at high HCl concentrations where $D_F < D_{Cl}$, but they do not apply at low HCl concentrations where D_F may become equal to or even larger than D_{Cl}. In this region negatively charged fluoride complexes must be formed which are adsorbed by the resin. Using equation 6 the following values for $\Sigma(MF_i)_F/(m_t)_F$ were computed for $1M$ HF solutions

7 *M* HCl: W(VI) 0.92; Mo(VI) 0.72; U(VI) 0.52
11 *M* HCl: W(VI) 0.84; Mo(VI) 0.27; U(VI) <0.05

Thus the fraction of the metal complexed by fluoride ions at a given acidity is largest for W(VI), least for U(VI), with Mo(VI) lying intermediate, *i.e.*, this fraction does not follow the order of the elements in the periodic table. Adsorbabilities at low HCl concentrations where D_F rises rapidly with decreasing *M* HCl and where $D_F > D_{Cl}$ follow the same pattern, *i.e.*, W(VI) shows highest adsorption, U(VI) least adsorption, although the difference between W(VI) and Mo(VI) is less marked than at high HCl concentrations.

No computations of the stability constants of the fluoride complexes of these elements will be given at this time since their determination involves detailed knowledge of the change of species in chloride solutions as well as variations of the activity coefficients with ionic strength, particularly at high HCl concentrations.

Acknowledgment.—The authors are greatly indebted to Mrs. L. W. Magnusson, Jr., for valuable technical assistance.

OAK RIDGE, TENN.

[CONTRIBUTION FROM VARIAN ASSOCIATES]

The Electron Withdrawal Power of Substituent Groups

BY B. P. DAILEY[1] AND J. N. SHOOLERY

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A study of chemical shifts in the nuclear magnetic resonance spectra of ethyl and methyl derivatives of a number of organic substituent groups has been made. It was desired to find out how the electronegativity of an atom changes when it forms a part of different substituent groups and to attempt to derive a table of the electron withdrawal power of the substituent groups. A simple relationship between proton "chemical shifts" and the ionic character of the chemical bond to the proton has been established by the regularities existing in the experimental results of this study. It is shown that the electron withdrawal power of a substituent group is largely determined by the electronegativity of the first atom in the group.

Introduction

The use of electronegativities as a guide in studying electron withdrawal effects in chemistry has at least one serious drawback. The electronegativity of an atom is accurately defined for an atom forming a diatomic molecule but it is difficult to predict the changes in electronegativity which an atom will experience when it forms part of a polyatomic molecule.

The present study of chemical shifts in nuclear magnetic resonances was undertaken to attempt to discover how the electronegativity of an atom changes when it forms a part of different substituent groups and if possible to derive a table of the electron withdrawal power of the substituent groups.

The magnetic resonance absorption of a proton chemically bonded to another atom in molecule occurs at a value of the magnetic field which is influenced by the electronic structure of the molecule. The theoretical discussion of the calculation of chemical shifts presented by Saika and Slichter[2] makes it appear that the chemical shifts for protons can be rather simply related to the ionicity of the chemical bond to the proton. They divide the contributing factors into three terms: (1) the diamagnetic correction for the atom in question arising largely from the bonding electron during the period it occupies an atomic 1s orbital centered about the proton (2) the paramagnetic term for the atom in question. This term should be zero for an atomic 1s orbital. (3) The contribution from other atoms.

For a given chemical bond such as the C–H bond, the largest contribution of the type designated as (3) above should remain constant so that as different substituent groups are bonded to the carbon atom the shifts in the proton magnetic resonance can be used to measure the change in the ionicity of the C–H bond and the relative electron withdrawal power of the substituent groups.

