SOME USES AND REACTIONS OF
LITHIUM ALUMINUM HYDRIDE

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ABSTRACT

A method for determining the concentration of lithium aluminum hydride ($LiAlH_4$) is described involving the hydrolysis of the reagent at constant temperature and measurement of the evolved hydrogen by change in pressure.

The apparent active hydrogen content of several organic compounds was determined using an ether solution of the reagent. In most cases, the expected number of hydrogen atoms was found and the reagent behaved like the Grignard reagent, although the reaction was sometimes more vigorous. The keto-enol tautomers investigated behaved as though they were only partially enolized, whereas with the Grignard reagent, similar compounds act as though they exist only in the enol form.

Preliminary studies indicated that $LiAlH_4$ may be used successfully for the simultaneous determination of active hydrogen and certain reducible functional groups.

Hydrogenolysis of several alkyl halides with $LiAlH_4$ was accomplished by using more stringent conditions than are usually necessary in reducing organic compounds with this reagent. This hydrogenolysis was also accomplished with lithium hydride using a small amount of $LiAlH_4$ as the hydrogen carrier.

PROBLEM STATUS

This is an interim report on a phase of this problem, which is being discontinued temporarily.

AUTHORIZATION

NRL Problem C01-07R (BuAer Problem TED NRL 3401)

SOME USES AND REACTIONS OF
LITHIUM ALUMINUM HYDRIDE

INTRODUCTION

Lithium aluminum hydride was first prepared by Dr. H. I. Schlesinger and his co-workers at the University of Chicago.[1] In preliminary studies of its reaction with organic substances, it showed considerable promise as a synthetic tool. As a result, Dr. W. G. Brown, also of the University of Chicago, undertook to expand such studies.

The reagent is prepared through the reaction of lithium hydride and aluminum chloride in ether solution.[1,2] It is a vigorous agent for the reduction of various types of organic compounds[3,4,5,6] and a valuable analytical tool for the determination of active hydrogen[7,8,9] and functional groups.[7,9]

DETERMINATION OF LITHIUM ALUMINUM HYDRIDE IN SOLUTION

Method of Analysis

Inasmuch as lithium aluminum hydride is often prepared and used in ether solution, a method was sought for the determination of its concentration without removal of the solvent. It has been shown[2] that lithium aluminum hydride is decomposed by water to liberate hydrogen quantitatively according to the equation

$$LiAlH_4 + 4H_2O \longrightarrow LiOH + Al(OH)_3 + 4H_2$$

The present method of analysis is based on this reaction and an apparatus was designed and constructed in which a known volume of solution is hydrolyzed and the evolved hydrogen measured by change in pressure.

Since the hydrogen is determined by pressure change, the error due to variation in the vapor pressure of ether with temperature may be considerable. This error is practically eliminated, however, by maintaining the decomposition flask at 0°C with crushed ice and water. Although it would be desirable to keep the entire apparatus at 0°C, it was found that by reducing the volume of the exposed portion to a minimum, sufficiently satisfactory results are

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obtained. Use of the apparatus with the flask maintained at a higher temperature led to erratic results.

Apparatus

The apparatus used is shown in Figure 1.   The decomposition flask is a 2-liter, round-bottomed flask with a 35/20 spherical socket joint.   A 10-ml buret having a pressure-equalizing by-pass and take-off arm is attached to the flask.   The buret is closed by a tightly fitting rubber stopper.
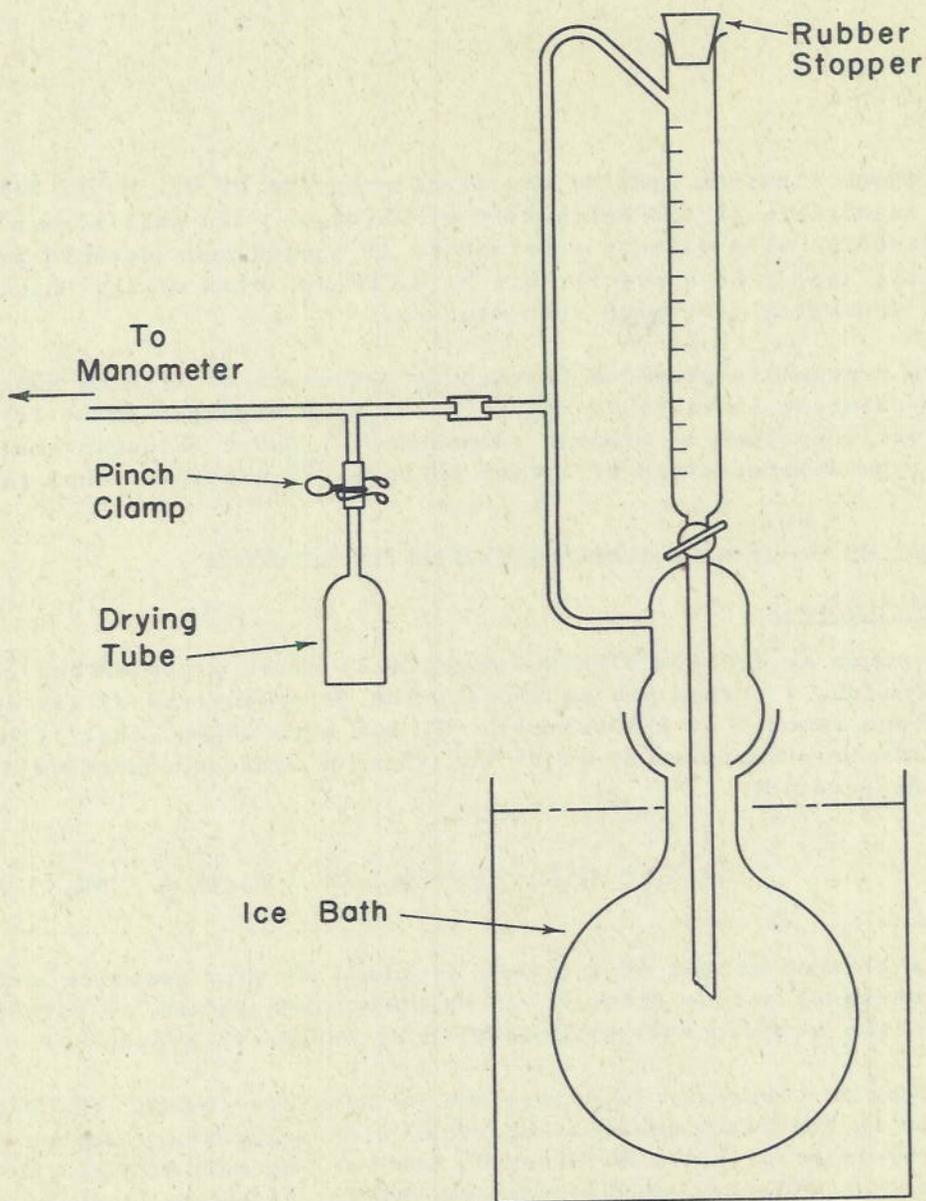

