METALLIC SALTS OF ALCOHOLS AND ALCOHOL ANALOGS

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I. INTRODUCTION

It is frequently said that chemical literature abounds in references to the preparation and properties of compounds which are as yet useless. Precisely the opposite is true of metallic salts of alcohols and their analogs, for, in spite of a long record of usefulness, they have rarely been studied for their own sake. Although they partake of the characteristics of both organic and inorganic compounds, their structural intricacies, limited to the organic anion, have only within recent years interested the organic chemist, while his inorganic fellow has never been eager to deal with salts containing hydrocarbon radicals. Moreover, the same reactivity that makes such compounds valuable in synthetic work renders them difficult to isolate and study.

The present discussion is designed to summarize existing knowledge of the chemistry of these salts. It does not by any means purport to be a catalog of all literature references dealing with its title; to compile an exhaustive bibliography of the uses of sodium ethoxide alone would be an extremely formidable task. It is inevitable, therefore, that most details must be obtained by reference to the original sources. Every effort has been made, however, to avoid the omission of any general method of preparation or type reaction. In addition, tables have been constructed setting forth most of the known physical properties and many of the reactions of salts of alcohol types.

Practically all the compounds under discussion are derived from alcohols, amines, mercaptans, or hydrocarbons, i.e., from alcohols or their analogs in the ammonia, hydrogen sulfide, or methane systems, according to the ideas and nomenclature developed by Franklin (117). These views give additional significance to the marked chemical resemblance among such apparently unrelated compounds as $Ca(OCH_3)_2$, $Na_2NC_6H_5$, KSC_2H_5, and $NaCH_2CH_3$.

All such salts may evidently be represented by a general formula $M_x(AR_n)_y$. M represents any metal or highly electropositive radical;[1] A may be any polyvalent element; and R denotes hydrogen or any monovalent radical derived from the hydrogen compounds of the elements of Group IVB (C, Si, Ge, Sn, Pb).[2] The subscripts x, n, and y merely satisfy valence requirements. If every R is a hydrogen atom, the compound is not considered a salt of an alcohol type except in a formal way, like that in which water is called the simplest alcohol.

The nomenclature of these salts is reasonably uniform; usage has sanctioned the employment of such names as "metal alkyl oxide," "metal alkyl sulfide" (mercaptide), "metal alkyl amide," and "metal alkyl methide."[3] The nomenclature recommended for organometallic compounds by the Committee on Nomenclature, Spelling and Pronunciation of the American Chemical Society (78) is admirable from an organic standpoint, but it quite obscures the polar nature of such compounds as possess this constitution. Despite its frequent occurrence, particularly in German

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[1] For definitions see KRAUS: J. Am. Chem. Soc. **44**, 1217–39 (1922); **46**, 2196–2204 (1924).

[2] Kraus has suggested that the saturated hydrogen compounds of these elements be known collectively as hydranes.

[3] The system of naming hydrocarbon radicals suggested by Vorländer (J. prakt. Chem. [2] **59**, 247 (1899)) and adopted in Bernthsen-Sudborough's "Textbook of Organic Chemistry" (D. van Nostrand Co., New York, 1931) is followed in this paper. "The term *alkyl* group comprises all such monovalent radicals, whether of the aliphatic series, e.g., CH_3, C_2H_5, or of the aromatic, e.g., C_6H_5, $CH_3 \cdot C_6H_4$, $C_6H_5CH_2$, etc. The purely aliphatic alkyl radicals are termed *alphyl* groups, and the aromatic, aryl."

chemical literature, the term "alcoholate" applied to the salt of an alcohol (239a) is distinctly objectionable, since by analogy to "hydrate" (78) and "ammonate," it is used correctly only in referring to a salt containing alcohol of crystallization, like $CaCl_2 \cdot 2C_2H_5OH$.

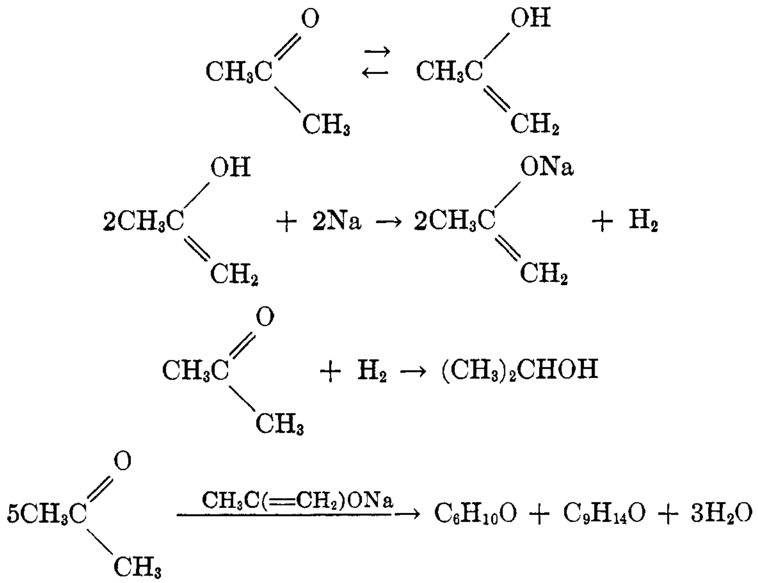
A study of the frequency with which various elements or groups occur in described compounds reveals that the radical R is commonly derived from a saturated hydrocarbon. Substituted silicane (227), germane (219, 233, 218), or stannane (60) radicals, as in $KOGe(C_2H_5)_3$ and $NaNHSn(C_6H_5)_3$, are rare, and lead derivatives of this kind are not yet known.

The nature of M is less limited. Metal alkyls have excited sufficient intrinsic interest so that investigators have succeeded in preparing members of the group representative of most of the common metals. The wealth of data on zinc dialkyls may even encourage a venture outside the realm of true salts, in the hope of bringing back ideas yet untried therein. The lack of spectacular properties in salts of amines, mercaptans (thiols), and alcohols has confined the study of these compounds almost entirely to those containing an alkali metal. Simple or alkylated ammonium groups and one tetraalkyl arsonium form (163) are the only positive radicals proved capable of yielding solid salts of alcohol types, although substituted phosphonium ethoxides (167) have been examined in solution. The only salts of other metals which have attracted more than casual attention are the alkoxides of aluminum, thallium, the alkaline earth metals, and zinc; the aryl amides of calcium and zinc; and some mercaptides of the heavy metals.

The variation of the middle element A is restricted to Subgroups B of Groups IV, V, and VI. Oxygen, carbon, or sulfur most frequently occupies this central position, although nitrogen derivatives are attaining increased familiarity. Salts containing selenium, tellurium, phosphorus, arsenic, or antimony have been partially or wholly neglected because of the disagreeable and poisonous nature of the parent substances, although Job and his coworkers (194, 195, 193) have demonstrated the possibility of establishing such metal–element linkages by securing the mixed compounds $C_6H_5P(MgBr)_2$ and $C_6H_5As(MgBr)_2$. Largely through the efforts of Kraus, four other elements—silicon (213, 217, 227), germanium (219, 233, 216, 218, 230), tin (220, 229, 225, 226), and lead (114)—have been shown to form salts of the type $NaAR_3$ in liquid ammonia or amines. The formally similar compounds of boron (234, 236, 235, 28), aluminum (237), and gallium (231), which constitute the only instances in which an element outside Groups IV, V, and VI enters such a combination, are probably abnormal in electron configuration. No doubt atoms of elements of Groups II and III already carrying alkyl radicals are incapable of combining with other metals, for Kraus and Kurtz (224) were unable to prepare $NaHgC_6H_5$ by reducing phenylmercuric chloride, C_6H_5HgCl, with sodium.

II. PREPARATION BY OXIDATION-REDUCTION REACTIONS

A widely used method for preparing salts of alcohol types involves the reduction of some part of an organic molecule, usually by a metal. Since the latter must supply electrons with some facility, sodium and potassium are most important in this rôle. The organic material may be volatilized and passed over the heated metal, or the reaction may be realized in solution. In an undiluted compound, the presence of an alkali metal and the heat of reaction often lead to rearrangements and polymerization, while any nascent hydrogen is likely to produce undesirable reduction, as it does in the action of sodium upon acetone.



$$CH_3C(=O)CH_3 \rightleftarrows CH_3C(OH)=CH_2$$

$$2CH_3C(OH)=CH_2 + 2Na \rightarrow 2CH_3C(ONa)=CH_2 + H_2$$

$$CH_3C(=O)CH_3 + H_2 \rightarrow (CH_3)_2CHOH$$

$$5CH_3C(=O)CH_3 \xrightarrow{CH_3C(=CH_2)ONa} C_6H_{10}O + C_9H_{14}O + 3H_2O$$

Of the various solvents (liquid ammonia, ethers, hydrocarbons) capable of moderating the former of these effects, liquid ammonia is by far the best. Its capacity for dissolving metals unchanged makes possible a homogeneous reaction of controllable speed, while its slight tendency toward autoionization precludes destructive ammonolysis of nearly all salts of alcohol types except the more reactive metal alkyls and their silicon analogs, e.g., NaC_2H_5, KC_6H_5, and $NaSi(C_2H_5)_3$.

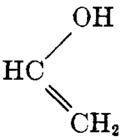
1. *The action of organic acids on metals*

The action of a metal on an alcohol or an alcohol analog exemplifies a familiar kind of oxidation-reduction,—the displacement of hydrogen from an acid by a metal (408). This historically important reaction was first applied by Liebig (251) to the preparation of sodium ethoxide, and was subsequently of service to Gladstone and Tribe (138), who first obtained aluminum alkoxides.

$$3C_2H_5OH + Al \rightarrow Al(OC_2H_5)_3 + 3/2\ H_2$$

The metal or an alloy is caused to react with the pure or dissolved alcohol type, various catalysts (iodine, stannic chloride, nitrobenzene, boron trioxide, or almost any compound of a heavy metal) sometimes being valuable accelerators. The reaction velocity diminishes progressively as the number and molecular weight of hydrocarbon groups attached to the central atom increases, and decreases also when the organic compound contains moisture (347).

For a given metal, the extent of reaction with different alcohol types depends largely upon the acidities of the latter, which vary with their structure. The acidities of corresponding acids in different systems of compounds are qualitatively related to each other as the acidities of the parent substances are related; these assume the order (acidity of) $H_2S > H_2O > NH_3 > CH_4$. Within a system, the nature and number of R groups in the compound $M_x(AR_n)_y$ have a decided influence. Aryl radicals linked to the central element A produce more acidity than alphyl radicals. The ionizability of hydrogen attached to A is also enhanced by an increased number of aryl groups similarly bound to that element, as is illustrated by the relative acidities of methane, toluene, diphenylmethane, and triphenylmethane. On the other hand, the escaping tendency of the proton seems to vary inversely as the number of alkyl radicals substituent on the main carbon or other atom of an R group; thus primary alcohols are stronger acids than secondary ones, which in turn surpass the tertiary forms. Because of the double bond in the R group, the acidity of enolic forms of monoaldehydes and monoketones and their analogs, like



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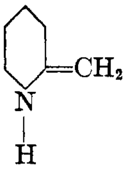


is probably rather high. It is difficult to verify this by measuring the rate at which these compounds react with metals, since, although the equilibrated mixture of tautomers may be practically devoid of the enol (acidic) form, the tautomeric shift will replenish the decreasing supply of that form. When several hydrogen atoms are linked to the same central atom, as in aniline or methane, the replacement of one hydrogen atom by metal invariably diminishes the acidity of the compound materially. This accords with the observation that salts in which the molecule contains more than one atom of even an alkali metal are extremely rare.

