

**Figure 12.** Comprehensive reaction scheme and data of the excited-state proton transfer in the methanol solution of 3-HX (deaerated) and of the relaxation processes both in the ground and excited states.

In the tautomer formation in the excited state, there may be two possible mechanisms: the simultaneous formation of tautomer from a hydrogen-bonding 3-HX with two methanol molecules and a step-wise formation by proton transfer from methanol to anion (probably to carbonyl oxygen). However, the latter mechanism, the step-wise formation, may be negligible or at least insignificant because the TSLE fluorescence spectrum of tautomer is not significant in the second laser excitation of the transient absorption band of the anion, as mentioned above. Therefore, it seems that the anion and tautomer are generated individually from their respective excited states of one and two methanol H-bonding complexes of 3-HX. This excited-state behavior is in contrast to the fact that the ground-state tautomer relaxes stepwise to the parent molecule through the formation of anion by releasing a proton from carbonyl oxygen. The proposed mechanism and data are shown in Figure 12.

The excited-state anion and tautomer dissipate their excitation energy with lifetimes of 5.9 and 0.6 ns to the respective ground

states. The transient absorption and TSLE time-resolved fluorescence spectra demonstrated a notable evidence of the anion formation from tautomer in the ground state—the fact that the ground-state anion is generated not only from the energy dissipation of this excited state but also from the ground-state tautomer ( $\tau = \sim 4.1 \mu\text{s}$ ). The rise of TSLE fluorescence intensity reflects the latter slow process (T  $\rightarrow$  A). Further, the very long lifetime of the ground-state anion ( $\sim 100 \mu\text{s}$ ) implies a very slow reaction rate of the reverse proton transfer to the parent molecule. On the other hand, a weak fluorescence signal due to the stable ground-state anion was detected only by dye laser excitation as mentioned in the Experimental Section. Therefore, a small amount of the stable anion present in the solvent which is generated by a simple ground-state dissociation may be involved in the reaction scheme.<sup>13,14</sup> However, the reaction kinetics and dynamics obtained by the transient absorption and TSLE fluorescence cannot be disturbed by this stable anion. In the aerated solution, neither rise of TSLE fluorescence intensity in the variable delay plots was observed nor rise of the transient absorption at 340–360 nm owing to the anion was detected. The fact is consistent with the short lifetime ( $\tau = 300\text{--}400 \text{ ns}$ ) of the ground-state tautomer, which seems to imply the oxygenation reaction in aerated condition as mentioned in the last section.

**Acknowledgment.** This work was supported by a Grand-in-Aid for Scientific Research (No. 58470125) from the Ministry of Education, Science and Culture of Japan.

**Registry No.** 3-Hydroxyxanthone, 3722-51-8.

(13) A similar stable anion formation of methyl salicylate and related compounds in alcohols was encountered in the case of TSLE fluorescence study on the excited-state proton transfer: Nishiya, A.; Yamauchi, S.; Hirota, N.; Fujiwara, Y.; Itoh, M., to be published.

(14) Kloepper, W.; Naundorf, G. *J. Lumin.* **1974**, *8*, 457.

## Free Cyclohexyl Cations from the Decay of Tritiated Cyclohexane

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**Abstract:** The question concerning the existence, the stability, and the isomerization rate of free, unstabilized cyclohexyl cation has been addressed by using the decay technique. Labeled cyclohexyl ions, unsolvated and free of counterions, have been generated in gaseous and liquid systems by the decay of a constituent atom of multitritiated cyclohexane. The daughter ions possess up to ca. 30 kcal mol<sup>-1</sup> excess internal energy, being formed in a geometry reminiscent of the neutral parent rather than in the most stable structure of the cyclohexyl cation. The analysis of the tritiated products from the reaction of the decay ions with suitable nucleophiles in different environments has provided compelling evidence for the existence of free cyclohexyl ion as a legitimate ionic intermediate having a lifetime of at least 10<sup>-8</sup>–10<sup>-7</sup> s. The cation corresponds to a local minimum on the C<sub>6</sub>H<sub>11</sub><sup>+</sup> energy surface, whose depth, deduced from the rate of isomerization to the more stable 1-methylcyclopentyl structure, is estimated below 10 kcal mol<sup>-1</sup>. The results confirm earlier conclusions from a radiolytic study and provide, in addition, useful information on the relative reaction rate of free cyclohexyl and 1-methylcyclopentyl cations toward several nucleophiles.

