again contained amorphous oxide, which was purified, dried and analyzed. The precipitate from the Carius was weighed and then extracted with 2% ammonia to separate the iodide and chloride.

Substance, 0.1176; AgI, 0.1284; AgCl, 0.0404. Found: I, 58.98; Cl, 8.49.

Another sample was then made, and analyzed, using the cyanide method for the indirect analysis. The composition was close to that of the previous sample.

Substance, 0.2033; AgI + AgCl, 0.2924; Ag, 0.1560. Found: I, 58.09; Cl, 9.01.
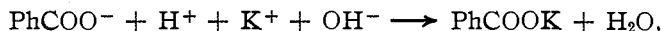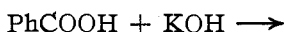
MINNEAPOLIS, MINN.

ORGANIC ADDITIVE COMPOUNDS OF POTASSIUM HYDROXIDE.

BY WILLIAM M. DEHN AND RUTH E. MERLING.
Received September 22, 1917.

When benzoic acid reacts with potassium hydroxide in aqueous solution, the following equations are universally regarded as adequate to describe the mechanism of chemical reaction:

$$PhCOOH + KOH \longrightarrow$$
$$PhCOO^- + H^+ + K^+ + OH^- \longrightarrow PhCOOK + H_2O,$$

for here we are dealing with a simple case of the action of an acid on a base. Preliminary ionization, followed by the formation of non-ionizable water, is assumed to be the *sine qua non* of this reaction.

The ionic theory rests so securely on experimental facts, interprets so many chemical phenomena, and is grounded so universally in chemical opinion, that sight is frequently lost of the fact that it rests on assumptions and possibly may color and mislead. Its interpretation of the mechanism of chemical reaction of acids and bases require: (1) preliminary ionic dissociation of both the acid and the base, (2) subsequent association of their ions to yield molecular salt and molecular water, and (3) association of the salt with water to form the hydrated salt.

Since the experimental facts of this paper are not at all in agreement with these assumptions, we shall re-open for discussion the ionic interpretation of the interaction of acids and bases.

According to this theory the first phenomenon of a chemical reaction is *dissociation*. The reality and possibility of initial dissociation are especially questioned by the findings of this paper. For when brought together in anhydrous ether, not only acids and bases but also a host of other reactive compounds yield *additive* compounds, as the first and, in most cases, the only recognizable products. Therefore, the alternate view, that of *initial association*, instead of dissociation, presents itself. Now, it cannot be denied that the first chemical activity is either a disso-

ciation or an association.   Inasmuch as the *initial* ionic dissociation in anhydrous ether is merely assumed, and the experimental facts do not accord with this assumption, it may be profitable to examine the alternate association theory.

Since, as far as tested, the included associated compounds formed in either give with water the same products that have been recognized as formed when water is the original solvent, it is possible that *association is the initial reaction even in water*.   Since water transforms the ether-associated compounds and yields the usual ionic equilibria, it is conceivable and probable that *ionization is the final effect instead of the initial cause of chemical reactions*.

The absence of any *cause* of ionization except the "specific influence" of the solvent, degrees of ionization varying with the mass of the solvent; the unsaturated and consequential additive nature of all ionizable compounds; the independence, on the one hand, of chemical reactivity and solubility and, on the other hand, probably of chemical reactivity and ionization; studies of reactions in non-ionizing solvents; the extensive recognization of molecular compounds; all these and other evidences point to an independence of the two phenomena, chemical reactivity and ionization.

The increasing difficulties of reconciling to the ionic basis all chemical reactions, especially the great bulk of organic reactions, certainly should bear closer scrutiny.   For example, take the case of acetone, which with potash[1] yields $(CH_3)_2CO.KOH$ and with hydrogenbromide[2] yields $(CH_3)_2$-$CO.HBr$.   Or consider the ester and other additive compounds of this paper, on the one hand, and analogous additive compounds with acids, on the other hand.   The latter compounds, illustrating "the basic properties of oxygen," are described by McIntosh,[3] Kendall[4] and others.[5]   Ionic explanations of the formation of these oppositely constituted compounds are inadequate,[6] if not absurd; but, without the use of any initial dissocia-

[1] Vaubel, *J. prakt. Chem.*, [2] **43**, 599 (1891).

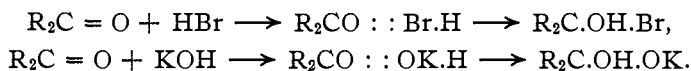[2] Maass and McIntosh, THIS JOURNAL, **34**, 1286 (1912).

[3] *J. Chem. Soc.*, **85**, 919, 1098 (1904); THIS JOURNAL, **27**, 26, 1013 (1905); **28**, 588 (1906); **30**, 1097 (1908); **32**, 542 (1910); **33**, 71, 542 (1911); **34**, 1273 (1912).

