Chemical Ionization Mass Spectrometry. V. Cycloparaffins

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Abstract: The chemical ionization mass spectra of cycloparaffins have been determined. The compounds investigated consisted of ten cyclopentanes, eleven cyclohexanes, cycloheptane, cyclooctane, four bicycloalkanes, and perdeuteriocyclohexane. The $(\mathrm{MW} - 1)^+$ ions are the most intense in the spectra with the intensity values for all but one compound ranging between approximately 0.40 and 0.75 of the total cycloparaffin ionization. The intensities of the $(\mathrm{MW} - 1)^+$ ions for the alkylcyclopentanes and alkylcyclohexanes can be correlated semiquantitatively with the structures of the molecules in terms of the random attack localized reaction concept of chemical ionization. The spectra reflect the presence of methyl groups in the structures of the cycloalkane molecules. Cyclic olefin ions are formed which give information about the ring present. The experiments with cyclo-C_6D_{12} show that the $C_6D_{11}^+$ ion is formed with essentially no isotopic mixing, and it is suggested that CH_5^+ may in part act as a Lewis acid to affect hydride (or deuteride) ion abstraction. The equal intensities of $C_3D_7^+$ and $C_3D_6H^+$ ions formed from cyclo-C_6D_{12} indicate that the formation of these ions involves considerable structural rearrangement, and the possibility of major structural rearrangements is also indicated by ions formed in certain other cycloalkanes.

We report here the results of our investigations of the chemical ionization mass spectra of a number of cycloparaffins. Our purpose in undertaking the work is to provide a body of data about chemical ionization mass spectrometry with the hope that a basis will thus be provided for elucidating the interesting chemistry of gaseous ionic reactions and for developing a practically useful technique of analytical mass spectrometry. A general description of chemical ionization mass spectrometry has been given,[2] and in previous papers reports have been given of the chemical ionization mass spectra of esters,[3a] paraffins,[4] and aromatic hydrocarbons.[3b] In the present study of cycloparaffins (as in the earlier studies) methane is used as the reactant gas, and we may briefly summarize the chemical ionization technique by stating that by maintaining a high pressure (1 torr) of CH_4 in the mass spectrometer ionization chamber a mixture of CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ is formed. These ions in turn react with added compounds (cycloalkanes in the case of this study) to produce the chemical ionization mass spectra of the added compounds.

Experimental Section

The measurements were made using the Esso chemical physics mass spectrometer and the chemical ionization procedures described previously.[2,3a,4] The source pressure of the methane used as reactant gas was maintained at 1.00 ± 0.01 torr. The temperature of the ionization chamber was 185°. The cycloparaffins investigated were API or NBS standard samples used as obtained except as follows. The cyclopentane and cyclohexane were Phillips research grade and were used as obtained. The cyclooctane and bicyclo[2.2.2]octane were obtained from the Aldrich Chemical Co., Milwaukee, Wis., and the Chemical Sample Co., Columbus, Ohio, respectively. Perdeuteriocyclohexane (cyclo-C_6D_{12}) was obtained from Merck Sharp and Dohme of Canada, Montreal, Que. For these compounds the spectral measurements were made on purified samples prepared by preparative scale gas chromatography.

Results and Discussion

Spectra were obtained for ten cyclopentanes, eleven cyclohexanes, cycloheptane, cyclooctane, four bicycloalkanes, and perdeuteriocyclohexane. The results are given in Table I. As is generally the case with chemical ionization, the spectra are quite simple, and for the monocycloalkanes they consist almost exclusively of two series of ions, namely, a main series with formula $C_nH_{2n-1}^+$ and a subsidiary series with formula $C_nH_{2n+1}^+$. Ions with m/e 68 and 82 are also observed. For the bicycloalkanes two series are formed also: one with formula $C_nH_{2n-3}^+$ and a subsidiary series with formula $C_nH_{2n-1}^+$, and in addition some mass 57 is observed with three of the bicycloalkanes. Many of the ions in the several series are of small intensity, and for almost all of the cycloalkanes studied most (>75%) of the ionization observed is carried by two to four ions. To simplify Table I, C^{13} isotope ions are not tabulated, although they are taken into account in calculating relative intensities. Thus the intensities given do not sum to unity.

MW^+ Ions. For a number of compounds the intensity at m/e = MW is somewhat larger than the C^{13} isotopic contribution from the always large m/e = MW − 1 ion. This suggests that some MW^+ ions are being formed, and those intensities in excess of the isotope correction are listed in Table I in a column labeled MW^+. Variation exists from one compound to another as to whether MW^+ ions are observed or not, and, when they are, considerable variation in intensity is observed. The MW^+ intensities listed are small differences of large quantities, and thus are subject to appreciable error. We are inclined to think that MW^+ ions can be formed with some compounds, probably by a charge exchange reaction with $C_2H_4^+$, which is present in the methane plasma to the extent of about 2%.

$(\mathrm{MW} + 1)^+$ Ions. For convenience the intensities of the $(\mathrm{MW} + 1)^+$ ions are collected in Table II, and it

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[1] (a) Central Basic Research Division; (b) Baytown Research and Development Division.

[2] M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **88**, 2621 (1966).

[3] (a) M. S. B. Munson and F. H. Field, *ibid.*, **88**, 4337 (1966); (b) *ibid.*, **89**, 1047 (1967).

[4] F. H. Field, M. S. B. Munson, and D. A. Becker, Advances in Chemistry, No. 58, American Chemical Society, Washington, D. C., 1966, p 167.

may be seen that these intensities are generally small, greater than 0.05 of the total ionization for only 5 of the 27 compounds. Formation of $(MW + 1)^+$ ions is not observed in alkanes larger than ethane when the CH_4 pressure is 1 torr,[4] and it must be concluded that all proton transfer to these compounds results in dissociation of either C–H or C–C bonds. However, cleavage of a C–C bond in the ring of a protonated cycloparaffin produces an ion of the same *m/e* in the $C_nH_{2n+1}^+$ series, which is doubtless the explanation for the observation of $(MW + 1)^+$ ions in the cycloalkanes. Ring-opening proton-transfer reactions are exothermic for all the cycloalkanes when the reactant ion is CH_5^+.

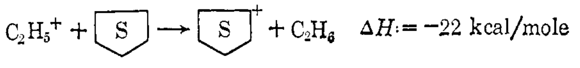
$$CH_5^+ + c\text{-}C_6H_{12} \longrightarrow n\text{-}C_6H_{13}^+ + CH_4 \quad \Delta H = -13 \text{ kcal/mole} \tag{1}$$

This heat of reaction is calculated using a value of $\Delta H_f(CH_5^+) = 229$ kcal/mole.[5] Heats of formation of the neutral compounds were taken from the API compilation,[6] and a value for $\Delta H_f(n\text{-}C_6H_{13}^+) = 205$ kcal/mole was estimated using Franklin's method of group equivalents.[4,7] For alkyl-substituted cycloalkanes rupture of the ring at the bond next to the side chain will produce a secondary carbonium ion with a consequent increase in the exothermicity of the reaction.