Aluminum, the alkali metals, and to a smaller extent those of the alkaline earth family, react more or less with all alcohols, mercaptans, and aromatic amines, although Kirner (208) has observed an anomalous failure of cold methyl mercaptan to attack sodium unless the relatively weaker acid, ethyl alcohol, is present. A semi-commercial process (49) for making sodium phenylamide by this method employs either excess aniline or a high-boiling hydrocarbon as solvent, and cuprous oxide, nickelous oxide, or cobaltous oxide as a catalyst (89) to reduce the temperature required. The action of cesium on liquid aliphatic amines (308), of calcium on aromatic amines (103), and of magnesium on alcohols is normal, but the instability of the salts toward heat renders the vapor method inapplicable to their preparation. That this limitation is not insurmountable is attested by Titherley's (384) preparation of potassium ethylamide from the gaseous amine, and Terentiev's (372) success in similarly securing magnesium aryl amides.

Only those hydrocarbons and analogs containing especially active hydrogen atoms (fluorene, triphenylmethane, triphenylstannane) are known to react as acids with alkali metals. It has been suggested, however, that under appropriate experimental conditions cesium may displace hydrogen from even alkanes (262).

The reaction of the highly electropositive metals with the more acidic hydrocarbons (76, 245), monohydric alcohols (59, 232, 414, 364), polyhydric alcohols (337), aromatic amines (302, 412), and pyrroles (116) is facilitated by dissolving the metals in liquid ammonia.

2. The reaction of metals with salts of alcohol types

The extent to which one metal displaces another from salts is governed by the relative positions of the two in the electrochemical series, if other variables are neglected. Since most salts of highly electropositive metals are more readily obtained by other means, such a process loses in importance as a preparative method. Another metal may displace zinc or mercury from an ester-like alkyl,

$$Zn(C_2H_5)_2 + 2Na \rightarrow 2NaC_2H_5 + Zn$$

but not infrequently, as in the case represented, the new metal alkyl cannot be isolated from the reaction mixture except as a double compound (402, 143). Lithium reacts with Grignard reagents in ether,

$$C_6H_5MgBr + Li \rightarrow LiC_6H_5 + LiBr + Mg$$

but the slowness of the displacement usually renders decomposition of the lithium alkyl by the ether unavoidable (330).

3. Direct combination of metals and free radicals

The mechanism of the displacements already discussed is believed by many authorities to include the action of the metal on free radicals. Even when this controversial point is disregarded, reactions may be found in which preëxistent radicals participate. Repeated corroborations of the discovery, by Paneth and his students (296, 297), that free alphyl groups can exist in a gas and can combine directly with metals, excite the thought that true salts of hydrocarbons should be so obtainable. Full confirmation of this prediction has been supplied by Simons and Dull (352), who have prepared sodium methyl and sodium ethyl by just such a method. Alkali metals are similarly attacked by free groups in ethereal solution (427), although triphenylmethyl yields only polymeric derivatives unless a metal amalgam or solution is employed (335). The monomolecular radicals R_2Ge, R_2Sn, and R_3Sn, while insoluble in liquid ammonia, react smoothly with a metal dissolved therein (220, 229, 216).

When a solution containing a salt of an alcohol type is electrolyzed, almost any metallic anode, unless it consists of a noble metal, is converted into the corresponding salt. Such disintegrations of the positive electrode have been observed in the electrolysis of sodium alkyls dissolved in zinc diethyl (158, 159), of Grignard reagents in diethyl ether (120), and of sodium alkoxides in alcohols (370, 369). The possibility exists, of course, that the reactivity responsible for the change is to be assigned to the anions themselves (427) rather than to the free groups resulting from their discharge.

4. Reduction of other organic compounds by metals

For some time after the discovery of the dissociation of hexaphenylethane, metallic potassium was used to estimate the magnitude of such dissociation in related hydrocarbons by removing the free radicals. It has since been shown that the degree of reactivity of a hydrocarbon toward a metal can indicate only the relative instability of the central bond; the alkali metals are now known to cleave undissociated molecules.

$$R_nA\text{—}A'R'_n + 2K \rightarrow KAR_n + KA'R'_n$$

Many compounds in which A and A′ are atoms of the same Group IV element fail to react unless the metal is dissolved in liquid ammonia, in which medium insolubility of most metals and ammonolysis of the products restrict the usefulness of the method. In general the carbon-carbon bond proves too stable to be broken unless each atom carries several aryl groups, as in $(C_6H_5)_2CH\text{—}CH(C_6H_5)_2$ and other polyphenylethanes (421, 71, 12). The silicon-silicon bond cannot be severed at all (213, 227), but sodium in liquid ammonia accomplishes normal reductions of germanium (219, 216, 218, 230) and tin (213) compounds of this type. However, the truth of the original report (413) that azobenzene can thus be cleaved to disodium phenylamide is doubtful (214).

To emphasize the extensive applicability of this kind of reduction, the following equations illustrating its occurrence are cited:

$$(C_6H_5)_2N\text{—}N(C_6H_5)_2 + 2K \rightarrow 2KN(C_6H_5)_2 \quad (335, 413, 331, 341)$$
$$C_6H_5S\text{—}SC_6H_5 + 2Na \rightarrow 2NaSC_6H_5 \quad (246, 277, 417, 365)$$
$$C_6H_5Se\text{—}SeC_6H_5 + 2Na \rightarrow 2NaSeC_6H_5 \quad (212)$$
$$(C_6H_5)_3CO\text{—}OC(C_6H_5)_3 + 2K \rightarrow 2KOC(C_6H_5)_3 \quad (444)$$

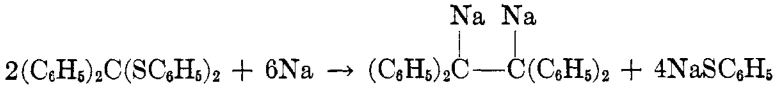
There has recently been reported (43) the cleavage of tetraphenyldiarsyl, $(C_6H_5)_2As\text{—}As(C_6H_5)_2$, by sodium-potassium alloy, but the resulting salt, the first representative of its type, was not isolated or studied except in its reaction with bromobenzene to yield triphenylarsine. It would be of interest to attempt a similar cleavage of cacodyl, $(CH_3)_2As\text{—}As(CH_3)_2$.

The reduction of diphenyl disulfide as expressed by the equation (248)

$$C_6H_5S\text{—}SC_6H_5 + Hg \rightleftarrows Hg(SC_6H_5)_2$$

may also be accomplished by other metals, including zinc and lead (293, 419, 246).

When the two central atoms are dissimilar and one of them is carbon, the stability of the connecting bond can scarcely be predicted. Neither $(C_2H_5)_3SiC_6H_5$ nor $(C_2H_5)_3SiCH_2C_6H_5$, the only tetraalkylsilicanes yet tested, undergoes cleavage by sodium in liquid ammonia (227). On the other hand, sodium splits dialkyl sulfides (343) and thioacetals (339),



$$2(C_6H_5)_2C(SC_6H_5)_2 + 6Na \rightarrow (C_6H_5)_2\overset{\overset{Na}{|}}{C}\text{—}\overset{\overset{Na}{|}}{C}(C_6H_5)_2 + 4NaSC_6H_5$$

although in liquid ammonia (232, 417) the metal alkyl ammonolyzes.

$$C_2H_5S\text{—}CH_2CH_3 + 2Na \rightarrow NaSC_2H_5 + NaCH_2CH_3$$
$$NaCH_2CH_3 + NH_3 \rightarrow NaNH_2 + C_2H_6$$

Tetraarylgermanes (219) and tetraalkylstannanes (229, 60) in the same solvent are cleaved by sodium, perhaps repeatedly.

$$(CH_3)_3Sn\text{—}CH_3 + 2Na + NH_3 \rightarrow NaSn(CH_3)_3 + NaNH_2 + CH_4$$
$$(CH_3)_2NaSn\text{—}CH_3 + 2Na + NH_3 \rightarrow Na_2Sn(CH_3)_2 + NaNH_2 + CH_4$$

Triphenylmethylamine is so weak an acid that its reaction with metallic potassium in liquid ammonia gives, not the expected salt, $(C_6H_5)_3CNHK$, but cleavage products (228).

$$(C_6H_5)_3C—NH_2 + 2K \rightarrow KC(C_6H_5)_3 + KNH_2$$

The ammono ether, trimethylamine, reacts with cesium at ordinary temperatures, but the reaction has not yet been studied (87). Aquo ethers are unaffected by sodium in liquid ammonia (232), unless one or both of the R groups is a stannyl or a germanyl radical, as in $(CH_3)_3SnOC_6H_5$ or $[(C_6H_5)_3Ge]_2O$ (219, 226, 218).

$$(CH_3)_3SnOC_6H_5 + 2Na \rightarrow NaSn(CH_3)_3 + NaOC_6H_5$$

Schorigin (342, 343) found that high-boiling aromatic ethers react at their boiling points with either sodium or sodium–potassium alloy; those having smaller molecular weights and lower boiling points require long heating with the metal in a sealed tube. At 200°C. aliphatic ethers of low molecular weight resist decomposition by an alkali metal alloy over extended periods (164), and even metallic cesium does not cleave diethyl ether at room temperature (87). In spite of the tendency of the new metal alkyl to decompose by reacting with unchanged ether or side-products of the reaction (2), Ziegler (444, 443) and others (69, 341, 340, 29a) make use of the Schorigin cleavage of aromatic ethers to obtain alkali metal salts of hydrocarbons.

$$(C_6H_5)_2CHOCH_3 + 2Na \rightarrow NaCH(C_6H_5)_2 + NaOCH_3$$

Almost no information is at hand relative to the stability of linkages in which carbon does not participate. Some early work of Chapman and Smith (58) indicates that alphyl nitrates are split normally by sodium,

$$C_2H_5O—NO_2 + 2Na \rightarrow NaOC_2H_5 + NaNO_2$$

and that alphyl nitrites undergo a similar cleavage by zinc,

$$2C_5H_{11}O—NO + Zn \rightarrow Zn(OC_5H_{11})_2 + 2NO$$

but react with sodium in a more complicated manner. More modern investigators (227, 217) report the splitting of the mixed hydranes $(C_2H_5)_3Si—Ge(C_6H_5)_3$ and $(C_6H_5)_3Si—Sn(CH_3)_3$,

$$(C_2H_5)_3Si—Ge(C_6H_5)_3 + 2K \rightarrow KSi(C_2H_5)_3 + KGe(C_6H_5)_3$$

by which the difficultly accessible silicon salts are obtained.