[4] *Ibid.*, **36**, 1222, 1722, 2498 (1914); **37**, 149 (1915); **38**, 1309, 1712 (1916).

[5] Friedel, *Bull. soc. chim.*, [1] **24**, 160, 241 (1875); Collie and Tickle, *J. Chem. Soc.*, **75**, 710 (1899); **77**, 1114 (1900); **85**, 973 (1904); Baeyer and Villiger, *Ber.*, **33**, 1438 (1900); **34**, 2679, 3612 (1901); **35**, 1201 (1902); Stobbe, *Ann.*, **370**, 93 (1909); Gomberg, *Ann.*, **370**, 142 (1909); **376**, 183 (1910); Vorländer, *Ann.*, **341**, 1 (1905); Wieland and Reischle, *Ber.*, **41**, 3671 (1908); Platnikov, *Ber.*, **42**, 1154 (1909); Hamfray, *J. Chem. Soc.*, **85**, 1443 (1905); Baly, *Ibid.*, **96**, 144 (1909); Willstätter and Pummerer, *Ber.*, **37**, 3740 (1904); **38**, 1461 (1905); Landolph, *Compt. rend.*, **36**, 1463; **96**, 580.

[6] Kendall maintains in all of his papers that the reactions are additive, instantaneous and ionic.   His chief argument that they are ionic is because they are instantaneous. Now, if this reasoning is correct, the reactions with KOH are not ionic because they are not instantaneous,

tion, these reactions, as discussed below, can easily be accounted for on the basis of association.

$$R_2C = O + HBr \longrightarrow R_2CO : : Br.H \longrightarrow R_2C.OH.Br,$$

$$R_2C = O + KOH \longrightarrow R_2CO : : OK.H \longrightarrow R_2C.OH.OK.$$

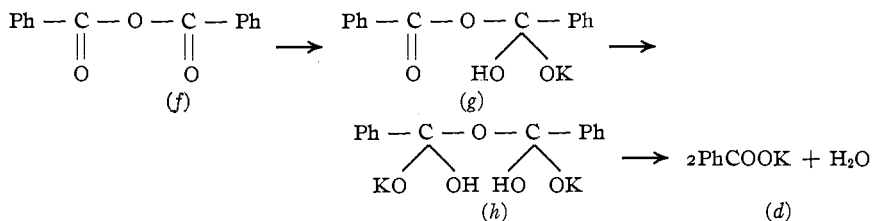When benzoic acid and solid potash are brought together in anhydrous ether, the following successive additions and decompositions are recognized:

```
2PhCOOH         Ph — C — O — C — Ph
+ 2KOH  ⟶          /\         ||        ⟶
   (a)          HO   OH       O
                         (b)
```

```
                Ph — C — O — C — Ph
                   /\          /\           ⟶  2PhCOOK + 2H₂O
                HO   OHHO   OK
                        (c)                         (d)
```
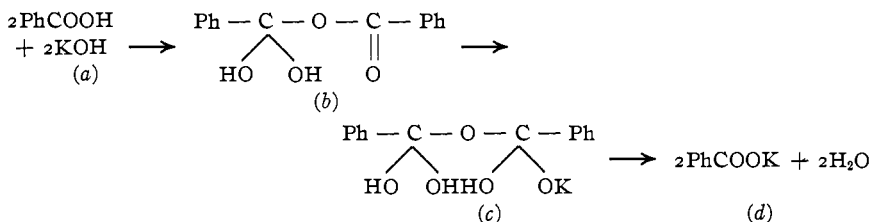
The bimolecular association (b) is proven by the measurements of Beckmann,[1] by the formation of the initial salt (c) and by collateral evidence.[2] Proofs of the formation of the initial salt (c) and the final salt (d) is represented.

When benzoic anhydride and solid potash were brought together in anhydrous ether, the following successive additions are recognized:

```
Ph — C — O — C — Ph       Ph — C — O — C — Ph
   ||         ||       ⟶      ||        /\          ⟶
   O          O               O       HO   OK
        (f)                         (g)
```

```
                Ph — C — O — C — Ph
                   /\          /\           ⟶  2PhCOOK + H₂O
                KO   OH HO   OK
                        (h)                         (d)
```

It is observed that the final salt (d) is the same, both with benzoic acid and with its anhydride; the intermediate salt (c) differs from salt (h).

The other acids studied are classified as follows:

NATURE OF SALTS FORMED.

2 Acid KOH.	Acid KOH.	Acid 2 KOH.
benzoic	benzoic	uric
malic	crotonic	meconic
cinnamic	dichloroacetic	succinic
	o-nitrobenzoic	gallic
	naphthionic	
	thioacetic	

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[1] Z. physik. Chem., **3**, 603 (1889); **6**, 457 (1890).