One observes in Table II interesting variations in the intensities of the $(MW + 1)^+$ ions. In particular, the $(MW + 1)^+$ intensities are relatively large in compounds containing the cyclopentane ring. Thus, the intensity of $(MW + 1)^+$ in cyclopentane itself is significantly greater than the $(MW + 1)^+$ intensities in the other unsubstituted monocyclic compounds, and the intensity in hydrindan (which contains a fused cyclopentyl ring) is double that of *trans*-decalin, which contains fused cyclohexyl rings. The addition of an alkyl side chain to both cyclopentane and cyclohexane lowers the $(MW + 1)^+$ intensities, but the intensities in the alkylcyclopentanes are significantly greater than those in the alkylcyclohexanes. Thus the average $(MW + 1)^+$ intensity for the alkylcyclopentanes is 0.036, whereas the average value for the alkylcyclohexanes is 0.011. We are quite at a loss to explain any of these observations concerning $(MW + 1)^+$ intensities.

$(MW - 1)^+$ Ions. The intensities of the $(MW - 1)^+$ ions are collected in Table II. The $(MW - 1)^+$ ions are for all compounds the most intense ions observed, with values ranging from 0.270 (*t*-butylcyclohexane) to 0.743 (cyclohexane). For *t*-butylcyclohexane the $(MW - 1)^+$ intensity is almost equaled by the $C_4H_9^+$ intensity, but this is the only compound in which the intensity of another ion is comparable with that of $(MW - 1)^+$.

The most obvious reaction producing these ions in the unsubstituted cycloalkanes is hydride abstraction by $C_2H_5^+$ or $C_3H_5^+$ to produce a cycloalkyl ion. Thus



$$C_2H_5^+ + \boxed{S} \longrightarrow \boxed{S}^+ + C_2H_6 \quad \Delta H = -22 \text{ kcal/mole} \tag{2}$$

However, with the straight-chain paraffins, $(MW - 1)^+$ alkyl ion formation comprises[4] only about 30% of the total chemical ionization, and this percentage becomes significantly smaller for the branched paraffins. The difference between these figures and the 50–70% $(MW - 1)^+$ intensities observed with the cycloparaffins is significant, and we believe that different factors or processes must be operating in the two classes of compounds.

The $(MW - 1)^+$ intensities in the alkylcyclohexanes are lower than the $(MW - 1)^+$ intensity in cyclohexane, and a considerable intensity variation is observed depending on the identity of the side chain(s) present. A similar dependence upon the nature of the side chains is observed in the alkylcyclopentanes, but the comparison with the $(MW - 1)^+$ intensity of unsubstituted cyclopentane does not show an obviously clear trend. In our study of the paraffinic hydrocarbons[4] we were able to make a semiquantitative correlation of the intensities of $(MW - 1)^+$ ions in branched paraffins with the number of so-called available hydrogens in the molecule, and it is of interest to attempt the same type of calculation with the alkylcycloalkanes. An available hydrogen is defined as a nonprimary hydrogen atom which is not attached to a carbon atom β to a branch point in the carbon chain, and the calculation is based on the postulate that chemical ionization involves a random attack of the reactant ion followed by a localized reaction. These reactions are assumed to be H^- abstraction or C–C fission for all C atoms except those β to a branch point for which it is assumed that C–C fission always follows any H^- abstraction which may occur. We make the calculation for the alkyl-substituted cycloalkanes by assuming that the relative amounts of attack on the ring and side chain are determined by the relative sizes of the ring and side chain, and we assume further that the chemical ionization reactions of the ring and side chain proceed independently of each other. Thus, we write

$$I_{MW-1} = \left(\frac{H_{RS}}{H_{RU}}\right)\left(\frac{C_R}{C_T}\right)I_{RU} + \frac{CH_2}{C_T}(0.32) + \frac{CH}{C_T}(0.032/2) \tag{3}$$

where H_{RS} = number of ring H atoms in the substituted cycloalkane (H atoms on carbons β to a *t*-butyl side chain are not counted); H_{RU} = number of ring H atoms in the corresponding unsubstituted cycloalkane (cyclopentane or cyclohexane); C_R = number of ring carbons; C_T = total number of carbons; I_{RU} = effective $(MW - 1)^+$ intensity for the unsubstituted cycloalkane; CH_2 = number of CH_2 groups in alkyl group (groups β to a C–C branch point are not counted); CH = number of CH groups in alkyl group (groups β to a C–C branch point are not counted).

The numerical factor of 0.32 written in eq 3 is the fraction of $(MW - 1)^+$ intensity observed to result from attack on a CH_2 group in a straight-chain paraffin. The quantity I_{RU} written in eq 3 stands for the effective $(MW - 1)^+$ intensity for cyclopentane or cyclohexane depending on whether the equation is used to calculate $(MW - 1)^+$ intensities for substituted cyclopentanes or substituted cyclohexanes. One's first thought is to use as the value of I_{RU} the observed $(MW - 1)^+$ in-

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[5] M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, 87, 3294 (1965).

[6] API Research Project 44, "Selected Values and Properties of Hydrocarbons and Related Compounds," Chemical Thermodynamics Properties Center, Texas A&M, College Station, Texas.

[7] J. L. Franklin, *J. Chem. Phys.*, 25, 2029 (1953).

Table I. Relative Ion Intensities for Cycloparaffins[a]

