Reactions of the Halogen Fluorosulfates, FOSO₂F, ClOSO₂F, BrOSO₂F, and Br(OSO₂F)₃

By WILLIAM P. GILBREATH and GEORGE H. CADY

The new reactive compound, chlorine fluorosulfate, $ClOSO_2F$, was produced by the combination of chlorine with peroxydisulfuryl difluoride, $S_2O_6F_2$, at about 125° under pressure. It combined with tetrafluoroethylene to form 2-chlorotetrafluoroethyl fluorosulfate. This type of behavior was found to be typical of the halogen(I) fluorosulfates of fluorine, chlorine, and bromine. They were added across the carbon–carbon double bond to bind the halogen atom to one of the carbon atoms and the fluorosulfate group to the other. Compounds obtained in this manner were: $C_2F_5OSO_2F$, $CCl_2FCCl_2OSO_2F$ $CF_2BrCF_2OSO_2F$, and perfluorocyclopentyl fluorosulfate. Fluorine fluorosulfate combined with sulfur tetrafluoride to form SF_5OSO_2F but the fluorosulfates of chlorine(I) and of bromine(I) did not react similarly. When used in excess, fluorine fluorosulfate combined with bromine to give a liquid product having the empirical composition $Br_2 \cdot 3SO_3F_2$. The same sort of material was formed by mixing equimolar amounts of BrF_3 and $Br(SO_3F)_3$. It was found also that the latter reactants tended to combine chemically in all proportions when mixed; therefore, the material $Br_2 \cdot 3SO_3F$ should be regarded as a non-stoichiometric compound.

The halogen fluorosulfates, $FOSO_2F$,[1] $BrOSO_2F$,[2] $Br(OSO_2F)_3$,[2] $I(OSO_2F)_3$,[2] and $IF_3(OSO_2F)_2$[3] have been characterized, but few of their reactions have been studied. One purpose of the present research was to increase the number of known chemical properties of these substances. Another purpose was to produce and identify a fluorosulfate of chlorine. Previous attempts to do this had been unsuccessful.[4] In this research, particular attention has been given to addition reactions of compounds containing the carbon–carbon double bond. This is because fluorine fluorosulfate contains an –OF group. Other compounds of this type, specifically CF_3OF and SF_5OF, break at the –OF bond when adding to the carbon–carbon double bond.[5-7] It has now been found that fluorine fluorosulfate behaves in the same way and that the other halogen fluorosulfates also break at the oxygen–halogen bond when adding across the double bond.

Bromine was observed to react with fluorine fluorosulfate at room temperature to form a golden yellow liquid of low volatility. The excess fluorine fluorosulfate could be distilled away, leaving a product having the definite composition $Br_2 \cdot 3SO_3F_2$. This formula suggested the possibility that the same material might result from mixing equimolar quantities of BrF_3 and $Br(SO_3F)_3$. When these were mixed, the product appeared to be identical with that formed from Br_2 and SO_3F_2. When ratios of BrF_3 and $Br(SO_3F)_3$ other than 1:1 were used they also gave a golden yellow liquid of very low volatility, and when BrF_3 was used in excess, it was not possible to remove all of the excess by vacuum pumping. The liquid continued to contain more moles of combined BrF_3 than of $Br(SO_3F)_3$. It was not found possible to study the system BrF_3–$Br(SO_3F)_3$ by measur-