The breaking by sodium of the titanium-oxygen bond in tetraethyl titanate (256) belongs to the rare type in which both fragments are not salts of the metal employed.

$$Ti(OC_2H_5)_4 + Na \rightarrow NaOC_2H_5 + Ti(OC_2H_5)_3$$

The complex decomposition of some carboxylic esters by the same metal (130, 119, 300, 45) involves a related scission of a carbon-oxygen bond, the primary reaction being of the type

$$OC(OC_6H_5)_2 + 2Na \rightarrow 2NaOC_6H_5 + CO$$

The reducing power of the alkali metals is equally competent to transform many halogen compounds into salts.

$$R_nAX + 2Na \rightarrow NaAR_n + NaX$$

Triaryl halides of carbon (335, 223, 143) and tin (220, 225) are most frequently subjected to this reduction, although lithium reacts very well with practically all alkyl halides (440, 438, 133, 422, 137, 71). Metals outside Group IA, if they have any effect, usually yield mixed salts of the Grignard type, $XMAR_n$; but it is now generally admitted that the Grignard reagent exists as an equilibrium mixture.

$$2RMgX \rightleftarrows MgR_2 + MgX_2$$

While phenylmercaptomercuric chloride cannot be prepared directly from the metal, its disproportionation is similar (247).

$$2C_6H_5SHgCl \rightleftarrows Hg(SC_6H_5)_2 + HgCl_2$$

Reductions of the type $R_nAX + 2Na$ remain undemonstrated for halides belonging to other than hydrane systems, chiefly because the excessive instability of such halogen derivatives (R_2NCl, $ROCl$, $RSCl$) renders their study difficult.

5. Reductions by means of salts of alcohol types

Much of the reducing potency of the metals is transmitted to their salts of alcohol types, as the recognized tendency of the latter to undergo oxidation shows. Ordinarily molecular oxygen causes complete disintegration, but in several tin (60) and germanium (219) compounds an irreversible conversion of a salt belonging to a hydrane system into an alkoxide is effected.

$$NaSn(C_6H_5)_3 + 1/2O_2 \rightarrow NaOSn(C_6H_5)_3$$

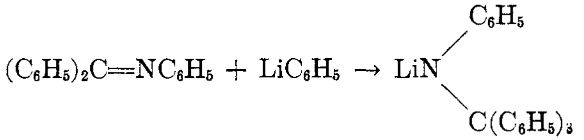
A related change is the addition of metal alkyls to various types of unsaturated linkages. Provided that no enolic form can be present to react as an acid, this addition may produce new salts of alcohol types. Under these conditions some aldehydes and ketones give alkoxides (336, 332, 133, 29a),

$$H_2C{=}O + NaC(C_6H_5)_3 \rightarrow NaOCH_2C(C_6H_5)_3$$

thioketones produce mercaptides (30),

$$(C_6H_5)_2C{=}S + NaCH(C_6H_5)_2 \rightarrow NaSC(C_6H_5)_2CH(C_6H_5)_2$$

ammono ketones yield alkyl amides (446, 432, 134),



$$(C_6H_5)_2C{=}NC_6H_5 + LiC_6H_5 \rightarrow LiN\begin{cases} C_6H_5 \\ C(C_6H_5)_3 \end{cases}$$

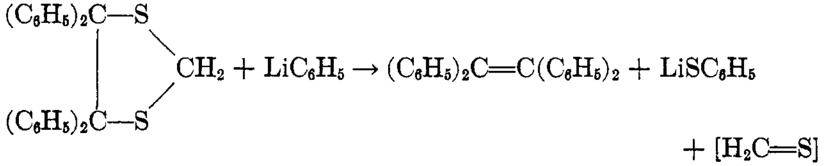
and some ethylenes form salts of other hydrocarbons (439, 431, 134).

$$C_6H_5CH{=}CH_2 + KC(CH_3)_2C_6H_5 \rightarrow KCHC_6H_5CH_2C(CH_3)_2C_6H_5$$

It is of purely theoretical interest to note that metal alkyls decompose ethers (2) and organic disulfides and diselenides (341), although not dialkyl sulfides (124).

$$C_2H_5OC_2H_5 + NaC_2H_5 \rightarrow NaOC_2H_5 + C_2H_4 + C_2H_6$$

Lithium phenyl breaks a carbon-sulfur bond in its reaction with a few cyclic sulfur compounds (338).



One sulfur atom in aromatic disulfides is likewise reduced by potassium diphenylamide (341), and even by some salts of thiols (249).

III. PREPARATION BY METATHETIC REACTIONS

1. *The action of organic acids on salts*

More than twenty years ago Stieglitz (363) pointed out facts which Brönsted's ideas have reëmphasized: many common hydrogen compounds act as weak acids, therefore sodium hydroxide is a salt and the reactions represented by the equations

$$NaOH + HCl \rightleftarrows NaCl + H_2O$$
$$NaNHC_6H_5 + HOH \rightleftarrows NaOH + C_6H_5NH_2$$

and

$$NaC_2H_5 + CH_3SH \rightleftarrows NaSCH_3 + C_2H_6$$

are exactly analogous.

If such reactions are to be employed in preparing salts, a list in which acids are arranged according to strength would be of material service. The extent of displacement, however, varies with temperature and with the effective concentrations of reactants and products. It is necessary, therefore, to specify the former, and to regulate the latter by avoiding the use of solvents in which there is an appreciable divergence in ionization or solubility of reagents and products. After justifying the assumption that salts of weak acids dissolved in diethyl ether are ionized to approximately the same extent, Conant and Wheland (72) established the relative acid strengths of a number of hydrocarbons by such a displacement method. Their results, supplemented by additional information on benzene (124, 430), are abbreviated in table 1, each acid being able to displace those below it more or less completely. It is questionable whether the relative affinities of organic radicals for the electron pair (207), which determine the acidities of their hydrogen compounds, have actually been measured by the relative rates of competitive reactions (6).

TABLE 1

Relative acidity of weak acids

1. Acetophenone	9. 1-Naphthyldiphenylmethane
2. Phenylacetylene	10. Diphenylmethane
3. Indene	11. 1,1-Diphenyl-2-methylethylene (1,1-diphenyl-1-propene)
4. Phenylfluorene	12. Cumene
5. Fluorene	13. Toluene
6. Xanthene	14. Benzene
7. Diphenyl(phenylphenyl)methane	15. Ethane
8. Triphenylmethane	

Until the systematic study, as begun by Conant and McEwen (70), of the acidities of amines, alcohols, and mercaptans is farther advanced, judgment must be based on such occasional displacements as have been reported. Sodium sulfide is said to fail to neutralize a mercaptan, and even sodium hydrosulfide produces only a partial reaction (44), so that the ability of cupric sulfide to remove mercaptans from their solutions in hydrocarbons is unusual and unexplained (354). While the soluble alkali metal mercaptides are better prepared by the action of the free acids on metallic hydroxides or alkoxides,

$$C_2H_5SH + NaOC_2H_5 \rightarrow NaSC_2H_5 + C_2H_5OH$$

the extreme insolubility of the mercaptides and alkyl selenides of heavier metals makes it possible to precipitate them in the presence of hydrochloric acid.

$$2CH_3SH + FeCl_2 \rightarrow Fe(SCH_3)_2 + 2HCl$$

Although the reaction between an alcohol and a strong alkali like sodium hydroxide is normally far from complete, commercial practice has utilized these cheap materials by continuous dehydration to increase the yield (188, 401, 399). Thallous ethoxide and sodium ethoxide are favored starting materials for preparing other alkoxides by alcoholysis.

$$C_6H_5OH + TlOC_2H_5 \rightarrow TlOC_6H_5 + C_2H_5OH$$

A novel synthesis is that in which a metal otherwise inert toward an alcohol reacts in the presence of oxygen or ozone (241, 199, 121, 84).

$$2Tl + 1/2O_2 + 2C_2H_5OH \rightarrow 2TlOC_2H_5 + H_2O$$

Copper (353, 354) and lead (298) apparently conduct themselves similarly.

Alkoxides may be secured by the alcoholysis of sodium amide (75, 318, 32, 33, 215), or of the nitride of lithium (108), sodium (405), magnesium (367a, 418), or calcium (275),

$$6C_2H_5OH + Mg_3N_2 \rightarrow 3Mg(OC_2H_5)_2 + 2NH_3$$

or of calcium hydride (418, 310),

$$2C_2H_5OH + CaH_2 \rightarrow Ca(OC_2H_5)_2 + 2H_2$$

or of a salt of a hydrocarbon (309, 385).

$$2CH_3OH + Zn(C_2H_5)_2 \rightarrow Zn(OCH_3)_2 + 2C_2H_6$$

The solvolysis of iron tricarbonyl, a covalent substance, produces impure ferrous methoxide (168),

$$2CH_3OH + Fe(CO)_3 \rightarrow Fe(OCH_3)_2 + H_2 + 3CO$$

whereas that of ferric formate is more typical in its incompleteness (174).

$$2CH_3OH + Fe(OOCH)_3 \rightarrow (HCOO)Fe(OCH_3)_2 + 2HCOOH$$

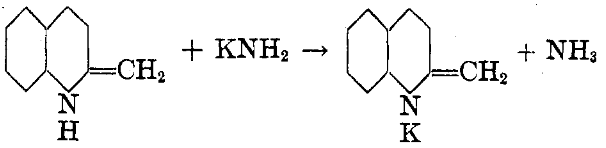
Neither the copper "salt" of acetoacetic ester (420) nor thorium tetra-acetyl acetone (38), each a chelate compound, is convertible to a pure alkoxide by an alcohol.

Schlenk, Hilleman, and Rodloff (332) have contributed to our very meager knowledge of salts of aldehyde enols by their study of sodium 2,2-diphenylvinyl oxide, prepared according to the equation

$$(C_6H_5)_2CHCHO + NaC(C_6H_5)_3 \rightarrow (C_6H_5)_2C{=}CHONa + (C_6H_5)_3CH$$

The acidic hydrogen of the >NH grouping in aromatic amines (384, 271, 414), pyrrole, carbazole, and indole (116), and enolic modifications of ammono ketones (31), is replaced by metal when these acids are treated with an alkali amide.

$$C_6H_5NH_2 + NaNH_2 \rightarrow NaNHC_6H_5 + NH_3$$



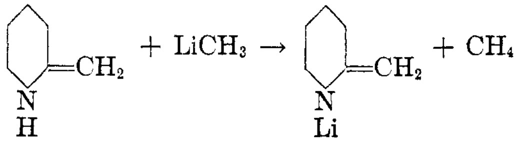
To note some isolated reactions of ammono acids, diethylamine reacts with lithium phenyl (442),

$$(C_2H_5)_2NH + LiC_6H_5 \rightarrow LiN(C_2H_5)_2 + C_6H_6$$

aromatic amines with magnesium diphenyl (329) or zinc dialkyls (115, 126),

$$2C_6H_5NH_2 + Zn(C_2H_5)_2 \rightarrow Zn(NHC_6N_5)_2 + 2C_2H_6$$

and ammono enols with lithium alkyls (446).