Compd no.	Compound name[c]	MW	Relative ion intensities[b]												
			C_3	C_4		C_5			C_6			C_7		C_8	
			43	55	57	68	69	71	82	83	85	97	99	111	113
	Cyclopentanes														
1	CyC_5	70	0.242	0.003	0.003	0.005	0.451	0.235							
2	$MeCyC_5$	84	0.181		0.070		0.117			0.418	0.120				
3	$EtCyC_5$	98	0.004	0.012	0.309	0.013	0.035	0.033		0.101		0.402	0.015		
4	*n*-$PrCyC_5$	112	0.034		0.123	0.002	0.029	0.128		0.021	0.016	0.050		0.534	0.025
5	*i*-$PrCyC_5$	112	0.029		0.164	0.009	0.014	0.118		0.001	0.019	0.170		0.425	0.020
6	*n*-$BuCyC_5$	126	0.014	0.002	0.076		0.092	0.095		0.050	0.056	0.015	0.010	0.037	
7	*n*-$C_{10}CyC_5$	210			0.011	0.003	0.011	0.024	0.003	0.040	0.021	0.088	0.020	0.055	0.021
8	*trans*-1,2-Me_2CyC_5	98	0.003	0.002	0.250		0.001	0.005		0.165		0.483	0.033		
9	1-Me-1-Et-CyC_5	112	0.010	0.002	0.112		0.008	0.114	0.011	0.048	0.038	0.161		0.472	0.023
10	1,1,3-Me_3-CyC_5	112	0.015	0.001	0.128		0.005	0.099		0.003	0.001	0.246		0.448	0.018
	Cyclohexanes														
11	CyC_6	84	0.064	0.001	0.016		0.012			0.743	0.086				
12	$MeCyC_6$	98	0.002	0.004	0.159		0.002	0.001		0.125		0.607	0.012		
13	$EtCyC_6$	112		0.048	0.043		0.003	0.044	0.013	0.030		0.062		0.720	0.008
14	*n*-$PrCyC_6$	126		0.004	0.048		0.043	0.057	0.019	0.025	0.042	0.036		0.053	
15	*i*-$PrCyC_6$	126		0.005	0.058		0.040	0.070	0.030	0.044	0.042	0.002	0.002	0.145	
16	*n*-$BuCyC_6$	140		0.001	0.046		0.026	0.034	0.017	0.099	0.033	0.048	0.016	0.019	
17	*i*-$BuCyC_6$	140		0.001	0.056		0.010	0.036	0.010	0.092	0.034	0.060	0.015	0.001	
18	*t*-$BuCyC_6$	140			0.244		0.003	0.030	0.004	0.092	0.024	0.015	0.007		0.001
19	*n*-$C_{10}CyC_6$	224		0.004	0.018		0.004	0.023	0.018	0.047	0.020	0.082	0.012	0.047	0.010
20	*trans*-1,2-Me_2CyC_6	112			0.030		0.003	0.036		0.001	0.001	0.184	0.001	0.664	0.010
21	1,1,3-Me_3CyC_6	126			0.015		0.010	0.026		0.004	0.011	0.001	0.001	0.277	0.001
	Other Cycloalkanes														
22	CyC_7	98	0.005	0.005	0.168		0.001	0.003		0.003		0.725	0.001		
23	CyC_8	112	0.004	0.008	0.124		0.063	0.128		0.005	0.001			0.573	0.006
	Bicycloalkanes														
				55	57	67	69		81	82	83	95	97	109	111
24	Bicyclo[2.2.2]-octane	110		0.017	0.005	0.008	0.147		0.005		0.009			0.550	0.147
25	*trans*-Hydrindan	124			0.016	0.004	0.119		0.013		0.066		0.018		
26	*trans*-Decalin	138			0.012		0.011		0.008		0.057	0.005	0.023		0.003
27	Cyclohexyl-CyC_6	166					0.001		0.003	0.018	0.043	0.003	0.038	0.024	

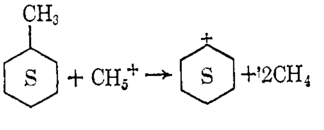
[a] CH_4 reactant; P_{CH_4} = 1.0 torr. [b] At the designated carbon atom and *m/e* values. [c] CyC_5 = cyclopentane; CyC_6 = cyclohexane; CyC_7

tensities for cyclopentane and cyclohexane, *i.e.*, 0.451 and 0.743, respectively (Table II).

Calculations based on this idea were made and gave satisfactory results for the alkylcyclohexanes but gave poorer agreement with the experimental values for the alkylcyclopentanes. In an effort to rationalize this discrepancy, we noted that $(MW + 1)^+$ intensities for the alkylcycloalkanes are appreciably smaller than the values found in the unsubstituted cycloalkanes, and this effect is particularly marked in the cyclopentane series. It seems reasonable to assume that at least some of the ionization which exists as $(MW + 1)^+$ ions in the cycloalkane exists as $(MW - 1)^+$ ions in the substituted cycloalkanes. Therefore, we assume that the value to be used for I_{RU} in eq 3 is the sum of the intensities observed in the unsubstituted cycloalkanes for the $(MW + 1)^+$ and the $(MW - 1)^+$ ions less the average intensity of the $(MW + 1)^+$ ions found in the substituted cycloalkanes. The actual values used are, for cyclopentane calculations, $I_{RU} = 0.451 + 0.235 - 0.036 = 0.677$ and, for cyclohexane calculations, $I_{RU} = 0.743 + 0.086 - 0.011 = 0.818$.

The $(MW - 1)^+$ intensities calculated in this way are given in Table III along with the experimental values for comparison. The over-all agreement seems to us to be good enough to provide support for the postulates on which the calculations are based, namely, the random attack localized reaction concept. Thus we may say that this postulate (plus the concept of β fission) constitutes a correlation for the $(MW - 1)^+$ ion intensities for normal paraffins, isoparaffins, and cycloparaffins. For the alkylcycloalkanes, the calculation seems to work best for the monoalkylcycloalkanes where the alkyl side chain is relatively long, that is, propyl or larger. This is probably to be expected, for chemical ionization occurring far out on the alkyl side chain would not be expected to influence reactions occurring on the cycloalkyl ring, and conversely. It is gratifying that intensity differences between *n*-propyl- and isopropylcycloalkanes and between *n*-, iso-, and *t*-butylcycloalkanes are accurately reflected by the calculated values.

$(MW - 15)^+$ Ions. Turning now to the intensities of $(MW - 15)^+$ ions, it may be observed from Table I that methyl loss processes in effect do not occur for the unsubstituted cycloalkanes and bicycloalkanes. In view of the molecular structures, this finding will surprise no one. By contrast, in the alkylcycloalkanes the formation of ions by loss of methyl groups is an important process. The reaction is strongly exothermic, and we write as a typical example



$\Delta H \simeq -39$ kcal/mole (4)

Relative ion intensities[b]																
C_9		C_{10}		C_{11}		C_{12}		C_{13}		C_{14}		C_{16}		C_{16}		MW^+
125	127	139	141	153	155	167	169	181	183	195	197	209	211	223	225	
								Cyclopentanes								
																0.004
																0.029
																0.018
																0.002
0.476	0.031															
0.040	0.019	0.028	0.012	0.017	0.008	0.006	0.004	0.003	0.008	0.009		0.408	0.040			
																0.008
								Cyclohexanes								
																0.021
																0.020
0.530	0.011															0.017
0.471	0.012															0.014
0.040		0.503	0.011													0.010
0.108		0.448	0.011													0.009
0.157	0.002	0.270	0.010													
0.033	0.012	0.025	0.010	0.018	0.005	0.010	0.003	0.007	0.002	0.006		0.018		0.430	0.013	
																0.003
0.578	0.007															
								Other Cycloalkanes								
																0.014
																0.012
								Bicycloalkanes								
123	125	137	139	151	153	165	167									
																0.033
0.558	0.088															0.022
0.001		0.704	0.041													0.026
0.007						0.713	0.033									

= cycloheptane; CyC_8 = cyclooctane.