Figure 1 - Apparatus for analysis of
lithium aluminum hydride

A standard ball-and-socket locking clamp is used to hold the joint between the flask and buret in order to prevent leakage. The take-off arm on the buret is connected through a T-tube to a manometer by means of small-bore tubing. A drying tube is attached to the T-tube with a short piece of rubber tubing which may be closed by a pinch clamp. Before use, the volume of the entire system is measured to within a few milliliters and the volume of the ungraduated lower portion of the buret above the stopcock is determined accurately.

Procedure

The decomposition flask is clamped into place and surrounded with crushed ice and ice water. A mixture of 160 ml of cold 10 percent sulfuric acid and 40 ml of cold ether is placed in the flask and the remainder of the apparatus is assembled and allowed to stand for 5 minutes with the pinch clamp closed. If a change of pressure is observed, the pinch clamp is opened momentarily and the process repeated until equilibrium is reached.

Approximately 10 ml of the lithium aluminum hydride-ether solution is added to the buret and the volume is estimated to within 0.01 to 0.02 ml. Then the system is closed and allowed to stand for a few minutes to insure that it is again at equilibrium. The solution is run into the flask slowly until the buret is drained. After equilibrium is reached (usually 5 to 10 minutes), the increase in pressure is read to 0.5 mm. The system is prepared for a subsequent analysis by opening the pinch clamp and re-equilibrating to atmospheric pressure. The concentration of hydride is calculated from the equation:

$$\text{Molarity} = \frac{\text{pressure increase (mm of Hg)} \times \text{net free volume (ml)}}{\text{volume of sample (ml)} \times 68{,}100}$$

The net free volume is the total volume of the system less the volume of all solutions added. The factor 68,100 combines the constants R, T, and the fact that 4 moles of hydrogen are liberated per mole of lithium aluminum hydride.

Results

Solutions at four different concentrations of lithium aluminum hydride in ether were analyzed by this procedure. As a check method, samples of these same solutions were decomposed by 1 N hydrochloric acid and the aluminum was determined by the method of Snyder.[10] The results of these determinations, given in Table 1, indicate that the method has good reproducibility and, for most purposes, is sufficiently accurate for the quantitative determination of lithium aluminum hydride in ether.

TABLE 1

Analyses of Lithium Aluminum Hydride Solutions

Soln. no.	Vol. of sample (ml)	Net free volume (ml)	Pressure increase (mm Hg)	Molarity found by hydrolysis	Molarity by Al method	Difference
1	8.35	1992	210	0.735	0.732	
	8.05	1984	204.5	0.740	0.714	
	10.00	1974	252.5	0.732	0.723	
				Av. 0.736	0.723	0.013
2	9.83	1990	236	0.701	0.710	
	9.90	1980	238	0.699	0.707	
	9.67	1971	231.5	0.693	0.710	
	8.32	1962	199.5	0.691		
				Av. 0.696	0.709	0.013
3	10.20	1990	162	0.464	0.474	
	10.55	1979	170	0.468	0.479	
	10.15	1969	169	0.481		
	10.40	1995	168.5	0.474		
	10.80	1984	173.5	0.468		
				Av. 0.471	0.477	0.006
4	11.40	1989	122	0.312	0.314	
	10.15	1978	108	0.309	0.319	
	10.50	1968	112	0.308	0.315	
	10.85	1957	117.5	0.311	0.312	
	10.55	1946	114	0.309		
	10.70	1936	116.5	0.309		
				Av. 0.310	0.315	0.005

This method of analysis has also been used with success for the deter-
mination of the concentration of lithium aluminum hydride in solvents other
than ethyl ether, such as dibutyl ether and tetrahydrofuran. It is indi-
cated that the method also may be used for determining solubility of the
hydride in solvents where solubility is low. In cases where a solvent other
than ethyl ether is used, instead of placing 40 ml of ethyl ether in the
decomposition flask prior to the determination, 40 ml of the solvent in
question is used.

No correction was made for the error introduced by solution of hydro-
gen due to increased pressure, since such loss of hydrogen lies within the experi-
mental error of this method. Under different experimental conditions, how-
ever, this error may become appreciable and a correction may be necessary.

**REACTION OF LITHIUM ALUMINUM HYDRIDE WITH COMPOUNDS CONTAINING
ACTIVE HYDROGEN**

Method of Determination

Lithium aluminum hydride reacts with many compounds containing active
hydrogen in a manner similar to that of the Grignard reagent, except that
hydrogen instead of a hydrocarbon is liberated. In order to study the
quantitative nature of this reaction, an apparatus was devised so that a
known amount of material could be added to an excess of reagent in ether
solution at 0°C and the liberated hydrogen measured by changes in pressure.
By this method, the apparent active hydrogen content of a number of organic
compounds was determined.