ing freezing points, because the golden liquids did not freeze upon cooling; instead, they became glassy. A study by n.m.r. was made, however, to learn whether $Br_2(SO_3F_2)_3$ would show its own fluorine nuclear resonances while either BrF_3 or $Br(SO_3F)_3$, when present in excess, would show its typical fluorine resonance. Various mixtures of BrF_3 with $Br(SO_3F)_3$ were tried at room temperature but for each mixture only two resonances were observed—one at the higher magnetic field, for fluorine atoms attached to bromine and one, at the lower field, for fluorine atoms attached to sulfur. The chemical shifts of the two types of resonance were measured with respect to the fluorine resonance of CCl_3F as an external standard. For the chemical shift of fluorine attached to bromine there was a nearly linear increase from 23 p.p.m. for pure BrF_3 to 48.9 p.p.m. for a 1:1 ratio of BrF_3 to $Br(SO_3F)_3$ and from there a nearly linear decrease to 44 p.p.m. for 17.6 mole % BrF_3. The chemical shift of the fluorine attached to sulfur changed slightly and in a nearly linear manner from −39 p.p.m. for pure $Br(SO_3F)_3$ to −41 p.p.m. at 90 mole % BrF_3. Although the maximum chemical shift for one type of fluorine at 50 mole % BrF_3 suggested something special about the composition $Br_2 \cdot 3SO_3F_2$, the most significant result of the n.m.r. observations was the implication that rapid exchange occurred involving various molecular or ionic species. Probably polymeric molecules existed in the system, and it is likely that ions such as BrF_2^+, $Br(SO_3F)_2^+$, $BrFSO_3F^+$, BrF_4^-, $BrF_3SO_3F^-$, $BrF_2(SO_3F)_2^-$, $BrF(SO_3F)_3^-$, and $Br(SO_3F)_4^-$ were present. Since BrF_3 and $Br(SO_3F)_3$ appeared to have chemical affinity over the entire range of composition, the yellow liquid of composition $Br_2(SO_3F_2)_3$ should be regarded as a non-stoichiometric compound. An additional bit of evidence about this system was obtained by condensing excess fluorine fluorosulfate upon a sample of dark red bromine(I) fluorosulfate, $BrOSO_2F$. When the mixture warmed to room temperature, it became yellow in color. The excess fluorine fluorosulfate was pumped away, leaving a liquid of the empirical compo-

(1) F. B. Dudley, G. H. Cady, and D. F. Eggers, *J. Am. Chem. Soc.*, **78**, 290 (1956).
(2) J. E. Roberts and G. H. Cady, *ibid.*, **82**, 352 (1960).
(3) J. E. Roberts and G. H. Cady, *ibid.*, **82**, 354 (1960).
(4) J. M. Shreeve and G. H. Cady, *ibid.*, **83**, 4251 (1961).
(5) R. S. Porter and G. H. Cady, *ibid.*, **79**, 5625 (1957).
(6) J. A. C. Allison and G. H. Cady, *ibid.*, **81**, 1089 (1959).
(7) S. M. Williamson and G. H. Cady, *Inorg. Chem.*, **1**, 673 (1962).

TABLE I

INFRARED SPECTRA, 2 TO 15 μ RANGE

(Frequencies in cm.$^{-1}$ units)

$C_2F_5SO_3F$	$C_5F_9SO_3F$	$CCl_2FCCl_2SO_3F$	$CH_2FCH_2SO_3F$?	$CClF_2CF_2SO_3F$	$CF_2BrCF_2SO_3F$
1500 vvs	1494 vs	1800 w	2870 w	1497 vs	2240 w
1382 w	1378 w	1482 vvs	1468 vs	1426 m	1498 vs
1249 vvs	1322 s	1243 vvs	1235 vs	1261 vs	1315 ms
1219 s	1288 w	1121 w	1095 m	1221 vs	1256 vs
1158 vs	1252 vs	1065 m	1036 vs	1185 vs	1217 s
1093 vvs	1230 vvs	984 vs	953 vs	1153 vs	1182 vs
1000 w	1155 s	938 s	832 vs	1123 vvs	1144 vs
887 s	1075 mw	896 m		985 vs	1113 vvs
843 vs	1038 w	830–852 vvs		872 m	1080 m
775 ms	990 vvs	741 w		843 s	1016 w
	849 vs			767 m	945–968 vs
	804 m				867 ms
	697 m				843 vs
					808 w
					766 ms
					730 w

sition BrF(SO₃F)₂. The fluorine n.m.r. spectrum was composed of two sharp resonances separated by 89 p.p.m. with an area ratio of 1:2, the smaller resonance peak being at a higher magnetic field than the larger. The observed chemical shift was the same as that expected for a 1:2 mixture of BrF₃ with Br(SO₃F)₃.

