

[CONTRIBUTION FROM THE DIVISION OF PURE CHEMISTRY, NATIONAL RESEARCH COUNCIL, OTTAWA, CANADA. ISSUED AS NRC No. 6415]

Free Radicals by Mass Spectrometry. XXIV. Ionization Potentials of Cycloalkyl Free Radicals and Cycloalkanes

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RECEIVED MARCH 25, 1961

Values have been obtained by electron impact for the vertical ionization potentials of some cycloalkyl free radicals. They were found to be: cyclopropyl 8.05 ± 0.1 , cyclobutyl 7.88 ± 0.05 , cyclopentyl 7.79 ± 0.03 and cyclohexyl 7.66 ± 0.05 e.v. The radicals were produced thermally by pyrolysis of appropriate cycloalkyl nitrites in a furnace leading to the ionization chamber of a mass spectrometer. Ionization potentials of the corresponding cycloalkanes and appearance potentials of radical ions in some derivatives also have been measured.

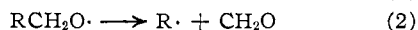
Introduction

This study was undertaken as an extension of recently published work³ on ionization potentials of alkyl radicals. Several recent papers⁴⁻⁶ have been concerned mainly with fragmentation processes in cyclic hydrocarbons, but no values, either direct or indirect, have been reported for ionization potentials of cycloalkyl free radicals.

Experimental

The mass spectrometer⁷ and thermal reactor⁸ have been described previously. The "low pressure" reactor used for these measurements consisted of a quartz tube, 1.5 mm. internal diameter, whose final 2 cm. was surrounded by a tantalum furnace element encased in a quartz sheath. The reactant gases, after passing through the furnace at a pressure of about 10^{-3} mm., entered directly into the ionization chamber through a 2 mm. aperture in the top plate.

Since alkyl nitrites have been found to be good sources for the production of alkyl free radicals,³ it was felt that cycloalkyl nitrites should also be suitable precursors for cyclic radicals. In the present work we have found that the cycloalkyl nitrites decompose in a manner analogous to the alkyl nitrites



where R· is cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl. The cyclic derivatives decomposed in the same temperature range as the alkyl nitrites (350–500°), indicating that the activation energy for reaction 1 is of the same order of magnitude in both cases, *i.e.*, 34–37 kcal./mole.⁹ Since the cycloalkoxy radicals could not be detected, it may be assumed that the activation energy for reaction 2 is quite low, presumably not greatly different from that for alkoxy radicals, 11–14 kcal./mole.⁹ The presence of cycloalkyl radicals during decomposition of the nitrite was initially established by the use of low energy electrons. A maximum in the yield of radicals was found at a furnace temperature in the region of 400–500°, and the ionization efficiency curves consequently were measured at this temperature.

Except for cyclopropyl, all radical yields were large, being 0.3 to 0.5 of the total ion current at the parent mass of the radical. No unexpected products appeared. A very low yield was found for cyclopropyl, the major mode of decomposition of the nitrite being that leading to the production of cyclopropyl carboxaldehyde.

The method used to determine the ionization potentials of radicals from the ionization efficiency curves for the

radical and a standard reference gas has been described.¹⁰ In this method the net radical ion current was obtained from the total peak height with 50 v. electrons by subtracting the contributions from fragment ions of undecomposed RCH_2ONO , of alcohols and aldehydes RCH_2OH and RCHO present either as impurities or as by-products and of the dimers RR and hydrocarbons RH produced by radical-radical reactions. The mass spectra of these components were determined in separate experiments using the pure compounds or in some cases were taken from the mass spectrometric literature. The logarithm of the ratio of the ion current at a given ionizing voltage to that calculated above at 50 v. was plotted as a function of the electron accelerating potential. The same procedure was used for a reference gas, either krypton or xenon, which was added to the gas stream. For all radicals reported the two curves were found to be parallel within 0.05 v. from 0.1% to 2% of the ion current at 50 v. The semi-logarithmic method also was used in determining the ionization potentials of cyclic hydrocarbons and the appearance potentials of fragment ions in some derivatives.

