Anal. Calcd. for [Co en trien]Cl_3: C, 25.84; H, 7.05; N, 22.64; Cl, 28.61; Co, 15.85. Found: C, 25.63; H, 6.98; N, 22.42; Cl, 28.57; Co, 15.93.

The salt can be purified more easily by conversion to the much less soluble iodide. Five grams (0.013 mole) of the salt in 20 cc. of water and 5 g. (0.033 mole) of sodium iodide in 10 cc. gave a crystalline iodide which was washed with cold water, recrystallized from 20 cc. of distilled water and dried in a vacuum over sulfuric acid.

Anal. Calcd. for [Co en trien]I_3: I, 58.92. Found: I, 58.67.

Attempts to resolve the ion, [Co en trien]$^{+++}$, from the bromide *dextro*-tartrate[7] and *dextro*-α-bromocamphor-π-sulfonate were not successful. The difficulty encountered was largely due to the extreme solubility of these salts.

Tetrakis-(ethylenediamine)-triethylenetetraminedicobalt(III) Chloride.—Thirty grams (0.105 mole) of finely ground *cis* or *trans*-dichloro-bis-(ethylenediamine)-cobalt(III) chloride, 11.5 g. (0.079 mole) of triethylenetetramine, and 500 cc. of absolute alcohol were allowed to react as described for the preparation of [Co en trien]Cl_3. An orange residue was formed, in practically theoretical amount. It was recrystallized from water and dried at 110°.

Anal. Calcd. for [Co_2 en_4 trien]Cl_6: C, 23.43; H, 7.02; N, 23.46; Cl, 29.65; Co, 16.43. Found: C, 23.23; H, 6.89; N, 23.58; Cl, 29.43; Co, 16.35.

Preparation and purification of the much less soluble iodide was accomplished by the method outlined for the corresponding [Co en trien]I_3.

Anal. Calcd. for [Co_2 en_4 trien]I_6: I, 60.14. Found: I, 59.93.

The resolution of this ion, [Co_2 en_4 trien]$^{+6}$, was not accomplished using the bromide *dextro*-tartrate[7] and the *dextro*-α-bromocamphor-π-sulfonate.

tris-(Triethylenetetramine)-dicobalt(III) Chloride.—Twenty grams (0.064 mole) of finely ground II or III, 9.6 g. (0.065 mole) of triethylenetetramine, and 300 cc. of absolute ethyl alcohol were allowed to react as described for the preparation of [Co en trien]Cl_3. A portion of the orange product was recrystallized from water and dried at 110°.

Anal. Calcd. for [Co_2 $trien_3$]Cl_6: C, 28.09; H, 7.07; N, 21.87; Cl, 27.64; Co, 15.32. Found: C, 27.87; H, 6.97; N, 21.93; Cl, 27.39; Co, 15.47.

The complex iodide was obtained by the addition of a small excess of sodium iodide solution to a solution of the complex chloride. This slightly soluble iodide was purified by recrystallization from water and dried in a vacuum over sulfuric acid.

Anal. Calcd. for [Co_2 $trien_3$]I_6:, I, 58.92. Found: I, 58.67.

Again all efforts to resolve this ion, [Co_2 $trien_3$]$^{+6}$, from the bromide *dextro*-tartrate[7] and *dextro*-α-bromocamphor-π-sulfonate were without avail.

Summary

Salts of the following cations containing triethylenetetramine and cobalt(III) have been prepared and some of their properties are described: [Co trien Cl_2]$^+$, [Co trien $(NO_2)_2$]$^+$, [Co trien CO_3]$^+$, [Co trien C_2O_4]$^+$, [Co trien $(NH_3)_2$]$^{+3}$, [Co en trien]$^{+3}$, [Co_2 en_4 trien]$^{+6}$, and [Co_2 $trien_3$]$^{+6}$.

A *cis*-configuration seems to be indicated for the ions, [Co trien Cl_2]$^+$ and [Co trien $(NO_2)_2$]$^+$.

An absorption band was obtained at approximately 2425 Å. for several *cis*-dinitrotetramminecobalt(III) compounds and this same band was less clearly shown by the corresponding *cis*-dichloro compounds.