Parts of the BrF₃–Br(SO₃F)₃ system probably were encountered by Woolf[8] in 1950. He reported a compound, BrF₂SO₃F, formed by the reaction of NOSO₃F with BrF₂SbF₆. He also reported the chemical combination of bromine trifluoride with sulfur trioxide.

Fluorine fluorosulfate was found to react slowly with sulfur tetrafluoride in a glass vessel at 70° to produce the previously known pentafluorosulfur fluorosulfate,[9,10] SF₅OSO₂F, in about 25% yield after a 3-hr. period. The analogous reactions using chlorine fluorosulfate or bromine fluorosulfate with sulfur tetrafluoride in a Monel metal reactor at 80° failed to give the hoped for addition products. Substances formed by these reactions included SO₂F₂, S₂O₅F₂, SF₆, and Cl₂ or Br₂.

The melting points of the new organo fluorosulfates produced by adding halogen fluorosulfates to alkenes generally were not obtained, since, on cooling, glasses rather than crystalline solids formed. Infrared spectra for these substances showed =S<(O)(O) stretching frequencies at 1468–1500 cm.$^{-1}$ (asymmetric) and 1235–1261 cm.$^{-1}$ (symmetric), S–F stretching frequency at 832–850 cm.$^{-1}$, and various C–F stretching modes between 1000 and 1382 cm.$^{-1}$. The spectra are given in Table I. With the exception of the material thought to be 2-fluoroethyl fluorosulfate these compounds were thermally stable at least up to their normal boiling points. They were not very soluble in water but were dissolved by common organic solvents.

Experimental

Chlorine Fluorosulfate, ClOSO₂F.—A 0.023-mole sample of

(8) A. A. Woolf, *J. Chem. Soc.*, 1053 (1950).
(9) H. J. Eméleus and K. J. Packer, *ibid.*, 771 (1962).
(10) C. I. Merrill, Ph.D. Thesis, University of Washington, 1962.

chlorine was condensed together with a 0.016-mole portion of peroxydisulfuryl difluoride, S₂O₆F₂, in a Monel metal reactor having an external diameter of 6.35 mm. and a volume of 5 ml. A valve on the reactor was closed to confine the materials. This vessel then was surrounded by a protective metal shield and was maintained at about 125° for 5 days. The product then was cooled to −78° and subjected to vacuum pumping for 20 hr. to remove the unreacted chlorine. This left behind a material which was nearly as pure ClOSO₂F as could be obtained by more complicated procedures tried in this study. It was found undesirable in general to transfer the substance from one part of the system to another because of its high reactivity with traces of water on the glass apparatus. Hydrolysis yielded a red viscous liquid of low volatility. A freshly distilled sample was a yellow liquid. Upon standing at room temperature the color gradually deepened and became red. Distillation again gave a yellow distillate but left behind a red material.

Properties of this substance, like those of others mentioned later, are given in Table II.

The mass spectrum at an ionization potential of 70 volts had peaks attributed to Cl⁺, SO₂F⁺, SO⁺, SOF⁺, SO₃⁺, SO₂⁺, and ClSO₂F⁺ in order of decreasing magnitude. Peaks for SiF₃⁺, Cl₂⁺, and HCl⁺ also were present. They probably were formed by the compound reacting with water on glass apparatus. The n.m.r. spectrum, at 56.4 Mc., had one resonance peak at a chemical shift of −33.9 p.p.m. relative to the external reference, CCl₃F. An impurity peak, probably due to S₂O₆F₂ or S₂O₅F₂, having one fortieth of the area of the principal peak, was present at a chemical shift (from CCl₃F) of −47.6 p.p.m.

