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THE REACTIONS OF H AND D ATOMS WITH CYCLIC AND PARAFFIN HYDROCARBONS¹

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Abstract

The reactions of H and D atoms, produced by the discharge method, with benzene, four cycloalkanes, and the corresponding normal paraffins have been investigated at room temperature. Methane is the major product of each reaction. Collision yields have been calculated on the basis of hydrocarbon disappearance and exchange. Of the cycloalkanes, cyclopropane is the most inert with cyclopentane the most reactive. Cyclopropane and cyclobutane do not exchange with D atoms but benzene, cyclopentane, and cyclohexane undergo considerable exchange. In the case of the normal paraffins the degree of exchange increases with increasing molecular weight.

It is concluded that the initial reaction

is responsible for the products formed in the reactions but other primary processes may be responsible for the exchange of these hydrocarbons.

The discharge method of producing H atoms has been widely used to study the primary processes in reactions of H atoms with hydrocarbons. The consensus of opinion at present is that H atoms react with paraffins by hydrogen abstraction to produce hydrocarbon radicals which then undergo rapid "atomic cracking" reactions. This belief is largely based on the appearance of methane as the major product in all such reactions. It seemed of some interest therefore to investigate the reaction of H atoms with benzene and with some of the cycloalkanes.

Materials

Cylinder hydrogen was freed from oxygen by passage over copper wool at 300°C., and through two traps cooled in liquid nitrogen. About 0.6% nitrogen still remained as an impurity.

Deuterium was obtained under pressure by reacting 99.6% D₂O with specially purified calcium turnings at 260°C. in an autoclave; traces of NH₃ formed from the Ca₃N₂ present in the calcium were readily frozen out. Analysis showed the deuterium contained no H₂ and not more than 10% HD for which appropriate corrections were made in the calculations.

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Cyclopropane was obtained from the Ohio Chemical Company and was rated as 99.5% pure. It was freed from noncondensable gases and subjected to several trap-to-trap distillations, the middle 1/3 fraction being retained.

Cyclobutane was prepared from cyclobutanone by the method of Roberts and Sauer (9). The cyclobutanone was obtained from the reaction of diazomethane with ketene. The cyclobutane was tested for impurities by carefully fractionating a sample in a modified Ward still (10) and analyzing the fractions in the mass spectrometer. Cyclopentane, the largest impurity, was present to the extent of 0.6 mole %; lighter hydrocarbons amounted to less than 0.07 mole %. An infrared spectrum of the gas was found to agree well with published spectra except for the presence of an absorption maximum at 1810 cm^{-1} for which no explanation has as yet been found.

National Bureau of Standards standard samples of cyclopentane and cyclohexane were dried by passage over phosphorus pentoxide and used without further purification.

Carefully purified and freshly distilled benzene was provided for us by Dr. L. Marion of this laboratory and was thoroughly degassed and dried over phosphorus pentoxide before use.

The normal paraffins were Phillip's "Research Grade" materials rated as 99.88% pure. These were degassed and subjected to several trap-to-trap distillations prior to use.

Experimental Procedure

The discharge tube was of the familiar Wood-Bonhoeffer type described in previous communications from this laboratory (11, 15). The hydrogen pressure was reduced from atmospheric to about 0.35 mm., and its flow rate (58 cc. at N.T.P. per min.) was controlled by a capillary leak at the inlet end and a throttle at the pump end of the system; throttling at the pump end was found to be necessary in order to minimize pressure fluctuations. Atom concentrations were measured before and after each experiment at the top and bottom of the reaction tube by means of Wrede-Harteck gauges (5, 17) used in conjunction with a thermocouple type Pirani gauge which was frequently calibrated for hydrogen and deuterium. The average of these readings was considered to represent the average atom concentration obtaining during the experiment.

The flow rate of the hydrocarbon was controlled by maintaining a fixed vapor pressure in a side tube of known volume. The pressure of the gas at room temperature in this volume was measured before and after each experiment; the difference then gave a measure of the total amount of hydrocarbon used in the experiment, from which the flow rate could be calculated. The reactant gases were mixed at a distance of 20 cm. from the discharge and flowed together down a cylindrical reaction tube; hydrogen atoms leaving the tube recom-

bined on platinum gauze. From the flow rates of the gases, their partial pressures, and the volume of the reaction tube it was possible to calculate the average time spent by a molecule in the tube; this reaction time was of the order of 0.6 sec.