EVANSTON, ILLINOIS RECEIVED FEBRUARY 20, 1948

[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Determination of Position of Tracer Atom in a Molecule: Mass Spectra of Some Deuterated Hydrocarbons[1]

BY JOHN TURKEVICH,[2] LEWIS FRIEDMAN,[2] ERNEST SOLOMON AND FRANCES M. WRIGHTSON[3]

The problem of determining the position of a tracer atom in a complex molecule arose during the study of the mechanism of catalytic reduction of acetone to propane with deuterium. Since the mass spectrum of a molecule consists of fragment ions obtained by rupture of valence bonds it was thought that the relative abundance of appropriate ions would indicate the position of an isotopic atom. Thus C_3H_7D-1 should give among others, ions of mass 16 and 15.

$$H_3C{-}CH_2{-}CH_2D \longrightarrow C_2H_5 + \underset{16}{CH_2D^+} + E$$

$$C_2H_4D + \underset{15}{CH_3^+} + E$$

While C_3H_7D-2 should give no ions of mass 16.

$$CH_3{-}CH_2D{-}CH_3 \longrightarrow C_2H_4D + \underset{15}{CH_3^+} + E$$

The purpose of this study was to establish the validity of this approach and to study in general the changes in the mass spectrographic pattern of hydrocarbons produced by replacing some of the hydrogens with deuterium. With this in mind monodeuteromethane, tetradeuteromethane, monodeuteroethane, monodeuteropropane-1 and monodeuteropropane-2 were prepared and studied on two standard mass spectrographs, that of Nier and the one of the Consolidated Engineering Corporation.

A mass spectrometric study of dideuteroethylene has been made by Delfosse and Hipple.[4] More recently Evans, Bauer and Beach[5] have investigated the mass spectrum of monodeuteromethane and Mohler and Dibeler,[6] mono- and dideuteroacetylenes. These studies show that the

---

[1] Presented at the meeting of the American Chemical Society in Atlantic City, April 15, 1947.

[2] Princeton University.

[3] M. W. Kellogg Co.

[4] J. Delfosse and J. A. Hipple, *Phys. Rev.*, **54**, 1060 (1938).

[5] M. Evans, N. Bauer and J. Y. Beach, *J. Chem. Phys.*, **14**, 701 (1946).

[6] F. L. Mohler and V. Dibeler, *Phys. Rev.*, **72**, 158A (1947).

carbon–deuterium bond does not break as readily as the carbon–hydrogen bond.

Experimental

The mass spectrometer was a Nier type[7] instrument. The gas analyzed was introduced into the spectrometer tube through a capillary leak. The gas pressure in the sample system was kept at 10 mm. The bombarding electrons responsible for the ionization and dissociation processes were accelerated from an incandescent tungsten filament through a slit into the ion gun by a potential of 67.5 volts.

The mass spectra were also determined in a Consolidated Engineering Corporation instrument.[8] In this case the electron accelerating voltage was 55 volts and the gas analyzed was permitted to leak into the spectrometer tube from a sample reservoir at a pressure of approximately 20 microns.

Materials

The monodeuteromethane was prepared by decomposing methylmagnesium iodide with 100% heavy water. The Grignard reagent was prepared by adding 14.5 g. of C. P. methyl iodide to 20 cc. of dry Eastman Kodak butyl ether and 2.8 g. of magnesium turnings in a 250-ml. round-bottom flask. The magnesium was carefully drilled from a block of pure metal without the aid of any cutting oils or fluids. The flask was fitted with a vertical water cooled reflux condenser which in turn was fitted at the top with a calcium chloride tube. The reaction was initiated by gentle heating and then controlled by cooling in a water-bath. The flask containing the Grignard reagent was attached to a vacuum line by means of a standard taper ground glass joint, cooled in Dry Ice and evacuated. The reagent was thoroughly out gassed by melting, freezing and then evacuating several times. A small quantity of heavy water vapor (approximately 10–15 cc., N. T. P. estimated from the volume of the products formed) was distilled into the flask containing the Grignard reagent. The purity of the methane was determined by abundance ratio of masses 16 and 17. The first sample gave for this ratio a value of 0.83. The reaction mixture was cooled in Dry Ice and this sample of gas pumped off. A second batch of heavy water vapor was distilled into the Grignard reagent and the ratio of 16 to 17 in the deuteromethane formed was found to be 0.73. In the third and fourth batches the values were found to be 0.710 and 0.709. The constant values observed indicate that the reagent had been cleaned up of any light water contamination and the limit of purity had been reached. A larger sample of gas was then generated for final analysis.