The reaction of chlorine fluorosulfate with water was violent and yielded oxygen as a product. In one case 24% of the oxidizing equivalent due to chlorine(I) was liberated as O₂ while the remainder (presumably present as HOCl) was found in solution by an iodometric titration. The proportions of O₂ and HOCl formed by hydrolysis varied from one run to another. Chlorine and sulfur were determined in the solution.

Reaction of Bromine with Fluorine Fluorosulfate.—A sample of bromine weighing not over 1 g. was condensed in a glass bulb cooled to −183°. An excess amount of fluorine fluorosulfate then was condensed in the bulb. As the temperature of the vessel rose to and remained at about 25° the substances reacted, giving a golden yellow liquid. The excess of fluorine fluorosulfate then was pumped away while the material was held at 15°. All of the bromine was present in the yellow product and the latter had a weight indicating that 3 moles of SO₃F₂ had combined with 1 mole of Br₂.

Anal. Calcd. for Br₂·3SO₃F₂: Br, 31.0; S, 18.7. Found: Br, 30.6; S, 17.0. The hydrolysis reaction used for the analysis was violent and some oxygen was produced.

Reaction of Fluorine Fluorosulfate with Iodine(III) Fluorosul-

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Table II

Properties of Compounds

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	ClSO$_3$F	C$_2$F$_5$SO$_3$F	C$_5$F$_9$SO$_3$F	FC$_2$Cl$_4$SO$_3$F	ClC$_2$F$_4$SO$_3$	BrC$_2$F$_4$SO$_3$F
M.p., °C.	−84.3 ± 0.3					
Vap. press. data: A^a	8.14352	7.9805	8.1160	7.9332	8.1136	7.8808
B^a	1674.5	1505	1912	2194	1719	1733
range, °C.	−23 to +45	−23 to +27	−18 to +87	38–164	−25 to +57	0–25
B.p. from eq. a, °C.	45.1	22.1	92.0	161.3	55.4	73.4
$\Delta H,^c$ kcal./mole	−7.66	−6.89	−8.75	−10.07	−7.86	−7.93
Trouton constant, e.u.	24.0	23.2	23.8	23.2	23.8	23.2
Density data: C^b	1.760	1.714	1.844	1.834	1.764	2.007
D^b	0.00247	0.00343	0.00258	0.00178	0.00228	0.00286
range, °C.	−70 to +20	0–20	3–30	0–30	0–30	0–27
d at 20°, g./cc.	1.711	1.645	1.792	1.798	1.718	1.950
Mol. wt., obsd.	133 ± 1.5	218 ± 1	330 ± 2	282 ± 7	234 ± 1	279 ± 1
theor.	134.5	218.1	330.1	284	234.5	279.0
% S, obsd.	24.4	14.2	9.6	10.2	11.6	
% S, theor.	23.8	14.7	9.7	11.2	13.6	
% Cl, obsd.	25.8			50.1	14.3	Br = 27.9
% Cl, theor.	26.4			50.0	15.1	Br = 28.6
% F, obsd.		47.7			41.8	35.3
% F, theor.		50.0			40.7	34.4

^{a} Vapor pressure constants in the equation (a) log P (mm.) $= A - B/T$ (°K.). ^{b} Density constants in the equation (b) d (g./cc.) $= C - Dt$ (°C.). ^{c} ΔH of vaporization, calculated from Clausius–Clapeyron equation.

fate.—Fluorine fluorosulfate reacted with iodine(III) fluorosulfate at 25°, forming peroxydisulfuryl difluoride and a colorless liquid having the properties of IF$_3$(SO$_3$F)$_2$.[3] The former was removed from the latter by vacuum pumping at room temperature.