The assumption of a simple relationship between shifts in proton resonances and the ionic character of the chemical bond to the proton is plausibly suggested by theoretical considerations but must, of course, be justified by regularities demonstrated in the experimental data. Such regularities were apparently established for ethyl derivatives in an earlier paper[3] and also by an analysis of the data of Meyer, Saika and Gutowsky.[4] However the results obtained in the more recent study by Meyer and Gutowsky[5] of methyl derivatives seemed to contradict the above generalizations. The object of this study was to measure the shifts in the proton magnetic resonances in the methyl and ethyl derivatives of a number of substituent groups so that the relations between the shifts and ionicity might be more firmly established and that these groups might therefore be arranged in order of their electron withdrawal power. Alternatively,

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[2] A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

[3] James N. Shoolery, *ibid.*, **21**, 1899 (1953).

[4] L. H. Meyer, A. Saika and H. S. Gutowsky, THIS JOURNAL, **75**, 4567 (1953).

[5] L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953).

the data could be used to assign effective values of the electronegativity of the substituent groups. This is a quantity which is not readily available from other physical data.

Experimental

The measurements were made with a Varian Model 4300 high resolution nuclear magnetic resonance spectrometer at a frequency of 30 Mc. and magnetic field of approximately 7050 gauss. Samples were contained in cylindrical glass tubes having an i.d. of 3 mm. These tubes were filled to a depth of approximately 7 cm. although a less than 1 centimeter length of the liquid column was actually contained within the receiver coil. The sample tubes were rotated at a speed of 500–800 r.p.m. within the crossed coil system by means of an air turbine in order to obtain better resolution. In all cases, the three peaks of the methyl resonance fine structure in the ethyl derivatives were cleanly resolved. The different compounds were dissolved in benzene which was used to obtain a reference resonance. The concentration of the solutions was ordinarily made up to be 50% benzene by volume.

The frequency separation of the resonance of interest from the benzene resonance was measured using the following modified procedure of Arnold and Packard.[6] An audio-frequency signal was superimposed upon the sawtooth sweep voltage fed to the field modulation coils. This produced sidebands on the observed resonances at frequencies whose difference from the central resonance frequency corresponded to the frequency of the signal from the audio oscillator. The audio oscillator was adjusted until the side band from the benzene resonance was super-imposed on the resonance which was being measured. At this point the frequency of the audio oscillator was checked with a Hewlett Packard frequency counter whose reading gave the desired frequency difference directly with an accuracy of better than one cycle. The resolution of the patterns was such that measured frequency differences could be duplicated during a different series of measurements made at a later data to ±one cycle.

Figure 1 gives the resonance pattern for a typical ethyl derivative. The center resonance of the triplet methyl pattern and the center of the quadruplet methylene pattern were measured for each of the ethyl derivatives. All measurements were made at room temperature.

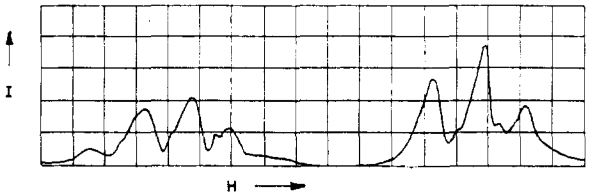

Fig. 1.—Ethyl bromide resonance pattern for a typical ethyl derivative.

The chemical shifts were measured as frequency differences in cycles from the benzene resonance frequency. These frequency differences may be converted to δ in parts per million by dividing by 30. Approximate chemical shifts based on the H_2O resonance as a reference may be obtained by subtracting 53 cycles from the reported frequency differences. However, as is discussed later, such a procedure neglects important effects due to bulk diamagnetic susceptibility corrections.

Materials.—The only requirement as to purity for the samples in this study was that they be sufficiently pure so that the methyl and methylene resonance could be recognized with no ambiguity.

The samples of methane, methyl chloride and methylamine were specially synthesized. The sample of ethyl fluoride was given us by the Jackson Laboratories of the E. I. du Pont de Nemours Co. The other samples were obtained commercially.