Monodeuteroethane was prepared in a similar manner by the decomposition of ethylmagnesium bromide with heavy water. Ethylmagnesium bromide was prepared by adding 11 g. of ethyl bromide to 10 cc. of dry butyl ether and 2.8 g. of magnesium turnings in a 250-ml. round-bottom flask. Mild heating was used to initiate the reaction. The Grignard reagent was decomposed by using successive batches of heavy water. The ratios of the abundances of the ions of masses 30 and 31 were 0.80 for the first batch and 0.79 for the second, third and final batches prepared.

Propane-D-1 and Propane-D-2 were prepared from the corresponding normal and isopropylmagnesium bromides and heavy water. Both alkyl halides were purified by fractional distillation. In the preparation of propane-D-1 the ratios of the abundances of the ions of mass 44 and 45 were 1.05, 1.00, 0.895, and finally 0.863 for the following four successive batches. In the preparation of propane-D-2 the ratios for these ions were 0.83, 0.725, 0.74 and 0.74.

A sample of **tetradeuteromethane** containing approximately 7% monoprotium trideuteromethane was given to us by Mr. M. W. Wright. This material was prepared by the decomposition of aluminum carbide with heavy water. Excess hydrogen formed was removed by freezing the deuteromethane in solid nitrogen and pumping off the more volatile components.

It should be pointed out that in the preparation of deuterium compounds by the Grignard reagent extreme care must be observed to avoid introduction of light hydrogen into the molecule. The following precautions were observed. In the first place the heavy water was added in small successive portions to the Grignard reagent and samples were analyzed for the highest masses in the mass spectrograph. Two criteria of purity could then be applied. Successive samples should show a constant low value for the mass one smaller than the maximum, as the hydrogen impurity is removed from the sample (thus the relative abundance of mass 30 from C_2H_5D should reach a steady minimal value). Another criterion is that the sensitivity coefficient (absolute intensity) of the ion of parent mass be the same as that of the corresponding light hydrogen compound.

The second method of determining the purity of the preparation is to determine the hydrogen–deuterium ratio in the product. In this method the hydrocarbon was oxidized by copper oxide at 500°. The water formed was condensed in a Dry Ice trap and the carbon dioxide pumped off. The water was decomposed over zinc at 330°. The hydrogen so formed was analyzed in a Nier type mass spectrometer for the deuterium–hydrogen ratio. The instrument was calibrated by measuring the ratio of masses three and two of hydrogen from standard heavy water samples whose deuterium content was known from density determinations. The following two examples illustrate the results obtained using some early impure compounds. A preparation of monodeuteroethane has a sensitivity coefficient for the parent mass of 15 while the value of the corresponding light hydrogen ethane was 20.0. Assuming that the sensitivity coefficient is independent of deuterium content, this result would indicate that the preparation of monodeutero compound was 75% pure. Combustion and deuterium analysis indicated 12.0% deuterium and the monodeuteroethane (theoretical value is 16.7%). Thus deuterium analysis indicates again a 73% purity. Another example is furnished by the experiments on monodeuteropropane-2. The sensitivity coefficient for the mass of parent ion was 12.0 while that of the light hydrogen compound was 24.56. This would indicate 49% purity. The deuterium analysis showed 6.45% deuterium (theoretical value for a monodeuteropropane is 12.5%), or a purity of 50%. Thus the purity determinations based on an assumption of equal sensitivity coefficients of the ion of parent mass irrespective of deuterium substitution lead to the same result as an ultimate analysis based on hydrogen deuterium analysis.

Results

The experimental results obtained are expressed in terms of the sensitivity coefficients of the ion of parent mass and relative ion intensities. The sensitivity coefficient of the ion of parent mass is the relative value of the ion current of the parent mass at an inlet pressure of one micron under identical operating conditions. The relative ion intensities are expressed in the following way. The intensity of ion of parent mass is given the value of 100 and the intensities of the other ions are presented relative to the intensity of the ion of parent mass. Using the sensitivity coefficient as given and the relative ion intensity one can obtain intensities of all other ions at the standard operating conditions of the instrument.

The data presented in Tables I, II and III permit a comparison of the results obtained by the two standard instruments: that of Nier and that

---

(7) A. O. Nier, *Rev. Sci. Inst.*, **11**, 212 (1940).

(8) Washburn, Wiley and Rock, *Ind. Eng. Chem., Anal. Ed.*, **15**, 541 (1943).

