Third penta-acetate m. p., 98°; $[\alpha]_D$ = —42°	Second hexa-acetate m. p., 139–40°; $[\alpha]_D$ = —31	The beta forms of some other than the butylene ring type.
Fourth penta-acetate m. p., 87°; $[\alpha]_D$ = +61°	Not yet known	The alpha forms of this second ring type.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. VIII. THE ELECTROLYTIC REDUCTION OF CARBONYL DERIVATIVES[1,2]

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Theoretical Discussion

One of the outstanding, fundamental problems in organic chemistry is that of the laws dictating and governing the phenomena of "polymerization," and to the student of carbohydrate and polysaccharide chemistry the factors giving rise to the polymerization of anhydro-sugars and polysaccharides present a subject of absorbing interest.

A correct interpretation of these factors would be of considerable value, not only in enabling us to obtain a clearer insight into the changes occurring in plant growth but also in connection with the manufacture of cellulose and allied products, and their industrial application.

There would seem to be little or no doubt but that the polymerization of anhydro-sugars and polysaccharides is intimately related to the "residual valence" of the carbonyl (CO) group, so that a determination of the relative magnitude of this, in derivatives containing the carbonyl radical (either active or latent), might be expected to yield valuable data regarding the tendency of a particular substance to undergo polymerization.

Up to the present time, attempts made to define the reactivity of the carbonyl group have been concerned with reactions involving the use of a second complex component and under conditions where the energy changes involved are of considerable magnitude.

Thus Stewart[3] has shown that when hydrogen attached to a carbon atom adjacent to the carbonyl group of a ketone is replaced by methyl, there results a decrease in the additive capacity of the carbonyl group for sodium bisulfite. The conclusion drawn from his experiments was that the reactivity of the carbonyl group is not peculiar to itself

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[1] This paper is constructed from a dissertation presented by Roland R. Read in June, 1922, to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.

[2] Communicated to the Organic Division, American Chemical Society, Birmingham, Alabama, April 1922.

[3] Stewart, *J. Chem. Soc.*, **87**, 185 (1905).

but is a function both of the surrounding groups and of the structure of the entire molecule.

Stewart and Baly[4] investigated the relation of the absorption spectra of ketones to their chemical structure and reached a similar conclusion.

Petrenko-Kritschenko[5] used the reaction between carbonyl derivatives and hydroxylamine, phenylhydrazine, and metallic bisulfite as a measure of the reactivity of the carbonyl group, expressing the results in terms of the amounts present at equilibrium. Stewart[3,4] followed the rate of such reactions and obtained results similar to those previously determined.

The rate of reaction between diphenyl ketene and the carbonyl group was used as a means for determining the reactivity of the latter by Staudinger and Kon[6] and they found that the configuration of the carbonyl derivatives exerted an influence on this reaction. The method was not found applicable, however, to aliphatic aldehydes and ketones (the simplest carbonyl derivatives) as these brought about polymerization of the diphenyl ketene.

The heat liberated during the formation of a Schiff base has been utilized by Eibner[7] as a measure of the reactivity. By means of this reaction the aldehydes were divided into: (a) a more reactive group, namely, those more soluble in water, such as formaldehyde, acetaldehyde and propionaldehyde; and (b), a less reactive group, those less soluble in water, namely, *iso*butyraldehyde, *iso*valeraldehyde, heptaldehyde, benzaldehyde and salicylaldehyde.

Hibbert[8] determined the relative reactivities of a series of ketones from a comparison of the amounts of methane liberated in "partition experiments" between 3 moles each of the ketones and one mole of α-naphthol when allowed to react with one mole of methylmagnesium iodide.

The results described in this paper were obtained in an investigation on the comparative activities of the carbonyl group in aldehydes and ketones as indicated by their behavior on reduction by electrolytic methods. Under such treatment the molecule is subjected to a minimum of external influence so that "lowering of cathode potential" and "current efficiency" might be expected to indicate, in some measure at least, the "reactivity of the carbonyl group," in other words its "residual valence." This, in turn, is probably closely connected with "tendency towards polymerization."