Apparatus

A diagram of the apparatus used is shown in Figure 2. The reaction
flask consisted of a 500-ml round-bottomed flask bearing a 35/20 spherical
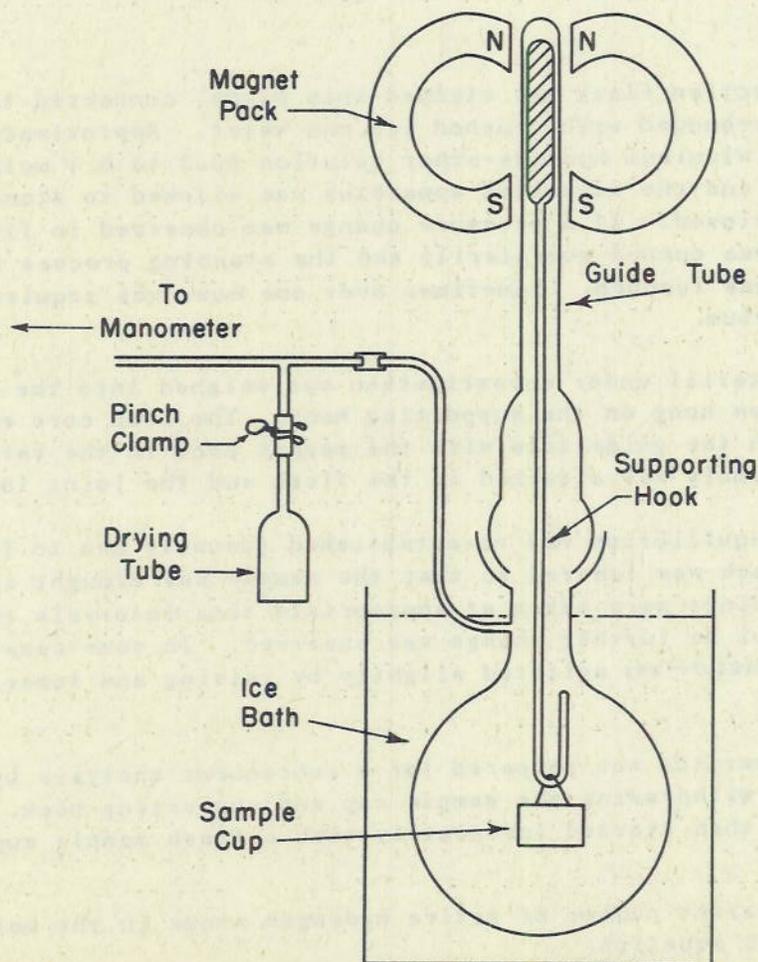
Figure 2 - Apparatus for determining active hydrogen

socket joint.   A take-off arm was attached to the neck and connected to a
manometer by small-bore tubing through a T-tube.   The T-tube was connected
to a drying tube with rubber tubing which could be closed by a pinch clamp.
The reaction flask was closed by a spherical ball joint carrying a 12- X
130-mm guide tube.   A clamp with an efficient locking device was used to
hold the joint together in order to prevent leakage.   The supporting hook
was made from glass rod joined to a sealed glass tube containing an iron
core.   The over-all length of the supporting hook was such that its lower
end almost touched the bottom of the flask when the magnet pack was in the
lowered position.   The magnet pack consisted of two Alnico magnets in
opposition mounted so that the pack passed over the guide tube easily. The
sample cup was made from 15-mm tubing and had a capacity of approximately
2 ml.   A handle was provided so that the cup could be suspended from the
supporting hook.

Before using the apparatus, the volume of the system was determined.
In addition to this apparatus, a second one similar in construction but
using a one-liter reaction flask was used for many of the determinations.

Procedure

The reaction flask was clamped into place, connected to the manom-
eter and surrounded with crushed ice and water.   Approximately 100 ml of
cold lithium aluminum hydride-ether solution (0.3 to 0.7 molar) was placed
in the flask and the assembled apparatus was allowed to stand with the
pinch clamp closed.   If a pressure change was observed in five minutes, the
pinch clamp was opened momentarily and the standing process repeated until
equilibrium was reached.   Sometimes over one hour was required to attain
this equilibrium.

The material under investigation was weighed into the sample cup
which was then hung on the supporting hook.   The iron core end of the hook
was placed in the guide tube with the magnet pack in the raised position
and this assembly was attached to the flask and the joint locked in place.

After equilibrium was re-established (usually ten to fifteen minutes),
the magnet pack was lowered so that the sample was brought into the solution.
Pressure readings were taken at appropriate time intervals (usually five
minutes) until no further change was observed.   In some cases, when reaction
was slow, the mixture was agitated slightly by raising and lowering the magnet
pack.

The apparatus was prepared for a subsequent analysis by releasing the
pressure and withdrawing the sample cup and supporting hook.   The next deter-
mination was then started immediately with a fresh sample cup and supporting
hook.

The apparent number of active hydrogen atoms in the molecule was calcu-
lated from the equation:

$$\text{No. active H atoms} = \frac{\text{pressure(mm) x net free vol. (ml)}}{\text{millimoles sample x 17,030}}$$

The pressure is the observed pressure increase less the small pressure in-
crease found by carrying out a blank determination without a sample. The
correction for the blank is not constant but varies with atmospheric con-
ditions and time. In those cases where reaction is rapid, this correction
is usually small--of the order of 1 to 3 mm. The net free volume is the
total volume of the system less the volume of the solutions added and the
volume of the supporting hook. The factor 17,030 combines the constants R
and T. Occasionally, for slow reactions, it was found necessary to apply a
correction for changes in barometric pressure. No correction was made, how-
ever, for the solubility of hydrogen due to increased pressure, since under
the conditions described, it is small and lies within the experimental
error of the method.

In general, the size of the sample was chosen so that a pressure change
of approximately 100 mm was obtained. For the apparatus described, the amount
of material ordinarily used varied from 0.1 to 0.4 gm depending on its molec-
ular weight and the number of active hydrogen atoms. Materials which were
suspected of not being dry were treated with anhydrous calcium sulfate or
phosphorus pentoxide.

Results and Discussion

The values found for the apparent active hydrogen content of a number
of typical organic compounds are presented in Table 2. Detailed data for
this work are given in Table 5 of Appendix I.

From this table, it can be seen that many of the simple alcohols, phenols,
and acids react with lithium aluminum hydride in ether to liberate hydrogen
in the expected manner and give results which are in good agreement with the
theoretical values. Although the reactions usually appeared to be complete
within a few seconds, several minutes were required to reach equilibrium.
The inconclusive results obtained with hydroquinone, succinic acid and tere-
phthalic acid may be due to the formation of insoluble material which coats
the crystals and inhibits further reaction. The anomalous results obtained
with resorcinol may be due to the formation of an insoluble product or to
partial reaction in the keto form. With the Grignard reagent, resorcinol
has been reported to show from one to two atoms of active hydrogen.[11,12,13]

The amines and amides tested showed the expected number of active hydro-
gen atoms and, with the exception of acetanilide, required prolonged reaction
periods. The extreme slowness of the reaction of diamylamine was unexpected.
The liberation of two hydrogens by primary amines and unsubstituted amides
by this reagent at $0^{\circ}C$ is of interest, since the Grignard reagent liberates
one hydrogen from such compounds at ordinary temperatures and the second on
heating.[14] Although the time required for complete liberation of hydrogen
by primary amines and unsubstituted amides was rather long, the first hydro-
gen was liberated rapidly, usually within five minutes. This behavior was
also observed for all other compounds tested which showed more than one atom
of apparent active hydrogen.

