be enhanced by a *higher* exothermicity of the formation process, and consequently of the excitation level of I, and by the reduced efficiency of collisional stabilization in the low-pressure systems. The conceivable, albeit admittedly unlikely, possibility that cyclohexanol arises from some kind of condensation-promoted skeletal isomerization of the 1-methylcyclopentyl ion



or from the skeletal isomerization of protonated 1-methylcyclopentanol



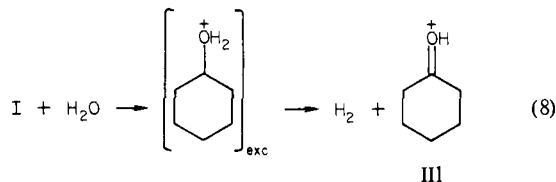
or from some skeletal isomerization induced by the deprotonation



is ruled out by the observation that 1-methylcyclopentanol is by far the major, if not the only, product formed from II, generated via hydride-ion abstraction from methylcyclopentane.

(14) The  $H_f^\circ$  values of protonated cyclohexanol and cyclohexanone were taken from: Jelus, B. L.; Murray, R. K.; Munson, B. *J. Am. Chem. Soc.* **1975**, *97*, 2362-65.

**Formation of Cyclohexanone.** Cyclohexanone is a major product from the systems containing  $c\text{-C}_6\text{H}_{12}$ , and the effect of  $\text{NH}_3$  on its yield suggests that ionic processes must be largely responsible for its formation. Among the possible ionic processes leading to cyclohexanone, one can consider the loss of  $\text{H}_2$  from protonated cyclohexanol, excited by the exothermicity of reaction 4a. It should be noted that the overall process



is exothermic<sup>14</sup> by ca. 7 kcal mol<sup>-1</sup>. Furthermore, loss of  $\text{H}_2$  from protonated cyclohexanol is the second most important fragmentation channel in the  $\text{H}_2$  CI spectra of alcohols,<sup>15</sup> and has been specifically observed in the  $\text{CH}_4$  and  $i\text{-C}_4\text{H}_{10}$  CI spectra of cyclohexanol.<sup>16,17</sup>

Reaction of  $\text{H}_3^+$  with cyclohexanol in systems at atmospheric pressure gives cyclohexanone in high yields. Cyclohexanone and isopropyl cyclohexyl ether are the major products from the reaction of  $i\text{-C}_3\text{H}_7^+$  ions with  $c\text{-C}_6\text{H}_{11}\text{OH}$ , their relative yields depending on the composition of the system. Formation of cyclohexanone in these experiments is likely to involve the intermediacy of III, an ionic species repeatedly observed<sup>16</sup> in the CI spectra of  $c\text{-C}_6\text{H}_{11}\text{OH}$ . In the reasonable<sup>18</sup> hypothesis that III is not formed

exclusively via direct hydride-ion abstraction from position 1 of cyclohexanol, but arises as well via the decomposition of an excited oxonium ion from the protonation or the alkylation of the alcohol, the significant yields of cyclohexanone obtained in the radiolytic experiments can be taken as inferential evidence for the occurrence of fragmentation processes analogous to reaction 8 even in high-pressure systems.

In any event, while a detailed mechanistic analysis of the processes responsible for the formation of cyclohexanone is beyond the scope of the present report, the six-membered cyclic structure of the ketone certainly does not contradict the view that most of the  $\text{C}_6\text{H}_{11}^+$  ions from  $c\text{-C}_6\text{H}_{12}$  retain the  $\text{C}_6$ -ring structure.

### Conclusion

The nature of the neutral products from the reaction of radiolytically formed  $\text{C}_6\text{H}_{11}^+$  ions with water provides compelling evidence for the existence of the cyclohexyl cation as a fully legitimate ionic intermediate in the dilute gas state, with a lifetime in excess of  $10^{-7}$  s. The discrepancy with previous conclusions can be rationalized if one considers that the latter were based on structural assay of  $\text{C}_6\text{H}_{11}^+$  ions by mass spectrometric techniques characterized by a relatively long interval ( $\geq 10^{-5}$  s) between the ionization act and the actual structural analysis. In the case of ionic species, such as the cyclohexyl cation, prone to isomerization, and in the absence of collisional stabilization, such delay is amply sufficient to allow substantial modifications of the original ionic population.

**Acknowledgment.** This research has been supported by the Italian National Research Council (C.N.R.).

(15) Aquilanti, V.; Galli, A.; Volpi, G. *Symp. Chem. Dynamics Padua* **1966**, 149-58.

(16) Cf.: (a) Reference 14. (b) Diakiv, V.; Goldsack, R. J.; Shannon, J. S.; Lacey, M. *J. Org. Mass Spectrom.* **1978**, *13*, 462-9. (c) Feuselau, C.; Green, M. M.; Jardine, I. *Ibid.* **1979**, *14*, 326-9. (d) Field, F. H. *J. Am. Chem. Soc.* **1970**, *72*, 2672-76.

(17) It should be noted that the most important fragmentation pathway in the CI spectra of cyclohexanol, i.e., the ionic dehydration of the alcohol, corresponds to the reverse of reaction 4a and cannot be detected in the present study, nor can it affect the measured yields, in that I generates once again.

(18) The hypothesis is supported by mass spectrometric evidence. For instance, the hydride-ion abstraction by  $\text{H}_3^+$  from cyclohexanol-1-*d* is highly regiospecific, position 1 being sharply favored (ref 16b), despite the highly indiscriminate nature of the reagent and the strongly exothermic character of its hydride-ion abstraction from *all* positions of the ring. This can be hardly explained without preliminary formation of an excited oxonium ion (ref 16d). Moreover, metastable decomposition of the oxonium ion from the attack of  $i\text{-C}_4\text{H}_9^+$  to cyclohexanol to yield III has been directly observed (ref 14).