### Introduction

While the occurrence of solvated c-C<sub>6</sub>H<sub>11</sub><sup>+</sup> as a charged intermediate in solution is well documented,<sup>1</sup> its existence as a free cation, either in the gas phase or in condensed media of low nucleophilicity, is uncertain at the present time. Indeed, until very recently the general consensus, based on the persistent failure to





detect unstabilized cyclohexyl cation **1** by mass spectrometric or NMR techniques, was that **1** does not exist at all in the free state, owing to its prompt rearrangement to the 1-methylcyclopentyl isomer **2**.<sup>2</sup>

(1) (a) Olah, G. A.; Schleyer, P. v. R., Eds. "Carbonium Ions"; Wiley-Interscience: New York, 1970; Vol. 2, Chapters 14 and 15. (b) For a theoretical approach to the energetics of the hydride shifts within c-C<sub>6</sub>H<sub>11</sub><sup>+</sup>, and to the relative stability of its chair and boat conformations, see: Dannenberg, J. J.; Abrams, C.; Decoret, C.; Rayez, J. C. *J. Org. Chem.* **1983**, *48*, 3315.

<sup>†</sup>University of Rome.





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**Table I.** Radioactive Products from the Decay of  $c\text{-C}_6\text{X}_{12}$  ( $X = \text{H}, \text{T}$ ) in the Gas Phase

system composition <sup>a</sup> (torr)	rel yields of products <sup>b</sup> (%)				fract of cyclohexyl deriv (%)
					
CMe <sub>4</sub> , 720; MeOH, 14.6	11	21		68	32
CMe <sub>4</sub> , 200; MeOH, 9.9	6	4		90	10
CMe <sub>4</sub> , 50; MeOH, 10.3				100	0
SiMe <sub>4</sub> , 400; MeOH, 13.4	5		23	72	28
SiMe <sub>4</sub> , 200; MeOH, 12.8	6		9	85	15
SiMe <sub>4</sub> , 50; MeOH, 9.0	3			97	3
$c\text{-C}_6\text{H}_{12}$ , 80; MeOH, 9.4				100	0
$c\text{-C}_6\text{H}_{12}$ , 20; MeOH, 7.8				100	0
$n\text{-C}_7\text{H}_{16}$ , 40; MeOH, 9.7				100	0
MeOH, 4.8				100	0
CMe <sub>4</sub> , 720; 1,4-C <sub>4</sub> H <sub>8</sub> Br <sub>2</sub> , 0.96	26			74	26
CMe <sub>4</sub> , 200; 1,4-C <sub>4</sub> H <sub>8</sub> Br <sub>2</sub> , 0.85				100	0
CMe <sub>4</sub> , 50; 1,4-C <sub>4</sub> H <sub>8</sub> Br, 0.72				100	0
$n\text{-C}_7\text{H}_{16}$ , 40; 1,4-C <sub>4</sub> H <sub>8</sub> Br <sub>2</sub> , 0.96				100	0

<sup>a</sup>All systems contained  $c\text{-C}_6\text{X}_{12}$ , ca. 1.3 mCi, 3.7 torr, and O<sub>2</sub>, 10 torr, as a radical scavenger. <sup>b</sup>Y = OMe and Br, standard deviation ca. 10%. detection limit, ca. 1%.

**Table II.** Radioactive Products from the Decay of  $c\text{-C}_6\text{X}_{12}$  ( $X = \text{H}, \text{T}$ ) in the Liquid Phase

system compn <sup>a</sup> (mol %)	rel yields of products <sup>b</sup> (%)				fract of cyclohexyl deriv (%)
					
MeOH, 100	49	51			100
CMe <sub>4</sub> , 97.4; MeOH, 2.6	54	43		3	97
$c\text{-C}_6\text{H}_{12}$ , 99; MeOH, 1.0	12	84		4	96
SiMe <sub>4</sub> , 100		42	58		100
SiMe <sub>4</sub> , 99; MeOH, 1.0	10	40	47	3	97
AcOH, 100	100				100
1,4-C <sub>4</sub> H <sub>8</sub> Br <sub>2</sub> , 100	100				100
SiMe <sub>4</sub> , 99; 1,4-C <sub>4</sub> H <sub>8</sub> Br <sub>2</sub> , 1.0	5	8	85	2	98

<sup>a</sup>All systems contained  $c\text{-C}_6\text{X}_{12}$ , 1–3 mCi. <sup>b</sup>Standard deviation ca. 10%, Y = OMe, Br, or AcO.