The energetics of this reaction were calculated estimating the heat of formation of the cyclohexyl ion using Franklin's method of group equivalents,[7] but with no inclusion of any strain energy in the ion. Thus the exothermicity given constitutes an upper limit. The $(MW - 15)^+$ intensities for the alkylcycloalkanes are listed in Table IV, and the third column gives the $(MW - 15)^+$ intensity per CH_3 group present in the molecule. From the second column, one immediately sees that the intensity depends upon the number of methyl groups present, and consequently for di- and trimethyl-substituted molecules the $(MW - 15)^+$ ions comprise significant portions of the chemical ionization mass spectra. From the third column one sees that for compounds with methyl groups attached directly to the cycloalkane ring the intensity per methyl group shows very little variation from one compound to another. Thus, for five compounds the values range from 0.081 to 0.092, and the highest value observed is 0.125. For the monosubstituted cycloalkanes the intensity per CH_3 group decreases as the size of the side chain increases. The decrease is not strictly monotonic, for the values for both isopropylcyclopentane and isopropylcyclohexane tend to be relatively high; but the trend undoubtedly exists. We showed previously[4] that in the paraffins the $(MW - 15)^+$ intensities are on the order of a few per cent for the normal compounds and appreciably higher for the branched compounds. In n-$C_{18}H_{38}$, for example, the intensity of $(MW - 15)^+$ is 0.032, which corresponds to a value of 0.016 per CH_3 group. This is quite comparable with the values observed in n-decylcyclopentane and n-decylcyclohexane, and it is obvious that the decreasing trend observed in the $(MW - 15)^+$ intensities as the length of the chain increases is merely a reflection of the fact that the methyl group is behaving more like a methyl group in an aliphatic molecule. This behavior is to be expected on the basis of the random attack isolated reaction hypothesis of chemical ionization, and similarly the constancy of the intensity per methyl group for the methylated cycloalkanes indicates a lack of interaction between groups, which is also compatible with the hypothesis. The intensities of the ions formed by methyl loss do not exhibit a significant dependence upon whether the ion formed is primary, secondary, or tertiary, and this is probably the consequence of the fact that the formations of all three types of ions are quite exothermic.

Ions with Lower *m/e* Values. A further inspection of Table I does not reveal any other general relationships between $C_nH_{2n\pm1}$ ionic intensities and molecular structure. The spectra do not reflect the presence of alkyl groups larger than methyl; that is, $(MW - 29)^+$ corresponding to loss of ethyl, $(MW - 43)^+$ for loss of propyl, etc., are not particularly pronounced in molecules containing these groups. The cycloalkyl groups

Table II. $(MW \pm 1)^+$ Intensities

Compound		Relative intensity	
No.	Name	$(MW + 1)^+$	$(MW - 1)^+$
	Unsubstituted Monocyclics		
1	Cyclopentane	0.235	0.451
11	Cyclohexane	0.086	0.743
22	Cycloheptane	0.001	0.725
23	Cyclooctane	0.006	0.573
	Unsubstituted Bicyclics		
24	Bicyclo[2.2.2]octane	0.147	0.550
25	*trans*-Hydrindan	0.088	0.558
26	*trans*-Decalin	0.041	0.704
27	Cyclohexylcyclohexane	0.033	0.713
	Alkylcyclopentanes		
2	Methylcyclopentane	0.120	0.418
3	Ethylcyclopentane	0.015	0.402
4	*n*-Propylcyclopentane	0.025	0.534
5	Isopropylcyclopentane	0.020	0.425
6	*n*-Butylcyclopentane	0.031	0.476
7	*n*-Decylcyclopentane	0.040	0.408
8	*trans*-1,2-Dimethylcyclopentane	0.033	0.483
9	1-Methyl-1-ethylcyclopentane	0.023	0.472
10	1,1,3-Trimethylcyclopentane	0.018	0.448
	Alkylcyclohexanes		
12	Methylcyclohexane	0.012	0.607
13	Ethylcyclohexane	0.008	0.720
14	*n*-Propylcyclohexane	0.011	0.530
15	Isopropylcyclohexane	0.012	0.471
16	*n*-Butylcyclohexane	0.011	0.503
17	Isobutylcyclohexane	0.011	0.448
18	*t*-Butylcyclohexane	0.010	0.270
19	*n*-Decylcyclohexane	0.013	0.430
20	*trans*-1,2-Dimethylcyclohexane	0.010	0.664
21	1,1,3-Trimethylcyclohexane	0.007	0.578

Table III. Calculated and Experimental $(MW - 1)^+$ Intensities

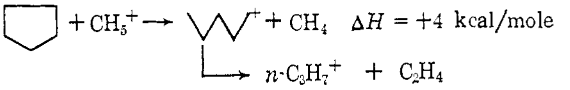
Substituent	Calcd	Exptl	Δ, %
	Cyclopentanes		
Me	0.51	0.42	21
Et	0.48	0.40	17
1,2-Me_2	0.39	0.48	19
n-Pr	0.47	0.53	11
i-Pr	0.41	0.43	5
1-Me-1-Et	0.46	0.47	2
1,1,3-Me_3	0.30	0.45	33
n-Bu	0.45	0.48	6
n-C_{10}	0.40	0.41	2
		Average	13
	Cyclohexanes		
Me	0.64	0.61	5
Et	0.60	0.72	17
1,2-Me_2	0.50	0.66	24
n-Pr	0.57	0.53	8
i-Pr	0.52	0.47	11
1,1,3-Me_3	0.41	0.58	28
n-Bu	0.55	0.50	10
i-Bu	0.52	0.45	16
t-Bu	0.29	0.27	7
n-C_{10}	0.46	0.43	7
		Average	13

Table IV. $(MW - 15)^+$ Intensities

Substituent	I_{MW-15}	I/N_{CH_3}	Type ion
	Cyclopentanes		
Me	0.117	0.117	Secondary
Et	0.101	0.101	Primary
n-Pr	0.050	0.050	Primary
i-Pr	0.170	0.085	Secondary
n-Bu	0.037	0.037	Primary
n-C_{10}	0.009	0.009	Primary
1,2-Me_2	0.165	0.083	Secondary
1-Me,1-Et	0.161	0.081	Primary + secondary
1,1,3-Me_3	0.246	0.082	Secondary + tertiary
	Cyclohexanes		
Me	0.125	0.125	Secondary
Et	0.062	0.062	Primary
n-Pr	0.053	0.053	Primary
i-Pr	0.145	0.073	Secondary
n-Bu	0.040	0.040	Primary
i-Bu	0.108	0.054	Secondary
t-Bu	0.157	0.052	Tertiary
n-C_{10}	0.018	0.018	Primary
1,2-Me_2	0.184	0.092	Tertiary
1,1,3-Me_3	0.277	0.092	Secondary + tertiary

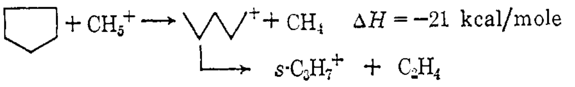
exhibit only a mild tendency to maintain their structural integrity; thus the ions formed by removal of alkyl side chains (*m/e* 69 for monosubstituted cyclopentanes and *m/e* 83 for monoalkyl-substituted cyclohexanes) are at best moderately intense, and, in addition, ions with *m/e* values less than 69 and 83 are oftentimes found in substituted and unsubstituted cyclopentane and cyclohexane, respectively.