TABLE I

RELATIVE ION INTENSITIES

Mass	CH_4 a	CH_4 b	CH_4 c	CH_3D a	CH_3D b	CH_3D c	CD_3H a	CD_4 a
20								100.0
19							100.0	
18							?	82.8
17				100.0	100.0	100.0	51.2	...
16	100.0	100.0	100.0	78.2	76.0	71.3	?	14.5
15	83.5	83.1	81.2	22.3	22.5	18.7	6.1	...
14	17.0	17.1	12.5	8.8	9.4	6.8	?	7.9
13	8.3	8.2	5.7	5.0	5.2	3.7	1.5	...
12	2.6	2.4	1.8	2.5	2.4	1.8	2.5	2.5
Total ions	211.4	...	...	216.8	...	...	...	207.7
Sensitivity coefficient of ion parent mass	61.8	...	...	65.0	...	...	63.3	63.3

[a] Consolidated Engineering Corporation Mass Spectrometer (M. W. Kellogg Company, Jersey City, N. J.). [b] Evans Bauer and Beach. [c] Nier type mass spectrometer. The values are corrected for C^{13} isotope.

TABLE II

RELATIVE ION INTENSITIES

Mass	C_2H_6 c	C_2H_6 a	C_2H_5D c	C_2H_5D a
31	...	...	100.0	100.0
30	100.0	100.0	73.1	74.3
29	76.5	78.0	330.4	320.1
28	393.4	394.0	196.3	(177.3)[a]
27	127.5	130.3	96.1	105.5
26	87.2	92.8	49.9	60.4
25	16.2	15.1	10.8	11.6
Total C_2 ions	800.8	810.2	856.6	....
16	...	0.2	6.2	8.5
15	12.5	17.9	9.7	18.2
14	8.4	12.2	5.4	(14.3)[a]
13	3.1	4.2	2.3	3.9
12	1.9	1.9	1.2	5.0
Total C_1 ions	25.9	36.4	24.8	....
Total ions	826.7	846.6	881.4	....

[a] Unreliable.

TABLE III

RELATIVE ION INTENSITIES

Mass	Propane c	Propane a	Propane D-1 c	Propane D-1 a	Propane D-2 c	Propane D-2 a
45	...	....	100.0	100.0	100.0	100.0
44	100.0	100.0	87.6	93.9	74.1	62.5
43	82.2	82.4	34.5	30.3	51.9	48.5
	21.0	20.1	47.6	53.9	40.2	51.6
41	43.4	46.3	35.7	41.6	56.6	36.0
40	8.7	7.4	36.7	39.9	23.2	31.9
39	55.7	62.9	44.0	57.4	13.1	49.4
38	...	17.3	....	18.2	....	14.6
37	...	10.5	....	11.3	....	8.9
Total C_3 ions	321.0	346.9	386.1	446.5	359.1	403.4
31[d]						
30	...	....	151.5	179.7	323.1	329.5
29	312.2	350.0	223.2	291.4	218.4	218.4
28	188.6	208.1	143.9	193.5	132.4	(60.0)[a]
27	113.5	142.3	77.1	122.3	85.2	89.9
26	24.4	30.1	17.5	28.4	20.2	18.7
Total C_2 ions	7638.7	730.5	613.5	815.3	779.3	.....
16	...	0.3	7.4	11.4	3.3	2.7
15	13.5	22.5	10.3	18.7	12.3	22.9
14	4.1	7.0	3.9	6.8	4.1	(1.0)[c]
13	1.5	2.1	1.2	2.3.	1.5	2.3
12	0.7	1.0	0.7	0.1	0.7	1.9
Total C_1	19.8	32.9	23.5	39.3	21.9	.....
Total ions[e]	979.5	1110.3	1023.1	1301.1	1160.3	.....

[d] Unreliable. [e] Total ions includes all peaks recorded.

of the Consolidated Engineering Corporation. One should first note in Table I the concordance of our results for monodeuteromethane obtained on the Consolidated instrument of the M. W. Kellogg Company at Jersey City with the results obtained by Evans, Bauer and Beach on a similar instrument on the West Coast. The values obtained on the Nier instrument at Princeton University are slightly lower.[9] An examination of the results of Tables II and III shows more marked differences in the individual values of the relative ion intensities for the various ethanes and propanes as obtained on the two different instruments. One must note, however, that the two instruments agree on both the order of abundance of the various ions and their magnitude. For that reason the results will be discussed for the most part in terms of the values obtained on the Nier instrument. The values obtained on the Consolidated instrument are placed in parentheses in the text of the paper.

Methane.—The sensitivity coefficients of the ion of parent mass for all three compounds CH_4, CH_3D and CD_4 is approximately the same.