In a previous report we have presented evidence for a lifetime of at least  $10^{-7}$  s for radiolytically generated  $c\text{-C}_6\text{H}_{11}^+$  ions in gases at pressures ranging from 40 to 720 torr.<sup>3</sup> In attempting to substantiate the radiolytic evidence, and to bring to a sharper focus the question concerning the stability of free cyclohexyl ion, we have resorted to the now well-established technique which exploits the decay of a radioactive atom in a tritiated precursor to generate free cations of well-defined structure.<sup>4</sup>

### Experimental Section

**Materials.** The chemicals and the gases used in the preparation of the decay systems, as inactive carriers or as reference standards in GLC, were obtained from commercial sources or prepared by unexceptional procedures. Multiply tritiated cyclohexane was obtained from the reaction of cyclohexene (5.2 mg, 0.063 mmol) with T<sub>2</sub> gas (5 Ci, 0.083 mmol) at 120 °C. The catalyst (5% Pt on charcoal) as well as the Pyrex reaction vessel had been previously equilibrated at 200 °C with several batches of T<sub>2</sub> in order to wash out any exchangeable protium. Blank reactions, carried out with D<sub>2</sub> instead of T<sub>2</sub> under otherwise identical conditions, gave quantitative yields of deuterated cyclohexanes, with an average D content of  $2.1 \pm 0.2$  atoms per molecule. The crude product from the reaction of T<sub>2</sub> with cyclohexene, thoroughly outgassed and repeatedly washed with H<sub>2</sub>, was diluted with a known amount of  $c\text{-C}_6\text{D}_{12}$  and assayed by GLC, which revealed the absence of any residual cyclohexene. The specific

activity of the diluted product, measured in a Tri-Carb liquid scintillation spectrometer, corresponded to an average T content of  $2.2 \pm 0.2$  atoms per molecule, in reasonable agreement with the results obtained in the blank runs. The usual NMR analysis of the intramolecular distribution of T was deemed unnecessary, given the equivalence of all hydrogen atoms of cyclohexane.

**Growth of the Decay Products.** The decay experiments were carried out according to procedures described elsewhere.<sup>5</sup> The gaseous systems were prepared by introducing ca. 1.3 mCi of purified  $c\text{-C}_6\text{X}_{12}$  ( $X = \text{H}, \text{T}$ ) into a carefully evacuated and outgassed 250-mL Pyrex vessel, equipped with a break-seal tip and containing the appropriate additives within fragile ampules. The required amounts of gaseous reagents (CMe<sub>4</sub>, SiMe<sub>4</sub>, O<sub>2</sub>, etc.) were then added by standard vacuum techniques, and the vessels were cooled to liquid nitrogen temperature and sealed off. The fragile ampules were then broken, and the contents of the vessel were allowed to come to room temperature and to mix. The liquid systems were prepared by dissolving 1–3 mCi of purified tritiated cyclohexane in the appropriate liquid reagent(s) in a 3.6-mL Pyrex vial, which was then cooled to liquid nitrogen and sealed, care being taken to fill the vessel as completely as possible. All samples were stored for periods of 9–12 months in the dark at 25 °C.

**Analysis of the Products.** The tritiated decay products were analyzed by radio-GLC. A Model C C. Erba gas chromatograph equipped with a hot-wire detector was used; the detector outlet was connected to a 10-mL internal flow proportional counter (Berthold Laboratorium AG) at 180 °C. Helium was used as the carrier gas, the effluents from the chromatograph being diluted with methane (1:1 v/v) to obtain a suitable counting gas. The identity of the products was established by comparing their capacity factors with those of authentic samples on at least two different columns. In many cases, inactive carriers were introduced into the decay system prior to radio-GLC to minimize possible losses of carrier-free products. These control analyses gave the same results, within the experimental errors, as the ones carried out by omitting the


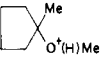




(2) (a) Wesdemiotis, C.; Wolfschütz, R.; Schwarz, H. *Tetrahedron* **1980**, *36*, 275. (b) Olah, G. A.; Bellinger, J. M.; Capas, C. A.; Lukas, J. *J. Am. Chem. Soc.* **1967**, *89*, 2692. (c) Olah, G. A.; Lukas, J. *J. Am. Chem. Soc.* **1968**, *90*, 933. (d) Arnett, E. M.; Petro, C. *J. Am. Chem. Soc.* **1978**, *100*, 5409.