Materials.—The nitrites were prepared from cyclic carbinols by the reaction of sodium nitrite and dilute sulfuric acid.¹¹ Cyclohexyl carbinol was obtained from Eastman Organic Chemicals, and the other alcohols were prepared by reaction of lithium aluminum hydride with commercially available carboxylic acid derivatives.¹² Side reactions which produced aldehydes RCHO in the decomposition of the nitrites in the reactor made it necessary to prepare the four cyclic carboxaldehydes. They were synthesized by catalytic dehydrogenation of the alcohols with copper chromium oxide, as described by Dunbar and Arnold¹³ for alkyl derivatives. Excellent yields were obtained for cyclohexyl, cyclopentyl and cyclobutyl carboxaldehydes. The reaction products of cyclopropyl carbinol were approximately equal amounts of *n*-butyraldehyde and cyclopropyl carboxaldehyde. However, the mass spectra were resolved readily.

Results and Discussion

Cycloalkyl Radicals.—The observed vertical ionization potentials of the cycloalkyl free radicals are listed in Table I. The deviations given were estimated from the reproducibility of a given measurement and are not intended to represent absolute limits of error. Since the radical yield for cyclopropyl was considerably less than for the others, a somewhat larger uncertainty has been assigned. Included in Table I are ionization potentials calculated by Franklin's group orbital method,¹⁴ using the same parameters employed in

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TABLE II

Compound	Electron impact		Photoionization ²⁰	Calcd.	
	This work	Lit.		This work	Lit.
Cyclopropane	10.53	10.23 ¹⁵	10.06	11.76	11.76 ¹⁴ , 11.29 ²¹
Cyclobutane	10.58	10.40	10.21-10.48 ¹⁴ , 11.04 ²¹
Cyclopentane	10.92	11.1 ¹⁶	10.53	10.90	10.80-10.97 ¹⁴ , 10.89 ²¹
Methylcyclopentane	10.45	10.57
Cyclohexane	10.50	11.0 ^{16,17} , 10.3 ¹⁸ 10.40 ¹⁹	9.88	10.40	10.21-10.48 ¹⁴ , 10.79 ²¹
Methylcyclohexane	10.19	9.85	10.26

the calculations for the propyl and butyl free radicals.³ The agreement is fairly good, although the experimental values do not show the alternation between odd and even numbered rings which is predicted by the calculation. This is in contrast to the ionization potentials of the corresponding cycloalkanes, as discussed below.

TABLE I

Radical	Ionization potential (volts)		Nos. of determinations
	Obsd.	Calcd.	
Cyclopropyl	8.05 ± 0.1	8.31	4
Cyclobutyl	7.88 ± .05	7.77	3
Cyclopentyl	7.79 ± .03	7.90	7
Cyclohexyl	7.66 ± .05	7.86	3

The structures of the radicals C₃H₅ and C₆H₁₁ were established unequivocally as cyclopentyl and cyclohexyl by comparing the observed mass spectra of their dimers with those taken from the API catalog of mass spectral data for bicyclopentyl and bicyclohexyl. The mass spectrum for the observed dimer of the C₄H₇ radical was clearly not that of 1,7-octadiene, the dimer of the butenyl radical CH₂CH₂CH=CH₂, which would be produced if ring cleavage had occurred. Although mass spectral data for bicyclobutyl were not available for comparison, there seems to be no doubt that the radical was cyclobutyl. The identity of the C₃H₅ radical is less unambiguous, in view of the possibility of a rearrangement of the cyclopropyl radical to the more stable allyl radical. Measurement of the ionization potential at a furnace temperature of 400° gave 8.05 v. as shown in Table I. On increasing the furnace temperature to 800°, the observed ionization potential rose to 8.18 v., the difference being significantly larger than the repeatability of a given measurement. Since I (allyl) has been found previously to be 8.16 v.,¹⁰ this suggests the possibility that the cyclopropyl radical rearranged to allyl in the furnace at the higher temperature. With regard to this observation it should be noted that, owing to the numerous collisions with the walls of the ionization chamber prior to ionization, the temperature of the radicals being ionized is essentially independent of the furnace temperature. Since the mass spectrum of bicyclopentyl is not known, an identification of the radical from the observed spectrum of the dimer could not be made at either temperature.