Work of Previous Investigators on the Electrolytic Reduction of Carbonyl Derivatives

Aldehydes.—This field has been only slightly investigated. O'Brien Gunn[9] patented the reduction of glucose on a graphite cathode in dilute sulfuric acid, claiming a 98% yield of mannitol. Loeb[10] tried, without success, to carry out the same reduction using

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[4] Stewart and Baly, *J. Chem. Soc.*, **89**, 489 (1906).

[5] Petrenko-Kritschenko, *J. prakt. Chem.*, **61**, 431 (1900); **62**, 315 (1900); *Ber.*, **34**, 1699, 1702 (1901); *Ann.*, **341**, 150 (1905).

[6] Staudinger and Kon, *Ann.*, **384**, 38 (1911).

[7] Eibner, *Ann.*, **302**, 335 (1899).

[8] Hibbert, *J. Chem. Soc.*, **101**, 341 (1912).

[9] O'Brien Gunn, Ger. pat., 140,318, **1900**.

[10] Loeb, *Z. Elektrochem.*, **6**, 1 (1910).

a lead cathode and platinum anode, while Findlay and Williams,[11] using lead electrodes, also failed to carry out this reduction. These investigators reached the conclusion that the method employed by O'Brien Gunn did not yield mannitol.

Ellis and McElroy[12] patented the reduction of formic acid to methyl alcohol and formaldehyde, the latter not being reduced at low current density. According to Knudsen[13] the reduction of formaldehyde on a lead cathode, using a high current density, gives methyl alcohol.

The reduction of acetaldehyde in dil. sulfuric acid solution on a mercury cathode at very high current density is said to yield 2,3-butylene glycol, while in alkaline solution the claim is made for the formation of the 1,3 derivative, lead, nickel and platinized platinum cathodes being employed in the latter case.[14]

Pascal[15] patented the reduction of acetaldehyde to ethyl alcohol on lead cathodes, his use of platinum, iron oxide and carbon anodes indicating that high cathode potentials are not necessary for this reduction.

According to Law[16] crotonaldehyde is reduced on a lead cathode to butyl alcohol with a very high yield.

Schepss[17] investigated the reducing action of the cadmium cathode under conditions of high current density and elevated temperature and found that propionaldehyde gave propyl alcohol and propane, while heptaldehyde gave heptane almost exclusively.

Ketones.—The reduction of acetone[18] has been the subject of numerous investigations. It is reduced to pinacol, *iso*propyl alcohol and propane on lead and mercury cathodes, in acid or alkaline solution. With cadmium as cathode the main product is propane.

Methylethyl ketone[19] behaves in an analogous manner.

Iso-amylmethyl ketone[20] gives the corresponding hydrocarbon when reduced at a cadmium cathode.

Unfortunately, many of the results obtained on electrolytic reduction cannot be duplicated as essential data regarding the current density, temperature, etc., are lacking. For the same reason it is impossible to apply such data to other experimental work, especially where such are to be used in an effort to predict the course of a specific reaction under given experimental conditions.

"Lowering of Cathode Potential," "Current-Efficiency" and "Reactivity of the Carbonyl Group"

There are two factors which serve to indicate the "tendency towards reduction" of a carbonyl derivative, namely, (1) the lowering of the cathode potential, that is, the amount by which the cathode is rendered less negative with respect to the solution, and (2) the "current efficiency."

The "Lowering of Cathode Potential."—It is well-known that molecular hydrogen is not evolved from different metals at the same cathode

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[11] Findlay and Williams, *Chem. Age*, **4**, 396 (1921).

[12] Ellis and McElroy, U. S. pat. 867,575, **1907**.

[13] Knudsen, *Ber.*, **42**, 3994 (1909).

[14] Ger. pat. 277, 392, **1913.**

[15] Pascal, Brit. pat. 140,115, **1918**; 140,527, **1918.**

[16] Law, *J. Chem. Soc.*, **101,** 1016 (1912).

[17] Schepss, *Ber.*, **46,** 2564 (1913).