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TABLE 2

Determination of Active Hydrogen

Name of Compounds	Time to reach equilibrium (min.)	No. of active H atoms found	
(Alcohols and Phenols)			
n-Decanol	5-10	1.00	1.02
Benzyl alcohol	5-10	1.06	
Heptanol-2	5-10	1.02	
Cyclohexanol	5-10	0.98	1.01
t-Amyl alcohol	5-10	0.97	1.00
2-Methyl-2,4-pentanediol	5-10	2.01	2.01
α-Naphthol	10-20	1.05	1.03
β-Naphthol	5-10	1.05	1.08
Resorcinol	50-140	1.53	1.56
Hydroquinone		....*	
(Acids)			
n-Caprylic acid	5-10	1.03	1.03
2-Ethylhexoic acid	5-10	1.02	
Benzoic acid	5-10	0.99	0.99
o-Bromobenzoic acid	10-15	1.00	
Succinic acid		....*	
Terephthalic acid		....*	
(Amines and Amides)			
Cyclohexylamine	115	2.08	
Diamylamine	375	0.94	
Tributylamine		None**	
Aniline	50	1.99	2.05
β-Naphthylamine	70-80	2.04	1.99
2-Ethylhexanoamide	60	2.05	
Acetanilide	5-10	0.98	
(Nitro Compounds)			
Nitrobenzene	35	2.08	
o-Nitrotoluene	100	2.03	
Nitromethane	120-250	2.40	2.75

TABLE 2 (Cont.)

Name of Compounds	Time to reach equilibrium (min.)	No. of active H atoms found	
(Tautomeric Compounds)			
Acetyl acetone	5-10	0.94	0.95
Ethyl acetoacetate	5-10	.56	.57
Diethyl malonate	5-10	.56	.57
Diethyl methylmalonate	5-10	.25	.28
Diethyl ethylmalonate	5-10	.22	.25
Diethyl *i*-propylmalonate	5-10	.18	.21
Diethyl *n*-butylmalonate	5-10	.22	.26
Diethyl *i*-butylmalonate	5-10	.22	.25
Diethyl benzylmalonate	5-10	.19	.21
(Miscellaneous)			
Acetophenone	5-10	0.07	0.05
Propiophenone	5-10	0.05	0.08
Octyl mercaptan	5-10	1.00	1.01
Dioctyl thioether		None**	
Ethyl palmitate		None**	
Phenylhydrazine	70-125	Erratic***	

* Reaction with these compounds was slight and too slow to obtain significant results.

** These compounds gave less than 0.02 atom of active hydrogen.

*** Values obtained were 3.01, 2.68, 3.47, 3.90 and 3.20.

Nitrobenzene and nitrotoluene showed two apparent active hydrogen atoms. With the Grignard reagent nitrobenzene has been reported as showing from 1.0 to 1.9 active hydrogens depending on the particular reagent used.[15] In contrast to the aromatic nitro compounds, nitromethane gave erratic results showing more than two apparent active hydrogens. With the Grignard reagent, values of less than one have been reported for nitromethane.[11,16]

The reaction of lithium aluminum hydride with compounds exhibiting keto-enol tautomerism was rapid and the results indicated that the compounds behaved as though they were partially enolized. In this connection it is interesting to note that diethyl malonate reacted as though it were approximately 56 percent enolized, yet the substituted diethyl malonates gave values which ranged from 18 to 28 percent. With the Grignard reagent

acetylacetone, ethyl acetoacetate and diethyl malonate have been reported to react as though they existed entirely in the mono-enol form.[12,14] In contrast to the Grignard reagent, it appears that lithium aluminum hydride reacts with the keto form of these compounds rapidly enough so that complete enolization cannot occur.

Definite conclusions cannot be drawn from the values obtained for aceto-phenone and propiophenone; however, it is indicated that these compounds re-acted as though they were partially enolized. In this respect, it is of interest that acetophenone has been reported to react with the Grignard reagent as though it were approximately 12-15 percent enolized in isoamyl ether and 78 percent enolized in pyridine or dioxane.[17,18]

Although the reaction of phenylhydrazine with lithium aluminum hydride gave erratic results, it was surprising that in three out of five determi-nations more than three apparent active hydrogen atoms were found. This sug-gested partial cleavage of the N-N bond. Confirmation of this cleavage was obtained by detection of ammonia upon hydrolysis of such a reaction mixture. In every case, the liberation of the first two hydrogens was rapid, occur-ring within five minutes.

PRELIMINARY STUDIES ON THE DETERMINATION OF FUNCTIONAL GROUPS WITH LITHIUM ALUMINUM HYDRIDE

Method of Determination

The active hydrogen studies indicated that many compounds react more readily with lithium aluminum hydride than with the Grignard reagent. In view of this, an apparatus was developed to study the quantitative reaction of lithium aluminum hydride with functional groups. Since the object of this study was merely to demonstrate the feasibility of using such a method for determining functional groups, only preliminary studies were conducted. Since this work was completed, Hochstein and Brown[7] have presented an excellent paper on the use of lithium aluminum hydride for the determination of active hydrogen and functional groups.