Discussion

There are a number of difficulties which arise in the theoretical interpretation of chemical shifts as ordinarily measured. If the resonance of interest is measured for the pure compound against an external reference, then the contribution due to the bulk diamagnetic susceptibility correction may have to be considered. These corrections have been ignored in much of the earlier work but to the accuracy of the present measurements are by no means negligible. In fact, the calculated correction for methyl iodide is 58 cycles while for benzene it is only 38 cycles.

It was assumed in planning this experiment that if two substances form a perfect solution then the diamagnetic correction for each of them would be the same and the frequency differences measured in solution should correspond closely to the true frequency difference corrected for diamagnetic susceptibility effects. As is discussed later, evidence obtained in some special experiments casts some doubt on this hypothesis. This procedure, however, gives rise to a further hazard to theoretical interpretation of chemical shifts measured in solution, namely, the possibility of effects due to molecular association. There is little chemical evidence that there are any large effects due to solvation or association of any of the ethyl and methyl derivatives studied in benzene solution. The good general agreement for a number of the ethyl derivatives, between the earlier results obtained[3] using pure substances and a substitution technique, with the results of this study on benzene solutions seems to rule out the presence of solution effects for the majority of the substances studied.

Because of the possibility of difficulty with diamagnetic susceptibility corrections and with solution effects, however, it appears that theoretical interpretation of chemical shifts would be most straightforward and reliable if they can be measured against an internal standard reference within the same molecule. Fortunately, this is possible in the measurements made using ethyl derivatives. It can be safely assumed that the electron withdrawal power of the substituent groups is nearly completely attenuated by the C–C bond so that the proton resonance in the methyl group should remain reasonably well fixed in frequency in the absence of solution and diamagnetic susceptibility effects.

Then the difference in chemical shifts ($\Delta CH_3 - \Delta CH_2$) between the methyl and methylene resonances in an ethyl derivative should furnish a reliable measure of the electron withdrawal power of the substituent group.

If we assume that the order of electron-withdrawal power for the substituent groups is correctly determined by the results for the ethyl derivatives, then two questions can be answered by comparing the results for the two series of ethyl and methyl derivatives. In Fig. 2 ($\Delta CH_3 - \Delta CH_2$) for the ethyl derivatives is plotted against the methyl resonance frequency for the corresponding methyl derivatives. A good linear relationship is obtained. This would seem to indicate that the effects due to differences in the diamagnetic susceptibility correction in the methyl series had been largely eliminated by measuring the resonances against the

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(6) J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

benzene resonance as a standard in benzene solutions. Also it would appear to demonstrate that the chemical shifts in both the ethyl and methyl series were similarly related to the ionicity of the C–H bonds in question.

It should be pointed out that although the chemical shifts measured in benzene solution for methyl halides in this study agree quite well with the results obtained for the ethyl halides they are in qualitative disagreement with the results obtained for the pure methyl halides by Gutowsky and co-workers.[4,5]

Table II presents the results of this study and that of Meyer, Saika and Gutowsky for the methyl halides and a number of other methyl and ethyl derivatives calculated as values of the chemical shift in cycles from the H_2O resonance. In converting the data of this study the value of the chemical shift from benzene to water was taken as 53 cycles. The data of Meyer, Saika and Gutowsky was converted by multiplying the δ value ($\delta = 10^5 \times (H_r - H_c)/H_r$) by -300. There remains some question as to the relative position of the methane resonance for pure methane with respect to water since Gutowsky and Hoffman[7] report this as $\delta = -0.33$.

Meyer and Gutowsky suggest that the failure of their results for the methyl halides to correlate in the expected fashion with the relative electronegativities is due to double bond character in the carbon–halogen bonds. While this is a plausible explanation for compounds containing more than one halogen atom bonded to a single carbon there is very little independent evidence supporting double bond character in the simple methyl halides. The accurate microwave structural data of Miller, Aamodt, Dousmanis, Townes and Kraitchman[8] show that none of the carbon–halogen bonds in the series CH_3Cl, CH_3Br and CH_3I are shorter than the sum of the single bond radii.