The condensable products were trapped out at liquid nitrogen temperature, their volume measured at room temperature, and their composition determined by separation in a Ward still followed by mass spectrometer analysis of the various fractions.

The noncondensable products passed through a "Leybold" diffusion pump and were adsorbed on silica gel at liquid nitrogen temperature. After an experiment the silica gel was maintained at liquid nitrogen temperature and opened to a "megavac" oil pump for 15 min. in order to desorb most of the hydrogen. "Davco" technical grade silica gel was found to be the most suitable material for this purpose since the use of a more "active" gel made the desorption exceedingly slow. The amounts of methane and ethane lost by this procedure were shown to be negligible by blank experiments made with known gas mixtures and by the excellent material balances obtained in all the experiments. The trap was then warmed to room temperature and the gas toeplered into a gas burette where its volume was measured. An aliquot was isolated in a sample bulb for subsequent mass spectrometer analysis. From the amount of hydrocarbon which had undergone reaction (subsequently referred to as the amount decomposed) and the reaction time it was possible to calculate the rate of the initial process.

There are several objections frequently raised against this method of calculating the rate of the initial reaction. First the concentration of H atoms decreases down the reaction tube as the reaction takes place; calculated corrections for this effect are complicated and generally inaccurate. However, the use of the mass spectrometer and other improved analytical procedures has made it possible to work with very small quantities of hydrocarbon gases. Consequently, we were able to reduce the flow rate of the hydrocarbon to less than 1/50th that of the H atoms, thereby greatly minimizing this source of error.

The practice of equating the rate of disappearance of the hydrocarbon to the rate of the primary step can also be criticized. A secondary reaction which could regenerate the hydrocarbon, such as the combination of an atom with the hydrocarbon radical would, of course, vitiate this procedure. This objection may be overcome by the use of deuterium in place of hydrogen; the amount of hydrocarbon which has been exchanged can then be determined by means of a mass spectrometer and added to the amount decomposed in order to calculate the true rate of the initial step. In order to interpret the mass spectra it was necessary to assume that the ion sensitivity (ion current per centimeter partial pressure) for the parent peak of a hydrocarbon does not change appreciably when the hydrocarbon is deuterated; evidence from work on methane

and ethane indicates that this assumption is reasonably valid. Corrections were made for the contributions to each parent peak from the cracking in the mass spectrometer of more deuterated hydrocarbon molecules, and for the C^{13} isotope. This involves the additional assumption that all the deuterated hydrocarbons have similar cracking patterns, but since these corrections were always small for the hydrocarbons investigated, this assumption does not introduce a serious error. It should be emphasized that the use of the mass spectrometer provides a much more positive and sensitive test for deuteration than any other method. The amount of each isotopic species of the compound can be measured independently and added together to give a true value of the percentage of the hydrocarbon which has undergone exchange, whereas the procedure of combusting the hydrocarbon and analyzing the resultant water gives only the over-all deuterium content of the sample. Further, there is no possibility of error arising from the presence of deuterium or deuterated reaction products in the sample.

Products of the Reactions

Methane was by far the most important product in the reactions of H and D atoms with all the hydrocarbons. Analysis of the methane produced in experiments with D atoms showed it to be over 80% CD_4 , with the remainder being mainly CD_3H .

Methane was found to be the only product of the reaction of H or D atoms with cyclopropane. This is neither in agreement with Gunning and Steacie (4), who found no evidence for reaction of cyclopropane with H atoms produced by mercury photosensitization, nor with Dingle and LeRoy (3) who found no reaction with H atoms produced by the thermal dissociation of H_2 . It was necessary, therefore, to investigate the reaction in detail to ensure that the methane in our experiments did not arise from any extraneous sources. Blank experiments, conducted in the absence of cyclopropane, produced some methane by the reaction of H atoms with the "apiezon" grease on the standard taper joints connecting the Wrede gauges and the hydrocarbon inlet tube with the reaction vessel. These joints were, therefore, eliminated from the apparatus and subsequent blank experiments produced no appreciable amounts of methane.