Perfluoroethyl Fluorosulfate.—Fluorine fluorosulfate at 1:3 dilution with dry nitrogen was slowly added over a 20-hr. period to tetrafluoroethylene at 1:7 dilution in a 2.2-l. bulb. The reaction, which was violent, was further moderated by a collar of solid carbon dioxide fixed around the neck of the reaction vessel and by a bath at −30° over the lower portion of the vessel. After a nearly stoichiometric amount of fluorine fluorosulfate had been added, the nitrogen was pumped away while the reaction product was held at −183°. Separation of the products by vapor phase chromatography showed about a 40% yield of C$_2$F$_5$SO$_3$F.

The mass spectrum showed the following major species, in order of decreasing abundance: C$_2$F$_5$$^+$, CF$_3$$^+$, SO$_2F^+$, COF$^+$, CF$^+$, CF$_2$$^+$, SO$^+$, CO$^+$, CF$_3SO_3$$^+$, SOF$^+$, and C$_2F_5SO_3$$^+$. The n.m.r. spectrum showed the fluorosulfate fluorine split into a triplet by the methylene fluorine atoms (α), which themselves were broken first into a doublet by the fluorosulfate fluorine and then into a quadruplet by the three equivalent methyl fluorine atoms (β). The β-fluorine resonance was split into a triplet by the methylene fluorine atoms. The following coupling and shielding values were obtained: $J_{SF-\alpha} = 8.2$ c.p.s., $J_{\alpha\beta} = 2.4$ c.p.s., $\delta_{SF} = -49.4$ p.p.m., $\delta_\alpha = 86.1$ p.p.m., $\delta_\beta = 88.5$ p.p.m. relative to CCl$_3$F.

Perfluorocyclopentyl Fluorosulfate.—Undiluted fluorine fluorosulfate was added slowly at room temperature to perfluorocyclopentene, initially at 100 mm. pressure, yielding a colorless liquid which then was purified by vapor phase chromatography. The somewhat cloudy product was dried with anhydrous sodium sulfate.

The mass spectrum had many peaks, the most prominent ones being for SO$_2$F$^+$, C$_3$F$_5$$^+$, CF$_3$$^+$, and C$_2F_4$$^+$. A small parent peak also was observed. The n.m.r. spectrum due to fluorine was that expected for a substance having the structure of perfluorocyclopentyl fluorosulfate. There was evidence for one fluorine atom attached to the α-carbon; two structurally different kinds of fluorine atoms, β and β', on each β-carbon atom and two structurally different kinds of fluorine atoms, γ and γ', on each γ-carbon atom. Values found for spin-spin coupling constants, J, and for chemical shifts, δ, with reference to CCl$_3$F, were as follows: $J_{\beta\beta'} = 262$ c.p.s., $J_{\gamma\gamma'} = 261$ c.p.s., $\delta_\beta = 122.45$

p.p.m., $\delta_{\beta'} = 130.48$ p.p.m., $\delta_\gamma = 130.07$ p.p.m., $\delta_{\gamma'} = 132.27$ p.p.m., $\delta_\alpha = 132.43$ p.p.m., $\delta_{SF} = -51.24$ p.p.m. A detailed analysis of the spectrum is given in a thesis.[11]

The observed intensity ratios for the different types of fluorine atoms in the n.m.r. spectrum were within 5% of those calculated for C$_5$F$_9$SO$_3$F.

2-Fluorotetrachloroethyl Fluorosulfate.—About 4 ml. of tetrachloroethylene was condensed in a 500-ml. glass reactor, and undiluted fluorine fluorosulfate vapor then was added rather rapidly at room temperature. A fog formed and settled out as a pale yellow liquid. The product was refined by distillation, giving 2-fluorotetrachloroethyl fluorosulfate in a yield of about 90%.

The mass spectrum revealed the following most prevalent species, in order of decreasing abundance: CClO$^+$, CCl$_3$$^+$, CCl$_2F^+$, C$_2Cl_4F^+$, CCl$_2$$^+$, and CCl$_2SO_3F^+$. The largest m/e found was 263 (C$_2$Cl$_4$SO$_3$F$^+$). The n.m.r. spectrum consisted of only two simple resonances, as expected. The sulfur and carbon fluorine resonances occurred at shifts of −50.4 and +67.0 p.p.m. relative to CCl$_3$F and had an area ratio of 1 to 1.1.