(3) Attinà, M.; Cacace, F.; Giacomello, P. *J. Am. Chem. Soc.* **1981**, *103*, 4711.

(4) (a) Cacace, F. *Adv. Phys. Org. Chem.* **1970**, *8*, 79. (b) Cacace, F. "Kinetics of Ion-Molecule Reactions"; Ausloos, P., Ed.; Plenum Press: New York, 1979; p 199. (c) Cacace, F. In "Hot Atom Chemistry", Tatsuo Matsumura, Ed.; Kodansha: Tokyo, 1984; p 161.

(5) Angelini, G.; Fornarini, S.; Speranza, M. *J. Am. Chem. Soc.* **1982**, *104*, 4773 and references therein.

Table III. Trapping Reactions and Their Energetics

trapping reactions	$\Delta H^\circ$ (kcal mol <sup>-1</sup> )	neutral product <sup>a</sup>
(4) 1 + MeOH $\rightarrow$ c-C <sub>6</sub> X <sub>11</sub> O <sup>+</sup> (H)Me	-33 <sup>b</sup>	c-C <sub>6</sub> X <sub>11</sub> OMe
(5) 1 + MeOH $\rightarrow$ c-C <sub>6</sub> X <sub>10</sub> + MeOH <sub>2</sub> <sup>+</sup>	0 <sup>c</sup>	c-C <sub>6</sub> X <sub>10</sub>
(6) 1 + Br(CH <sub>2</sub> ) <sub>4</sub> Br $\rightarrow$ c-C <sub>6</sub> X <sub>11</sub> Br + 	$\leq +1.5$ <sup>d</sup>	c-C <sub>6</sub> X <sub>11</sub> Br
(7) 1 + SiMe <sub>4</sub> $\rightarrow$ c-C <sub>6</sub> X <sub>11</sub> Me + SiMe <sub>3</sub> <sup>+</sup>	-68 <sup>e</sup>	c-C <sub>6</sub> X <sub>11</sub> Me
(8) 1 + SiMe <sub>4</sub> $\rightarrow$ c-C <sub>6</sub> X <sub>10</sub> + CH <sub>4</sub> + SiMe <sub>3</sub> <sup>+</sup>	-50 <sup>f</sup>	c-C <sub>6</sub> X <sub>10</sub>
(9) 2 + MeOH $\rightarrow$ 	-23 <sup>g</sup>	
(10) 2 + MeOH $\nrightarrow$  + MeOH <sub>2</sub> <sup>+</sup>	+14 <sup>h</sup>	
(11) 2 + SiMe <sub>4</sub> $\rightarrow$  + SiMe <sub>3</sub> <sup>+</sup>	-53 <sup>i</sup>	

<sup>a</sup>  $H_f^\circ$  values of neutral species from ref 11 and 12, or estimated by standard group methods with data from the same sources. <sup>b</sup> PA of c-C<sub>6</sub>H<sub>11</sub>OMe assumed equal to that of *i*-Pr-O-Me, ref 13,  $H_f^\circ$  of 1 from ref 14b. <sup>c</sup> PA of methanol from ref 13 and 14. <sup>d</sup>  $H_f^\circ$  of c-C<sub>6</sub>H<sub>8</sub>Br<sup>+</sup> based on the data from ref 15. <sup>e</sup> Based on data from ref 14 and 16. <sup>f</sup> Based on data from ref 16. <sup>g</sup> PA of the ether assumed equal to that of *tert*-butyl methyl ether,  $H_f^\circ$  of 2 from ref 13 and 14. <sup>h</sup> PA from ref 13 and 14. <sup>i</sup> Based on data from ref 14 and 16.

addition of carriers. The following columns were used: (i) a 2.5-m-long, 3-mm-i.d. stainless-steel column, packed with GP 80-100 mesh Carbo-pack G/0.1% SP-1000, operated at 70-140 °C; (ii) a 2.5-m-long, 3-mm-i.d. stainless-steel column, packed with 1,2,3-tris(2-cyanoethoxy)-propane, 10% w/w on 100-120 mesh Chromosorb P AW, operated at 40 °C; (iii) two 3-mm-i.d. stainless-steel columns, 1.8-m and 5.0-m long, packed with SP-1200 (5% w/w) + Bentone 34 (1.75% w/w) on 100-120 mesh Supelcoport, operated at 70-110 °C.