Few mechanisms can be advanced at present for the formation of most of the ions appreciably smaller than MW in the several spectra, and a rather marked lack of consistency is sometimes observed in the spectra of compounds of similar structure. For example, if one considers the homologous series of compounds between cyclopentane and cyclooctane, cyclopentane forms an intense ion at *m/e* 43, but cyclohexane produces only a rather weak ion at *m/e* 43 and no other intense small fragment ion. By contrast, cycloheptane forms moderately intense ions at *m/e* 57 and 71 and a weaker ion at *m/e* 69. The cause of this behavior is quite unknown. The formation of these alkyl ions from the cycloalkanes presents somewhat of an energetic problem. For the formation of *m/e* 43 from cyclopentane, the mechanism producing the ion without rearrangement is



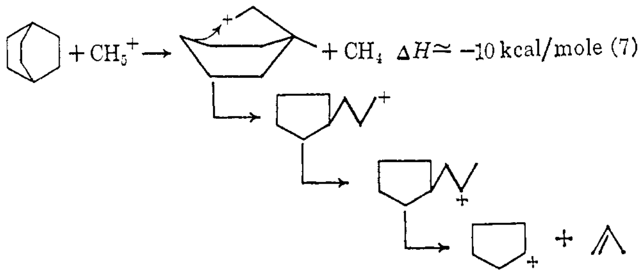
(5)

For the formation of the alkyl ions from cyclohexane, cycloheptane, and cyclooctane, the endothermicities of the reactions are somewhat greater, *i.e.*, about 8 kcal/mole. The endothermicity in reaction 5 is small enough that the occurrence of the reaction cannot definitely be excluded on energetic grounds, but the possibility of exclusion becomes somewhat stronger in the more endothermic reactions of cycloheptane and cyclooctane. If rearrangement to branched alkyl ions is allowed, the reactions become quite strongly exothermic. Thus



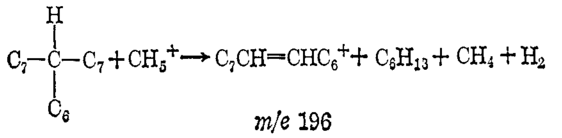
(6)

Some of the bicycloalkanes produce fairly intense ions which can be formed only by rearrangement or a process involving the breaking of three bonds. Thus one observes an intensity of 15% at *m/e* 69 in bicyclo[2.2.2]-octane, and an intensity of 12% at the same mass number in hydrindan. We cannot calculate the energies involved in the triple bond-breaking process, but we estimate that they will be quite unfavorable. The formation of the observed ions by rearrangement processes seems much more reasonable, and one can even present a guess as to possible rearrangement processes. Thus for formation of *m/e* 69 for bicyclo[2.2.2]octane, the mechanism shown in eq 7 is presented. The heat of reaction is calculated estimating about 5 kcal/mole strain energy in the cyclopentyl ion. Somewhat similar reactions can be written for the formation of *m/e* 69 and 83 from hydrindan and of *m/e* 83 from decalin. However, the relative intensities of these ions cannot be explained in terms of the mechanisms which can be advanced. In our previous work with the aliphatic branched paraffins we observed the formation of ions which could not be obtained from the parent molecules by straightforward bond-breaking processes, and the conclusion to be drawn from that work and from this is that rearrangement is probably involved (and possibly extensively involved) in the formation of ions of mass appreciably smaller than MW.



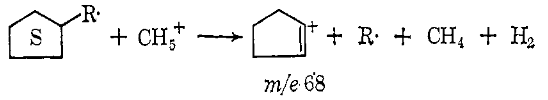
Ions with *m/e* 68 and 82. Ions with one or the other of these masses are observed in the spectra of almost all of the substituted cycloalkanes wherein at least one of the substituents on the ring is larger than methyl (see Table I). Three exceptions to this general behavior are observed: (1) cyclopentane has an intensity of 0.005 at *m/e* 68, (2) *n*-butylcyclopentane has ions at neither *m/e* 68 nor 82, and (3) *n*-decylcyclopentane exhibits ions at both *m/e* 68 and 82. For compounds for which these ions are formed, the intensities vary from 0.002 to 0.030 of the total ionization, and the intensities are generally higher for the substituted cyclohexanes than for the substituted cyclopentanes. The substituted cyclohexanes uniformly produce ions with *m/e* 82, but the substituted cyclopentanes produce ions with *m/e* 68 except for *n*-decylcyclopentane mentioned above and 1-methyl-1-ethylcyclopentane.

m/e values of 68 and 82 correspond to cyclopentene and cyclohexene ions, and the appearance of these olefin ions is reminiscent of the behavior of branched alkanes observed in previous studies.[4] There we found that the presence in the molecule of a branch larger than methyl gave rise to the formation of an olefin ion corresponding to the removal of the branch, for example

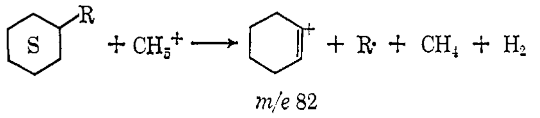


$$C_7\text{—}\underset{C_6}{\overset{H}{C}}\text{—}C_7 + CH_5^+ \rightarrow \underset{m/e\ 196}{C_7CH{=}CHC_6^+} + C_6H_{13} + CH_4 + H_2 \quad (8)$$

In the cycloalkanes studied in the present work, the branch to be removed is the substituent on the cycloalkyl ring, and thus we write

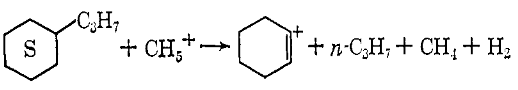


(9a)