As previously mentioned, the hydrogen contained about 0.6% nitrogen which formed ammonia in the discharge tube. To eliminate any possible effect of this impurity one experiment was conducted by first passing the hydrogen through a long, thin glass helix immersed in liquid hydrogen. This was found to remove the nitrogen but had no effect on the amount of methane produced.

To ensure that no cyclopropane was diffusing back into the discharge the hydrocarbon inlet tube was bent away from the discharge and experiments were conducted over a considerable range of cyclopropane flow rates; in each case the amount of methane produced was the same percentage of the cyclopropane used.

It was later discovered that small methane peaks were present in the mass spectra of tank hydrogen even after the hydrogen had been purified by passage through a palladium tube. Presumably, the methane was formed in some way in the mass spectrometer itself. To correct this, a standard hydrogen sample was measured in the mass spectrometer before each analysis at a pressure equal to the partial hydrogen pressure in the sample to be analyzed. The height of the mass 16 peak obtained from the hydrogen spectrum was then taken as the residual peak height to be subtracted from the sample spectrum.

Finally, to test whether the methane was formed from any impurity present in the cyclopropane, unreacted cyclopropane was recovered from one experiment and used in a subsequent experiment; the percentage of methane formed was found to be the same in each case. We can safely conclude, therefore, that methane is a true product of the reaction of H atoms with cyclopropane under our experiment conditions. No deuterated cyclopropane was recovered from any of the deuterium experiments.

In the case of cyclobutane, methane was again the sole product of the reaction with H and D atoms, while no measurable amount of deuterated cyclobutane could be detected.

With cyclopentane and cyclohexane, methane accounted for over 90% of the reaction products, with small amounts of other light hydrocarbons also being formed. To illustrate the order of magnitude of these products, the results of the mass spectrometer analyses of the products of the H atom-cyclopentane reaction are reported in Table I. In the deuterium experiments considerable exchange was found to occur. It was found, however, that the ratio of the amount of hydrocarbon decomposed to the amount exchanged was not constant but increased with increasing D atom concentration.

The green fluorescence reported by Bonhoeffer and Harteck (1) for the reaction of H atoms with benzene was observed in several of our experiments. About 85% of the decomposed benzene appeared as methane, the other 15% being comprised of all the straight chain hydrocarbons containing six carbon

TABLE I
PRODUCTS OF THE H ATOM - CYCLOPENTANE REACTION

Cyclopentane flow, cc. per min. N.T.P.	H atom flow, cc. per min. N.T.P.	% Cyclopentane which reacted to form							Cyclo- pentane unreacted	Mass balance
		CH ₄	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂	C ₃ H ₈	C ₃ H ₆	C ₄ H ₁₀		
0.692	14.8	26.8	1.3	...	0.70	0.4	0.05	...	74.0	103
0.373	16.6	23.9	2.9	.05	0.68	1.4	0.3	...	74.0	103
0.508	13.3	14.3	0.4	...	0.29	0.7	0.15	.04	78.2	94
0.518	10.1	11.4	0.2	...	0.23	0.8	0.2	...	81.3	94
0.201	20.1	33.0	1.2	...	0.32	0.9	0.2	...	63.6	99
0.060	10.2	42.6	2.8	.02	1.09	1.5	0.3	.30	52.0	101
0.042	11.8	36.6	0.50	...	1.15	0.5	0.03	...	51.7	90
0.173	14.7	29.0	0.80	...	1.30	0.2	0.15	...	66.0	98

atoms or less. This is a good indication of the complexity of the secondary reactions involved; apparently once the hydrocarbon radical is formed, it undergoes rapid atomic cracking and hydrogenation reactions until the relatively inert methane molecule is formed. There was no evidence for the formation of any cyclohexane or cyclohexene, which might have been expected in the event of hydrogenation of the benzene without ring split. The benzene recovered after reaction with D atoms was found to have undergone exchange to a considerable extent.