Since the bulk diamagnetic susceptibility corrections are large compared to the differences between the resonant frequencies for the methyl halides, difficulties in the interpretation of the data for the pure compounds might perhaps be expected. As indicated previously, such difficulties can be eliminated only for series of compounds such as the ethyl halides for which one of the resonances can serve as an intramolecular standard. It is interesting to note that the trend of the data for the ethyl halides agrees with that observed for the methyl halides in benzene solution but is opposite to that for the data of Meyer and Gutowsky obtained with the pure compounds. This is true not only for the data obtained using solutions of the ethyl halides in benzene but also for the earlier data on the pure ethyl halides.

It is perhaps significant that serious disagreement with the data of Meyer, Saika and Gutowsky occurred only when dealing with molecules such as CH_3I having unusually large diamagnetic susceptibilities. For the majority of compounds, agreement with the data of Meyer and Gutowsky was obtained within the combined probable error of the two sets of measurements.

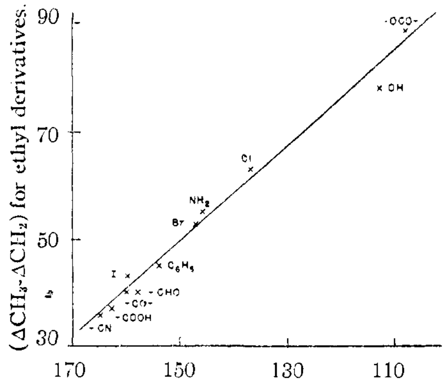

Fig. 2.—Comparison of chemical shifts for corresponding ethyl and methyl derivatives.

It should be noted that all of the results measured in solution represent larger frequency differences than those measured for the pure substances. The data suggest that there is a roughly constant correction of perhaps 5 cycles due to diamagnetic susceptibility for all substances having average values of the bulk diamagnetic susceptibility K. For substances having very large values of K such as CH_3I or CH_3Br the frequency difference should be much larger, perhaps as large as the differences of 54 and 32 cycles which were observed. However, the difference in the bulk diamagnetic susceptibility correction in going from pure benzene to pure CH_3I in cylindrical tubes has a calculated value of only 18 cycles.

The following experiment was performed in an attempt to investigate these bulk effects. The chemical shift of the methyl resonance frequency of methyl iodide was determined with respect to both benzene and water. The CH_3I was present first in a solution whose composition was 10% CH_3I in 90% benzene, then 90% CH_3I in 10% benzene. The water sample was substituted as an external frequency standard.

The frequency of the benzene resonance shifted by 30 cycles when compared to the water standard in going from the more dilute to the more concentrated methyl iodide solution. The methyl resonance in CH_3I shifted 43 cycles (toward lower fields) in going from the more dilute to the more concentrated solutions.

These frequency shifts are two or three times larger than would be expected from calculations of the bulk diamagnetic susceptibility correction. However they are in the right direction and occur for a substance which has a very large value of K. If the frequency shifts were due only to bulk diamagnetic susceptibility effects the 13 cycle difference in the shifts for benzene and CH_3I in the experiment above would certainly not be expected.

It is possible that some sort of intermolecular association produces this difference in frequency shifts.

Several experiments were performed to investigate this possibility. For one critical case, measurements were made of a solution of CH_3I in

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(7) H. S. Gutowsky and C. J. Hoffman, *J. Chem. Phys.*, **19**, 1259 (1951).

(8) S. L. Miller, L. C. Aamodt, G. Dousmanis, C. H. Townes and J. Kraitchman, *ibid.*, **20**, 1112 (1952).