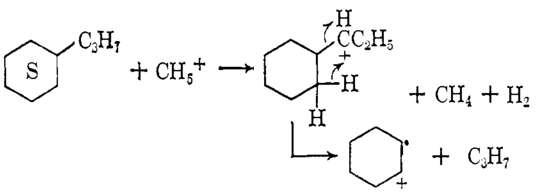
(9b)

where R must be larger than CH_3. We pointed out[4] that for branched aliphatic paraffins these reactions are strongly endothermic and run unexplainedly counter to the general proscription on endothermic ion–molecule reactions. The reactions in the cycloalkanes are similarly endothermic; for example



$\Delta H = +21$ kcal/mole (10)

We can write an electronic mechanism for reaction 10 analogous to that written for reactions such as (8), *i.e.*



(11)

We do not understand why these reactions occur in the face of the strong endothermicities, but it begins to seem that they are a general characteristic of the chemical ionization reactions of branched saturated hydrocarbons. Reactions 9a and 9b are particularly valuable in that they provide structural information about the size of the cycloalkane ring. In the case of polysubstituted cycloalkane rings, the olefin ion formed will be substituted and the information obtained will relate to the size of the ring plus substituents (other than the one removed). Thus we see in Table I that the olefin ion formed in 1-methyl-1-ethylcyclopentane has *m/e* 82, which probably corresponds to methylcyclopentene ion.

We have no explanation for the apparent lack of olefin ion formation in *n*-butylcyclopentane and for the formation of two olefin ions in *n*-decylcyclopentane. In spite of these uncertainties, we believe that the formation of olefin ions will be of practical use in chemical ionization mass spectrometry.

Studies Using cyclo-C_6D_{12}. The most powerful technique developed for identifying the reactions by which ions in mass spectra are produced is the isotopic tracer technique using deuterated compounds. In view of the many mechanistic problems which await solution in chemical ionization mass spectrometry, the application of the deuterium-isotope technique to chemical ionization mass spectrometry is much to be desired. However, two basic problems exist which do not exist in electron-impact ionization mass spectrometry, and these must be investigated before the isotope technique can be utilized. In electron-impact ionization mass spectrometry, the ions are formed and collected in a completely isolated environment, and the distribution of isotopic atoms present in the original molecule among the several fragment ions formed can occur only as a result of unimolecular reactions of the molecule ions. In chemical ionization mass spectrometry, on the other hand, this ionic isolation does not exist at all. In the first place, the ions are produced by interaction with reactant ions, which in general will have a different isotopic distribution from that in the compound of interest. If extensive exchange occurs in the chemical ionization process, determination of consequent reactions by isotope distribution determinations will be effectively precluded. In the second place, an ion once formed by chemical ionization is not isolated, for in general it will undergo a number of collisions with reactant gas molecules before it passes out of the ionization chamber. The occurrence of isotopic exchange during these collisions would also seriously interfere with mechanism determinations.

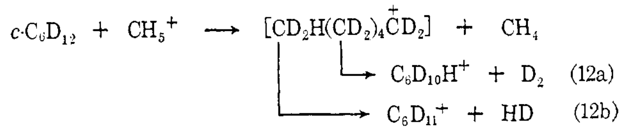
As our first contribution to this problem, we have investigated the chemical ionization of perdeuterated cyclohexane, cyclo-C_6D_{12}, using methane as the reactant gas, and the results are given in Table V. The relative intensities of the several types of ions formed from cyclo-C_6D_{12} agree with the intensities of the corresponding ions from cyclo-C_6H_{12}. The intensity observed at *m/e* 95 corresponds exactly to the C^{13} contribution from the large $C_6D_{11}^+$ intensity at *m/e* 94. The presence of an ion with intensity 0.045 at *m/e* 93 could result from isotopic exchange with methane ions during the chemical ionization process, from the presence of $C_6D_{11}H$ impurity in the deuterated cyclohexane, or from exchange reactions of the $C_6D_{11}^+$ ions with methane. Consequently the electron-impact mass spectrum of the cyclo-C_6D_{12} was obtained using the Esso chemical physics mass spectrometer in the electron-impact mode of operation and also in a CEC Model 21-103 mass spectrometer. Ions at *m/e* 95 were observed indicating the presence of $C_6D_{11}H$. The intensities of *m/e* 95 and 96 were used to obtain a quantitative determination of the amount of $C_6D_{11}H$, and values of 7.9 and 5.7% were obtained from the measurements on the chemical physics mass spectrometer and the CEC mass spectrometer, respectively. The ion at *m/e* 93 in the chemical ionization mass spectrum can be taken as a measure of the amount of cyclo-$C_6D_{11}H$, and from this value and the intensity of *m/e* 94 one calculates that the concentration of cyclo-$C_6D_{11}H$ in the deuterated cyclohexane is 7.0%. The agreement with the electron-impact values, particularly the chemical physics mass spectrometer value, is satisfactory, and we conclude that a zero or negligible amount of exchange is involved in the formation of the observed $C_6D_{10}H^+$ ion.

Table V. Relative Intensities for cyclo-C_6D_{12} and cyclo-C_6H_{12}

cyclo-C_6D_{12}				cyclo-C_6H_{12}		
m/e	Ion	I_{rel}		I_{rel}	Ion	*m/e*
46	$C_3D_3H_4^+$	0.002	0.057	0.064	$C_3H_7^+$	43
47	$C_3D_4H_3^+$	0.001				
49	$C_3D_6H^+$	0.028				
50	$C_3D_7^+$	0.026				
62	$C_4D_5H_4^+$	0.001	0.022	0.016	$C_4H_9^+$	57
64	$C_4D_7H_2^+$	0.005				
65	$C_4D_8H^+$	0.012				
66	$C_4D_9^+$	0.004				
93	$C_6D_{10}H^+$	0.045				
94	$C_6D_{11}^+$	0.667		0.743	$C_6H_{11}^+$	83
95	$C^{12}{}_5C^{13}D_{11}^+$	0.043				
96	$C_6D_{12}^+ + C_6D_{11}H_2^+$	0.036		0.021	$C_6H_{12}^+$	84
97	$C_6D_{12}H^+$	0.103		0.083	$C_6H_{13}^+$	85
98	$C^{12}{}_5C^{13}D_{12}H^+$	0.008				

From the concentration of $C_6D_{11}H$ present, one calculates that the intensity of $C_6D_{11}H_2^+$ (*m/e* 96) is 0.007 of the total ionization, which means that the intensity of $C_6D_{12}^+$ is 0.029. This is quite comparable with the molecule-ion formation in cyclo-C_6H_{12}, 0.021, and indicates that no significant amount of exchange is occurring in the formation of the ions at *m/e* 96. The intensity of $C_6D_{12}H^+$ (*m/e* 97) is somewhat greater than is observed in cyclo-C_6H_{12}, and this indicates that no loss of protonated cyclo-C_6D_{12} is occurring by exchange processes. The intensity of *m/e* 98 results completely from C^{13} contribution from the ions at *m/e* 97. Thus, the results in the molecular weight region for deuterated cyclohexane are that no exchange occurs in the chemical ionization process or in the subsequent travels of the ions out of the ionization chamber.