[18] Merck, Ger. pat. 113,719, **1899.** Tafel and Schmitz, *Z. Elecktrochem.*, **8,** 281 (1902). Elbs and Brand, *ibid.*, **8,** 783 (1902).

[19] Elbs and Brand, Ref. 18.

[20] Tafel, *Ber.*, **42,** 3146 (1909).

potential, and this phenomenon of "overvoltage" may be defined as the difference in potential between a cathode and a reversible hydrogen electrode in the same solution. The addition of a reducible substance, for example, a carbonyl derivative (aldehyde or ketone), to the cathode compartment, results in a change in the cathode potential, and the extent to which this is lowered may serve to indicate the "ease of reduction" of the free, or latent, carbonyl group.

"Current Efficiency."—Since the reduction of compounds reducible only with difficulty is always accompanied by the evolution of hydrogen, the efficiency of reduction can be readily followed by a comparison of the volume of hydrogen liberated from the cathode with that in a gas-coulometer operating in series. This is referred to later as the "Efficiency of Reduction."

In the presence of easily reducible substances the entire amount of hydrogen produced at the cathode may be absorbed. In such cases the relative ease of reduction of two compounds can often be determined by comparing the maximum current densities at which reduction occurs with 100% efficiency, all conditions being as nearly alike as possible.

The rate of reduction and the depolarizing action of any compound under given conditions are functions of the temperature and of the concentration of the depolarizer; the surface condition of the cathode is also a factor affecting its reducing activity.

It is a commonly accepted fact that as the potential of a cathode increases the reducing power of that electrode also increases.

The electrolyte to be used is dependent on the stability and solubility of the substance to be reduced. In general, aqueous solutions of acids or alkalies in various concentrations are employed. An approximately neutral electrolyte can be maintained by having present a weak acid, such as boric acid; or a substance capable of yielding a weak acid, such as ethyl acetate. Alcoholic solutions may also be employed.

The "Lowering of Cathode Potential" as a Measure of the Reactivity of the Carbonyl Group

Behavior of Aldehydes.—The results obtained may be summarized as follows.

Under the same experimental conditions, namely nature of electrolyte, temperature, etc., the lowering of cathode potential, using lead electrodes, is found in the case of aldehydes to vary markedly with (**a**) the saturated or unsaturated character; (**b**) the length of the chain; (**c**) the spatial relations of the atoms in the molecule; and (d) the character of the groups comprising the molecule.

(**a**) *Saturated and unsaturated aldehydes.*—While with *n*-butyraldehyde the maximum lowering of the cathode potential amounts to only 0.12 volt, with the analogous unsaturated crotonaldehyde this amounts to 0.58 volt. The high value of 0.58 volt for furfuraldehyde is also not without interest.

(b), (c) *Length of chain and spatial relations.*—The values obtained for acetaldehyde, propionaldehyde, *iso*butyraldehyde, and *n*-butyraldehyde, are 0.30, 0.30, 0.17 and 0.12, respectively. The method outlined using the present technique, is thus of no value in distinguishing between the residual valence of the carbonyl group in acetaldehyde and propionaldehyde. In the case of *iso*butyraldehyde and *n*-butyraldehyde, however, the strongly positive influence exerted by the hydrogen atoms in the critical 5,6 positions to the carbonyl group makes itself felt in a reduction of the cathode potential from that of 0.30 volt in the case of acetaldehyde, to 0.17 and 0.12 in the case of *iso*- and *n*-butyraldehyde, respectively. This behavior is in general agreement with that shown by such aldehydes with respect to their reactivity towards sodium bisulfite and other reagents.

(d) *Character of groups in molecule.*—The influence exerted by the substitution of hydrogen by hydroxyl is shown in the increase in value from 0.12 to 0.25 volt in the case of *n*-butyraldehyde and acetaldol, respectively.

Ketones.—The lowering of the cathode potential for dimethyl-, methylethyl- and methylpropyl ketone was found to be 0.06, 0.06 and 0.04 volt, respectively.