Cycloalkanes.—The observed ionization potentials of the four cycloalkanes and two methyl derivatives are listed in Table II, together with

previous electron impact¹⁵⁻¹⁹ and photoionization²⁰ values. Included also are ionization potentials calculated by Franklin¹⁴ using the group orbital method and a set of values which we have calculated by the same method using the parameters employed above for the ionization potentials of the free radicals. Some values recently calculated by Streitwieser²¹ using the "ω-technique" are also given.

The agreement between the experimental values obtained in this work and the electron impact values from the literature is, with one or two exceptions, reasonably good. The electron impact values, however, are consistently higher, by about 0.5 v., than the photoionization values. This difference is appreciably larger than for branched paraffins, olefins and cyclic olefins. For these compounds the difference between electron impact and photoionization rarely exceeds 0.2 v. and is smaller in many cases.²² Both sets of data, however, show that the ionization potentials of cycloalkanes do not follow the customary sequence common to other homologous series, of a rapid initial decrease followed by a slower diminution. Instead, the ionization potential of cyclopropane is nearly the same as that of cyclobutane and cyclohexane and nearly a volt lower than that of propane. Moreover, the ionization potential of cyclopentane is about 0.5 v. higher than those of other members of the series. As pointed out by Franklin,¹⁴ the group orbital calculation predicts the even-numbered rings to have the same ionization potential, while those of the odd-numbered rings decrease rapidly toward this value. This causes the calculated ionization potentials to be alternately high and low among the series, with a rapidly decreasing amplitude of variation. The experimental results appear to bear this out, although the agreement is obscured in part by the low value observed for cyclopropane. With this exception, the agreement between the present experimental and calculated values is remarkably close. For cyclopropane itself, the loss of overlap in the carbon orbitals resulting from the strained configuration

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evidently greatly facilitates the removal of an electron. The observed ionization potential is, in fact, closer to that of propylene than that of propane. The calculated value, on the other hand, corresponds to a structure with normal C-C bonds, since the method of calculation takes no account of the strained configuration in the ring. For cyclobutane and higher members of the series, the agreement between observed and calculated results indicates that, in as far as vertical ionization potentials are concerned, the residual ring strain can be ignored.

Appearance Potentials.—The appearance potentials $A(R_1^+)$ found for the $C_nH_{2n-1}^+$ ions formed from a number of cycloalkanes are given in Table III, together with values of ionic heats of formation $\Delta H_f(R_1^+)$ calculated from the relation

$$\Delta H_f(R_1^+) \leq A(R_1^+) - \Delta H_f(R_2) + \Delta H_f(R_1R_2)$$

In addition to the usual question as to the excess energy involved in this relation, there is a strong possibility that these appearance potentials correspond to ions which have an olefinic rather than a cyclic structure. In a study of the dissociative ionization of methyl- C^{13} -cyclopentane, Stevenson⁴ found that about 50% of the C_5 ions retain the labelled methyl carbon. This indicates strongly that the $C_5H_9^+$ ion formed by 75 v. electrons is not a cyclopentyl ion resulting from simple C-C bond rupture but is formed instead by dissociation of a hexene ion produced by isomerization of the parent methylcyclopentane ion. It is not clear whether $C_nH_{2n-1}^+$ ions formed at or near the appearance potential thresholds given in Table III are also olefinic ions resulting from isomerization of the parent ion, but in the absence of evidence to the contrary one must accept Stevenson's conclusion⁴ that these appearance potentials should not be employed to deduce energetic properties for cycloalkyl radicals or ions. A comparison of the heats of formation of these ions with those of ions known to be olefinic would be of value in deciding this question, but as can be seen from Table III, values are available only for $C_3H_5^+$ and $C_4H_7^+$. When combined with the ionization potentials of the radicals, the heats of formation of the $C_4H_7^+$ and $C_5H_9^+$ ions lead to C-H bond dissociation energies in cyclobutane and cyclopentane which are around 10 kcal./mole lower than would be expected on reasonable grounds. It seems quite probable, therefore, that these appearance potentials correspond to the formation of olefinic $C_4H_7^+$ and $C_5H_9^+$ ions, with possibly some excitational energy. This agrees with Stevenson's conclusions concerning the $C_5H_9^+$ ion.