The fact that no isotopically mixed analogs of $C_6D_{11}^+$ (*m/e* 94) are observed is of significance. In particular, within the limits of our experimental accuracy, no $C_6D_{10}H^+$ ions other than those from the cyclo-$C_6D_{11}H$ impurity are observed. The $C_6D_{11}^+$ ion (*m/e* 94) could be either a cyclohexyl ion formed by abstraction of a deuteride ion from the parent molecule, or alternatively it could be an open-chain alkenyl ion formed by protonation followed by ring opening and loss of a hydrogen molecule. However, the most probable path for this reaction is



$$\begin{array}{l} c\text{-}C_6D_{12} + CH_5^+ \longrightarrow [CD_2H(CD_2)_4\overset{+}{C}D_2] + CH_4 \\ \qquad\qquad\qquad\qquad \longrightarrow C_6D_{10}H^+ + D_2 \quad (12a) \\ \qquad\qquad\qquad\qquad \longrightarrow C_6D_{11}^+ + HD \quad (12b) \end{array}$$

and the fact that no $C_6D_{10}H^+$ is observed requires one to accept the quite incredible fact that reaction 12b occurs to the complete exclusion of 12a. One can show that the formation of ion $CD_2{=}CD(CD_2)_3C^+D_2$ is 17 kcal/mole endothermic, and the postulate of the formation of an open-chain ion becomes very dubious. These results lead us to the conclusion that the $C_6D_{11}^+$ ions have the cyclohexyl structure and are doubtlessly formed by the deuteride ion abstraction process. Deuteride ion abstraction by the $C_2H_5^+$ and $C_3H_5^+$ components of the methane plasma is easy enough to understand, but, in addition, the results suggest that CH_5^+ must also effect a deuteride ion abstraction. We mentioned earlier that the $(MW - 1)^+$ intensity in cyclo-C_6H_{12} is appreciably higher than would be expected by a straightforward analogy with aliphatic paraffin behavior. In addition, CH_5^+ comprises approximately half the ions in the methane plasma, but the cyclohexane ions other than $(MW - 1)^+$ ions amount to only about 30% of the total cyclohexane ionization, and thus either CH_5^+ ions are not reacting completely, or else the CH_5^+ ions are somehow forming cyclohexyl ions. The ionization sensitivity of cyclohexane is not particularly low, and we do not believe that the reaction cross-section for CH_5^+ with cyclohexane is abnormally low. Consequently, we believe that CH_5^+ is producing cyclohexyl ions. Two indistinguishable and essentially equivalent mechanisms can be thought to operate. One can think that CH_5^+ acts as a Brønsted acid and donates a proton, but with the restriction that the donated proton invariably reacts with a hydrogen atom of the cyclohexane to produce a cyclohexyl ion. Alternatively, CH_5^+ can be thought of as a Lewis acid which abstracts a hydride ion and dissociates to $H_2 + CH_4$ in the process. In summary, it would appear that if CH_5^+ donates a proton it does not become at all equivalent to the other hydrogens in the cyclohexane molecule, or, alternatively, H^- is abstracted without proton donation.

The results for the small fragment ions from cyclo-C_6D_{12} are given in Table VI. The relative intensities have been corrected for the impurity cyclo-$C_6D_{11}H$, and the values given in the last column are the relative amounts of the several isotopic distributions within each type of fragment ion observed, *i.e.*, propyl or butyl. The amounts of propyl and butyl ions formed from cyclohexane are small, particularly the butyl ion, and the amounts of the individual ions observed at some of the *m/e* values are very small. The presence of propyl ions at *m/e* 46 and 47 and of butyl ions at *m/e* 62 and 64 shows that some multiple exchange of protium and deuterium occurs either in the formation of these fragment ions or, much less likely in our opinion, in subsequent collisions with methane molecules. However, the intensities of these ions are small, and the uncertainties large enough so that discussion is not warranted.

Table VI. Fragment Ions from cyclo-C_6D_{12}

m/e	Formula	I_{rel}	% of ion group
	Propyl Ions		
46	$C_3D_3H_4^+$	0.002	3.5
47	$C_3D_4H_3^+$	0.001	1.8
49	$C_3D_6H^+$	0.027	47.3
50	$C_3D_7^+$	0.027	47.3
	Total	0.057	
	Butyl Ions		
62	$C_4D_5H_4^+$	0.001	4.5
64	$C_4D_7H_2^+$	0.005	22.7
65	$C_4D_8H^+$	0.012	54.7
66	$C_4H_9^+$	0.004	18.2
	Total	0.022	

It is of interest that the $C_3D_6H^+$ and $C_3D_7^+$ (*m/e* 49 and 50, respectively) are formed with equal intensities. One can be almost certain that propyl ions are formed in a sequence starting with protonation of the cyclohexane and passing through open-chain hexyl ions as intermediates. The *n*-hexyl ion which presumably is the first product of the ring-opening proton attack would initially have to have the added proton and the charge center at opposite ends of the molecule. The equal intensities of $C_3D_6H^+$ and $C_3D_7^+$ observed experimentally require that in the hexyl ions which decompose to give the propyl ions the added protium and the charge center must be in the same half of the ion for half the time. Since the protium and the charge center start their existence at opposite ends of the hexyl ions, the results indicate that extensive rearrangement of the ion and migration of the charge center occur before the ion decomposes into smaller fragments. Somewhat the same conclusion can be drawn from the butyl ions in that both $C_4D_8H^+$ and $C_4D_9^+$ are observed, but the matter is beclouded by the fact that these ions are not observed in equal intensity and, further, an appreciable amount of an ion involving greater protium exchange ($C_4D_7H_2^+$, *m/e* 64) is observed.

Our conclusions based on the deuterated fragment ions from cyclo-C_6D_{12} must be looked upon as being tentative, but we are of the opinion that chemical ionization of cyclohexane involves the following features. The $(MW - 1)^+$ ion is formed by a hydride ion abstraction process wherein the reactant ions are $C_2H_5^+$ and, to a lesser extent, CH_5^+. In addition, the CH_5^+ ions can act as a Brønsted acid transferring a proton to the cyclohexane. A fraction of the protonated C_6H_{12} exists long enough to be collected as such in the mass spectrometer, and the remainder decomposes by carbon–carbon bond fission to give smaller fragment ions. Extensive rearrangements can occur during the lifetime of the protonated C_6H_{12}. This conclusion is in keeping with the finding discussed earlier that fragment ions are observed in the spectra of certain cycloalkanes (and also paraffins) which cannot be formed by simple bond fission processes. It should be mentioned that this postulate of rearrangement and perhaps even a considerable mobility of molecular structure in the formation of smaller fragment ions is not necessarily in conflict with our postulate that chemical ionization of saturated hydrocarbons involves a random attack and localized reaction process. It is merely necessary that the localized reaction be thought of as applying solely to the initial reaction of the attacking ion.