Single experiments were made with each of the normal paraffins for comparison purposes. The reaction products were almost exclusively methane in each case. All the normal paraffins were found to be partially exchanged in the deuterium experiments.

Calculation and Discussion of Collision Yields

The collision yield can be defined as:

The rate of the primary process

The number of collisions per cc. per sec.

The numerator is determined experimentally; the denominator, the collision number, can be calculated from kinetic theory. The values for the collision diameters used in these calculations were obtained from viscosity data (13); 2.1 Å for H, 4.2 for C₃H₈, 4.8 for C₄H₁₀, 5.2 for C₅H₁₂, 5.8 for C₆H₁₄, 4.0 for cyclo-C₃H₆, 5.2 for cyclo-C₆H₁₂, and 5.0 for C₆H₆. Values of 4.4 and 4.8 Å were obtained by interpolation for cyclo-C₄H₈ and cyclo-C₅H₁₀ respectively. The details of the calculations of collision yields for the cycloalkanes are shown in Table II. The experiments marked D in column 1 of the table refer to deuterium experi-

TABLE II
CALCULATION OF COLLISION YIELDS FOR THE CYCLOALKANES

Hydrocarbon flow, cc. per min. at NTP	Atom flow, cc. per min. at NTP	Partial pressure of atoms, mm. Hg	Reaction time, sec.	Z in reaction time(a)	Per cent methane formed	Per cent other products(b)	Per cent exchange	Collision yield for reaction × 10 ⁷	Collision yield exchange × 10 ⁷
<i>Cyclopropane</i>									
.113	38.4	.175	.59	25.8 × 10 ⁹	2.50	<0.1		.097	
.430	12.9	.070	.67	11.3	0.50			.044	
.588	10.1	.056	.68	9.2	1.17			.127	
.225	9.5	.052	.68	8.4	0.90			.107	
1.092	12.1	.066	.68	11.0	1.32			.120	
.916	20.5	.105	.64	21.8	2.05			.094	
.244	45.1	.193	.58	27.0	1.16			.043	
.635	29.0	.133	.62	19.8	2.10			.106	
.660	18.9	.098	.65	15.3	2.03			.133	
.160	11.5	.063	.68	10.7	2.76			.258	
.269	14.3	.082	.65	12.9	1.45			.112	
.252	15.1	.092	.67	14.7	1.36			.092	
.406	14.3	.089	.70	14.9	1.36			.091	
.257	19.9	.109	.62	16.3	2.30			.141	
.050(D)	20.6	.140	.88	21.0	4.4	<0.1	0	.21	0
.046(D)	4.1	.035	.97	5.8	2.9		0	.50	0
.067(D)	20.0	.137	.90	16.3	5.8		0	.36	0
.104(D)	14.5	.105	.92	21.0	4.5		0	.21	0