Aromatic amines similarly liberate the weak acid H_2 when they act upon the hydrides of sodium, potassium (90), or calcium (103, 101).

$$2C_6H_5NH_2 + CaH_2 \rightarrow Ca(NHC_6H_5)_2 + H_2$$

Although most alkyl amides are readily decomposed by water and alcohols, sodium diphenylamide has been partially precipitated from ether (61) as a product of the reaction represented by the equation

$$(C_6H_5)_2NH + NaOC_2H_5 \rightarrow NaN(C_6H_5)_2 + C_2H_5OH$$

Moreover, fusion methods have succeeded in completing the reaction between potassium hydroxide and pyrrole by volatilizing the water formed (9, 65).

$$C_4H_4NH + KOH \rightarrow KNC_4H_4 + H_2O$$

The potassium salts of carbazole (141, 66, 346) and of fluorene (407, 7) have been secured in the same way.

Nevertheless, few metallic derivatives in which the central element belongs to Group IV are accessible by displacement reactions, because of the weakness of the hydranes as acids. One hydrocarbon sometimes causes the liberation of another (72).

$$(C_6H_5)_2CH_2 + NaCH_2C_6H_5 \rightarrow NaCH(C_6H_5)_2 + C_6H_5CH_3$$

Fluorene (408, 128) and indene (409, 129) react normally when heated with sodium amide or with sodium in the presence of gaseous ammonia. In addition, hydrocarbons containing the benzohydryl group, $(C_6H_5)_2CH—$, are sufficiently acidic in liquid ammonia to decompose potassium amide (434). On the other hand, even the irregularity of the behavior of trimethylstannane (226)

$$(CH_3)_3SnH + NaNH_2 \rightarrow NaSn(CH_3)_3 + NH_3 \text{ (30 per cent)}$$

$$(CH_3)_3SnH + 2NaNH_2 \rightarrow NaSn(CH_3)_3 + (CH_3)_3SnNH_2 + H_2 \text{ (70 per cent)}$$

is probably less than that of many other hydranes.

It is perhaps appropriate to refer briefly to ammonium salts of alcohol types, since it may be supposed that they are formed in small amounts by the action of a simple or substituted ammonium hydroxide upon an acid:

$$C_6H_5OH + NH_4OH \rightarrow NH_4OC_6H_5 + H_2O$$

Actually the salts so formed can no more be isolated than can ammonium hydroxide itself. Instead, they are secured by the action of an acid on a base (ammonia or an amine) in the Brönsted sense:

$$(C_6H_5)_3CH + CH_3NH_2 \rightarrow CH_3NH_3C(C_6H_5)_3$$

Such reactions have no claim to consideration among acid–salt metatheses, but lack sufficient importance to warrant assigning them to an especially created subdivision.

2. Metatheses between two salts

The most widely applicable reaction for preparing salts of alcohol types containing any desired metal, a metathesis between two salts, has never been exploited commensurately with its value. Since formation of a precipitate is a convenient process insuring completion of the reaction, the solvent is chosen with a view toward promoting that effect.

Employment of this double decomposition has been confined mainly to the preparation of alkoxides. Chablay (59) has demonstrated its utility in liquid ammonia, where a reaction like that represented by the equation

$$Pb(NO_3)_2 + 2NaOC_2H_5 \rightarrow Pb(OC_2H_5)_2 + 2NaNO_3$$

reaches completion by virtue of the small solubility of plumbous ethoxide. Thallous formate, treated with sodium ethoxide in absolute alcohol, yields a precipitate of oily thallous ethoxide (269).

$$HCOOTl + NaOC_2H_5 \rightarrow TlOC_2H_5 + HCOONa$$

Upon other occasions it is the by-product which is insoluble; sodium chloride is precipitated from alcohol in the synthesis of ferric ethoxide (377),

$$FeCl_3 + 3NaOC_2H_5 \rightarrow Fe(OC_2H_5)_3 + 3NaCl$$

chromic ethoxide (375), lithium ethoxide (197), and others (267). Corresponding metatheses in the methane and the ammonia systems enabled Schlenk and Holtz (333, 334) to obtain some remarkable ammonium salts of hydrocarbons

$$(CH_3)_4NCl + (C_6H_5)_3CNa \rightarrow (CH_3)_4NC(C_6H_5)_3 + NaCl$$

and amines.

$$(CH_3)_4NCl + (C_6H_5)_2NNa \rightarrow (CH_3)_4NN(C_6H_5)_2 + NaCl$$

According to Ziegler and Dersh (441), lithium benzyl and some other organolithium compounds are best prepared by the action of lithium phenyl on the corresponding Grignard reagent.

$$C_6H_5CH_2MgBr + LiC_6H_5 \rightarrow LiCH_2C_6H_5 + C_6H_5MgBr$$

3. *The reaction of salts with other organic compounds*

When alkalies saponify esters, neutralization of the excess alkali by the alcohol may be a secondary change.

$$CH_3COOC_2H_5 + 2NaOH \rightarrow CH_3COONa + NaOC_2H_5 + H_2O$$

A similar conversion occurs during the fusion of aromatic sulfonic acids with sodium hydroxide or sodium amide (34).

$$C_6H_5SO_3Na + 2NaNH_2 \rightarrow NaNHC_6H_5 + Na_2SO_3 + NH_3$$

At elevated temperatures, various reagents—fused alkalies (253, 8, 123), aluminum chloride (266), and sodium ethoxide (265)—decompose ethers, sometimes with the initial production of salts of alcohol types; such salts, however, tend to decompose at the temperature required.

In liquid ammonia, sodium amide adds to the free radicals triphenylmethyl (433) and trimethylstannyl (226) in the sense of the equation

$$2(CH_3)_3Sn + NaNH_2 \rightarrow NaSn(CH_3)_3 + (CH_3)_3SnNH_2$$

Dialkyl disulfides undergo an apparently related reaction,

$$(C_6H_5)_2S_2 + 2K_2S \rightleftarrows 2KSC_6H_5 + KS{-}SK$$

which is represented as reaching equilibrium, because different authors (295, 178) have reported such exchanges to proceed in opposite directions.

IV. PHYSICAL PROPERTIES

Any exposition of the properties of salts of alcohols and alcohol analogs may well have as its theme the recurring fact that the transition from heteropolar salts to homopolar ortho esters is a stepwise process. This transition correlates well with that noticeable among metallic halides and oxides. Metals of Groups I and II, with the exception of beryllium and mercury, form salts of alcohol types which are rather involatile and insoluble in most solvents (see tables 2, 3, 4, 5, 6), but predisposed toward ionization if dissolved. Derivatives of all non-metals, antimony, and the tetravalent forms of titanium, germanium, tin, and lead have some or all of the characteristics of organic compounds—definite and relatively low melting points and boiling points, solubility in organic solvents, and

TABLE 2

Properties of salts of alcohols

SALT	COLOR	FORM	SOLUBILITY			REFERENCES
			ROH	NH_3	Organic solvents	
$LiOC_2H_5$	White	C	+	–	(+)	(59, 197, 414, 108)
$NaOC_2H_5$	White	A	+	–	–	(404, 380, 59, 26, 232)
KOC_2H_5	White	A	+	–	–?	(59, 26, 232)
$Cu(OCH_3)_2$	Blue?	A	–	?	?	(370)
$Mg(OCH_3)_2$	White	C	(+)	?	(+)	(368, 370, 26, 373, 41, 57)
$Zn(OCH_3)_2$	White	A	–	–	–	(385, 26, 267)
$Hg(OCH_3)_2$?	Orange	A	–	?	?	(171)
$Ca(OC_2H_5)_2$	White	A	+	–	(+)?	(88, 299, 59, 26)
$Ba(OC_2H_5)_2$	White	A	+	–	–	(88, 59, 26)
$Sr(OC_2H_5)_2$	White	A	+	–	?	(59)
$Al(OC_2H_5)_3$	White	C	–	?	(+)	(381, 74, 26, 386, 390)
$TlOC_2H_5$	White*	C	+	–	+	(241, 59, 121, 84, 64, 269, 351)
$Ti(OC_2H_5)_3$	Violet	A	–	?	–	(256)
$Zr(OC_6H_5)_4$	White	C	+	?	+	(192, 267)
$Pb(OCH_3)_2$	White	A	–	–	?	(370, 298, 59)
$Cr(OC_2H_5)_3$	Green	A	(+)	?	(+)?	(375)
$Fe(OCH_3)_2$	Violet	A	–	?	–	(168)
$Fe(OC_2H_5)_3$	Brown	C	(+)	?	(+)	(377)

C = crystalline; A = amorphous. An asterisk denotes that the compound is liquid at ordinary temperatures.

A + sign indicates a considerable solubility.

A (+) sign represents partial solubility.

A – sign indicates practical insolubility.

TABLE 3

Properties of salts of mercaptans

SALT	COLOR	FORM	SOLUBILITY		REFERENCES
			Water	Organic solvents	
$NaSC_2H_5$	White	C	+	(+)	(209, 301)
KSC_2H_5	White	A	+	(+)	(437)
$CuSC_2H_5$	Yellow	A	−	(+)	(209, 97, 354)
$AgSC_2H_5$	Yellow	C	−	?	(395, 360, 209)
$AuSC_2H_5$	White	A	−	(+)	(437, 165)
$Zn(SC_2H_5)_2$	White	C	−	?	(209)
$Cd(SC_2H_5)_2$	White	C	−	?	(209)
$Hg(SC_2H_5)_2$	White	C	−	+	(437, 209)
$TlSC_2H_5$	Yellow	A	(+)	?	(209)
$Sn(SC_2H_5)_2$	Yellow	A?	−	?	(209)
$Pb(SC_2H_5)_2$	Yellow	C	−	+	(437, 209)
$Bi(SC_2H_5)_3$	Orange	C	−	+	(209)
$Fe(SC_2H_5)_2$	Black	A	−	−	(209, 259)
$Ni(SC_2H_5)_2$	Brown	A	−	−	(209, 261)
$Co(SC_2H_5)_2$	Brown	A	−	(+)?	(209)
$Rh(SC_2H_5)_2$	Yellow	A	−	(+)?	(209, 281)
$Pd(SC_2H_5)_2$	Yellow	A	−	−?	(209, 281)
$Ir(SC_2H_5)_2$	Orange	A	−	(+)	(176, 281)
$Pt(SC_2H_5)_2$	Yellow	A	−	−?	(209, 281, 305)
$Pt(SC_2H_5)_4$	Orange	A	−	−	(176, 281)

See note accompanying table 2.

TABLE 4

Properties of salts of amines

SALT	COLOR	FORM	SOLUBILITY			REFERENCES
			RNH_2	NH_3	Organic solvents	
$NaNHC_6H_5$	White	A	+	+	(+)	(384, 302, 412, 372, 89, 90)
$NaN(C_6H_5)_2$	White	C	+	+	(+)	(384, 302, 412)
$KNHC_2H_5$	White	A	+	+	(+)?	(384)
$KN(C_6H_5)_2$	White	A	+	+	(+)	(155, 116)
$CsNHCH_3$	White	A	+	+	−	(308)
$AgNC_4H_4$	White	?	?	+	?	(116)
$Mg(NHC_6H_5)_2$	White	A	?	?	−	(372, 329)
$Mg(NC_4H_4)_2$	White	A?	?	(+)	?	(116)
$Zn(NHC_6H_5)_2$	White	A	?	?	−	(115, 126)
$Zn[N(C_6H_5)_2]_2$	White	A	?	?	−	(115, 126)
$Ca(NHC_6H_5)_2$	White	A	(+)	?	−	(103)
$Ca[N(C_6H_5)_2]_2$	White	A	(+)	(+)	−	(103)

See note accompanying table 2.