[2] The constitution of benzoic anhydride is, of course, closely related. Gerhardt's potassium salt evidently is an associated form. Jahresb., 1852, 450. Abnormal melting points of benzoic acid. Beilstein, Ann., **132**, 318 (1864).

All of these salts, when first formed, are additive[1] compounds; later they may or may not yield the simple anhydrous salt.   Proofs of these conclusions are as follows:

(1) The initial and final percentages of composition demonstrate the progressive nature of the reactions.

(2) Titrations with acids or with alkalies further demonstrate the nature of the compounds.

(3) The initial presence of all of the water in the precipitate, and the progressive loss of this water from the precipitate in most of the cases studied.

(4) The inability of the anhydrous compounds to take up a molecule of water from an ether solution of the same.

Proofs afforded by (1) and (2) are sufficiently evident, and demonstrate the non-ionic nature of the reactions.   The latter is further proven by the initial location of the water.[2]   If the reactions were ionic, water would be formed immediately, on account of its slight degree, if ionization would appear as such in the ether,[3] and ultimately would yield the hydrated salt in equilibria with the anhydrous salt.   But *pure hydrated salts are first formed* and these subsequently may or may not yield water and the anhydrous salt.   In other words, these experiments clearly demonstrate that these reactions in anhydrous ether are additive and are not ionic.

Furthermore, not only acids but all other organic compounds containing carbonyl groups thus add whole molecules of potassium hydroxide.

Acid..............................	$R.CO.OH$	$\longrightarrow$ $R.COK.(OH)_2$
Aldehyde........................	$R.CO.H$	$\longrightarrow$ $R.COK.H(OH)$
Ketone..........................	R_2CO	$\longrightarrow$ $R_2COK.(OH)$
Ester...........................	$R.CO.OR$	$\longrightarrow$ $R.COK.OR(OH)$
Amide...........................	$R.CO.NH_2$	$\longrightarrow$ $R.COK.NH_2(OH)$
Urethane........................	$RO.CO.NH_2$	$\longrightarrow$ $RO.COK.NH_2(OH)$
Acid halide.....................	$R.CO.X$	$\longrightarrow$ $R.COK.X(OH)$
Anhydride, etc..................		

It may be observed that:

(1) All of these potassium compounds are *salts*.

(2) The conventional definitions of an acid are not sufficiently inclusive and exclusive.

[1] Most organic compounds tend to *associate* in the common solvents.   Consult tables and bibliography in Turner's "Monograph on Molecular Association," pp. 119–167 (1915).

[2] Since KOH is a dehydrating agent, when present in excess, it keeps the ether free from water.   Precipitates, tending to give up water easily, as in cases of the alcohols, esters, etc., finally become more or less liquid.   Usually the residual KOH does not become liquid.   When an excess of compound is treated with KOH and all of the latter disappears, no water appears in the ether.

[3] The absence of water in the ether was proven by anhydrous copper sulfate. Usually the mixture of precipitate and ether gave a positive test for water.

(3) The reactive group of most organic compounds is the carbonyl[1] group.

(4) Reaction takes place by addition on the carbonyl group. This addition is, of course, of the following nature:

$$= CO + K \longrightarrow = C - OK$$
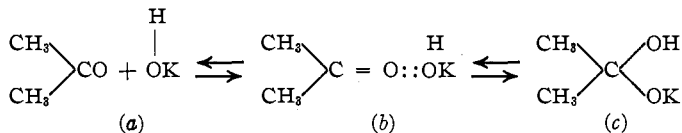$$\quad\quad\quad | \quad\quad\quad\quad\quad \searrow OH$$
$$\quad\quad\quad OH$$
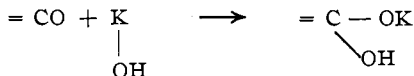
When hydrated acids are considered *trihydroxylated*, and aldehydes and ketones *dihydroxylated*, and alcohols *monohydroxylated*

$$\begin{array}{cccc} \nearrow OH & & & \\ R.C.OH & RH.C.OH & R_2.C.OH & RH_2C.OH \\ \searrow OH & \searrow OH & \searrow OH & \end{array}$$

it is observed that these compounds differ in degree and not in kind, hence it is not surprizing that all of them form salts.

Reactions with aldehydes, though by no means so rapid as with acids, are quite rapid; with aromatic ketones, somewhat slower; with acetone, very slow but definitely progressive.