TABLE III—Continued

Hydrocarbon flow, cc. per min. NTP	Atom flow, cc. per min. at NTP	Partial pressure of atoms, mm. Hg.	Reaction time, sec.	Z in reaction time ^(a)	Per cent methane formed	Per cent other products ^(b)	Per cent exchange	Collision yield for reaction $\times 10^7$	Collision yield exchange $\times 10^7$
<i>Cyclobutane</i>									
.267	16.1	.097	.67	17.9	13.4	>0.1		.75	
.253	13.5	.082	.67	15.1	12.8			.85	
.168	11.2	.068	.70	12.6	17.1			1.4	
.077	9.4	.059	.71	10.9	17.8			1.6	
.227	10.0	.065	.70	11.9	12.9			1.1	
.134	13.8	.082	.69	14.6	14.9			1.0	
.171(D)	10.0	.064	1.00	12.7	33.6	>0.1	0	2.6	0
.253(D)	9.2	.053	1.02	10.7	34.0		0	3.2	0
.043(D)	12.0	.073	.99	14.3	23.0		0	1.6	0
<i>Cyclopentane</i>									
.692	14.8	.049	.55	8.2	26.8	2.4			
.373	16.6	.059	.55	9.9	23.9	5.3			
.508	13.3	.041	.51	7.7	14.3	1.6			
.518	10.1	.031	.55	6.1	11.4	1.4			
.201	20.0	.066	.51	10.2	33.0	2.6			
.169	14.7	.052	.54	8.4	29.0	2.4			
.223(D)	8.30	.077	.82	14.0	47.8		26.4	3.4	1.9
.143(D)	8.30	.077	.82	14.0	55.9		34.0	4.0	2.4
.096(D)	3.87	.037	.86	7.1	41.4		35.7	5.9	5.1
.190(D)	5.46	.050	.83	9.3	33.1		41.7	3.6	4.4
.266(D)	3.75	.032	.87	6.2	24.0		51.0	3.9	8.3
.270(D)	3.36	.032	.85	6.1	24.0		50.2	3.9	8.3
.502(D)	Diffusion into Discharge								
.269(D)	1.91	.017	.79	3.8	18.6		43.8	4.9	11.6
.202(D)	2.49	.020	.77	3.7	26.0		41.8	7.0	11.2
.060(D)	1.91	.016	.82	2.6	17.4		54.2	6.2	20.9
.119(D)	3.20	.028	.77	4.8	32.0		46.0	6.7	9.5
.319(D)	1.47	.013	.77	2.1	11.8		40.7	5.6	19.4
.249(D)	1.40	.013	.77	2.1	12.4		37.5	5.9	17.5
.280(D)	1.75	.017	.75	2.8	16.9		40.2	6.0	14.4
<i>Cyclohexane</i>									
.381	14.0	.060	.43	9.9	11.6	1.5		1.3	
.376	14.5	.063	.43	10.5	8.9	1.1		1.0	
.390	9.3	.044	.45	7.6	5.8	0.5		0.82	
.079	5.5	.026	.46	4.6	8.7	1.0		1.80	
.092	6.4	.032	.47	5.7	10.4	0.5		1.90	
.101	4.7	.024	.46	4.3	6.5	0.4		1.61	
.108(D)	8.3	.056	.60	9.1	30.1		33.0	3.3	3.6

(a) The number of collisions of 1 hydrocarbon molecule with H or D atoms in the reaction time.

(b) In the deuterium experiments other products when determined are grouped together with the methane.

ments. The collision yields for all the hydrocarbons along with their mean deviations are shown in Table III. Column 2 of Table III gives the collision yields for the hydrogen experiments calculated from the rate of hydrocarbon disappearance. Column 4 gives the same data for the deuterium experiments,

while column 6 gives the collision yields for the exchange process; column 7 is the sum of columns 4 and 6. The average value for the percentage of hydrocarbon which has undergone exchange is given in column 6; this will, of course, depend upon the D atom concentration. Activation energies are given in column 3 for the H atom reactions and in column 8 for the D atom reactions; the latter were calculated from the combined collision yields for exchange and decomposition. In making these calculations a value of 0.1 has been chosen for the steric factor, in the expression

$$\text{collision yield} = A.e^{-E/RT}$$

since this has been the custom in the past in dealing with H atom reactions. However, a great deal of evidence is accumulating which indicates that many free radical reactions have very low steric factors (*ca.* 10^{-4}). There appears to be no way at present of deciding if steric factors are low for H atom reactions. If they also should prove to be very low then the activation energies reported may be greatly in error. However, this has no effect on any arguments concerning relative reactivity which are based on collision yields.

The reason for the uncertainty in the case of benzene becomes apparent when the stoichiometry of the reaction is considered. At least 18 H atoms are required to transform one molecule of benzene into methane. Since this reaction is rapid there is a serious depletion of H atoms even at the flow rates used in these experiments, which results in too low a value for the collision yield. (Robb and Melville (7) have recently reported a collision yield of 7×10^{-4} for this reaction calculated from the rate of hydrogen atom disappearance.)