## Results

The relative yields of the tritiated products from the decay of c-C<sub>6</sub>X<sub>12</sub> are given in Tables I and II, which refer respectively to gaseous and liquid systems. Accurate measurement of the absolute yields (defined by the ratio of the activity found in a given product to the total activity of the decay ions formed in the system) is not essential to evaluate the extent of isomerization of cyclohexyl cations. Nevertheless, consideration of the absolute yields is useful in order to verify whether the processes studied represent, indeed, major reaction channels of the daughter ions. This appears to be the case in the systems investigated, since the combined absolute yields of the products isolated are roughly 60-80%.<sup>6</sup>

The most significant features of the experimental results can be outlined as follows.

(i) In liquid systems the product pattern is characterized by the almost quantitative (96-100%) retention of the cyclohexyl structure, irrespective of the specific nucleophile used to trap the decay ions.

(ii) In gaseous hydrocarbons, isomerization to the 1-methylcyclopentyl structure predominates to an extent depending on the total pressure of the system, rather than on the nature of the specific nucleophile used. Thus, no cyclohexyl derivative can be detected at all in hydrocarbon gases below 400 torr. At higher pressures, the fraction of cyclohexyl derivatives is approximately the same in systems containing MeOH or 1,4-dibromobutane. At any given pressure the extent of isomerization is somewhat lower in SiMe<sub>4</sub>, which acts as a nucleophilic reagent as well as a moderating gas.

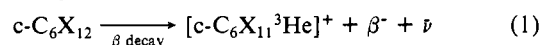
(iii) Cyclohexyl derivatives from liquid and gaseous systems containing MeOH consist of a mixture of cyclohexyl methyl ether and cyclohexene, while no olefins (isomeric methylcyclopentenes or methylenecyclopentane) accompany 1-methylcyclopentyl methyl ether. Formation of methylcyclohexane from the gaseous and liquid systems containing SiMe<sub>4</sub> contrasts with the absence of

detectable amounts of 1,1-dimethylcyclopentane.

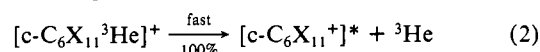
## Discussion

**The Reagent.** Since the concentration of c-C<sub>6</sub>X<sub>12</sub> and therefore the specific activity of the system have deliberately been kept at a very low level, the otherwise conceivable contribution of radiolytic processes to the formation of tritiated products is practically suppressed.<sup>7</sup> Consequently, in this study, the labeled decay ions represent the only significant source of the products isolated, and a brief outline of their formation process is in order.

No experimental data on the unimolecular, decay-induced fragmentation pattern of tritiated cyclohexane are currently available. Nevertheless, the theoretical, mass spectrometric, and radiochemical evidence concerning other hydrocarbons, including the strictly related c-C<sub>4</sub>H<sub>7</sub>T and c-C<sub>5</sub>H<sub>9</sub>T,<sup>8</sup> allows one to delineate with reasonable confidence the molecular consequences of the c-C<sub>6</sub>X<sub>12</sub> decay. The nuclear event is expected to generate, in a time (10<sup>-15</sup> s) very short on the chemical scale, a primary daughter ion. According to the unique distribution of excitation energy



following tritium decay, well documented by theoretical results and "charge" mass spectrometry, up to 20% of the daughter ions are formed in excited electronic states, which causes their prompt and extensive fragmentation, irrespective of the environment. The remaining daughter ions (ca. 80%), formed in their electronic ground state without appreciable recoil energy, nevertheless undergo prompt and quantitative loss of a neutral <sup>3</sup>He atom, owing to the inherently repulsive nature of the C-He interaction.<sup>9</sup> The



excess internal energy of the cyclohexyl cations from the decay of c-C<sub>6</sub>X<sub>12</sub> is of particular relevance to the present study. In this connection, it should be noted that even in the absence of other excitation mechanisms, the sudden nuclear transition generates daughter ions whose geometry, reminiscent of the neutral parent, does not correspond to the most stable structure of the cyclohexyl cation. The upper limit of such deformation energy can roughly be set around 30 kcal mol<sup>-1</sup>, in analogy with the results of theo-