The CH_3D pattern had been previously reported by Evans, Bauer and Beach and our results using the Consolidated instrument agree with those they reported. The results we obtained with the Nier instrument are slightly lower. The CH_3D pattern is different from that of CH_4 and CD_4. Evans, Bauer and Beach have made a detailed analysis of this difference in terms of statistics and the relative dissociation probabilities of the C–H and C–D bonds in CH_3D and of the CH bond in CH_4 compared to the C–H bond in CH_3D. We shall limit ourselves to a more elementary analysis. The number of processes of ionization increases from five to six when one goes from CH_4 to CH_3D while the sum total of the ion currents

---

[9] This may be due to differences in the ambient temperatures of the ionization chambers in the two instruments.

remains the same (211.4, 216.8, 207.7). This brings of necessity a redistribution of the cracking pattern. This kind of redistribution is not statistical as has been pointed out by Evans, Bauer and Beach in the case of CH_3D and by Delfosse and Hipple for $C_2H_2D_2$.

The mass 16 in the spectrum of CH_3D results from the removal of a hydrogen atom and an electron from the molecule. Statistically this should correspond to $^3/_4$ the value obtained for the removal of a hydrogen from CH_4 or 60.9 (62.6). The observed values are 71.3 (78.2) indicating that the hydrogen removal is 1.17 (1.25) more probable if the carbon atom contains a deuterium atom. The mass 15 may arise from two processes. It may arise from a removal of two hydrogens from CH_3D and should have $^3/_6$ the value of the CH_2^+ produced from CH_4 or 6.2 (8.5). The second process is the removal of a deuterium from CH_3D. The statistical value should be one-quarter of the removal of a hydrogen from CH_4 or 20.3 (20.9). The total for the two processes is 26.5 (29.4) and is larger than the experimentally observed value 18.7 (22.3). If one assumes that the probability of breaking a deuterium–carbon bond is one-half that of breaking a hydrogen–carbon bond while the breaking of a hydrogen–carbon bond is 1.17 more probable if the carbon atom contains a deuterium atom we get a predicted value of 18.4 (21.1) in better agreement with experimental values 18.7 (22.3). The mass 14 arises again from two processes. The first produces a CD^+ which should be one-third of the CH^+ from CH_4 or 1.9 (2.8). If we multiply this by 1.17 we get 2.2 (3.5). The second is due to CH_2^+ which should be $^3/_6$ of the CH_2^+ peak of CH_4 or 6.2 (8.5). If we multiply this by (0.5) (1.17) we get 3.8 (5.0). The predicted value is thus 6.0 (8.5) where the experimental value is 6.8 (8.8).

A part of the CD_3H pattern can be obtained from the 7% CD_3H impurity in CD_4 sample by considering the relative intensities of the ions of odd mass in the spectrum of CD_4 (after correcting for the 1.1% C^{13} isotope). One then obtains 100 for the CD_3H^+ and 51.2 for the CD_2H^+. The other masses cannot be obtained from the data available. For CD_2H^+, on purely statistical grounds, one would expect three-quarters of 83.5, or 62.6. An interpretation of the CD_3H spectrum must await synthesis of pure CD_3H.

The CD_4 as prepared contained 7.2% CD_3H as revealed by ions of odd mass. The spectrum of CD_4 should consist solely of ions of even mass when a correction is made for the contribution due to 1.1% C^{13} isotope. The presence of an impurity of 7.2% CD_3H affects the spectrum but slightly since the currents for even masses from this molecule would be small in view of the small amount of the impurity present. The only correction applied was to the mass 18 where it was calculated on statistical grounds to be $7.2 \times 0.835 \times {}^1/_4 = 1.5$. The value in Table I is so corrected. The process of removing a hydrogen from CH_4 to give CH_3^+ has the value 83.5 while the similar process of removal of D from CD_4 has the value 82.8.

The removal of two hydrogens from CH_4 gives the value of 17.0 while the corresponding process in CD_4 has the value 14.5. The removal of three hydrogens from CH_4 gives a value of 8.34 while that of three deuteriums from CD_4 is 7.85. One thus sees that the probability of breaking a carbon–deuterium bond in tetradeuterium methane is the same as the probability of breaking a carbon–hydrogen bond in tetrahydrogen methane. The probability of breaking a carbon hydrogen bond is greater if there is a carbon–deuterium bond present and also the probability of breaking a carbon–deuterium bond is less if there is a carbon–hydrogen bond present.