It will be seen from Table III that cyclopropane is more inert than the other cycloalkanes, with cyclopentane being the most reactive. It is interesting to note that this is the same order of reactivity found by Trotman-Dickenson and Steacie (16) for the reactions of methyl radicals with the cycloalkanes. The inertness of cyclopropane may seem somewhat surprising although the rate

TABLE III
COLLISION YIELDS AND ACTIVATION ENERGIES

Hydrocarbon	H atoms		D atoms				
	Collision Yield $\times 10^7$	Activation energy, kcal.	Collision yield for reaction $\times 10^7$	Average % exchange	Collision yield for exchange $\times 10^7$	Total Collision yield $\times 10^7$	Activation energy, kcal.
Cyclopropane	$0.11 \pm .03$	9.5	$.34 \pm .11$	0	0	$.34 \pm 1.1$	9.3
Cyclobutane	$1.1 \pm .3$	8.2	$2.5 \pm .5$	0	0	$2.5 \pm .5$	7.7
Cyclopentane	$3.0 \pm .6$	7.5	5.2 ± 1.1	40	10.4 ± 5.0	15.6 ± 6.1	6.6
Cyclohexane	$1.4 \pm .4$	8.0	3.3	33	3.6	6.9	7.2
Benzene	> 5	< 7	> 5	> 40	> 10	> 15	< 6
Propane	0.46	8.6	1.13	6	.21	1.2	8.0
<i>n</i> -Butane	0.31	8.9	.65	13	.50	1.5	7.9
<i>n</i> -Pentane	0.59	8.5	.66	36	1.38	2.0	7.8
<i>n</i> -Hexane	0.22	9.1	.94	50	1.90	2.8	8.0

determining step probably does not involve the strained ring configuration but rather the rupture of a C-H bond which could be stronger than the C-H bond in normal paraffins. With the exception of cyclopropane the cycloalkanes react somewhat more rapidly than their straight chain counterparts. The fact that the cyclic hydrocarbons possess only secondary bonds scarcely seems sufficient cause for these differences.

Since only single experiments were conducted with each of the normal paraffins no significance can be attributed to the differences in their collision yields, which are within the estimated experimental error. The collision yields compare quite favorably with previously published values.

The percentage decompositions in the deuterium experiments are all somewhat larger than for the corresponding H atom experiments. Since the atoms do not possess zero point energies the differences, if real, must be attributed to the energy differences in the activated complexes. However, these differences may be largely superficial since it was noted during blank experiments that the D atom concentrations decreased more slowly with time than did the H atom concentrations. Hence the procedure of using the average of the atom concentrations measured before and after each experiment may involve errors sufficiently large to account for the different rates.* The main point of interest in the deuterium experiments lies in the degree to which the hydrocarbons are exchanged. In the case of cyclopropane and cyclobutane no exchange occurs, while cyclopentane, cyclohexane, and benzene undergo considerable exchange. In the case of the normal paraffins it will be seen that the degree of exchange increases with increasing molecular weight. This appears to be in disagreement with the work of Steacie and Parlee (12) who found that C_3H_8 does not exchange with D atoms at room temperature, and with Trenner, Morikawa, and Taylor (14) who found no exchange with either C_3H_8 or $n-C_4H_{10}$. However, we have already mentioned that the mass spectrometer method is much more positive and sensitive a test than those employed by these workers. Thus the 6% exchange which we observed in the case of propane (which was mainly C_3H_7D) would correspond to less than 1% deuterium content by the method of Steacie and Parlee.

The exchange of a hydrocarbon may be conceived to occur by one of the following mechanisms:

* It may be argued that the reaction time is greater in the case of deuterium owing to its slower flow rate. Experimental measurements showed the relative flow rates of H_2 and D_2 to be 1.41, i.e., the inverse ratio of the square roots of their masses. From the kinetic theory of viscous flow it can be shown that this corresponds to equal collision diameters for H_2 and D_2 . Since the reduced masses in the expression for the collision number are nearly in the inverse ratio of the square roots of the masses of H_2 to D_2 these effects should nearly cancel.

The reaction of methyl radicals with H_2 has been shown to occur with an activation energy of about 9 kcal. and a low steric factor. It is to be expected that the activation energy should probably increase and the steric factor decrease for reaction A (2) with more complicated hydrocarbon radicals. Hence mechanism A would not be expected to play a very important part in exchange processes at room temperature. However, the increase in the ratio of hydrocarbon decomposed to hydrocarbon exchanged with increasing atom concentration observed in the case of cyclopentane suggests that this mechanism may contribute slightly to the exchange process.