The value of $\Delta H_f(C_5H_9^+) \leq 239$ kcal./mole is quite significantly higher than that for allyl, which is 220 kcal./mole.²³ When combined with $I(\text{cyclopropyl})$, however, the derived C-H bond dissociation

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TABLE III
APPEARANCE POTENTIALS AND HEATS OF FORMATION OF IONS OF FORMULA $C_nH_{2n-1}^+$, (NOT NECESSARILY CYCLIC)

Compound	Ion	Appearance potential (volt)		ΔH_f ion (kcal./mole)	ΔH_f of corresp. olefinic ion
		Lit.	This work		
Cyclopropane	$C_3H_5^+$	12.1 ¹⁴	12.06	$\leq 239^a$	220 ²³
Cyclobutane	$C_4H_7^+$...	11.24	$\leq 213^b$	204-206 ²²
Methylcyclopentane	$C_5H_9^+$...	10.95	$\leq 195^c$
Cyclohexane	$C_6H_{11}^+$...	11.66	$\leq 187^c$
Methylcyclohexane	$C_7H_{13}^+$...	10.95	$\leq 184^c$

^a $\Delta H_f(\text{cyclopropane}) = +12.74$ kcal./mole, J. W. Knowlton and F. D. Rossini, *J. Res. National Bureau of Standards*, **43**, 113 (1949). ^b $\Delta H_f(\text{cyclobutane}) = +6.3$ kcal./mole, J. Coops and S. Kaarsemaker, *Rec. Trav. Chim. Pays-Bas*, **69**, 1364 (1950). This value appears to be a little high by comparison with the rest of the series. ^c Heats of formation of cycloalkanes taken from F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.

energy in cyclopropane, ≤ 92.5 kcal./mole, also appears to be lower than might be expected, although not to such a large extent as for $C_4H_7^+$ and $C_5H_9^+$. There is reason to believe that the dissociation energy of the C-H bond in cyclopropane is more nearly like a primary C-H bond (~ 98 kcal./mole) than a secondary C-H bond (~ 93 kcal./mole). For instance, the activation energy for abstraction of a hydrogen atom by methyl radical is around 10.3 kcal./mole.²⁴ This is essentially the same as the corresponding activation energy for abstraction of a primary hydrogen as in ethane or neopentane. Abstraction of a secondary hydrogen on the other hand, as in *n*-butane and *n*-pentane, requires an activation energy of about 8.3 kcal./mole.²⁴ Although such comparisons are not always reliable, one may reasonably doubt that the C-H bond dissociation energy in cyclopropane is as low as 92.5 kcal./mole. It seems probable, therefore, that the $C_3H_5^+$ ion formed from cyclopropane at the appearance potential is not a cyclopropyl ion but an allyl ion with a large amount of excitation energy.

The appearance potentials for $C_6H_{11}^+$ ions from cyclohexane and methylcyclohexane both give about 186 kcal./mole for $\Delta H_f(C_6H_{11}^+)$. When combined with $I(\text{cyclohexyl}) = 7.66$ v., this gives $\Delta H_f(\text{cyclohexyl}) \leq 9$ kcal./mole and $D(\text{cyclohexyl-H}) \leq 91$ kcal./mole. In contrast to the other members of this series, this value for the bond dissociation energy appears not unreasonable by comparison with secondary C-H bonds in other hydrocarbons. There is a possibility, then, that the $C_6H_{11}^+$ ion formed by the dissociative ionization of cyclohexane and methylcyclohexane is actually a cyclohexyl ion formed by simple bond fission, rather than by a rearrangement to an olefinic ion as occurs with the C_3 - C_5 cycloalkanes.

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