Ethanes.—The mass spectra of ethane and monodeuteroethane are presented in Table II. The sensitivity coefficients of the parent masses were found to be approximately the same. The total number of ions formed from ethane (827–847) is slightly less than the total from monodeuteroethane (881). The relative ion intensities are different first because new masses 31 (C_2H_5D) and 16 (CH_2D) appear and secondly because alternative processes involving the removal of either D or 2H atoms give ions of the same mass. Ninety-five per cent. of the ions are in the C_2 group indicating that it is easier to break C–H bonds than the –C–C bonds. The total number of ions in the C_2 group in deuteroethane 857 is greater than in ethane 801 (824). In the C_2 group mass 30 arises from the loss of a hydrogen and an electron from deuteroethane. Its value should be $^5/_6 \times (1.17)$ of that observed for the 29 peak in ethane or 74.6 (81.2). The experimental value is 73.1 (74.3). The mass 29 arises by two processes: (a) the removal of a deuterium and an electron which should be equal to $^1/_6 \times (0.5)$ the value of removing a hydrogen from ethane 76.5 (78.0) or 6.5 (6.5); (b) removal of two hydrogens and an electron from deuteroethane which should be $^{10}/_{15} \times (1.17)$ of a similar process in ethane 393 (394) or 307 (328). The predicted value is 314 (335) while the observed value is 330 (320). The mass 28 arises again two processes (a) the removal of three hydrogens and an electron which should be $^{10}/_{20} \times (1.17)$ of analogous process for ethane 127.5 (130.3) or 74.6 (81.4) and (b) the removal of a deuterium, hydrogen and electron which should be $^5/_{15}$ of the removal of two hydrogens from ethane 393.4 (394) or 131 (131). The predicted value is 206 (213) while the observed value is 196. The agreement with experiment is better if one drops the weighing factors (1.17) and (0.5) for the simultaneous removal of an H and a D.

Mass 27 arises from (a) removal of 4 hydrogen atoms and an electron from C_2H_5D and should be equal to $^5/_{15}$ of (1.17) 87.2 (92.8) or 34.0 (38.6), (b) removal of 3 hydrogen and one deuterium atom and an electron. The value for this process should be $^{10}/_{20}$ of 127.5 (130.3) or 63.8 (65.2). The total is 98 (104). The observed value is 96 (105.5). The mass 26 arises from (a) removal of five hydrogens and an electron from C_2H_5D and should be equal to $^{1}/_{5} \times (1.17) \times 16.2\ (15.1) =$ 3.8 (3.8) and (b) removal of three hydrogen and one deuterium and electron. The value for this process should be $^{10}/_{20} \times 87.2\ (92.8)$ or 43.6 (46.4). The total predicted value is 47.4 (50.2) as contrasted with the experimental value of 49 9 (60.4). The mass 25 arises from sole process of removal of four hydrogens and a deuterium atom and an electron. This should be equal to $^{5}/_{6}$ of 16.2 (15.1) = 13.5 (12.6) whereas the experimental value is 10.8 (11.6).

The C_1 group constitutes about 3% of the total ions produced from ethane. The values for the ethane are 25.9 (36.4) and for the deuteroethane 24.8. The mass 16 in monodeuteroethane arises from a split of the molecule in two and should be one-half of the mass 15 from ethane or 6.2 (9.0). The experimentally observed values are 6.2 (8.5). The close concordance between the predicted and experimentally observed results indicates that the presence of the deuterium isotope does not appreciably affect the probability of breaking the C—C bond. The mass 15 in monodeuteroethane arises from CH_3^+ and CHD^+. The amount of the CH_3^+ can be calculated as one-half the 15 peak in C_2H_6 or 6.2 (8.5). The amount of the CHD^+ is $^{1}/_{2} \times {}^{2}/_{3} \times (1.17)$ of the CH_2^+ from C_2H_6 or 3.3 (5.1). The total is therefore 9.5 (13.6) while the observed value is 9.7 (18.2).

The value of 14 peak in C_2H_5D is due to contributions of CH_2 and CD^+. The CH_2^+ that comes from CH_3 is $^{1}/_{2}$ of 8.4 or 4.2 and the amount that comes from CH_2D is $^{1}/_{2} \times {}^{1}/_{3}\ (0.5) \times 8.4$ or 0.7. The CD^+ that comes from CDH_2 should be $^{1}/_{2}$ $(3.1) \times {}^{4}/_{6} = 0.7$. The total is $4.2 + 0.7 + 0.7 = 5.6$. The value obtained on the Nier instrument is 5.4.