C_2H_5I. Within the error of measurement, the difference in resonance frequencies of CH_3 in CH_3I and CH_2 in C_2H_5I was the same as the value calculated from the measurements made on benzene solutions. The difference in resonance frequencies of the CH_3 group in C_2H_5Br and the CH_3 group in nitromethane measured using a solution of C_2H_5Br in nitromethane agreed within 2 cycles with the frequency predicted from the data obtained using benzene solutions. The frequency difference between the benzene resonance and the CH_3 resonance in methanol changed by no more than 3 cycles over a 10-fold range of methanol concentrations.

In column five of Table I, frequency differences are given for a number of molecules which measure the magnitude of the proton spin–spin interaction. These frequency differences were measured with an accuracy of perhaps ±1 cycle. It seems evident that the size of the spin–spin interaction is not simply related to the ionic character of the chemical bonds through which the effect is transmitted. There is a real variation in the frequency differences measured between, let us say, ethanol and ethyl nitrate, but it is not obvious from consideration of these results upon what variables this variation depends.

TABLE I

ETHYL AND METHYL RESONANCES MEASURED FROM BENZENE REFERENCE

Compd.	CH_2 resonance, cycles	CH_3 resonance, cycles	$(\Delta CH_3 - \Delta CH_2)$, cycles	Spin–spin separation, cycles
Ethyl mercaptan	+150	+182	32	5.9
Methane		+195		
Cyclohexane	+170			
n-Hexane	+176	+188		
Diethyl sulfide	+144	+184	40	6.9
Ethyl thiocyanate	+138	+181	43	6.4
Ethyl cyanide	+155	+190	35	
Methyl cyanide		+165		
Propionic acid	+150	+187	37	
Acetic acid		+162		
Propionaldehyde	+152	+191	39	
Acetaldehyde		+158		
Methyl ethyl ketone	+151	+190	39	
Ethyl iodide	+130	+172	42	8.5
Methyl iodide		+161		
Ethylbenzene	+139	+182	43	7.2
Toluene		+154		
Ethyl bromide	+122	+175	53	
Methyl bromide		+148		
Ethylamine	+130	+185	55	
Methylamine		+147		
Ethyl chloride	+114.0	+178	64	7.1
Methyl chloride		+137		
Methyl vinyl ether		+119		
Ethanol	+104	+181	77	5.7
Methanol		+114		
Ethyl acetate	+ 95	+184	89	
Methyl salicylate		+107		
Diethyl sulfate	+ 94	+183	89	6.2
Diethyl sulfite	+ 96	+185	89	7.2
Nitroethane	+ 89	+180	91	8.6
Nitromethane		+ 96		
Ethyl nitrate	+ 90	+185	95	8.9
Ethyl fluoride	+ 86	+182	96	

Conclusions

In general, the existence of a simple relationship between proton "chemical shifts" and the ionic character of the chemical bond to the proton would seem to be clearly established by the regularities which can be shown to exist in the experimental results of this study.

In Fig. 3 the values of $\Delta CH_3 - \Delta CH_2$ for the ethyl halides are plotted against the values of the electronegativities of the corresponding halogen as given by Huggins.[9] As may be seen, a linear relationship exists which may be expressed by the equation

$$\text{electronegativity} = 0.02315(\Delta CH_3 - \Delta CH_2) + 1.71$$

Using the observed values of $(\Delta CH_3 - \Delta CH_2)$ and this equation the values of the relative electronegativities of the substituent groups given in Table III may be derived. In order to do this, it is necessary to assume that the linear relationship established for the halogen substituents will hold for the other substituent groups also. As a rough approximation, this is probably justified for those cases in which the bond between the methylene group and the substituent involves orbitals of the same symmetry as those in the corresponding bonds in the ethyl halides. The equa-