Now, since acetone is miscible with ether in all proportions, the question of solubility, as in some cases, does not necessarily condition reactions. Why then is acetone so sluggish toward potassium hydroxide? In accordance with previous experiments, it has been recognized that an inhibitory state intervenes between free molecules and their molecular compounds. To illustrate with acetone:

$$\begin{array}{ccc} & H & \\ CH_3\diagdown & | & CH_3\diagdown \quad\quad H \quad\quad CH_3\diagdown \quad \diagup OH \\ \quad\quad >CO + OK \rightleftarrows \quad\quad >C = O::OK \rightleftarrows \quad\quad >C \\ CH_3\diagup & & CH_3\diagup \quad\quad\quad\quad CH_3\diagup \quad \diagdown OK \\ (a) & & (b) \quad\quad\quad\quad\quad (c) \end{array}$$

Here two assumptions are made:

(1) The residual valences of the two reacting molecules cohere.[2]

(2) The energy of the new system, or of its component parts, promote the molecular rearrangement.

Now, it is easily understood that among a host of chemical reactions either state (a) only can exist, or state (a) may reversibly tend to progress to state (b) but not to state (c), or state (a) may progress to (b) and only slowly to state (c), or state (a) may progress rapidly to state (c).

With acetone in anhydrous ether it is conceivable that the methyl

[1] THIS JOURNAL, **38**, 1317 (1916). Kendall demonstrates that addition may take place both on the carbonyl and hydroxyl oxygen atoms. See also Hoogewerff and van Dorp, *Rec. trav. chim. Pays-Bas*, **21**, 363 (1902).

[2] The above reactions do not indicate how KOH may add without a preliminary dissociation. Indeed, it may erroneously have been concluded that such preliminary dissociation was intended. However, this was not the case.

groups only slowly influence the change from (b) to (c). However, if the energy of the system is increased by heat, acetone and potash without a solvent yield at once[1] the addition compound.

Evidences for the existence of the intermediate state (b) are as follows:

(1) The extensively recognized tendency of organic compounds to exist in equilibria of molecular compounds[2] in most solvents.

(2) The isolation and proof of intermediate compounds in many cases, thus demonstrating progressive chemical changes.
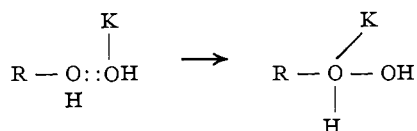
(3) The sluggishness or non-reactivity of many compounds similar to acetone, under some conditions but not under other conditions.

(4) The existence of oxonium compounds, as voluminously described in the literature.

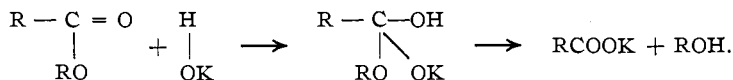(5) The phenomenon of non-interchangeability of radicles[3] in certain reactions.

(6) The accelerating influence of sunlight in many of these reactions.

In respect to the oxonium salts, it is here observed that the potash additive compounds of alcohols and phenols are of great interest. Their formation is elucidated by the following equation:

$$\underset{\text{H}}{\overset{\overset{\textstyle\text{K}}{|}}{\text{R} - \text{O} : : \text{OH}}} \quad \longrightarrow \quad \underset{\text{H}}{\overset{\overset{\textstyle\text{K}}{\diagup}}{\text{R} - \text{O} - \text{OH}}}$$

With some alcohols and phenols the reactions are rapid; with others, quite slow. With o-nitrophenol[4] the reaction is complete in a day or two; with p-nitrophenol the reaction was just recognizable after months of standing.

The reactions with esters are especially interesting, for the light they throw on the mechanics of saponification.

$$\underset{\text{RO}}{\overset{\overset{\textstyle\text{R} - \text{C} = \text{O}}{|}}{}} + \underset{\text{OK}}{\overset{\overset{\textstyle\text{H}}{|}}{}} \longrightarrow \underset{\text{RO}\ \ \text{OK}}{\overset{\textstyle\text{R} - \text{C} - \text{OH}}{\diagdown}} \longrightarrow \text{RCOOK} + \text{ROH.}$$

The alcohol split off may and, indeed does, take up another molecule of KOH, hence after long standing the percentage of potassium in the precipitates approach the requirements of the formula RCOOR.2KOH. It was found that the alcohols finally yield precipitates whose concentra-

[1] Vaubel, J. prakt. Chem., [2] 43, 599 (1891).

[2] See Turner's "Monograph on Molecular Association."

[3] THIS JOURNAL, 36, 2095 (1914); 37, 2124 (1915); 39, 2444 (1917).

[4] This observation and preliminary experiments with the isomeric nitrobenzaldehydes and nitrocresols reacting with potash in anhydrous ether, lead to conclusions contrary to the findings of Auwers (Z. physik. Chem., 40, 513 (1902) and Kremann (Ber., 39, 1022 (1906); Monatsh., 27, 627 (1906)), in respect to the additive powers of these isomers.

tion of potassium exceed the requirement of the formula ROH.KOH. Since compounds of this kind easily lose water, which dissolves more potash, the alcoholates finally are contaminated by free potash. Therefore, esters finally yield with potash, the following compounds and mixtures:

$$\begin{array}{c} RC-OK \\ RO \diagdown OH \end{array} \longrightarrow RCOOK + ROH.KOH \longrightarrow RCOOK + ROK + KOH.H_2O$$

$$\qquad (a) \qquad\qquad\qquad (b) \qquad\qquad\qquad\qquad (c)$$

Proofs of the composition of the initial precipitate (a) were obtained by a study of ethyl salicylate. After its early formation, filtering and washing with ether, it gave the following:

(1) Its percentage of potassium was in close agreement with the theoretical percentage.