Apparatus

A diagram of the apparatus is shown in Figure 3. Three burets are used. Buret A (capacity 10 ml) is for the lithium aluminum hydride-ether reagent; buret B (capacity 25 ml) is for dry ether; and buret C (capacity 25 ml) is for 10 percent sulfuric acid solution. Burets A and B are pro-tected by drying tubes and are attached to reservoirs containing reagent and dry ether respectively. These burets which are filled by applying gentle suction through the drying tubes, carry 2-way stopcocks and are attached to the inlet tube as shown in the diagram. Provisions are made for sweeping the inlet tube and reaction flask with dry hydrogen. The reaction vessel is a 250-ml Erlenmeyer flask connected to the remainder of
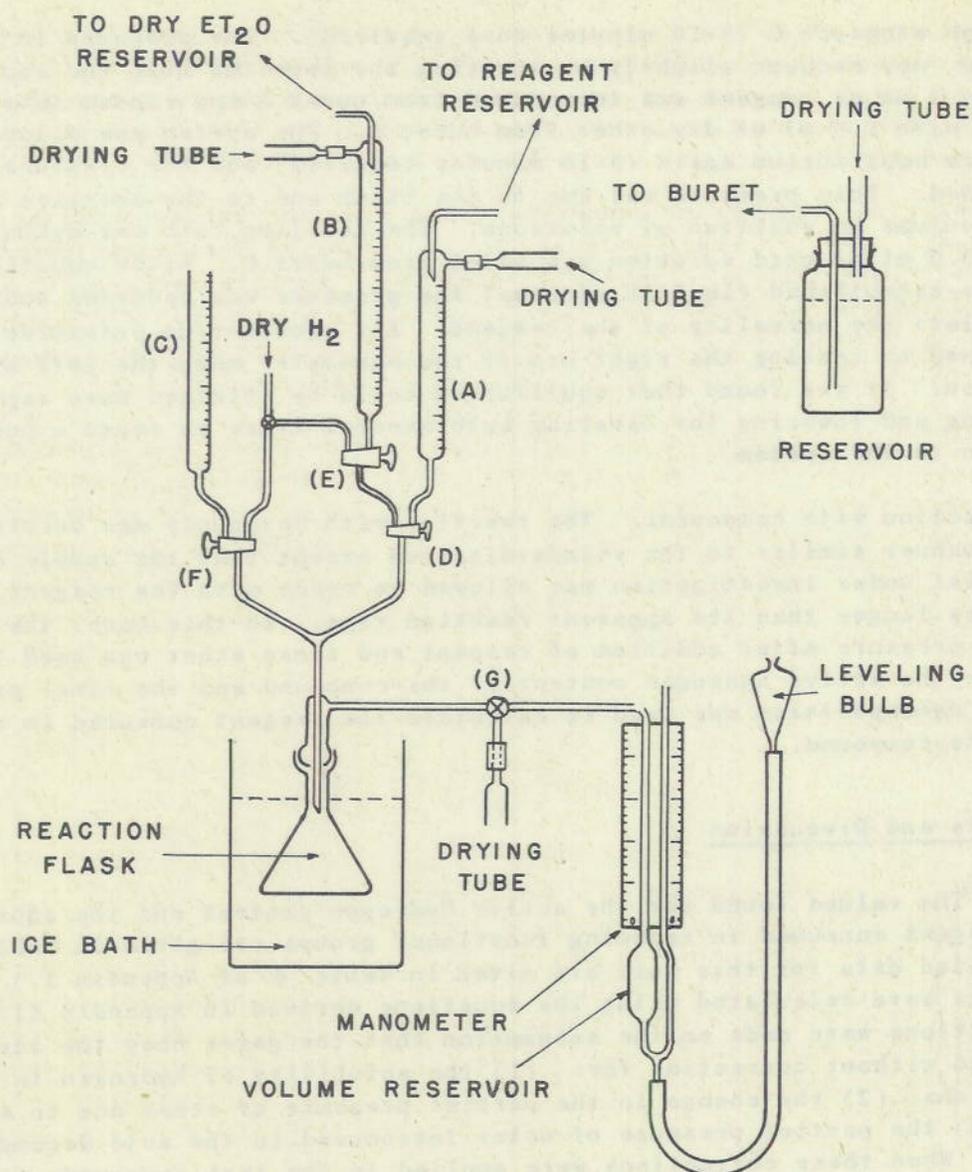
Figure 3 - Apparatus for determination of functional groups

the apparatus by a 28/12 spherical ball-and-socket joint. The take-off
arm is connected to a differential mercury manometer which has a leveling
device. One arm of the manometer has an expanded chamber to act as a
volume reservoir. Before using the apparatus, the volume of the system
was determined.

Procedure

A) Standardization of reagent: A clean, dry reaction flask was clamped into
place and surrounded with crushed ice and water. The system was swept out
for 2 minutes by passing dry hydrogen (1 to 2 liters per min.) through stop-
cocks D, E, and F and out through G. Fifteen milliliters of dry ether was
then added from buret B and the system was allowed to come to 0-0 equili-
brium at atmospheric pressure by occasional venting of the excess pressure

through stopcock G (5-10 minutes were required). The pressure in the
system was reduced slightly by lowering the leveling bulb and approxi-
mately 3 ml of reagent was introduced from buret A and rinsed into the
flask with 5.0 ml of dry ether from buret B. The system was allowed to
come to equilibrium again (5-10 minutes required) and the pressure was
recorded. This pressure was due to the blank and to the decrease in the
free volume by addition of solutions. The leveling bulb was again lowered
and 10.0 ml of acid solution was added from buret C. After equilibrium
was re-established (in 5-10 minutes) the pressure was recorded and used to
calculate the normality of the reagent. All equilibrium pressures were
obtained by reading the right arm of the manometer when the left arm was
at zero. It was found that equilibrium could be attained more rapidly by
raising and lowering the leveling bulb several times to cause a pumping
action in the system.

B) Reaction with compounds: The reaction with compounds was carried out
in a manner similar to the standardization except that the sample of the
material under investigation was allowed to react with the reagent for 30
minutes longer than its apparent reaction time. In this case, the equili-
brium pressure after addition of reagent and rinse ether was used to cal-
culate the active hydrogen content of the compound and the final pressure
after decomposition was used to calculate the reagent consumed in reduc-
ing the compound.

Results and Discussion

The values found for the active hydrogen content and the equivalents
of reagent consumed in reducing functional groups are given in Table 3.
(Detailed data for this work are given in Table 6 of Appendix I.) These
results were calculated using the equations derived in Appendix II. The
derivations were made on the assumption that the gases obey the ideal gas
law and without correcting for: (1) the solubility of hydrogen in the
solutions; (2) the change in the partial pressure of ether due to solutes;
and (3) the partial pressure of water introduced in the acid decomposition
step. When these corrections were applied to the test compounds given in
Table 3, no significant improvement in the results was obtained and it was
therefore concluded that they were unnecessary under the conditions described.

The results given in Table 3 indicate that the simple nitriles,
ketones and esters tested behaved in the expected fashion in that they showed
very little active hydrogen and consumed the expected equivalents of reagent.

Benzoic acid and acetanilide showed the expected number of active hydro-
gen atoms but failed to consume the theoretical equivalents of reagent. These
low results may be due to either incomplete reaction because of formation
of an insoluble compound, or to an unexpected reaction. It is interesting
to note that at higher temperatures, acids have been found to consume two
equivalents of reagent.[7] Experimental work with several other acids showed
a behavior similar to that of benzoic acid.

TABLE 3

Reaction with Functional Groups

Name of compound	No. of active H found	Equiv. of reagent consumed
Benzonitrile	0.03	2.01
2-Ethylhexanonitrile	0.02	1.93
Acetophenone	0.01	0.95
Cyclohexanone	0.02	0.97
Cyclohexanone	0.04	1.03
2-Octanone	0.09	1.15
Dibutyl phthalate	0.05	4.04
Diethyl sebacate	0.03	3.65
2-Ethylhexyl acetate	0.06	2.10
Ethyl palmitate	0.02	2.03
Ethyl palmitate	0.04	2.01
Benzoic acid	0.98	0.90
Acetanilide	0.97	0.58
Diethyl malonate	0.39	3.68
Diethyl malonate	0.49	3.32

Diethyl malonate gave active hydrogen values slightly lower than those shown in Table 2 -- possibly due to the difference in the experimental conditions. The results in Table 3 indicate that the equivalents of reagent consumed by malonic ester give the expected value for a di-ester less the active hydrogen value.