(6) The data required to calculate the absolute yields include the absolute activity of the products, the initial activity of c-C<sub>6</sub>X<sub>12</sub>, its isotopic composition, the storage time, and the decay rate of tritium. Significant experimental uncertainties affect several of the above data, in particular the absolute activity of the products, whose measurement depends on the counting efficiency of the internal-flow proportional detectors.

(7) Radiolytic processes are entirely negligible as a source of tritiated products in comparison with the decay of the labeled parent, provided that the concentration of the latter, and therefore the specific activity of the system, is sufficiently low. For a discussion of this topic, cf. ref 4.

(8) Pobo, L. G.; Wexler, S.; Caronna, S. *Radiochim. Acta.* **1973**, *19*, 5.

(9) Ikuda, S.; Iwata, S.; Imamura, M. *J. Chem. Phys.* **1977**, *66*, 4671. For a general survey, see ref 4a and Wexler (Wexler, S. "Actions Chimiques et Biologiques des Radiations"; Haissinsky, M., Ed.; Masson et Cie: Paris, 1965; Vol. 8, p 110).

retical calculations concerning correspondingly deformed species, e.g., pyramidal methyl ions.<sup>10</sup>

In conclusion, the decay of a tritium atom of  $c\text{-C}_6\text{X}_{12}$  can be expected to give high yields (ca. 80%) of labeled cyclohexyl cations, characterized by excess vibrational energy (up to ca. 30 kcal mol<sup>-1</sup>) arising from the relaxation of their initially deformed structure to the most stable geometry.

**The Trapping Reactions.** The reactions chosen to sample the population of isomeric  $\text{C}_6\text{X}_{11}^+$  ions, their energetics, and their neutral end products are illustrated in Table III. The results outlined in the previous section show that the labeled decay ions are effectively trapped by the nucleophiles used, both in gaseous and in liquid systems, giving high yields of the expected neutral products. Even more relevant to the specific purpose of this study, the measured isomeric composition of the  $\text{C}_6\text{X}_{11}^+$  ions appears to be fairly independent of the particular nucleophile used to trap the charged precursors. Thus, the 32% fraction of the ions which retain the cyclohexyl structure in  $\text{CMe}_4$  at 720 torr, deduced from the reaction with  $\text{MeOH}$ , compares well with the 26% fraction deduced from the reaction with 1,4-dibromobutane, and with the 28% fraction measured in  $\text{SiMe}_4$  at 400 torr.

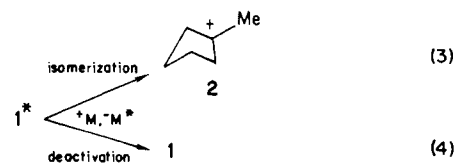
The composition of the products from systems containing two different nucleophiles allows a rough estimate of the relative efficiency of the reactions listed in Table III. Thus, the apparent  $k_3/k_7$  ratio deduced from the relative yields of the corresponding neutral products ranges from 6.5 in  $\text{SiMe}_4$  at 400 torr to ca. 20 in liquid  $\text{SiMe}_4$ . The apparent  $k_6/k_7$  ratio in liquid  $\text{SiMe}_4$  containing 1 mol % 1,4-dibromobutane denotes also a significant bias (ca. 5.8:1) of the  $c\text{-C}_6\text{X}_{11}^+$  ion for the latter nucleophile. Despite its exothermic character, reaction 11 does not occur to any detectable extent in gaseous systems containing both  $\text{SiMe}_4$  and  $\text{MeOH}$ , or in liquid  $\text{SiMe}_4$ . Finally, formation of methylcyclopentene via deprotonation of **2** does not occur, which can be rationalized by considering the endothermic character of process 10.