(2) With water it yielded an oil and the odor of ethyl salicylate.[1] Acidifying the precipitate increased the oil but precipitated no free salicylic acid.

(3) The theoretical quantity of alkali was titrated with 0.1 N hydrochloric acid, in accordance with the reaction

$$C_7H_7O_4K + H_2O \longrightarrow C_7H_6O_3 + KOH + H_2O.$$

(4) When boiled with water and finally acidified with hydrochloric acid, free salicylic acid was precipitated.

The formation of the mixtures (b) and (c) was proven by the hygroscopic nature of the last precipitates and by comparisons of the total potassium and the titrable potassium contained in such precipitates.

Another interesting interpretation afforded by these reactions is Cannizaro's.[2]

$$2R.C=O \quad H \qquad R-C-OH \quad O=C-R$$
$$\begin{array}{ccc} | & + & | \\ H & & OK \end{array} \longrightarrow \begin{array}{ccc} |\diagdown & + & | \\ H\ \ OK & & H \end{array} \longrightarrow$$
$$R-C-O-C-R$$
$$\begin{array}{cc} \diagup\diagdown \ \ . \ |\diagdown & \longrightarrow RCOOK + HOH_2C.R. \\ KO\ \ H\ \ \ HO\ H \end{array}$$

This and other reactions will be studied in detail from the starting point of alkali additive compounds.

Experimental Methods.

Bottles of convenient size were filled with anhydrous ether, care being exercized to avoid contact with atmospheric moisture. Sufficient substance for a homogeneous solution was added and finally a clean, dry lump of potash. On standing a crust was most frequently formed on the potash; this usually could be shaken off; sometimes a glass rod was

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[1] If some of the precipitate was placed on water, spinning motions were produced. This disturbance of surface tension may also be demonstrated most beautifully by a short piece of wool yarn moistened at one end by ethyl salicylate. When placed on water, boat-like motions continue for many minutes.

[2] *Ber.*, 14, 2394 (1881). In this connection see also Nef, *Ann.*, 298, 302 (1897).

used to remove the crust. Often the precipitate forming could be seen to increase and sometimes it increased so that it occupied the entire ether volume. Some of the bottles were placed in direct sunlight to promote reactions. Finally the precipitates were separated either by decantation or by rapid filtering through a porcelain funnel. After washing with anhydrous ether, the precipitates were dried and, if not hygroscopic, were shaken through a fine sieve to separate lumps of unchanged potash.

The precipitates were treated with sulfuric acid, evaporated, incinerated and weighed as K_2SO_4. The loss of water, etc., was determined by heating at 100–110° in desiccators heated in a steam bath. The latter precaution was necessary to avoid absorption of atmospheric carbon dioxide.

The losses of weight often differed widely from the theoretical percentages of water, owing to: (1) the hygroscopic nature of the addition compounds, (2) the presence of one hydroxyl group only, (3) the simultaneous evolution of ammonia, alcohol, etc., (4) incomplete desiccation at the temperature and time employed. Of course, careful regulation of the time and temperature of heating could give apparent agreement of the theoretical and determined percentages of water. However, the percentages of potassium, easily determined with great accuracy, were the best indications of the true composition of the precipitates.

It must be remembered that some of the reactions are progressive, consequently the composition of the precipitates may vary. Other conditions that may influence the composition of the precipitates are as follows: (1) concentration of the reacting substance, (2) fineness of division of the potash employed, (3) length of time of standing, and (4) frequency of shaking. The time of standing varied from a few minutes to many weeks or months. Unless otherwise stated, the time used was the maximum, averaging about ten weeks.

The character of some precipitates was studied by titration. For example, benzaldehyde gave the following data:

	Immediate precipitate.	2nd day.	3rd day.	4th day.	5th day.
Acidity..............	32.55	1.82	—3.09	—6.19	—15.12
Total K..............	14.85	23.24	24.26	24.35	24.50

Since the benzaldehyde contained benzoic acid, the reaction at first was rapid and $(C_6H_5COOH)_2.KOH$ was largely formed. Theoretical acidity, 40.65%; K, 13.02%. As successive precipitates were filtered out, the new precipitate finally approached the composition of $C_6H_5CH.OH.OK$, whose theoretical alkalinity, calculated as K, and total K is 24.11%. Since an equimolecular mixture of $C_6H_5COOK.H_2O$ and $C_6H_5CH_2OK$, formed according to Cannizaro's reaction, has the same percentage of potassium but an alkalinity of only one-half, this reaction must be more closely studied. The final precipitate gave off the odor of benzaldehyde.