TABLE 5

Properties of salts of hydrocarbons

SALT	COLOR	FORM	SOLUBILITY		REFERENCES
			NH_3	Organic solvents	
LiC_2H_5	White	C	−	(+)	(426)
$LiC(C_6H_5)_3$	Red	C	+	+	(426)
$LiCH_2C_6H_5$	Red	C	(+)?	+	(426)
NaC_2H_5	White	A	−	−	(426)
$NaC(C_6H_5)_3$	Red	C	+	+	(426)
$NaCH_2C_6H_5$	Red	C	(+)?	(+)	(426)
KCH_3	White	A	−	−	(426)
$KC(C_6H_5)_3$	Red	C	+	+	(426)
$RbC(C_6H_5)_3$	Red	C	+	(+)	(143)
$CsC(C_6H_5)_3$	Red	C	+	(+)	(143)
CuC_6H_5	White	A	−?	−	(306)
AgC_6H_5	Brown	A	−?	−	(238, 306)
$Mg(C_6H_5)_2$	White	C	(+)?	+	(196)
$Ca[C(C_6H_5)_3]_2$	Red	?	+	(+)?	(223)
$Zn(C_2H_5)_2$	White*	C	−	+	(122)

See note accompanying table 2.

TABLE 6

Known properties of ammonium salts of alcohol types

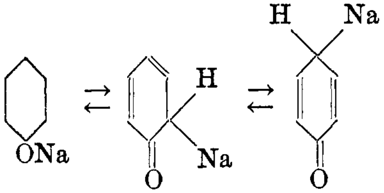
SALT	FORM	SOLUBILITY	REFERENCES
$(CH_3)_4NC(C_6H_5)_3$	Red powder	Soluble in pyridine only	(333)
$(CH_3)_4NN(C_6H_5)_2$	Green-yellow needles	Soluble in pyridine only	(334)
$(CH_3)_3C_6H_5NOC_6H_5$	White fusible powder	Soluble in water	(163)
$(CH_3)_3C_6H_5NSC_6H_5$	White fusible powder	Soluble in water	(163)
$CH_3NH_3C(C_6H_5)_3$	Pink solid	Insoluble in liquid NH_3	(433)
$C_6H_5NH_3OC_6H_5$	White fusible powder	Soluble in water and organic solvents	(180, 100, 250, 179)
$CH_3NH_3OC_6H_5$	White fusible powder	Soluble in methylamine	(132)
$NH_4C(C_6H_5)_3$	Pink solid	Insoluble in liquid NH_3	(223)
$NH_4SC_6H_5$	White crystals	Insoluble in liquid NH_3	(232, 414, 417)

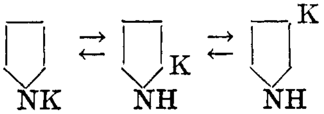
inability to support electrolytic conduction. All other metals, including mercury and beryllium, yield compounds intermediate in nature between salts and esters.

The many similarities between parent substances and alcohol types in each system create expectations that salts of the two should be equally comparable. That such resemblances indeed exist is most clearly seen in the methane system (compare $NaCH_3$ and $NaCH_2CH_3$), but sodium hydroxide and a sodium alkoxide also exhibit numerous likenesses.

During the formative period of structural organic chemistry, the constitution of sodium alkoxides was naturally uncertain. Wanklyn considered sodium ethoxide the "hydrate" of a radical called "ethylenesodium," $(C_2H_4Na)OH$, and held that in that salt as well as in sodium alkyls the metal is trivalent (403, 127). The arguments which finally prevailed over this view and which led to the commonly accepted structural formula, CH_3CH_2ONa, were the replaceability of only one hydrogen atom per molecule, and the fact that in ethers prepared by the Williamson synthesis the alkyl group introduced is known to be linked through oxygen (243).

It is maintained by Hückel (182), against much opposition, that salts of alcohol types can always exist in tautomeric forms.



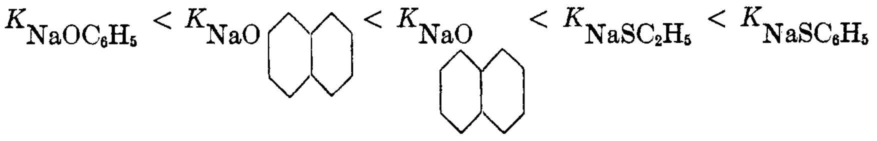


The organometallic isomers are supposed to be present in solution in nonionizing media, whereas alcohols and other ionizing solvents favor the existence of the orthodox form.

A number of theories have been proposed to account for the color of some metallic salts of triphenylmethane and related acids, but the only one yet extended to apply to all salts of alcohol types is that of Hantzsch. In pursuance of his general theory of pseudo acids, Hantzsch (149, 150) holds that two isomeric forms of a salt of an alcohol type are possible, a covalent and an electrovalent form. The colored salts of triphenylmethane and diphenylamine are electrovalent forms in which the anion contains a quinoid benzene ring. Modern theories of atomic linkages, however, cast grave doubt upon the possibility of existence of two distinct electroisomers.

Molecular weight determinations have shown sodium ethyl dissolved in zinc diethyl (160), ferric ethoxide in ethyl alcohol (377), and alkali metal salts of simple alcohols dissolved therein (24), to be monomolecular at low concentrations. Sodium and potassium salts of menthol and of the enolic forms of camphor, menthone, and acetophenone dissolved in organic solvents (24), as well as the solvates present in concentrated solutions of alkali alkyls in zinc diethyl (160), exist as at least double molecules, their molecular condition varying with the nature of the solvent. Although older cryoscopic data (381) were interpreted as indicating that aluminum alkoxides in benzene are monomolecular, it is now well-established that both aluminum (390) and thallium (351) alkoxides are considerably associated in that solvent. According to calculations of dipole moments based on their dielectric constants, the polymeric forms of the aluminum salts are symmetrically constituted and probably have a ring structure (390).

A number of investigators have concerned themselves with the heats of formation of alkali metal alkoxides and related salts (83, 84, 85, 27), and with the degree of hydrolysis suffered by alkoxides at various dilutions (139, 379, 283, 46, 406, 56). Bent and Gilfillan (29) have reported that potassium triphenylmethyl behaves as a true salt in a voltaic cell. From conductance measurements made on this and other organoalkali salts dissolved in pyridine, Ziegler and Wollschitt (445) concluded that under these conditions the compounds are highly polar and non-associated. The same relatively high conductances are characteristic of solutions of sodium triphenylmethyl, sodium triphenylgermanyl, and sodium triphenylstannyl in liquid ammonia (213, 222). In this solvent sodium phenylamide is a better electrolyte than sodium amide (213); sodium triphenylmethyl is better than sodium trimethylmethyl; and the dissociation constants of the salts of alcohols and thiols studied (221) assume the order:



$$K_{\mathrm{NaOC_6H_5}} < K_{\mathrm{NaO}} < K_{\mathrm{NaO}} < K_{\mathrm{NaSC_2H_5}} < K_{\mathrm{NaSC_6H_5}}$$

A consideration of these facts led Kraus and Johnson (221) to point out that an increase in the size of the anion produces an increase in conductance. A comparison of sodium hydroxide with a sodium alkoxide in this respect has not been made, because no non-reactive solvent for both salts is known. Alcohols have served as solvents in measurements of conductances (379, 311, 350, 211, 411, 170, 20) and decomposition potentials (55) of alkoxides. Data on refractive indices substantiate the electrical evidence that higher alcohols cannot cause ionization of sodium alkoxides dissolved therein (379, 50).

By way of a summary, it may be concluded that the salt-like character of the salt $M_x(AR_n)_y$ tends to be increased by the following changes:

(a) Increased electropositive nature of M, as indicated by the electrochemical series. Example: sodium phenoxide, $NaOC_6H_5$, is more salt-like than aluminum phenoxide, $Al(OC_6H_5)_3$.

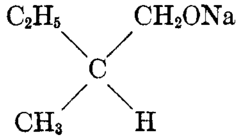
(b) Decreased valence of M. Example: titanium triethoxide, $Ti(OC_2H_5)_3$, is more salt-like than tetraethyl titanate, $Ti(OC_2H_5)_4$.

(c) Increased electronegative nature of A. This may be intrinsic (zinc methoxide, $Zn(OCH_3)_2$, is more salt-like than zinc diethyl, $Zn(CH_2CH_3)_2$), or it may be induced by changes in the kind and number of R groups substituent on the central element.

V. CHEMICAL PROPERTIES

1. Pyrogenetic reactions

In the case of optically active alkoxides like



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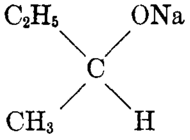


decomposition by heat is preceded by racemization. A theory of the mechanism of such transformations, proposed by Hückel and Naab (183, 181) and accepted in subsequent work (362), holds that steric rearrangements of alkoxides always occur at the asymmetric carbon atom or one immediately adjacent thereto, and that they proceed through intermediate formation of a salt of an enolic form.

Not many other salts of alcohol types have been so carefully studied as regards pyrolytic reactions, although all are subject to thermal decomposition; indeed, silver phenyl (238, 306) and many salts of enolic forms of aldehydes and ketones, e.g., sodium vinyl oxide (118), $CH_2{=}CHONa$, are unstable even at ordinary temperatures. Judging from the work of Norris (289), it is of prime importance to control all variables (time, temperature, and pressure), if data on the kinds and amounts of products are to have any significance. In the simple destructive distillations which are our chief source of information, such control has usually been neglected. These studies are further complicated by numerous simultaneous and consecutive side reactions, as Nef (284) and Fry and coworkers (123) have shown.

$$\mathrm{NaOH + C_6H_5OH \rightarrow NaOC_6H_5 + H_2O}$$
$$\mathrm{NaOC_2H_5 \rightarrow NaOH + C_2H_4}$$
$$\mathrm{C_2H_4 \rightarrow 2C + 2H_2}$$
$$\mathrm{NaOH + C_2H_5OH \rightarrow CH_3COONa + H_2}$$
$$\mathrm{CH_3COONa + NaOH \rightarrow Na_2CO_3 + CH_4}$$

Differences in the nature of alkyl groups present vary the course of the reaction in each system; sodium methoxide, sodium ethoxide, and sodium phenoxide yield compounds dissimilar in quality and quantity. (See table 7.) When it is added that decomposition products of corresponding salts of different metals are often widely divergent in character, the absence of inclusive rules is accountable. Two minor uses of pyrolytic reactions involving aluminum salts are noteworthy. The destructive distillation of aluminum aryl oxides produces good yields of aromatic ethers (138, 382, 74, 273), while similar treatment of the alphyl oxides leaves a residue of activated aluminum oxide particularly valuable as a dehydration catalyst (5).