TABLE II

Compd.	$(\Delta CH_3 - \Delta H_2O)$, cycles This study	Meyer, Saika and Gutowsky[3]	Compd.	$(\Delta CH_3 - \Delta H_2O)$, cycles This study	Meyer, Saika, and Gutowsky[3]
CH_3I	+108	+ 54	C_2H_5COOH	+134	+126
CH_3Br	+ 95	+ 63	CH_3COOH	+109	+ 96
CH_3Cl	+ 84	+ 69	$C_2H_5NH_2$	+132	+126
CH_3OH	+ 61	+ 51	CH_3CN	+112	+102
CH_3NH_2	+ 94	+ 82	Methyl salicylate	+ 54	+ 51
CH_3NO_2	+ 43	+ 39	Cyclohexane	+117	+117
CH_3CHO	+105	+102	C_2H_5CHO	+138	+129
C_2H_5OH	+128	+120	$C_2H_5NO_2$	+132	+120

TABLE III

RELATIVE ELECTRONEGATIVITY OF SUBSTITUENT GROUPS

Groups	$(\Delta CH_3 - \Delta CH_2)$ for ethyl derivatives, cycles	Calcd. electronegativity[a]	Electronegativity of first atom
-SH	32	2.45	2.6
-CN	35	2.52	2.6
-COOH	37	2.57	2.6
-CHO	39	2.61	2.6
-CO-	39	2.61	2.6
-S-	40	2.64	2.6
-I	42	2.68	2.65
-SCN	43	2.70	2.6
$-C_6H_5$	43	2.70	2.6
-Br	53	2.94	2.95
$-NH_2$	55	2.99	3.05
-Cl	64	3.19	3.15
-OH	77	3.51	3.5
-OCO-	89	3.83	3.5
$-SO_4-$	89	3.83	3.5
$-SO_3-$	89	3.83	3.5
$-NO_3$	95	3.91	3.5
-F	96	3.93	3.90

[a] Electronegativity = $0.02315\,(\Delta CH_3 - \Delta CH_2) + 1.71$.

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(9) M. L. Huggins, THIS JOURNAL, **75**, 4123 (1953).

tion given above definitely does not hold for the case of ethane where the methylene–substituent bond involves a 1s orbital. ($\Delta CH_3 - \Delta CH_2$) for ethane is of course zero rather than 20 cycles as predicted by the equation.

Nevertheless the equation is probably reasonably satisfactory as a guide to interpolating between the electronegativity values of the halogens. All of the substituents, except hydrogen, form bonds to the methylene group using an orbital which is primarily a p orbital and similar in symmetry to that used by the halogens.

Table III seems to indicate that the electron withdrawal power of a substituent group is largely determined by the electronegativity of the first atom in the group. The chief variations are observed in the lowering of the group electronegativity of –SH with respect to –S– and –SCN, of NH_2 and OH by the presence of the hydrogen atoms in the group. The presence of linkages such as –C–, –N– and –S– seems to substantially increase the group electronegativity.

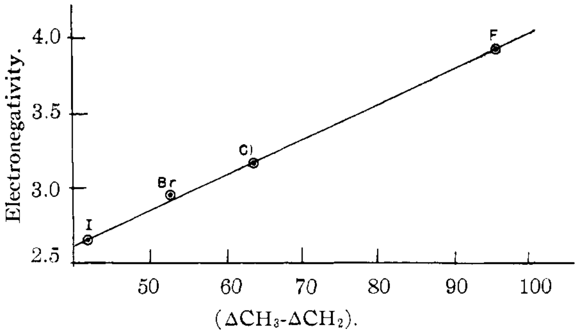

Fig. 3.—Chemical shift *vs.* electronegativity for the ethyl halides.

It is interesting to note that while the electronegativities are not simply related, the value of ($\Delta CH_3 - \Delta CH_2$) for ethyl bromide is exactly the average of the values for ethyl chloride and ethyl iodide.

Palo Alto, Cal.