**Existence of Free, Unstabilized Cyclohexyl Cation.** As a background for the discussion of the results and their relevance to the problem addressed by this study, it is useful to briefly outline the unique features of the technique used as a source of the charged reagent. Of particular mechanistic note is that the decay ions are formed in an entirely free state, their charge being balanced by a remote electron rather than by an adjacent counterion. In the gaseous systems, the decay ions are of course unsolvated. Even in the liquid phase, the time required for a reactive encounter is in general much shorter than that for the rotational relaxation of the solvent molecules in the field of the suddenly generated cation. Consequently, a good case can be made for characterizing the decay ion as free of an organized solvation shell when the reaction with the nucleophile occurs.<sup>17</sup> Finally, trapping the decay ions requires a comparatively short time,  $10^{-8}$ – $10^{-7}$  s in the gas phase and  $10^{-13}$ – $10^{-11}$  s in liquid systems. This allows effective interception and characterization of charged intermediates prone to fast isomerization, as in the case in point.

From the above considerations, it seems legitimate to conclude that the observed formation of tritiated cyclohexyl derivatives unequivocally shows that free, unstabilized  $c\text{-C}_6\text{X}_{11}^+$  cations do exist in the dilute gas state, as well as in the liquid phase, surviving isomerization for at least  $10^{-8}$ – $10^{-7}$  s, the time required

for their interception by the nucleophilic reagent at the lowest concentrations of the latter used in the present study. Such a lifetime entitles free cyclohexyl cation to the rank of a fully legitimate ionic intermediate, necessarily corresponding to a local minimum on the  $\text{C}_6\text{H}_{11}^+$  energy surface.

**Stability and Isomerization of Cyclohexyl Cation.** The dramatic difference in the isomeric composition of the products from the liquid and the gaseous systems and its steep pressure dependence in the gas phase show that collisional deactivation is essential to stabilize the cyclohexyl cations from the decay, removing the excess internal energy associated with their structural deformation. The isomeric composition of the products is determined in each system by the competition of the processes



Stabilization **4** prevails in the liquid systems, while isomerization **3** predominates in the gas phase, becoming practically complete at the lower pressures.

The extensive isomerization observed even at 720 torr suggests that the rate of process **3** is comparable to the collision frequency at that pressure, in the order of  $10^{10}$  s<sup>-1</sup>. Assuming that the excess internal energy of **1\*** amounts to 30 kcal mol<sup>-1</sup> (vide supra), a rough estimate of the activation barrier of process **3** can be obtained by applying the classical RRKM treatment, which leads to values of 5–9 kcal mol<sup>-1</sup>, depending on the number of effective oscillators chosen. Without discounting the well-known limitations of such calculations, and their sensitivity to the assumptions made, there is little doubt that the activation barrier of process **3** is remarkably low, most likely below 10 kcal mol<sup>-1</sup>. The conclusion is independently supported by the appreciable isomerization undergone in gases at atmospheric pressure by  $c\text{-C}_6\text{H}_{11}^+$  ions, formed via hydride ion abstraction from  $c\text{-C}_6\text{H}_{12}$  by  $i\text{-C}_3\text{H}_7^+$ , despite the limited energy released<sup>3,14b</sup> and its partition between the products.

While the present results confirm the facile **1** → **2** rearrangement, they provide no information concerning its mechanism. No products whose formation could unambiguously be traced to the interception of  $c\text{-C}_3\text{H}_9\text{-CH}_2^+$  or bicyclohexylium ions could be detected, not even in neat liquid methanol. Such negative evidence suggests that if the above species are actually involved in the ring contraction, as suggested by previous studies,<sup>18</sup> they are best characterized as ionic transition states.

## Conclusion

The results provide convincing evidence for the existence of free, unstabilized cyclohexyl cation **1** in the dilute gas state, as well as in the liquid phase, with a lifetime of at least  $10^{-8}$ – $10^{-7}$  s, in agreement with the conclusions from a preliminary radiolytic study.<sup>3</sup> While on the  $\text{C}_6\text{H}_{11}^+$  energy surface structure **1** is characterized by a local minimum, the latter must be relatively shallow, since the energy barrier for isomerization to the 1-methylcyclopentyl structure **2** is probably lower than 10 kcal mol<sup>-1</sup>. This finding provides a satisfactory explanation of the persistent failure to detect and characterize gaseous  $c\text{-C}_6\text{H}_{11}^+$  with other experimental techniques, in particular with structurally diagnostic mass spectrometric methods.<sup>2a</sup> In fact, taking into account the remarkably low activation barrier of the isomerization process **3**, complete rearrangement of **1** is expected to occur well before structural assay under the conditions typical of mass spectrometric experiments.<sup>19</sup>