Presumably tetraalkylammonium alphyl oxides (274, 272, 397, 1, 189), tetraalkylammonium (146) and tetraalkylarsonium (121a) salts of alkanes, and hydrazinium methoxide (82) can exist only at low temperatures. The reactions which should give rise to them at higher ones yield only decomposition products.

$$\mathrm{8(CH_3)_3C_2H_5NBr + 8NaOC_2H_5 \rightarrow 8(CH_3)_3N + (C_2H_5)_2O + 14C_2H_4 + 7H_2O}$$
$$\mathrm{(C_2H_5)_4NBr + LiC_2H_5 \rightarrow (C_2H_5)_3N + C_2H_6 + C_2H_4 + LiBr}$$
$$\mathrm{N_2H_5Cl + NaOCH_3 \rightarrow N_2H_4 + CH_3OH + NaCl}$$

The implied pyrolysis of the intermediate salts follows the same course as that taken by more stable derivatives of this kind (163, 157, 167).

$$\mathrm{(CH_3)_3C_6H_5NOC_6H_5 \rightarrow C_6H_5N(CH_3)_3 + C_6H_5OCH_3}$$
$$\mathrm{[(CH_3)_2CHCH_2]_4NC_2H_5 \rightarrow [(CH_3)_2CHCH_2]_3N + (CH_3)_2CHCH_2CH_2CH_3}$$

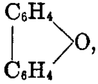
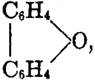
2. Metathetic reactions

Mention has already been made of the fact that metallic derivatives of alcohol types may be secured by a metathesis between two salts, one of which is often a halide:

$$\mathrm{CrCl_3 + 3NaOC_2H_5 \rightarrow Cr(OC_2H_5)_3 + 3NaCl}$$

TABLE 7

Pyrolysis of salts of alcohol types

SALT	TEMPERATURE	MAIN PRODUCTS REPORTED	REFERENCES
	degrees C.		
$NaOCH_3$	260–400	Na_2CO_3, Na_2C_2, C, H_2, CH_4	(23, 98)
$NaOC_2H_5$	250–350	NaOH, Na_2CO_3, CH_3COONa, Na_2C_2?, C, H_2, CH_4, C_2H_4	(404, 270, 284, 73, 98)
$NaOC_6H_5$	450–500	NaOH, C, CH_4, C_2H_6, C_6H_6, $(C_6H_5)_2$	(98, 110, 175, 173)
$NaOCH(CH_3)_2$	200	NaOH, $CH_3CH{=}CH_2$	(40)
$Mg(OCH_3)_2$	80	MgO, H_2, CO, CH_4	(368)
$Zn[OCH_2CH(CH_3)_2]_2$	?	[ZnO]?, H_2, CO, CO_2, C_nH_{2n+2}, C_nH_{2n}, ROH, RCHO, RCOOR	(385)
$Ca(OC_2H_5)_2$	?	$CaCO_3$, $(CH_3)_2CO$, H_2, CH_4	(88)
$Ca(OC_6H_5)_2$	?	[CaO]?,  $\left.\begin{array}{l}C_6H_4\\ \vert\\ C_6H_4\end{array}\right\rangle O$, C_6H_6, H_2O	(396)
$Ba(OC_2H_5)_2$	?	$BaCO_3$, C, H_2, C_2H_4, CH_4, C_2H_6, C_4H_{10}	(239a, 64, 88)
$Al(OC_6H_5)_3$	265	Al_2O_3, $(C_6H_5)_2O$	(138, 382, 74, 273)
$TlOC_2H_5$	?	Tl, C_2H_5OH, CH_3COOH, H_2	(241)
$Pb(OC_6H_5)_2$	?	[Pb]?,  $\left.\begin{array}{l}C_6H_4\\ \vert\\ C_6H_4\end{array}\right\rangle O$, H_2O	(140, 25)
$NaSCH_3$	200	Na_2S, Na_2S_2, $[(CH_3)_2S]$?	(437, 209, 301)
Mercaptides of Au, Hg, Pt	Various	Metal, dialkyl disulfide	(95, 209, 294, 165)
Other mercaptides	Various	Metallic sulfide, dialkyl sulfide	(202, 360, 95, 209)
$AgSeC_6H_5$	?	Ag, $(C_6H_5)_2Se_2$	(93)
$KNHC_2H_5$	300?	KCN, C, H_2	(384)
$KNHC_6H_5$	?	KCN, C	(172)
$KNC_{12}H_8$	400?	KCN, C, NH_3, $C_{12}H_8NH$	(62)
$CsNHCH_3$	120	CsCN, H_2	(308)
$CsNHC_2H_5$	110	[CsCN]?, H_2, C_nH_{2n+2}, C_nH_{2n}	(308)
$NaCH_3$	200	Na_2C_2, Na, CH_4	(37, 54)
NaC_2H_5	100	NaH, C_2H_4, C_2H_0, $[Na_2C_2]$?	(37, 54)
LiC_2H_5	120	LiH (50 per cent)	(378)
LiC_2H_5	250	Unsaturated hydrocarbons, C_2H_6, H_2	(121a)
LiC_4H_9	173	Butylene, butane, H_2	(121a)
CuC_6H_5	80	Cu, $(C_6H_5)_2$	(306)
AgC_6H_5	−18	Ag, $(C_6H_5)_2$	(238, 306)
$Mg(C_6H_5)_2$	175	MgH_2, C_2H_4	(196)
$NaSn(CH_3)_3$	75	Na–Sn alloy, $[Sn(CH_3)_4]$?, hydrocarbons	(229)

When the reacting halide is highly covalent, one product is an ortho ester of an inorganic acid.

$$TiCl_4 + 4NaOC_2H_5 \rightarrow Ti(OC_2H_5)_4 + 4NaCl$$

It may be recalled that the Grignard reagent is favored as a means for preparing organometallic derivatives by this method.

$$BiCl_3 + 3CH_3MgCl \rightarrow Bi(CH_3)_3 + 3MgCl_2$$

The similarity of all these reactions to that represented by the equation

$$C_2H_5Br + NaOC_6H_5 \rightarrow C_2H_5OC_6H_5 + NaBr$$

is so marked that we may regard them as modifications of the original Williamson synthesis. This synthesis, in which alkoxides play a part similar to that of metallic hydroxides in saponification, is subject to all the limitations that might be anticipated from this analogy. Aryl halides readily surrender their halogen only when a copper catalyst is present (391). Again, a hydrogen atom may combine with one of halogen bound to an adjacent carbon atom, producing unsaturation:

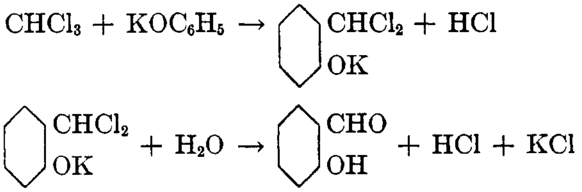
$$(CH_3)_2CH{-}CBr(CH_3)_2 \xrightarrow{KOCH_3} (CH_3)_2C{=}C(CH_3)_2 + HBr$$

Britton (49) reported that temperature considerably influences the course of the reaction between sodium phenylamide and phenyl chloride; at 180°C. the chief product is diphenylamine, whereas at 250°C. *o*-aminobiphenyl is obtained in 45 per cent yield.

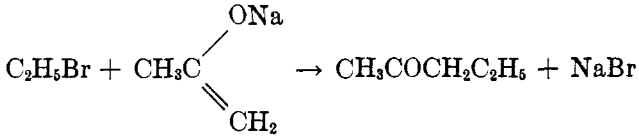
The behavior of polyhalogenated hydrocarbons is difficult of prediction. Sodium ethoxide couples normally with chloropicrin (152) and chloroform (201),

$$CHCl_3 + 3NaOC_2H_5 \rightarrow CH(OC_2H_5)_3 + 3NaCl$$

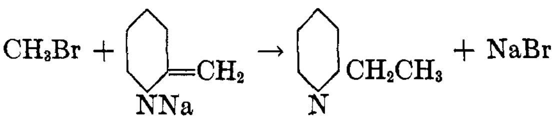
but aryl oxides and mercaptides may either give the expected ortho esters (125, 16) or undergo ring substitution or oxidation, depending on experimental conditions (35, 285, 257, 25, 216). The Tiemann-Reimer reaction is one of these abnormal cases:



Chloroform and carbon tetrachloride react similarly with potassium pyrrole, yielding α-pyrrolealdehyde (19) and α-pyrrolecarboxylic acid (67), respectively. When employed in a Williamson synthesis, salts of enols may yield, instead of the expected ether-like compounds, the isomeric alkylated keto forms (33).



$$C_2H_5Br + CH_3C\begin{matrix}\diagup ONa \\ \diagdown\!\!\diagdown CH_2\end{matrix} \rightarrow CH_3COCH_2C_2H_5 + NaBr$$



It is Hückel's (182) contention that most of these and other so-called "abnormal" Williamson reactions are normal couplings involving the organometallic forms of salts of alcohol types.

Under proper control, nevertheless, the Williamson reaction attains quantitative precision in the Stephanow method for determination of covalent halogen (361, 320). Its freedom from side reactions and the possibility of varying the degree of ionization of the reacting salt by changing the solvent make this coupling eminently suitable for studies in reaction kinetics.

Just as sodium ethoxide, in the Williamson synthesis, is employed to supply an $—OC_2H_5$ group, salts in other systems (sodium mercaptides, lead mercaptides, sodium diaryl amides, etc.) are used to introduce the negative groups they contain.

$$2C_6H_5Br + Pb(SC_2H_5)_2 \rightarrow 2C_6H_5SC_2H_5 + PbBr_2$$

Zinc dialkyls have been superseded by Grignard reagents in most fields, but they are still superior to their competitors for preparing pure hydrocarbons from tertiary alphyl halides (286).

$$2(CH_3)_3CCl + Zn(C_2H_5)_2 \rightarrow 2(CH_3)_3CC_2H_5 + ZnCl_2$$

Closely allied to the Williamson synthesis are other reactions in which the rôle of the halogen is played by some other negative group:

$$(CH_3)_2SO_4 + 2NaOC_6H_5 \rightarrow 2CH_3OC_6H_5 + Na_2SO_4$$

It is well authenticated, however, that esters of fatty acids are not saponified by alcoholic solutions of alkoxides unless water is present to liberate metallic hydroxides (291, 52, 145, 355, 349, 4, 191).

More difficulty is encountered in classifying a high-temperature process which affords a means for replacing many hydrogen atoms by alkyl groups,

$$C_6H_5NH_2 + NaOC_2H_5 \rightarrow C_6H_5NHC_2H_5 + NaOH$$

since it is evidently not a true variation of the Williamson reaction. Nitrogen compounds are especially susceptible to such alkylation, which has proved successful for pyrroles (109), pyrazolones (425), and amines (284, 244). If an acyl group is present, as in acetamide or acetanilide, the metallic hydroxide formed effects its removal (345).

$$CH_3CONH_2 + NaOC_2H_5 \rightarrow C_2H_5NH_2 + CH_3COONa$$

In some instances, particularly when alcohols (284, 144, 410, 181) are alkylated, the side reactions produced by sodium alkoxides are so dominant that it is necessary to substitute salts of aluminum or magnesium.