HYDROGENOLYSIS OF ALKYL HALIDES BY LITHIUM ALUMINUM HYDRIDE

Nature of the Reaction

Although lithium aluminum hydride reduces many compounds rapidly and completely in ethyl ether at reflux temperature,[3,4,5,6] its reaction with alkyl halides is more sluggish. This difficulty may be overcome by the use of such solvents as tetrahydrofuran, which permit the employment of higher temperatures. The reactions have been further accelerated and the yields improved by a new procedure using lithium hydride, which also greatly decreases the amount of lithium aluminum hydride necessary to complete the reaction.

Experimental results indicate that not all four hydrogen atoms show the same reactivity toward alkyl halides, and that the reaction probably

proceeds in at least two steps, as represented by the equations:

$$LiAlH_4 + RX \longrightarrow RH + LiX + AlH_3$$

$$AlH_3 + 3 RX \longrightarrow AlX_3 + 3 RH .$$

Of these steps, the first is presumed to be much more rapid than the second.

As shown in Table 4, when the molar ratio of reagent to the more active halides was greater than 1.0 the reactions proceeded rapidly and to completion. When the ratio was approximately 0.25 (the calculated value to replace all four hydrogens), the reactions were sluggish. The stepwise course of the reaction would account for the fact that more than one hydrogen per mole of reagent is consumed and that all four hydrogens are not replaced in a reasonable time.

Since aluminum hydride reacts with lithium hydride in ether to produce lithium aluminum hydride,[19] it was reasoned that alkyl halides could be hydrogenated by means of lithium hydride with only a small amount of lithium aluminum hydride present. This hydrogenolysis was found to proceed rapidly and to completion. Under these conditions the reaction may be represented as:

$$RX + LiH \xrightarrow{\text{LiAlH}_4} RH + LiX.$$
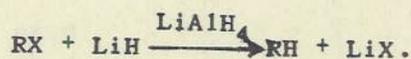
It is evident that lithium aluminum hydride acts as a hydrogen carrier, as shown by the fact that no reaction was found to occur with lithium hydride alone. The use of lithium hydride greatly reduces the amount of lithium aluminum hydride necessary and minimizes the possibility of the formation of aluminum halide.

In general, it was found that alkyl bromides react more readily than alkyl chlorides with lithium aluminum hydride. Primary halides react more readily than secondary halides which in turn are more reactive than tertiary halides. Alicyclic and aromatic halides proved very unreactive.

The reaction of 1,2-dibromoöctane with lithium aluminum hydride to give a moderate amount of olefin was surprising, since (except for a trace in the reaction product of bromocyclohexane) olefins were not observed in the reaction products of the other alkyl halides. No attempt was made to identify this olefin.

Method

In order to accelerate the reaction of lithium aluminum hydride with alkyl halides, it was necessary to use temperatures higher than that of refluxing ethyl ether. This temperature should be kept below 100°C, however

TABLE 4

Hydrogenolysis of Alkyl Halides

Compound	Solvent	Hrs. Reflux	Moles LiAlH$_4$/ mole RX	Moles LiH/ mole RX	Product	Yield (%)
1-Bromoöctane	Et$_2$O	1	0.25	2.0	n-octane	40
"	"	3	0.25	2.0	"	72
"	Bu$_2$O	1[1]	0.28	0		32
"	"	3[1]	0.28	0		64
"	THF[2]	0.5	0.13	1.5		96
"	"	1	0.03	1.5	"	95
"	"	1	0.36	0	"	61
"	"	1	0.8	0	"	96
"	"	2	0	1.5	---	0
1-Chlorododecane	"	2.5	0.8	0	n-dodecane	80
"	"	5	0.8	0	"	86
"	"	0.5	1.25	0	"	98
3-(Bromomethyl)-heptane	"	1	0.25	2.0	3-methylheptane	98
3-(Chloromethyl)-heptane	"	1	0.17	2.0	"	52
"	"	3	0.4	3.0	"	96
"	Et$_2$O	3	0.25	2.0	---	0
Benzyl chloride	THF	1	0.13	1.5	toluene	98
2-Bromoheptane	"	1	0.8	0	n-heptane	76
"	"	1	0.13	1.5	"	92
Bromocyclohexane	"	1	1.25	0	cyclohexane[3]	10
Chlorocyclohexane	"	1	0.13	1.5	---	0
5-Chloro-5-n-butylnonane	"	1	0.4	3.0	---	0
p-Bromotoluene	"	1	0.25	1.75	toluene	4
"	"	3	0.25	2.0	"	14
1,2-Dibromoöctane	"	1	0.25	3.0	n-octane[4]	80

[1] Reaction maintained at 85°. [2] Tetrahydrofuran. [3] Contained a trace of olefin. [4] In addition to the n-octane the reaction product contained 14 percent olefin calculated as octene.

since this is the incipient decomposition point of the reagent. Tetrahydro-
furan was found to be an excellent reaction medium because it is a good sol-
vent for the reagent,[2] it is miscible with water and it has a suitable boil-
ing point. Di-*iso*-propyl ether, although having the proper boiling point, was
found to be a poor solvent for the reagent. Di-*n*-butyl ether, in which the
reagent is suitably soluble, requires an externally controlled temperature
for the reaction, and in one instance of its use, there was a sudden rise in
temperature of the reaction mixture with consequent decomposition of reagent.

Apparatus and Procedure

The hydrogenolysis of 1-bromoóctane serves as an example of the method
used.   A mixture of 0.13 mole (5 g) of lithium aluminum hydride (from Metal Hydrides,
Inc., Beverly, Massachusetts) and 1.5 moles (12 g) of lithium hydride (100
mesh) was placed in a one-liter, three-necked flask equipped with a Hirschberg
stirrer and a reflux condenser fitted with a calcium chloride tube. A
thermometer was inserted through the center stopper parallel to the stirrer
shaft. The flask was cooled and 300 ml of tetrahydrofuran was added, with
stirring. The solution was then heated to reflux. One mole (193 g) of 1-bromo
óctane was added from a dropping funnel at such a rate to maintain moderate
reflux without external heating (approximately 45 minutes). The mixture
was refluxed for another hour, then cooled to 10°C. Approximately 100 ml
of a mixture of tetrahydrofuran/water, (60/40 by volume) was added very
cautiously with stirring, keeping the temperature below 20°C. The mixture
was transferred slowly with stirring into a two-liter beaker containing 80
ml of sulfuric acid in ice and water. The product layer was separated, washed
twice with one-liter portions of water, dried over anhydrous potassium car-
bonate and distilled through a 60-plate Stedman column. A 96 percent yield
of *n*-octane, b.p. 125° (uncorrected), n_D^{20} 1.3975, was obtained.