Finally, since the results obtained with the decay technique concern free ionic species, they lend themselves to a useful com-

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parison with those of theoretical approaches. A calculated value of the heat of formation of **1** (169 kcal mol<sup>-1</sup>) has been reported without specifying its most stable conformation.<sup>20</sup> Very recently, MINDO/3 and MNDO calculations concerning the boat and chair conformations of **1** and the transition states of 1-2, 1-3, and 1-4 hydride shifts have been published. A "facile" **1** → **2** rearrangement has been noted in the course of the calculations,

consistent with the evidence presented in this study, but unfortunately the specific reaction pathway has not been studied in detail.<sup>1b</sup>

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**Registry No.** MeOH, 67-56-1; 1,4-C<sub>4</sub>H<sub>8</sub>Br, 110-52-1; cyclohexylum, 22499-63-4; cyclohexane-t<sub>2</sub>, 84142-46-1; cyclohexene, 110-83-8.

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## Optical Activity of Monoolefins: RPA Calculations and Extraction of the Mechanisms in Kirkwood's Theory. Application to (-)-*trans*-Cyclooctene and (3*R*)-3-Methylcyclopentene

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**Abstract:** We present ab initio extended basis set calculations of the electronic (UV and CD) spectra of (-)-*trans*-cyclooctene and (3*R*)-3-methylcyclopentene in the random phase approximation (RPA). The nature of the excitations is discussed by means of approximate improved virtual orbitals (IVO's), transition densities, and charge rearrangement densities, and we use spectrum simulations to assist the comparison with experimental results. When a basis of localized molecular orbitals is used and effective bond transition moments are introduced, the RPA expression for the rotatory strength is cast in a form isomorphic with Kirkwood's original theory of optical rotatory power, and we present the resulting analysis of the chiroptical properties of the title compounds. To assist this analysis and to establish connection to previous work, we include calculations on ethylene and *trans*-2-butene, distorted as in (-)-*trans*-cyclooctene. Our computed results for ethylene and the other title molecules give a very satisfactory account of olefin spectra, for both valence and Rydberg excitations. The IVO contour plots of the  $\pi \rightarrow 3p$  Rydberg excitations show that the effective quantization axes of the 3p IVO's are governed by the gross shape of the molecule as opposed to the local symmetry of the chromophore. The Kirkwood analysis shows that the mechanisms for the chiroptical properties of the title compounds are quite different.

### I. Introduction

Over the years, the electronic spectra and the circular dichroism (CD) of monoolefins have been studied theoretically and experimentally from two different points of view. One perspective is the elucidation of the electronic properties of the ethylenic double bond, through the study of the combined effects of low-symmetry and restricted-motion molecular environments on the spectra. This viewpoint is exemplified by spectroscopic studies<sup>2,3</sup> and by electron impact<sup>4</sup> and photoelectron studies.<sup>5</sup> For the chiral molecules studied in ref 2 and 3, one gains in addition that the selection rules and intensity distributions in CD are quite different from those of ordinary absorption spectra.<sup>6,7</sup> The other perspective is to use the ethylenic chromophore as a structural probe, motivated largely by the success of the octant rule<sup>7</sup> for carbonyl compounds. This approach is represented by a number of studies combining experimental data and theoretical models in an attempt to generate rules for structure-CD correlations in rigid monoolefins.<sup>8-15</sup> Of

course, the two approaches are closely related since meaningful structure correlations presuppose secure spectral assignments.

Ethylene itself has been a computational favorite since the dawn of quantum chemistry (for leading references, see ref 16-18), whereas ab initio calculations on larger monoolefins are quite sparse.<sup>19</sup> Among chiral monoolefins, attention has been focused on two systems, namely (3*R*)-3-methylcyclopentene (Figure 1), whose low-lying excitations were treated recently by an ab initio SCF method,<sup>20</sup> and (-)-*trans*-cyclooctene (Figure 2), whose  $\pi \rightarrow \pi^*$  excitation has been studied by semiempirical<sup>21</sup> and minimal basis set ab initio methods<sup>22</sup> and for which twisted butene<sup>23,24</sup> and

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