Metatheses between acids and salts find numerous minor uses. Because alkoxides of alkali metals and aluminum, when dissolved in organic liquids, tend to produce a precipitate of metallic hydroxide by reaction with water, they have been of service in determining the dryness of ether (314), alcohols (162), and pyridine (104). Sulfur compounds in benzene are detected by their conversion of soluble thallous ethoxide into insoluble thallous sulfide (269). Again, zinc diethyl dissolved in pyridine comports itself like a Grignard reagent in testing for active hydrogen atoms (154).

$$Zn(C_2H_5)_2 + 2H^+ \rightarrow Zn^{++} + 2C_2H_6$$

In some cases salts of alcohol types are involved in withdrawing undesirable acids from solution. Mercaptans are removed, in the "sweetening" of petroleum, as their lead salts. The drying of an alcohol by means of the corresponding alkoxide of sodium (79, 356), calcium (242, 310), magnesium (41, 254), or aluminum (105, 153, 400) depends upon regeneration of the alcohol by hydrolysis of the salt. Whether a particular alkoxide is suitable for the purpose depends on its oxidizability and solubility relationships; it is desirable that the solubility of the alkoxide shall be high and that of the hydroxide low (79, 51, 290). Less frequently alkoxides are used to abstract water (203, 386) or hydrochloric acid (204, 386) formed in the course of a reaction. The splitting out of hydrogen halide from adjacent carbon atoms is catalyzed as well as forced to completion by these alkalies.

In other instances the acid or the salt produced by metathesis is desired. The former is the case when salts of alcohol types, made as purification intermediates, are hydrolyzed to yield mercaptans, pyrroles (65), carbazole (141), or the more acidic hydrocarbons like fluorene (408, 7, 128) and indene (409, 129). Salts of alcohols (especially of phenols) are sometimes preferred to the free acids as antiseptics and disinfectants, because of the higher solubility and lower toxicity of the salts. Sodium derivatives of weak organic acids like phthalimide (148), acetoacetic ester, acid amides (42, 119), and higher alcohols (388, 321, 316), are conveniently secured by neutralizing these acids with sodium ethoxide or sodium methoxide. Even sodium alkyls are reported valuable for preparing salts of alkylated acetonitriles (186), and aluminum alkoxides for manufacturing aluminum carboxylates (187). Exceptionally pure salts of inorganic acids are similarly accessible; hydrogen sulfide (317, 197, 312) and hydrogen selenide (387, 21) form hydrosulfides and hydroselenides of alkali metals,

$$H_2S + NaOC_2H_5 \rightarrow NaSH + C_2H_5OH$$

and electrolyte-free colloidal hydroxides of iron and chromium are produced by hydrolysis of the metallic ethoxides (375, 376, 377).

$$3H_2O + Fe(OC_2H_5)_3 \rightarrow Fe(OH)_3 + 3C_2H_5OH$$

3. Oxidation-reduction reactions

To avoid occasion for misapprehension it should be explained that a few oxidations of salts of alcohol types are later discussed as addition reactions. Such a process as the addition of sodium alkyls to molecular oxygen is incidentally an oxidation, but it corresponds more closely to the addition of sodium alkoxides to carbon dioxide.

If these conversions are excluded, the primary products of oxidation are a new metallic salt and a coupled pair of organic residues:

$$2NaAR_n + O_2 \rightarrow Na_2O_2 + R_nA\text{—}AR_n$$

If R_nA— is capable of existing as a free radical, further oxidation is likely to produce a peroxide, $R_nA\text{—}O\text{—}O\text{—}AR_n$. The oxygen representative RO—OR is usually too unstable to persist, and consequently there result aldehydes, carboxylic acids, and more complex degradation fragments. A very active oxidant, e.g., a halogen, may enter the disintegration residues as a substituent.

Instances in which salts of metals other than sodium or potassium have been oxidized to recognizable products are rare; a notable exception is the preparation of aliphatic sulfonic acids by boiling lead mercaptides with nitric acid (287). Of the reductions tabulated in table 8, the only ones of consequence are those accomplished by alkoxides. Since reducing power seems to vary inversely as extent of ionization, alkoxides of high molecular weight far surpass aryl oxides in this respect, while alkoxides of low molecular weight are of intermediate potency. In practice, ionization is minimized by maintaining the concentration of the solution at a high level and adding benzene or some similar non-ionizing medium (366). The work of Diels and Rhodius (92), in which they achieved reduction, by sodium amyloxide, of diverse unsaturated molecules (see table 8), has been adversely criticized by Toussaint (386), but is otherwise generally

TABLE 8

Reductions by salts of alcohol types

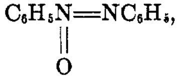
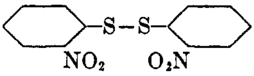
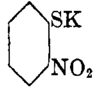
REDUCING AGENT	OXIDIZING AGENT	MAIN PRODUCTS REPORTED	REFERENCES
NaOR......	O_2	RCOONa, H_2O, Na_2O_2	(161, 284, 48, 14, 169)
	Cl_2	RCl, RCHO, RCOOH, substituted derivatives, NaCl	(258, 323, 73)
	Br_2	ROH, RBr, RCOOH, substituted derivatives, NaBr, RCOONa	(258, 348, 22)
	I_2	Polyiodo hydrocarbons, ROH, HCOOR, NaI, RCOONa	(53, 258, 206, 278, 47, 184)
	CrO_3, MnO_2	RCHO, RCOOH	(73)
	S_2O_3	Na_2SO_3, $Na_2S_2O_3$, $Na_2S_3O_6$, etc.	(394, 424)
	HNO_3	RNO_2, CO_2	(73)
	NO	N_2O, RCHO	(415, 416)
	$C_6H_5N_3$	$C_6H_5NH_2$, *N*-phenyl triazole, N_2, NaOH	(36, 37)
	Aromatic nitro compounds	Azoxy, azo, hydrazo or amino compounds, $Na_2C_2O_4$	(366, 255, 80, 112)
	Aromatic azo compounds	Hydrazo compounds, alkylated amines	(92)
	$C_6H_5N{=}CHC_6H_5$	$C_6H_5NHCH_2C_6H_5$	(92)
	$C_6H_5CH{=}CHCOOH$	$C_6H_5CH_2CH_2COOH$	(92)
KOR.......	Aromatic nitroso compounds	Azoxy compounds	(344, 151)
	C_6H_5NHOH	 $C_6H_5\underset{\overset{\Vert}{O}}{N}{=}NC_6H_5$, $C_6H_5N{=}NC_6H_5$	(17, 18)
NaSR......	O_2	R_2S_2, NaOH	(209, 39)
	I_2	R_2S_2, NaI	(257)
	S	R_2S_2, Na_2S_2	(39)
	Na_2S_2	R_2S_2, Na_2S	(39)
	$K_2S_2O_8$	R_2S_2, K_2SO_4, Na_2SO_4	(94)
	$SOCl_2$, SO_2Cl_2	R_2S_2, SO_2, NaCl	(77)
	$R'SSO_2R'$	$RSSR'$, $R'SO_2Na$	(113)
	$(R'SO_2)_2S$	R_2S_2, $R'SO_2Na$, $R'SO_2SNa$	(113)
	$R'SSO_3Na$	$RSSR'$, Na_2SO_3	(113)
	$Na_2S_3O_6$	R_2S_2, Na_2SO_3, $Na_2S_2O_3$	(113)
	$Na_2S_4O_6$	R_2S_2, $Na_2S_2O_3$	(113)
	$C_6H_5ICl_2$	R_2S_2, C_6H_5I, NaCl	(436)
	$C_6H_5NO_2$	R_2S_2, $C_6H_5NH_2$	(209)
	CBr_3NO_2	R_2S_2, CO_2, N_2, CO, NO, N_2O_3, NaBr	(239)
	CCl_4	R_2S_2, $CH(SR)_3$	(13)

TABLE 8—*Concluded*

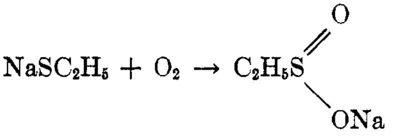
REDUCING AGENT	OXIDIZING AGENT	MAIN PRODUCTS REPORTED	REFERENCES
KSR	K_2S_2	R_2S_2, K_2S	(178)
	NH_2OH	R_2S_2, NH_3, KOH	(106)
		R_2S_2, 	(249)
	CCl_3NO_2	R_2S_2, CO_2, N_2, KCl	(285)
NaNHR	O_2	RN═NR, NaOH	(384, 10)
	$C_6H_5NO_2$	$C_6H_5N{=}NC_6H_5$, phenazine	(423)
$NaNR_2$	I_2	$R_2N—NR_2$, NaI	(61)
KNHR	O_2	RN═NR, [KOH]	(10)
KNR_2	$(C_6H_5)_2S_2$	$R_2NSC_6H_5$, KSC_6H_5	(341)
NaR	O_2	ROOR or R—R, Na_2O_2	(335, 228, 428)
	$(C_6H_5)_2S_2$	RSC_6H_5, $NaSC_6H_5$	(341)
	$(C_6H_5)_2Se_2$	$RSeC_6H_5$, $NaSeC_6H_5$	(341)

accepted as valid. Aldehydes present seem to influence the rate of reduction of aromatic nitro compounds by potassium ethoxide in a manner yet unexplained (15).

One of the most instructive oxidations of a salt not referable to the water system was studied by Klason (209). Sodium ethyl sulfide in solution is oxidized to diethyl disulfide,

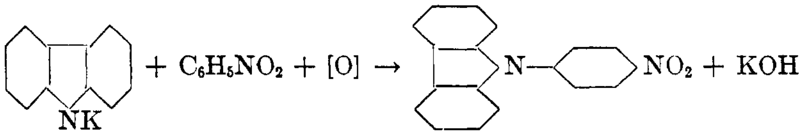
$$2NaSC_2H_5 + 1/2O_2 + H_2O \rightarrow 2NaOH + (C_2H_5)_2S_2$$

but when dry it merely adds to molecular oxygen, forming sodium ethyl sulfinate.



$$NaSC_2H_5 + O_2 \rightarrow C_2H_5S(=O)ONa$$

An extremely peculiar combination of oxidation and alkylation occurs when the potassium salt of carbazole is heated with excess nitrobenzene (86).

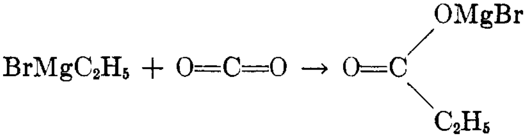


The additional nitrobenzene seems to supply the necessary oxygen, but no mechanism for the reaction has been suggested.

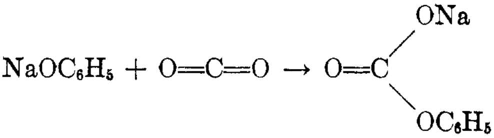
Compounds of disputed structure are formed when nitric acid acts on mercaptides of divalent iron, nickel, or cobalt. Manchot (260) defends the belief that $Fe(NO)_2SR$, for example, is a covalent derivative of monovalent iron, while Reihlen (307) prefers a polymeric formula requiring main valence linkages through nitrogen and oxygen.