Benzoic Acid and KOH.—When a concentrated ether solution of benzoic acid is treated with solid potash, a white amorphous mass, quickly increasing in volume by shaking, is formed. If filtered after a few minutes, washed with ether, dried and analyzed, the following data with different preparations may be obtained:

Calc. for $C_6H_5COOH.KOH$: K, 21.95%; H_2O, 10.11%.
Calc. for $(C_6H_5COOH).KOH$: K, 13.02%; H_2O, 6.00%.
Found: K, 14.22%, 13.83%, 13.20%, 13.52%.

The ether solution from these precipitates gave no test for water.

If a less concentrated solution of benzoic acid is treated with an excess of potash and is permitted to stand with frequent shaking for many days, needles and coral-like formations are observed. Finally a voluminous amorphous mass is obtained.

Calc. for C_6H_5COOK: K, 24.42%. Found: K, 25.02%, 24.61%.

The ether solution, filtered and evaporated, gave a trace of residue, thus indicating soluble solid phases. After long standing with an excess of potash, the percentage of potassium in the precipitate steadily increases.

Calc. for $C_6H_5C(OK)_2OH$: K, 36.16%. Found: K, 26.51%, 27.35%.

Salts of Other Acids.

(a) *Two molecules of acid and one molecule of KOH.*

Cinnamic acid.—Calc. for $(C_9H_8O_2)_2.KOH$: K, 11.10%.
Found: K, 10.92%.
Malic acid.—Calc. for $(C_4H_6O_5)_2.KOH$: K, 12.06%.
Found: K, 13.60%.

(b) *One molecule of acid and one molecule of KOH.*

Crotonic acid.—Calc. for $C_4H_6O_2.KOH$: K, 27.48%; H_2O, 12.67%.
Found: K, 27.75%; H_2O, 8.40%.
Dichloroacetic acid.—Calc. for $C_2H_2Cl_2O_2.KOH$: K, 21.13%.
Found: K, 22.24%.
Naphthionic acid.—Calc. for $C_{10}H_9O_3NS.KOH$: K, 14.00%.
Found: K, 13.88%.
o-Nitrobenzoic acid.—Calc. for $C_7H_5O_4N.KOH$: K, 17.52%; H_2O, 8.07%.
Found: K, 18.91%; H_2O, 3.66%.

Thioacetic Acid.—Transparent prisms.

Calc. for $CH_3COSH.KOH$: K, 29.57%.
Found: K, 29.90%.

(c) *One molecule of acid and two molecules of KOH.*

Succinic acid.—Calc. for $C_4H_6O_4.2KOH$: K, 33.96%; H_2O, 14.63%.
Found: K (a) 37.83%, (b) 34.50%; H_2O, 13.28%.
Meconic acid.—Calc. for $C_7H_4O_7.2KOH$: K, 25.04%; H_2O, 5.76%.
Found: K, 25.15%; H_2O, 2.29%.
Fumaric acid.—Calc. for $C_4H_4O_4KOH$: K, 46.11%.
Found: K, 46.68%.
Uric acid.—Calc. for $C_5H_4O_8N_4.2KOH$: K, 27.90%.
Found: K, 26.87%.

Acid Anhydrides.

Benzoic Anhydrides.—The reaction is slower with the anhydride than with benzoic acid. It gives at first the *additive compound* and finally the hydrated and the anhydrous potassium benzoates.

Calc. for $C_{14}H_{10}O_3$.KOH:	K, 13.85%;	H_2O, 6.38%.
Found: (early ppt.)	K, 13.43%;	H_2O, 3.17%.
Found: (later ppt.)	K, 14.77%.	
Found: (old ppts.)	K, 22.23%; 24.03%.	

Phthalic anhydride.—Calc. for $(C_8H_4O_3)_2$.KOH: K, 12.49%; 0.5H_2O, 2.89%.
Found: K, 12.86%; H_2O, 3.04%.

Aldehydes.

Benzaldehyde.—An immediate precipitate was formed and continued to be added to for a number of days.

Calc. for C_7H_6O.KOH:	K, 24.11%; 0.5H_2O, 5.55%.	
Found: (a)	K, 24.32%;	H_2O, 4.15%.
Found: (b)	K, 24.33%;	H_2O, 3.89%.

Cinnamic aldehyde.—Calc. for C_9H_8O.KOH: K, 20.77%; 0.5H_2O, 4.78%.
Found: K, 18.88%; H_2O, 4.05%.

Anisaldehyde.—Calc. for $C_7H_8O_2$.KOH: K, 20.34%; H_2O, 9.37%.
Found: K, 21.61%; loss wt., 10.26%.