Variations from this procedure are given in Table 4. In all cases,
from 0.3 to 1.0 mole of alkyl halide was used. In some cases, e.g., 3-(chloro-
methyl)-heptane, it was necessary to continue heating throughout the addi-
tion of the alkyl halide in order to maintain a steady reflux. In the case
of the normal paraffins it was possible to eliminate the distillation pro-
cedure by means of several additional water washes followed by washing with
cold concentrated sulfuric acid.

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APPENDIX I

TABLE 5

Active Hydrogen Data

Compound	Sample wt. (gm)	Millimoles sample	Net free vol. of system (ml)	Obs. press. increase (mm Hg)	Corr. press. increase (mm Hg)	Active H. found	Time to reach equilibrium (min)
n-Decanol	0.9126	5.76	1033	97	95	1.00	5-10
"	0.5230	3.30	1031	58	55.5	1.02	5-10
Benzyl alcohol	0.3307	3.06	459.5	120.5	118.5	1.06	5-10
Heptanol-2	0.3198	2.75	458	106.5	104.5	1.02	5-10
Cyclohexanol	0.6370	6.36	1043	104	102	0.98	5-10
"	0.6158	6.14	1045	103	101	1.01	5-10
t-Amyl alcohol	0.5276	5.98	993	100.5	99	0.97	5-10
"	0.5154	5.85	995	103	100.5	1.00	5-10
2-Methyl-2,4-pentanediol	0.3768	3.19	999	113	109.5	2.01	5-10
"	0.3830	3.24	1001	113	110.5	2.01	5-10
α-Naphthol	0.7389	5.12	987	95	92.5	1.05	10-20
"	0.4292	2.92	459.5	113.5	111	1.03	10-20
ß-Naphthol	0.4352	3.02	997	56	54	1.05	5-10
"	0.3754	2.60	989	51	48.5	1.08	5-10
Resorcinol	0.7996	7.26	1006	189	187.5	1.53	50
"	0.2236	2.03	461	126.	117	1.56	140
Hydroquinone	0.2113	1.92	464	reaction too slight		----	----
n-Caprylic acid	0.8591	5.95	995	107	105	1.03	5-10
"	0.8767	6.08	997	109	107	1.03	5-10
2-Ethylhexoic acid	0.8208	5.69	978	103	101	1.02	5-10
Benzoic acid	0.7417	6.07	1033	101	99	0.99	5-10
"	0.6508	5.33	1039	88	86	0.99	5-10
o-Bromobenzoic acid	0.8643	4.31	993	78.5	74.5	1.00	10-15
Succinic acid	0.3478	2.94	1035	reaction too slight		----	----
Terephthalic acid	0.4537	2.73	1001	120	115.5	2.08	115
Cyclohexylamine	0.3247	3.28	1003	79.5	76.5	0.94	375
Diamylamine	0.7583	4.82	1009	3	1	0.01	*
Tributylamine	0.8491	4.67	1016	126.5	123	1.99	50
Aniline	0.3506	3.76	1035	120	117.5	2.05	50
"	0.3101	3.33	989	122.5	119.5	2.04	70
ß-Naphthylamine	0.4884	3.41	991	106	102.5	1.99	80
"	0.4315	3.01	991	150.5	147	2.05	60
2-Ethylhexenamide	0.5943	4.14	982	125.5	123.5	0.98	5-10
Acetanilide	0.9912	7.33	986				

TABLE 5 (Cont.)

Compound	Sample wt. (gm)	Millimoles sample	Net free vol. of system (ml)	Obs. press. increase (mm Hg)	Corr. press. increase (mm Hg)	Active H found	Time to reach equilibrium (min.)
Nitrobenzene	0.5065	4.12	994	148	147	2.08	35
o-Nitrotoluene	0.5146	3.75	1004	132.5	129.5	2.03	100
Nitromethane	0.2503	4.10	1002	167.5	166.5	2.40	120
"	0.1264	2.07	1007	100	96	2.75	250
Acetyl acetone	0.5824	5.83	988	96.5	94.5	0.94	5-10
"	0.3055	3.05	465.5	108	106	0.95	5-10
Ethyl acetoacetate	0.3808	2.93	462.5	62	60	0.56	5-10
"	0.7656	5.88	984	60	58	0.57	5-10
Diethyl malonate	0.3755	2.345	462	50.5	48.5	0.56	5-10
"	0.3594	2.24	467	48	46	0.57	5-10
" methylmalonate	0.8706	4.99	1000	23	21	0.25	5-10
"	0.4210	2.41	463.5	27	25	0.28	5-10
" ethylmalonate	0.4052	2.15	468.5	19.5	17.5	0.22	5-10
"	0.4683	2.49	465	24.5	22.5	0.25	5-10
" i-propylmalonate	0.6152	3.05	470	21.5	19.5	0.18	5-10
"	1.3705	6.78	996	26.5	24.5	0.21	5-10
" n-butylmalonate	0.5272	2.435	469.5	21	19	0.22	5-10
"	1.1381	5.25	998	26.5	23.5	0.26	5-10
" i-butylmalonate	0.7120	3.29	471.5	28.5	26.5	0.22	5-10
"	1.1055	5.10	998	24	22	0.25	5-10
" benzylmalonate	0.5568	2.22	471	17	15	0.19	5-10
"	1.2353	4.94	1002	20	17.5	0.21	5-10
Acetophenone	0.4869	4.05	462.5	12	10	0.07	5-10
"	0.6040	5.02	464	14	12	0.05	5-10
Propiophenone	0.4462	3.32	477.5	7.5	5.5	0.05	5-10
"	0.4613	3.43	465.5	12	10	0.08	5-10
Octyl mercaptan	0.8689	5.94	1031	100.5	97.5	1.00	5-10
"	0.9330	6.38	1033	109.5	106.5	1.01	5-10
Dioctyl thioether	1.008	3.91	1014	1.5	0	0	*
Ethyl palmitate	1.0602	2.76	1012	1.5	0	0	*
Phenylhydrazine	0.2033	1.88	1011	99	95	3.01	80
"	0.2326	2.15	932	109.5	105.5	2.68	75
"	0.2469	2.28	1051	132	128	3.47	125
"	0.2409	2.23	987	147.5	146	3.90	90
"	0.2265	2.10	989	117	115.5	3.20	70

* Allowed to react 10 minutes.