Propanes.—The mass spectra of propane, propane D-1 and propane D-2 are presented in Table III. The presence of only one deuterium in the deuterated propanes is established by the absence of masses higher than 45. The sensitivity coefficients of the three propanes examined were the same. The total number of ions was 979.5 (1110), 1023 (1301) and 1160, respectively, and cannot be considered equal within the experimental error. The C_3 group contains about one-third of the ions. An analysis of the ions formed is difficult. The high value of the 44 peak in the D-1 and the low value in the D-2 compound seems to indicate that the primary carbon-hydrogen bond is more strongly held than the secondary and it is the secondary hydrogen that comes off first. A detailed discussion of the C_3 ions in the deuterium compounds must be postponed until further deuterium compounds are synthesized and studied. The C_2 group contains about two-thirds of the ions. The mass 30 results from the loss of a methyl radical and an electron from the deuteropropane. In the case of the D-1 compound its value should be equal to one-half of the mass 29 for propane or 156 (175). The observed value 151.5 (180) is in good agreement. In the case of the D-2 compound the value of the 30 mass should be equal to the value of the 29 mass in propane or 312 (350). The experimental values are 323 (330). The explanation for the value of the 29 mass in propane D-1 is satisfactory. It can arise in two ways

$$CH_3CH_2{-}CHD_2 \longrightarrow CH_4 + C_2DH_3 + E$$

and its value should be one-half times $^{4}/_{5}$ the value of the 28 peak in propane 75.5 (83). The other process is

$$CH_3{\cdot}CH_2{\cdot}CDH_2 \longrightarrow CDH_2 + CH_3{\cdot}CH_2^+ + E$$

which should be one-half the value of the 29 peak in propane or 156 (175). The total is 232 (258) to be compared with the experimental 223 (291). The value of the 29 mass in propane D-2 can arise only from a removal of a CH_4 from the molecule and should be equal to the 28 peak in propane, or 189 (208). The value found experimentally is 218 (218).

The C_1 group contains about 2% of the total ions. The mass 16 should occur only in the case of propane D-1 where it should be equal to one-half the value for the 15 mass in propane or 6.7 (11.2). The observed values are 7.4 (11.4) in good agreement with prediction. There should be no 16 mass in propane D-2. The small value obtained for this mass may be due to re-arrangement in the preparation of the deuterated propane. The mass 15 for propane D-2 should be the same as that from propane, *i.e.*, 13.5 (22.5). The experimental value is 12.3 (22.9) in good agreement with calculation. The value for propane D-1 arises by two processes

$$CH_3{\cdot}CH_2CH_2D \longrightarrow CH_3^+ + CH_2{\cdot}CHD$$

or one-half the value for propane 6.7 (11.2) and

$$CH_3{\cdot}CH_2CH_2D \longrightarrow CHD^+ + CH_2{\cdot}\dot{C}H_3$$

or two-thirds of the value for mass 14 (2.7, 4.7) from propane to give a predicted value of 9.4 (15.9). The experimental value is 10.3 (18.7). Thus we see that the C_1 group provides unequivocal evidence for the disposition of the deuterium atoms in the molecule.

In conclusion it may be stated that one can determine the position of the tracer atom in a propane molecule by examination of the intensities of masses 30 and 16. Furthermore, one can reconstruct the fine details of the mass spectrum of monodeuteromethane, monodeuteroethane using the assumption of equal probability of rupture of hydrogen carbon bonds, a 7/6 factor for a carbon–hydrogen bond on a carbon atom that has deuterium and a one-half factor for a carbon–deuterium bond. One further drops these factors if both D and H are removed simultaneously.

Conclusion

1. Monodeuteromethane, tetradeuteromethane, monodeuteroethane, monodeuteropropane-1 and monodeuteropropane-2 have been synthesized and their mass spectra determined on a Nier type and a Consolidated mass spectrometer.

2. A method of calculating the mass spectrum of monodeuteromethane and monodeuteroethane from the corresponding light hydrogen compounds, has been indicated.