Furfural.—Calc. for C_5H_4O.KOH: K, 25.70%; 0.5H_2O, 2.57%.
Found: K, 25.65%; H_2O, 1.06%.

Propionaldehyde.—Calc. for C_3H_6O.KOH: K, 33.29%; H_2O, 15.78%.
Found: K, 30.13%; loss, 11.72%.

Ketones.

Acetone.—The reaction proceeds very slowly.

Calc. for C_3H_6O.KOH:	K, 34.25%; 0.5H_2O, 15.78%.	
Found:	K, 34.40%; loss,	

Acetylacetone.—Calc. for $C_5H_8O_2$.KOH: K, 25.04%; H_2O, 11.53%.
Found: K, 25.60%; loss, 15.96%.

Benzoylacetone.—Calc. for $C_{10}H_{10}O_2$.KOH: K, 17.92%; H_2O, 8.26%.
Found: (a) K, 18.56%; H_2O, 1.74%.
Found: (b) K, 19.60%; H_2O, 1.44%.

Esters.

Ethyl salicylate.—Calc. for $C_8H_{10}O_3$.KOH: K, 17.92%.
Found: K, 18.05%.

Ethyl acetate.—Calc. for $C_4H_8O_2$.KOH: K, 29.59%; $C_2H_6O.H_2O$, 44.43%.
Calc. for $C_8H_8O_2$.2KOH: K, 39.04%; $C_2H_6O.H_2O$, 31.98%.
Found: K, 39.46%; loss wt., 14.77%.

Ethyl hippurate.—Calc. for $C_{11}H_{13}O_3$.KOH: K, 14.89%; H_2O, 6.84%.
Calc. for $C_{11}H_{13}O_3$.2KOH: K, 24.49%; H_2O, 5.64%.
Found: K, 17.58%; H_2O, 4.10%.

Benzyl benzoate.—Calc. for $C_{14}H_{12}O_2$.2KOH: K, 24.11%; H_2O, 5.92%.
Calc. for $C_{14}H_{12}O_2$.3KOH: K, 30.83%; H_2O, 4.73%.
Found: K, 29.81%; H_2O, 9.07%.

Ethyl malonate.—Calc. for $C_7H_{12}O_4$.2KOH: K, 26.14%; H_2O, 6.61%.
Calc. for $C_7H_{12}O_4$.3KOH: K, 39.57%; H_2O, 6.08%.
Found: K, 36.13%; H_2O, 11.00%.

Ethyl oleate.—Calc. for $C_{20}H_{38}O_2.KOH$:　　K, 10.67%; H_2O,　4.91%.
　　　　　　　Calc. for $C_{20}H_{38}O_2.KOH$:　　K, 18.51%; H_2O,　4.26%.
　　　　　　　Found:　　　　　　　　　　K, 16.01%; H_2O, 10.38%.
Diethyl tartrate.—Calc. for $C_8H_{14}O_6.KOH$:　K, 14.91%.
　　　　　　　Calc. for $C_8H_{14}O_6.2KOH$:　　K, 24.56%.
　　　　　　　Found:　　　　　　　　　　K, 19.73%.
Tributyrine.—Calc. for $C_{15}H_{26}O_6.3KOH$:　K, 24.94%; H_2O,　3.82%.
　　　　　　　Found: (*a*)　　　　　　　K, 25.84%; H_2O, 14.42%.
　　　　　　　Found: (*b*)　　　　　　　K, 24.99%; H_2O,　5.95%.
Tricapryline.—Calc. for $C_{27}H_{50}O_6.3KOH$:　K, 18.36%.
　　　　　　　Calc. for $C_{27}H_{50}O_6.4KOH$:　K, 22.51%.
　　　　　　　Found:　　　　　　　　　　K, 22.19%.

Amides.

Phenylacetamide.—Calc. for $C_8H_9ON.KOH$:　K, 20.45%; H_2O, 11.16%.
　　　　　　　Found:　　　　　　　　　　K, 20.08%; H_2O, 11.92%.
Acetamide.—Formed an oil.
　　　　　　　Calc. for $(C_2H_5ON)_4.KOH$:　K, 13.37%.
　　　　　　　Found:　　　　　　　　　　K, 14.88%.
Urethane.—Calc. for $C_3H_7O_2N.2KOH$:　K, 38.85%.
　　　　　　　Found:　　　　　　　　　　K, 39.98%.
Oxamide.—Calc. for $C_2H_4O_2N_2.KOH$:　K, 27.08%.
　　　　　　　Found:　　　　　　　　　　K, 27.42%.

Imides.

Succinimide.—Calc. for $C_4H_5O_2N.KOH$:　K, 25.20%.
　　　　　　　Found:　　　　　　　　　　K, 25.68%.
Phthalimide.—Calc. for $C_8H_5O_2N.KOH$:　K, 19.24%; $0.5H_2O$,　4.18%.
　　　　　　　Found: (*a*) 19.87%, (*b*)　K, 20.53%;　　H_2O,　4.12%.