4. Additive reactions

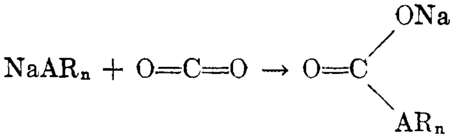
The previously noted addition of dry sodium mercaptide to oxygen is closely allied to reactions useful for the synthesis of carboxylic acids by the Grignard method,



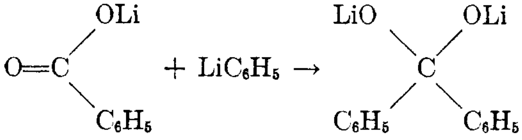
the Kolbe process,



and, in general, by the reaction



Grignard reagents and lithium aryls (134) sometimes add to the second double bond in carbon dioxide,



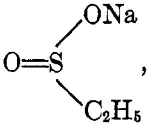
ketones being formed upon hydrolysis of the reaction product. The tendency of molecules of salts of alcohol types to add to carbon dioxide and other molecules containing multiple bonds may be judged from table 9.

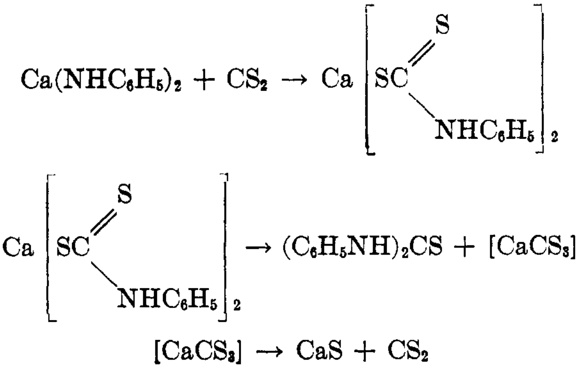
TABLE 9

Addition of salts to unsaturated molecules

MOLECULE	SALT					
	MR	RMgX	ZnR_2	$M(NHR)_n$	$M(OR)_n$	$M(SR)_n$
$R_2C{=}CR_2$	(+) (431)	− (328)	−	−	−	−
S	+ ?	+ (328)	?	?	−	(+) (96)
R_2CO	+ (426)	+ (328)	− (135)	+ (49)	(+) (393)	−?
RCOOR	+	+ (328)	− (135)	?	(+) (393, 99, 3, 325, 357	?
CO	+ (426)	(+)(111)	− ?	?	(+) (23, 359, 326)	?
O_2	+ (443)	+ (328)	− (122)	−	−	(+) (209)
CO_2	+ (136)	+ (328)	− (122)	(155, 103, 372)	(368, 382, 107)	− (177, 397, 210)
CS_2	+ (341)	+ (328)	− (122)	+ (103)	+	+ (280, 177)
SO_2	+ (426)	+ (328)	+ (122)	+ (103)	(324, 368, 315, 382)	+?

A + sign indicates ready reaction.
A (+) sign represents infrequent or difficult reaction.
A − sign denotes absence of reaction.

When Grignard reagents or other salts of hydrocarbons add in this manner, the resulting substances exhibit diminished reactivity, e.g.,  $O{=}S(ONa)C_2H_5$, from sulfur dioxide and sodium ethyl, is more stable toward heat and chemical reagents than sodium ethyl itself. Any similar product derived from a salt of another system, however, tends to be decomposed by water or increased temperature with regeneration of part or all of the unsaturated reagent (103, 107).

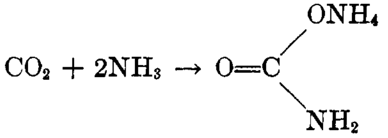


$$Ca(NHC_6H_5)_2 + CS_2 \rightarrow Ca\left[SC(=S)NHC_6H_5\right]_2$$

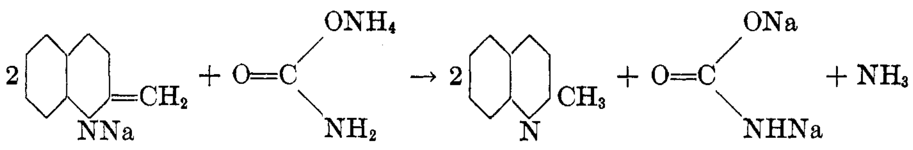
$$Ca\left[SC(=S)NHC_6H_5\right]_2 \rightarrow (C_6H_5NH)_2CS + [CaCS_3]$$

$$[CaCS_3] \rightarrow CaS + CS_2$$

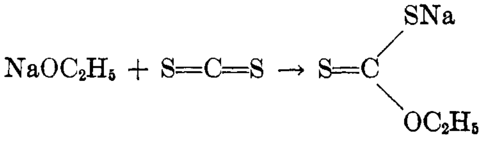
It may be hazarded that the anomalous failure of salts of enolic (enamic) forms of ammono ketones to add to carbon dioxide in liquid ammonia (31) is due to their considerable tendency to revert to the orthodox structure in the presence of even weak acids.



$$CO_2 + 2NH_3 \rightarrow O{=}C\begin{array}{l}/ONH_4\\ \backslash NH_2\end{array}$$



The addition of alkoxides to carbon disulfide produces the xanthates,



$$NaOC_2H_5 + S{=}C{=}S \rightarrow S{=}C\begin{array}{l}/SNa\\ \backslash OC_2H_5\end{array}$$

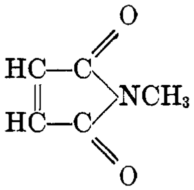
of commercial importance in fumigation and ore flotation processes.

Like many inorganic ortho acids of the water system, the derived ortho esters combine with many donor molecules (267, 327).

$$Ti(OC_2H_5)_4 + 2C_2H_5OH \rightarrow H_2[Ti(OC_2H_5)_6]$$
$$B(OCH_3)_3 + NaOCH_3 \rightarrow Na[B(OCH_3)_4]$$

Meerwein and Bersin (267) have proved that these alkoxo acids and salts surpass their hydroxyl analogs in stability, presumably because the coordinated groups can not easily split out molecules of an ether. The alkoxo acids, although less stable, may occasionally be isolated (377). Many of the so-called salts can even be dissolved in organic solvents and distilled, so that their polar nature must be feeble. The unusual stability and fusibility of the double compounds of alkali alkyls and zinc dialkyls (402, 143), together with their electrical behavior (156, 158, 159, 160), indicate that they belong to this group; consequently $NaC_2H_5 \cdot Zn(C_2H_5)_2$ is to be written as $Na[Zn(C_2H_5)_3]$. Nevertheless, salts of the type $M[BR_4]$ can not be secured by the reaction of boron trimethyl or boron triphenyl with an alkali metal alkyl (378).

The uncertainty concerning the structure of the brightly colored addition compounds between polynitro aromatic hydrocarbons and alkali alkoxides does not seriously detract from their merit for identifying the nitrated derivatives (190, 319, 392). Potassium aryl sulfides similarly add to chloropicrin (285), and unsaturated imides like



yield colored compounds with sodium alkoxides (303).

The metals of salts of alcohol types may themselves operate as coordination centers for many donor molecules, including those of alcohols, ethers, ketones, and esters. True alcoholates and etherates so obtained ($NaOC_2H_5 \cdot 2C_2H_5OH$ or $CH_3MgBr \cdot (C_2H_5)_2O$) differ little from the unsolvated salts in chemical properties, but may offer considerable resistance to removal of the solvent.

5. Catalytic effects

This field, a large one in itself, is thoroughly reviewed in Houben's reference work (264, 166, 203), and most of its practical aspects are discussed by Toussaint (386). The treatment here will therefore be confined to lending occasional supplementary emphasis.

Many of the studies in reaction kinetics which led Acree (263, 371, 279) to favor the "dual theory" of catalysis were concerned with alkali alkoxides. Whatever the mechanism may be, the effect of catalysis by alkoxides is evident in various migrations of multiple bonds, tautomeric shifts, and racemizations, the extent of the latter being a basis for quantitative determinations of salts of alcohols (389).

Alcoholyses in which esters exchange alkyl groups with alcohols

$$C_6H_5CH{=}CHCOOC_2H_5 + CH_3OH \xrightarrow{NaOC_2H_5} C_6H_5CH{=}CHCOOCH_3 + C_2H_5OH$$

require little additional description. Alkoxides of sodium, potassium, and aluminum are the usual catalysts, although Verley (393) and Terentiev (374) have employed the magnesium salts.

The aldol condensation is ordinarily induced by compounds other than sodium ethoxide, but the latter has received much notice in connection with the preparation of acetoacetic ester. Ethoxides of lithium (313) and calcium (299) lack the marked ability of the sodium salt to catalyze this famous reaction, the mechanism of which remains a subject of controversy.

Of much more industrial significance, especially in the manufacture of organic solvents, is a change which may be termed the generalized Cannizzaro reaction. It embraces all oxidation-reduction processes in which only the carbon atom of a carbonyl group and that of any organic molecule are the two active participants. The original Cannizzaro reaction, catalyzed by strong alkalies, may be represented by the equation

$$2RCHO + NaOH \rightarrow RCOONa + RCH_2OH$$

Subsequently Claisen (68) discovered that, if sodium alkoxides are employed as alkalies, the intermediate ester is not saponified:

$$2RCHO \rightarrow RCOOCH_2R$$

In 1906 Tischtschenko (383) reported an improvement in the yields of ester when the less caustic aluminum alkoxides are substituted for the alkaline catalysts. More recently published researches and patents (288, 292, 102, 200, 282, 81, 386) indicate that a "crossed" reaction between two different aldehydes is equally practical.

$$RCHO + R'CHO \rightarrow RCOOCH_2R'$$

Much interest has naturally centered about the relative catalytic values of salts of different metals, and the use of even zirconium alkoxides has been patented (185, 267a). Sodium alkoxides, as might be supposed, usually favor too many side reactions, particularly aldol condensations and resinification (393, 268). While symmetrical diacid alkoxides like $Mg(OR)_2$ are inferior in effectiveness to the mixed type XMgOR (142), it is the consensus of opinion that activated aluminum compounds excel (63, 102, 268, 304, 91, 198).

Examples of an additional variation of the generalized Cannizzaro reaction were first reported by Montagne and other investigators (252, 435, 358, 147, 284, 276) as ordinary reductions by means of alcoholic potash.

$$R_2CO + R'CH_2OH \xrightleftharpoons{R'CH_2OK} R_2CHOH + R'CHO$$

As Ponndorf (304) and Hückel and Naab (183) have pointed out, this modification always involves a reversible exchange of oxidation stages between the central carbon atom of a primary or secondary alcohol and that of a carbonyl group. The velocity of the reaction naturally varies with the reactivity of these two atoms and the efficacy of the catalyst. Verley (393), Dworzak (99), and others have proposed mechanisms based on addition compounds as intermediates, but no agreement has been reached. Although Bachmann (11) has obtained good yields using a sodium alkoxide as catalyst, the aluminum salts are generally preferred in spite of the increased seriousness of the Tischtschenko ester coupling as a side reaction (268, 322).

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