2-Fluoroethyl Fluorosulfate?—A small amount of 2-fluoroethyl fluorosulfate probably was prepared by slowly adding a 10:1 mixture of nitrogen and fluorine fluorosulfate to a 3:1 mixture of nitrogen and ethylene in a cold (−50°) vessel. The initial pressure of ethylene was about 100 mm. The reaction was very violent with mostly resinous materials being formed. In only two of the five attempts was any of the expected compound isolated. Since the identification of this compound was not absolutely certain, further space will not be devoted to the substance here. Details are given in a thesis.[11]

2-Chlorotetrafluoroethyl Fluorosulfate.—Tetrafluoroethylene diluted 1:1 with dry nitrogen was slowly added to gaseous chlorine fluorosulfate at room temperature and 200 mm. pressure. The resulting reaction was vigorous, and the expected product 2-chlorotetrafluoroethyl fluorosulfate was found to be formed in about 60% yield. The products were separated by gas chromatography. The following major species were noted in the mass spectrum: SO$_2$F$^+$, CF$_2$Cl$^+$, C$_2$F$_4$Cl$^+$, CF$^+$, CF$_2$SO$_3$$^+$, CF$_2$$^+$, C$_2F_5$$^+$, and SOF$^+$. C$_2F_3SO_3F^+$ was the heaviest species identified. The n.m.r. spectrum consisted of a triplet at −49.4 due to the fluorosulfate fluorine being split by its two nearest (α) fluorines, a triplet at 73.4 p.p.m. arising from the β-fluorines being split by the α pair, and two triplets centered at 87.0 p.p.m. belonging to the α-fluorines which were acted upon by the

(11) W. P. Gilbreath, Ph.D. Thesis, University of Washington, 1962.

β-fluorines and the fluorosulfate fluorine. The coupling constants (in c.p.s.) were: $J_{SF-\alpha} = 8.1$, $J_{\alpha\beta} = 3.3$.

2-Bromotetrafluoroethyl Fluorosulfate.—Tetrafluoroethylene, diluted 1:3 with nitrogen, was added slowly to red-black bromine(I) fluorosulfate, resulting in a clear solution. After purification by vacuum bulb to bulb distillation a yield of the compound of at least 75% based on bromine fluorosulfate consumption was recovered. Final purification was accomplished by gas chromatography. The principal peaks in the mass spectrum for mass numbers greater than 28 corresponded to the ions: SO_2F^+, $C_2F_4SO_3F^+$, $C_2F_4Br^+$, CF_2Br^+, $CF_2SO_3F^+$, $C_2F_5^+$, CF^+, FCO^+, SOF^+, and $CBrF^+$.

The n.m.r. spectrum of $BrC_2F_4SO_3F$ was very similar to that of $ClC_2F_4SO_3F$, described above. The following shielding and spin–spin coupling values were found: $\delta_{SF} = -49.4$, $\delta_\alpha = 86.1$, $\delta_\beta = 69.4$ (in p.p.m.); $J_{SF-\alpha} = 8.4$, $J_{\alpha\beta} = 3.1$.

CONTRIBUTION FROM THE ETHYL CORPORATION,
BATON ROUGE, LOUISIANA

Direct Synthesis of Complex Metal Hydrides[1,2]
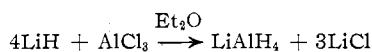
BY E. C. ASHBY, G. J. BRENDEL, AND H. E. REDMAN