Our experimental result that negligible isotopic mixing occurs in the formation of $C_6D_{11}^+$ ion and the conclusions based thereon are in accord with most of the findings of other workers. Aquilanti and Volpi[8] find that in the reaction of D_3^+ with C_3H_8, *i*-C_4H_{10}, and *n*-C_4H_{10}, the percentage of propyl or butyl ions retaining the deuterium atom ranges from 5 to 20%; that is, a very marked tendency to lose the D entity originally transferred from D_3^+ exists. These workers caution that hydride ion transfer by D_3^+ must always be considered as a possibility in the formation of $(MW - 1)^+$ ions (or $(MW - 2)^+$ in deuterated hydrocarbons), and our suggestion concerning the possibility that CH_5^+ acts as a Lewis acid is in keeping with this. On the other hand, Aquilanti and Volpi find that $C_2H_5^+$ and $C_2H_4D^+$ are formed with equal probabilities from $C_2H_6D^+$, and this behavior is also found by von Koch.[9] The hydrogens in the protonated ethane are considered to be equivalent. von Koch[10] also postulates that the hydrogens in CH_5^+ are equivalent, and it is possible that the properties of protonated methane and ethane are different from those of protonated higher paraffin hydrocarbons. Pettersson and Lindholm[11] report a contrary conclusion concerning propane; namely, in $C_3H_9^+$ all the hydrogens are equivalent. However,

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[8] V. Aquilanti and G. G. Volpi, *J. Chem. Phys.*, **44**, 2307 (1966).
[9] H. von Koch, *Arkiv Fysik*, **28**, 559 (1965).
[10] H. von Koch, *ibid.*, **28**, 529 (1965).
[11] E. Pettersson and E. Lindholm, *ibid.*, **24**, 49 (1963).

the data reported by Pettersson and Lindholm do not seem to us to warrant this conclusion. Haynes and Kebarle[12] find that the propyl ions formed by the reaction of methane reactant ions with C_3D_8 comprise the ion $C_3D_7^+$ and $C_3D_6H^+$ in relative amounts of 20:1. Roughly half the propyl ions are formed by deuteride ion abstraction reactions with $C_2H_5^+$ from methane, and thus decomposition of the $C_3D_8H^+$ ion formed by proton transfer from CH_5^+ produced $C_3D_7^+$ and $C_3D_6H^+$ ions roughly in the ratio of 10:1. One concludes that the transferred proton does not become equivalent to the other hydrogens in the propane.[13] In our opinion, the weight of evidence so far available is that with the possible exception of methane and ethane, hydrogen molecules ejected from a protonated saturated hydrocarbon contain a large fraction of the hydrogen entity initially transferred to the hydrocarbon.

Analytical Considerations. We have pointed out above that the alkylcycloalkanes produce ions in both the $C_nH_{2n+1}^+$ and $C_nH_{2n-1}^+$ series. We showed earlier[3] that aliphatic hydrocarbons produce only $C_nH_{2n+1}^+$ ions, and thus in the analysis of a mixture of aliphatic and cycloalkanes some interference may be expected. Fortunately for almost all practical purposes the interference will be small and can be neglected or approximate corrections can be applied. While an inspection of Table I reveals that some cycloalkanes produce alkyl ions with appreciable intensities, these ions invariably contain only three to five carbon atoms. Since analyses using methane reactant chemical ionization mass spectrometry will surely be restricted to relatively large molecules, alkyl ions containing three to five carbon atoms will not constitute restrictive interferences. The average intensity for $C_nH_{2n+1}^+$ with $m/e > 85$ is 0.0089, which comprises contributions from $(MW + 1)^+$ ions (average intensity = 0.026 for alkylcyclopentanes other than cyclopentane and methylcyclopentane and average intensity = 0.011 for alkylcyclohexanes other than cyclohexane) and alkyl ions with $m/e < MW + 1$ (average intensity 0.009). Thus meaningful interferences would be encountered only in the unlikely case of an analysis of trace amounts of aliphatic paraffins in cycloparaffins.

Acknowledgment. We wish to acknowledge with gratitude the assistance in obtaining the data given us by Mr. W. C. Gieger of the Baytown Laboratory and Mr. F. C. Petronis of the Linden Laboratory.

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[12] R. M. Haynes and P. Kebarle, *J. Chem. Phys.*, **45**, 3899 (1965).

[13] Haynes and Kebarle[12] state the opposite conclusion, but Professor Kebarle has informed us that this statement constitutes an inadvertent error.

Crystal Structure of 2,2-Diphenyl-1-picrylhydrazyl Free Radical[1]

Donald E. Williams

Contribution from the Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa 50010. *Received February 24, 1967*

Abstract: The crystal structure of the stable free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) has been determined from three-dimensional X-ray diffraction data. The molecular configuration around the second nitrogen is approximately trigonal planar with the phenyl groups twisted at angles of 49 and 22°. The bond at the digonal nitrogen is bent with a C–N–N angle of 118.5° and the attached picryl carbon is twisted 28.5° out of the plane of the trigonal hydrazine nitrogen. The nonplanarity of the hydrazyl backbone was not predicted from analyses of electron paramagnetic resonance measurements. The picryl ring plane is further inclined at an angle of 33° to the plane of the digonal nitrogen. The *o*-nitro groups are twisted out of the picryl ring plane by 25 and 55° while the *p*-nitro group is twisted by 13°. The stabilizing effect of the nitro groups on the radical is discussed. The hydrazyl N–N bond distance is 1.334 A, intermediate between expected values for single and double bonds. The benzene molecules of solvation are separated by normal van der Waals distances from the DPPH molecules; distances between DPPH molecules also are normal van der Waals contacts.

The stable free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) has been widely used as a homogeneous raddical detector[2a] and as a calibration standard for electron paramagnetic resonance (epr) spectrometers.[2b] The epr hyperfine splitting caused by the magnetic moments of the two hydrazyl nitrogen nuclei has been extensively studied and interpreted in terms of spin densities.[3] A very high resolution epr spectrum revealed additional hyperfine splittings which can be ascribed to the phenyl protons and/or nitro nitrogens.[4] Several proton magnetic resonance (pmr) investigations[5] have also shown the existence of spin density at the protons, and the Overhauser effect has been observed[6] with this substance.

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[1] This work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2047.

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