The radical recombination mechanism B provides an alternate fate for the hydrocarbon radical to that of "atomic cracking". It is similar to the mechanism first proposed by Taylor (14) to explain the high degree of deuteration of the methane formed in D atom reactions:

The quasi-deuteromethane can be stabilized only by collision with the wall or some other third body. The lifetime of the quasi-molecule is probably quite small and so there is a good probability of the splitting off of an H atom. This process recurs until there are only CD_3 radicals reacting with a large excess of D atoms and eventually a three body collision will occur to produce a stable CD_4 molecule.

Trenner, Morikawa, and Taylor (14) suggest that the three body restriction is also important for the combination of D atoms with propyl and butyl radicals, although their experimental evidence is not very clear. If exchange does occur by mechanism B then our results show that the three body restriction is much less important for the compounds investigated. Fig. 1 represents a typical mass spectrum of the cyclohexane recovered after reaction with D atoms. Mass 84 is the parent peak of cyclohexane and so the subsequent peaks will be nearly proportional to the amount of each deuterated cyclohexane present. We see that they decrease regularly from $C_6H_{11}D$ to C_6D_{12} , the reverse order to that observed for the deuteromethanes formed from this reaction. On the basis of mechanism B this simply means that for so complex a molecule sufficient degrees of freedom exist for the sharing of the excess energy that the collision time exceeds the average lifetime of the quasi-molecule, and the amounts of the various deuterocyclohexanes are those expected on a probability basis. The absence of deuteration in pairs also suggests that the excess energy does not remain localized at any single carbon atom in the molecule. Completely analogous spectra were obtained from the other hydrocarbons reacted with D atoms.

The reason for the absence of deuteration in the cases of cyclopropane and cyclobutane may lie in the strained structures of these compounds. Thus if the cyclopropyl and cyclobutyl radicals possess strain energy then they may be expected to decompose upon collision with a D atom with little likelihood of being stabilized. Cyclopentyl and cyclohexyl radicals on the other hand are relatively free from strain and could be readily stabilized.

FIG. 1.

In the case of the normal paraffins, mechanism B suggests that as the number of degrees of freedom increases, the average lifetime of the quasi-molecule should also increase. This predicts increased deuteration up the series which is in accord with experimental observation. However, we would expect the amount of exchange to increase at the expense of the amount decomposed if the rates of the initial process were the same for all the normal paraffins. Experimentally, the amount decomposed remains essentially constant throughout the series. To be tenable, mechanism B therefore requires an increasing rate for the initial process equal to the increasing rate of exchange. If this is so, then the collision yields for exchange reaction must be added to the collision yield for the decomposition reaction in order to obtain the collision yield of the primary process.

If mechanism C is operative then the collision yields should not be added since they represent different initial steps. The absence of exchange with cyclopropane and cyclobutane must be attributed to the inability of the strained

structures to undergo the Walden type inversion, whereas the increasing degree of exchange in the normal paraffins require the inversion to occur more readily the greater the number of degrees of freedom in the molecule. According to this mechanism deuteration need not occur at the expense of the decomposition reaction. It will also be unnecessary to invoke the concept of the three-body collision in this case to explain the mass spectra of the deuterated hydrocarbons. A comparison of our results with the two experiments of Robb and Melville (6) with *n*-hexane and cyclohexane lends support to this mechanism. They calculated collision yields from the rate of disappearance of H atoms which are in fair agreement with our collision yields calculated on the basis of decomposition alone, if the same values for collision diameters are used in both calculations. There is considerable disagreement, however, when their results are compared with the sum of our collision yields for decomposition and exchange. The use of mechanism C removes this discrepancy since there is no net decrease in atom concentration as a result of the exchange process.

Summing up then we may say that the reaction

followed by "atomic cracking" reactions is undoubtedly responsible for the products formed in the reactions of H and D atoms with benzene and the cycloalkanes as well as with normal paraffins. Other initial processes, however, may be responsible for the exchange of these hydrocarbons with D atoms.

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