The direct synthesis of $NaAlH_4$, $LiAlH_4$, $KAlH_4$, and $CsAlH_4$ from the elements has been accomplished. The reaction of the alkali metal, aluminum, and hydrogen proceeds at moderate temperatures and pressures to produce nearly quantitative yields of high purity alkali metal aluminum hydride. The method affords a convenient laboratory as well as commercial route to $NaAlH_4$ and $LiAlH_4$. The effects of temperature, pressure, solvent, and other variables have been determined. A mechanism for the reaction is discussed. The reaction of sodium, aluminum, hydrogen, and olefins to produce compounds of the structure $NaAlR_nH_{4-n}$ also has been accomplished. A promising route to unetherated $LiAlH_4$ has been found. The route involves the metathetical reaction of $NaAlH_4$ and $LiCl$ in diethyl ether. The effects of solvents and temperature on yield of $LiAlH_4$ have been investigated. A convenient method of isolation and purification of $LiAlH_4$ has been developed which produces $LiAlH_4$ in approximately 99% purity.

Introduction

The commercial process in use today for the preparation of $LiAlH_4$ involves the reaction of LiH with $AlCl_3$ in diethyl ether. This is the reaction originally used by Schlesinger and co-workers to prepare the first sample of $LiAlH_4$.[3]

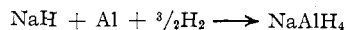$$4LiH + AlCl_3 \xrightarrow{\text{Et}_2\text{O}} LiAlH_4 + 3LiCl$$

This reaction proceeds in approximately 85% yield, producing a product of 95% purity when diethyl ether is used as a solvent. Unfortunately, for every four moles of LiH charged in this reaction, three are lost as by-product LiCl. Due to the high cost of lithium metal this fact is not insignificant.

This reaction has been extended to produce $NaAlH_4$ using tetrahydrofuran as a solvent, but in this case the reaction is more difficult. Yields and product purities are lower than for $LiAlH_4$. The failure of sodium hydride to work as well in this reaction is unfortunate, since Finholt has reported[4] the essential equivalency of $LiAlH_4$ and $NaAlH_4$ as reducing agents. The corresponding reaction of MgH_2 with $AlCl_3$ to produce $Mg(AlH_4)_2$ was reported by Wiberg,[5] and the reaction of CaH_2 with $AlCl_3$ was used by the Schlesinger group to prepare $Ca(AlH_4)_2$. Thus, the Schlesinger reaction involving an alkali or alkaline earth hydride and $AlCl_3$ is the only reaction used successfully up to now to prepare complex aluminum hydrides.

Results and Discussion

While studying the behavior of aluminum and hydrogen in the direct synthesis of triethylaluminum, we found that sodium hydride reacted with aluminum and hydrogen in an ether solvent to produce $NaAlH_4$ in quantitative yield.

$$NaH + Al + {}^3/_2H_2 \longrightarrow NaAlH_4$$

Initial experiments involved the reaction of NaH with activated aluminum powder in tetrahydrofuran at 140° and 5000 p.s.i. of hydrogen. Under these conditions $NaAlH_4$ was produced in quantitative yield in 4 hr. Substitution of sodium metal for NaH produced the same results at approximately the same rate. Hence, the direct synthesis of a complex metal hydride, from the elements, was achieved.[1,6,7]

$$Na + Al + 2H_2 \longrightarrow NaAlH_4$$
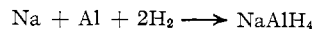
In contrast to the Schlesinger reaction, the direct synthesis uses only one mole of alkali metal per mole of product instead of four moles. The source of aluminum

(1) E. C. Ashby, French Patent 1,235,680, granted to Ethyl Corp., May 30, 1960.

(2) Presented at the Southwest–Southeast Regional Meeting of the American Chemical Society, New Orleans, La., December, 1961.

(3) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947).

(4) A. E. Finholt, E. C. Jacobson, A. E. Ogard, and P. Thompson, *ibid.*, **77**, 4163 (1955).

(5) E. Wiberg, *Angew. Chem.*, **65**, 16 (1953).

(6) Clasen later reported the same reaction, but with few details concerning the effect of variables (H. Clasen, *ibid.*, **73**, 322 (1961)).

(7) E. C. Ashby, *Chem. Ind.* (London), 208 (1962).