[Contribution from Chemistry Division, Argonne National Laboratory]

γ-Ray-induced Deuterium Gas–Water Exchange[1]

By Sheffield Gordon and Edwin J. Hart

Received February 11, 1955

Deuterium gas dissolved in light water has been found to undergo exchange with the protium of the water when these solutions are exposed to the γ-radiation of $Co.^{60}$ In neutral and acid solutions the major product of the exchange is hydrogen deuteride. Hydrogen is also formed in smaller yields. In alkaline solutions the hydrogen deuteride formation is suppressed whereas the hydrogen formation is unchanged over a wide range of *p*H's. The effects of *p*H, deuterium concentration and dose rate have been determined, and a mechanism is postulated.

Deuterium gas, when dissolved in water and exposed to Co^{60} γ-rays is found to undergo exchange with the protium of the water.[2] Two independent reactions appear to be occurring, and the stoichiometry can be accounted for by equations 1 and 2

$$D_2 + H_2O = HD + HDO \qquad (1)$$

$$D_2 + 2H_2O = H_2 + 2HDO \qquad (2)$$

Unexposed solutions of the gas do not give evidence of this exchange. The yield of reaction (1) is highly dependent upon *p*H in the range 0.5 to 13. The effect of *p*H, dosage rate and concentration of dissolved D_2 upon the yield of the exchange is reported in the present paper. Reaction (2) is independent of *p*H in the range 0.5 to 13. Evidence is provided for the existence of H atoms in irradiated solutions as well as evidence for the previously postulated ionization of the OH radical.[2,3] A mechanism is proposed for the exchange and its dependence on *p*H.

Experimental

Triply distilled water[3] was used in these experiments. Deuterium gas supplied by the Stuart Oxygen Co. and assaying >99.5% in deuterium atom content was used without further purification except to pass it through a liquid air trap. Two procedures were used to degas the water, dissolve the deuterium gas and fill the cells. The irradiation cells in experiments 1–14, inclusive, were cylindrical Pyrex cells about 2 cm. in diameter previously described.[4] The method of deaerating, saturating the water with deuterium gas, and filling the cells has been described.[5] Solutions and cells in experiments 14–23, inclusive, were prepared by using the syringe technique described previously.[3] The *p*H of the solutions was adjusted by adding buffers described in Table III. All *p*H's were measured on the stock solutions remaining after filling the cells, using a Leeds and Northrup *p*H meter, model 7663–A1. All solutions prepared by the above two procedures contained no gas phase and were irradiated with Co^{60} γ-rays in specially designed chambers.[6] The dosage rates were measured by use of the ferrous sulfate actinometer, and a value of 15.5 Fe^{+++}/100 e.v.[7] was used to convert chemical yield to electron volts/liter. After irradiation the gas was extracted from solution, and its volume and pressure were measured in a Van Slyke apparatus. The gas was then dried by passing it back and forth several times through a U-type liquid air trap, and mass spectrographic analysis made. The initial concentration of deuterium, $(D_2)_0$, was obtained on each series of runs by extracting and measuring the gas from the blank in the manner described. The spectrometer used for experiments 15–25, inclusive, was a Nier Consolidated instrument model 21–201 with dual collection. The peaks were measured by scanning magnetically, and single collection was used to measure the mass 4, 3 and 2 peaks separately. Pure deuterium, hydrogen and hydrogen deuteride were used to calibrate the instrument for peak sensitivity

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] S. Gordon, E. J. Hart and P. D. Walsh, Argonne National Laboratory Report No. UAC-406; S. Gordon and E. J. Hart, paper presented at September, 1952, ACS Meeting.

[3] E. J. Hart, S. Gordon and D. A. Hutchison, This Journal, **74**, 5548 (1952); **75**, 6165 (1953).

[4] E. J. Hart, *ibid.*, **73**, 68 (1951).

[5] E. J. Hart, *ibid.*, **74**, 4174 (1952).

[6] R. A. Blomgren, E. J. Hart and L. S. Markheim, *Rev. Sci. Instru.*, **24**, 298 (1953).

[7] E. J. Hart, *Ann. Revs. Phys. Chem.*, **5**, 139 (1954).