3. A method has been given to indicate the position of a deuterium atom in monodeuteropropanes.

RECEIVED JANUARY 27, 1948

[CONTRIBUTION FROM CHEMICAL LABORATORY, UNIVERSITY OF MISSOURI]

The Quantum Efficiency of the Mercury Sensitized Photochemical Decomposition of Hydrogen

BY LLOYD B. THOMAS AND WM. D. GWINN[1a]

Introduction

The reaction between mercury atoms excited by absorption of light of λ 2537 Å. and hydrogen molecules to produce hydrogen atoms was reported by Cario and Franck[1] in 1922. The analogous reaction between hydrogen molecules and mercury atoms excited by streaming electrons of controlled energy through the gas mixture has been carried out.[2] These and more recent studies in this laboratory have indicated that the 6^3P_1 state of mercury to which the photochemical reaction is ascribed may play only a slight part, if any, in the electron initiated reaction. The immediate occasion for undertaking the present study is to obtain the necessary reaction rate data to compare the kinetics of the electron and photon activated reactions in the hope that the mechanism of the former will be clarified.

Attention has been devoted by a number of investigators—Stuart, Zemansky, Bates[3] and Evans[4]—to the quenching of fluorescent resonance radiation from Hg^3P_1 atoms by collision of the Hg^3P_1 atoms with added foreign gas molecules. An over-all effective cross section for quenching is obtained through the method but it is not possible to distinguish between processes which may contribute to the quenching. By the method of the present paper it appears possible to determine the effective cross section for a specific process, *i.e.*, the interaction of Hg^3P_1 atoms with hydrogen molecules to cause their removal from the gas phase, presumably through dissociation.

Experimental

The reaction system and light source are shown in Fig. 1. The reaction cell is a cylinder of fused silica which has an internal length of 3.53 cm. and an internal diameter of 2.25 cm. The walls of the cell are lined with a thin cylinder of oxidized copper. The ends of the cylinder are flat polished fused silica windows 2 mm. thick and are fused on. The cell is attached to the rest of the system, which is of Pyrex, by a graded seal. The Pirani gage consists of a 0.0025 cm. platinum filament mounted as shown and immersed in a kerosene filled thermostat which is maintained at 30°. Precaution was taken to prevent a film of kerosene, which was found to absorb λ-2537, from creeping over the entrance window. The system in the thermostat was connected through a U-tube and mercury cut-off to a conventional high vacuum system with mercury condensation pump, McLeod gage, mercury cut-offs, and with no stopcocks in the high vacuum line. Hydrogen was admitted from a gas flame through a palladium tube. The pressure was brought to the desired values, as shown by the McLeod gage, through manipulation of the flame and cut-offs.

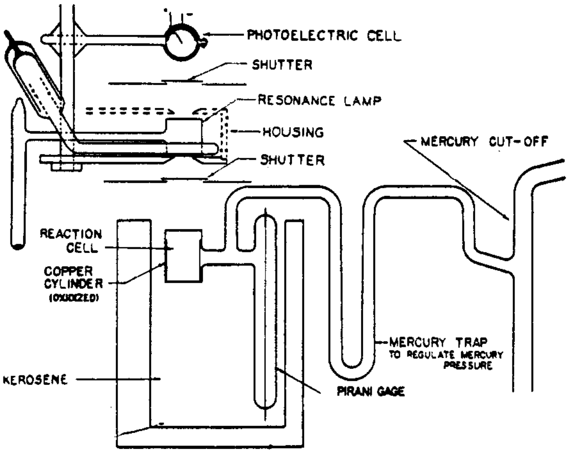

Fig. 1.—Experimental apparatus.

The light source is a monochromatic resonance lamp[5] which operates several degrees above room temperature and gives a very narrow line breadth—about 20% greater than the Doppler breadth at 30°. A fused silica photoelectric cell with a cadmiun coated cathode was mounted above the resonance lamp as shown and served as a check on the lamp intensity. The intensity of λ 2537 in this upper position was strictly proportional to that at the reaction cell window when the mercury vapor pressure in the resonance lamp cylinder was kept constant. The procedure in taking data is as follows: The thermostat is replaced by an oven. Oxygen is admitted to the system to about 10 mm. pressure. When the oven temperature becomes sufficiently high the oxygen pressure starts to diminish due to consumption by the copper of

---

[1a] Present address of W. D. G. is Department of Chemistry, University of California, Berkeley, Calif.

[1] Cario and Franck, *Z. Physik*, **11**, 155 (1922).

[2] Glockler and Thomas, THIS JOURNAL, **57**, 2352 (1935).

[3] A. C. G. Mitchell and M. W. Zemansky, "Resonance Radiation and Excited Atoms," Cambridge University Press, 1934.

[4] Evans, *J. Chem. Phys.*, **2**, 445 (1934).

[5] Thomas, *Rev. Sci. Inst.*, **12**, 309 (1941).