Alcohols.

Methyl.—Calc. for $CH_4O.KOH$:　　K, 44.36%.
　　　　　　　Found:　　　　　　　　　　K, 44.60%.

Ethyl.—Short, transparent, hygroscopic prisms.

　　　　　　　Calc. for $C_2H_6O.KOH$:　　K, 40.84%.
　　　　　　　Found: (*a*)　　　　　　　K, 40.30%.
　　　　　　　Found: (*b*) (long standing)　K, 59.20%.
　　　　　　　Found: (*b*) by titration　　K, 59.40%.
n-Heptyl.—Calc. for $C_7H_{16}O.KOH$:　K, 22.70%; H_2O, 10.46%.
　　　　　　　Found: (long standing)　　　K, 49.68%; H_2O,　8.02%.
Benzyl.—Calc. for $C_7H_8O.KOH$:　　K, 23.82%; H_2O, 10.97%.
　　　　　　　Found: (*a*)　　　　　　　K, 19.06%; loss, 32.54%.
　　　　　　　Found: (*b*)　　　　　　　K, 21.95%; loss, 36.22%.

Phenols.

m-Cresol.—Calc. for $C_6H_6O.KOH$:　K, 23.82%; H_2O, 10.99%.
　　　　　　　Found: (*a*)　　　　　　　K, 23.00%; H_2O, 10.07%.
　　　　　　　Found: (*b*)　　　　　　　K, 27.33%; H_2O, 12.21%.
p-Cresol.—Found:　　　　　　　　　　K, 22.76%; loss, 17.05%.
β-Naphthol.—Calc. for $C_{10}H_8O.KOH$:　K, 19.53%.
　　　　　　　Found:　　　　　　　　　　K, 19.52%.
Eugenol.—Calc. for $C_{10}H_{12}O_2.KOH$:　K, 17.75%; H_2O,　8.37%.
　　　　　　　Found:　　　　　　　　　　K, 16.75%; loss,　9.62%.

Tribromophenol.—Calc. for $C_6H_2OBr_3.KOH$: K, 10.11%; H_2O, 4.67%.
Found: K, 10.82%; loss, 6.70%.

o-Nitrophenol.—Clusters and moss-like masses of light yellow and red needles. When heated the mixture became uniformly deep red.

Calc. for $C_6H_5O_3N.KOH$: K, 20.03%; H_2O, 9.23%.
Found: K, 19.92%; loss, 11.21%.
Found: (by titration) K, 20.15%.
Phloroglucinol.—Calc. for $(C_6H_6O_3)_2.KOH$: K, 12.68%.
Calc. for $C_6H_6O_3.KOH$: K, 21.46%.
Found: (*a*) K 14.05% K, 14.97%.
Pyrogallol.—Found: K, 15.12%.

Miscellaneous Percentages of Potassium.—Gàllic acid, 24.08. Stearic acid, 20.10. Itaconic acid, 22.39. Salicylic acid, 21.33. Cyanuric acid, 30.13. Vanilline, 28.81. Guaiacol, 14.60. Aniline, 47.19. Acetanilide, 23.58. Citral, 41.45. Phorone, 40.16. Glycerol, a liquid, 15.58. Phenol, a liquid, 7.72. Resorcinol, 20.03. Catechol, 19.85. Amyl ether, 45.76. Anisol, 34.20. Veratrol, 26.32. Bornyl valerate, 40.47. Amyl formate, 41.50. Acetal, 43.40. Acetyl bromide, 29.10. Iodoform, 22.18. Ureas, 14.04. Carbon bisulfide very slowly formed beautiful, hygroscopic, bichromiate-colored crystals of 34.81% K. Phenolphthalein formed a deep red mass. These and other additive compounds with other alkalies will be investigated.

A few oxygen-containing compounds, such as raffinose, saccharine, camphor, etc., failed to show any reaction with potash.

SEATTLE, WASH.

THE ROLE OF ATMOSPHERIC OXYGEN AND ALKALI IN THE OXIDATION OF ACETONE WITH POTASSIUM PERMANGANATE. PYRUVIC ACID AS AN INTERMEDIATE PRODUCT.

BY EDGAR J. WITZEMANN.

Since our knowledge of the nature of the chemical equilibria active in oxidations is quite limited it is highly desirable that more work be done to extend this knowledge. The following paper deals with the oxidation of acetone with potassium permanganate in the presence of varying amounts of alkali at room temperature. The purpose of these experiments was fourfold:

(1) To study the relative participation of atmospheric oxygen in the oxidation of acetone.

(2) To study the relative yields of acetic, oxalic and carbonic acids and to note, if possible, the reasons for the variations.