TABLE 6
Functional Group Analysis Data

Compound	Weight (gm)	V	Volume (ml)			
			S_1	S_2	S_3	S_4
Standardization	-----	275	15.0	3.44	5.0	10.0
Diethyl malonate	0.2076	274	15.0	6.50	5.0	10.0
Standardization	-----	274	15.0	3.90	5.0	10.0
Diethyl malonate	0.1924	275	15.0	8.30	5.0	10.0
Standardization	-----	275	15.0	3.00	5.0	10.0
Benzoic Acid	0.2343	268.5	14.4	6.13	5.0	10.0
Standardization	-----	275	15.0	3.20	5.0	10.0
Acetanilide	0.1590	266	15.0	8.98	5.0	8.3
Standardization	-----	272	15.0	5.00	5.0	10.0
Ethyl palmitate	0.5334	275	15.0	5.00	5.0	10.0
" "	0.5180	280	15.0	5.00	5.0	10.0
Standardization	------	280.3	15.0	3.02	5.0	10.0
Diethyl sebacate	0.2162	268.8	15.0	6.50	5.0	10.0
Standardization	-----	268.8	15.0	2.97	5.0	10.0
2-Ethylhexanonitrile	0.1855	274.3	15.0	5.03	5.0	10.0
Acetophenone	0.5416	280.3	15.0	8.02	5.0	10.0
Cyclohexanone	0.4212	268.8	15.0	8.00	5.0	10.0
Standardization	-----	274.3	15.0	3.00	5.0	10.0
Benzonitrile	0.1617	268.8	15.0	6.04	5.0	10.0
2-Octanone	0.3723	280.3	15.0	6.05	5.0	10.0
2-Ethylhexyl acetate	0.2595	274.3	15.0	6.04	5.0	10.0
Cyclohexanone	0.3213	280.3	15.0	6.02	5.0	10.0
Dibutyl phthalate	0.2336	274.3	15.0	6.01	5.0	10.0

TABLE 6 (Cont.)

| Pressures (mm Hg) | | | Blank | Reagent | Active | Equiv. |
P_o	P_1	P_2	(millimoles H_2)	normality	hydrogen	reag. cons.
765	22	271.5	0.039	0.939	---	----
765	72	182.5	0.039	0.939	0.49	3.32
763	30	242.5	0.139	0.712	---	----
763	73	164	0.139	0.712	0.39	3.68
763	22.5	232	0.061	0.895	---	----
763	162.5	326	0.061	0.895	0.98	0.90
765	24	143.5	0.076	0.443	---	----
765	122	299	0.076	0.443	0.97	0.58
768.5	25.5	395	0.027	0.962	----	----
768	30	123	0.027	0.962	0.04	2.01
767	26.5	126.5	0.027	0.962	0.02	2.03
760	26	184	0.123	0.684	----	-----
761	38	155	0.123	0.684	0.03	3.65
758	29.5	209	0.157	0.770	----	----
758	36	120	0.157	0.770	0.02	1.93
759	42.5	187	0.157	0.770	0.01	0.95
759	48	203	0.157	0.770	0.02	0.97
765	27	201.5	0.126	0.747	----	----
765	38	152.5	0.126	0.747	0.03	2.01
762	50	132	0.126	0.747	0.09	1.15
761	40	147	0.126	0.747	0.06	2.10
760	43	129	0.126	0.747	0.04	1.03
760	37	130	0.126	0.747	0.05	4.04

APPENDIX II

Derivations of Equations Used in Functional Group Analysis

(A) Definition of terms

Step 1 = first addition of dry ether in procedure

Step 2 = addition of reagent and rinse dry ether

Step 3 = addition of sulfuric acid solution

P_o = atmospheric pressure

P_e = partial pressure of ether at 0^oC (185 mm)

P_{ho} = partial pressure of hydrogen after Step 1 = P_o-P_e

P_1 = observed pressure increase (recorded equilibrium pressure) after Step 2

P_{h1} = partial pressure of hydrogen after Step 2 = $P_{ho}+P_1$

P_2 = observed total pressure increase (recorded equilibrium pressure) after Step 3

P_{h2} = partial pressure of hydrogen after Step 3 = $P_{ho}+P_2$

V = total volume of system

S_1 = volume of ether added in Step 1

S_2 = volume of reagent added in Step 2

S_3 = volume of rinse ether added in Step 2

S_4 = volume of acid solution added in Step 3

n_1 = millimoles hydrogen present after Step 1

n_2 = millimoles hydrogen present after Step 2

n_3 = millimoles hydrogen present after Step 3

n_a = millimoles hydrogen liberated in Step 2 = n_2-n_1

n_b = millimoles hydrogen liberated in Step 3 = n_3-n_2

RT = 17,030 (all volumes in ml, pressures in mm Hg. and temperatures at 0^oC).

(B) Derivations

(1) Of n_a (millimoles hydrogen liberated in Step 2)

$$n_1 = \frac{P_{ho}(V-S_1)}{RT}$$

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$$n_2 = \frac{P_{h1}(V-S_1-S_2-S_3)}{RT}$$

$$n_a = n_2-n_1 = \frac{P_1(V-S_1)-(P_o+P_1-185)(S_2+S_3)}{17,030} \, .$$

(2) Of n_b (millimoles hydrogen liberated in Step 3)

$$n_3 = \frac{P_{h2}(V-S_1-S_2-S_3-S_4)}{RT}$$

$$n_b = n_3-n_2 = \frac{(P_2-P_1)(V-S_1-S_2-S_3)-(P_o+P_2-185)S_4}{17,030} \, .$$

(C) Calculations

   (1) Blank
        Blank = n_a(from standardization)

   (2) Normality of reagent

   $$N = \frac{n_a+n_b}{S_2} \, \text{(from standardization)}$$

   (3) Active hydrogen of a sample

   $$\text{No. active H atoms} = \frac{n_a-\text{blank}}{\text{millimoles sample}}$$

   (4) Reagent consumed by reaction with functional groups of sample

   $$\text{equivs. consumed/mole} = \frac{NS_2-n_a-n_b}{\text{millimoles sample}} \, .$$

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