The very marked drop in value from 0.30 volt in the case of acetaldehyde to that of 0.06 with acetone is in accordance with the pronounced difference in chemical reactivity of the two products, and a consequence of the replacement of hydrogen by the positive methyl group resulting in a considerable decrease in the negative character of the carbonyl group.

The effect of introducing an hydroxyl group is seen in an increase in value to 0.15 volt found in the case of hydroxybutylmethyl ketone (diacetone alcohol).

"Current Efficiency" as a Measure of the Reactivity of the Carbonyl Group

The "current efficiency," found with the various carbonyl derivatives is shown by plotting the hydrogen absorbed against the total hydrogen as measured in a coulometer operating in series.

Aldehydes (Saturated).—The curves for the saturated aldehydes are shown in Fig. 1.

It will be observed that the "current efficiency" of acetaldehyde, propionaldehyde, *iso*butyraldehyde, and *n*-butyraldehyde follows the same order as that of the decrease in cathode potential. Similarly, the replacement of hydrogen by hydroxyl (*n*-butyraldehyde and acetaldol) is also marked by a pronounced increase in "current efficiency."

With the saturated, non-substituted, aliphatic aldehydes the sole product of reduction in each case was found to be the corresponding saturated alcohol. There was no trace of any "glycol formation." With acetaldol the only product obtained was 1,3-butylene glycol.

Aldehydes (Unsaturated).—Crotonaldehyde was the only unsaturated aldehyde investigated and this was found to behave in an unexpected manner.

It is well known that crotonaldehyde on reduction by chemical methods, for example, with aluminum amalgam, the zinc-copper couple, iron and acetic acid, etc., yields a mixture of products consisting of a small amount of *n*-butyraldehyde and considerable quantities of *n*-butyl alcohol, crotyl alcohol and dipropenyl glycol, the amounts varying with the nature of the reducing agent and the conditions employed. Thus Charon[21] obtained the following yields by reducing with the zinc-copper couple in acetic acid solution: *n*-butyraldehyde, 2–3%; *n*-butyl alcohol, 3%; crotyl alcohol, 23%; dipropenyl glycol, 50–60%.

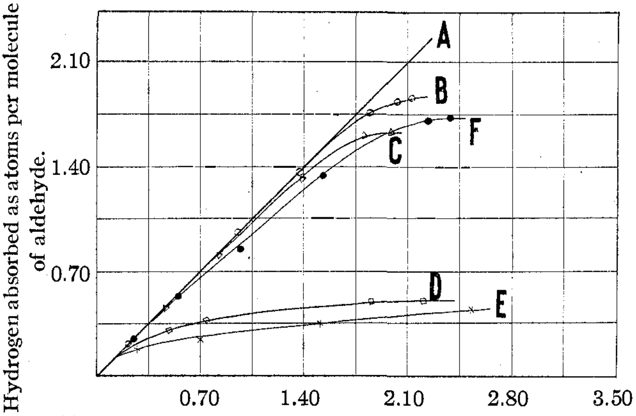

Fig. 1.—A, 100% efficiency; B, Acetaldehyde; C. Propionaldehyde; D, *iso*Butyraldehyde; E, Butyraldehyde; F, Acetaldol.

Considerable time and effort were spent in an endeavor to improve the yield of crotyl alcohol by various processes of chemical reduction, but without success.[22]

"Current Efficiency" of Crotonaldehyde.—Using lead electrodes and 2 *N* sulfuric acid as electrolyte, the two curves shown in Fig. 2 were obtained by plotting the total hydrogen against that absorbed as atoms of hydrogen per molecule of aldehyde. In Fig. 2 the "current efficiency" is plotted against the total hydrogen. It is evident that after the absorption of one atom of hydrogen per molecule of crotonaldehyde, no further

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[21] Charon, *Ann. chim. phys.*, [7] **17**, 197 (1899).

[22] It is intended to publish this work in a later paper.

reduction occurs, and that crotonaldehyde reduces much more readily than any of the saturated aldehydes investigated.

Nature of the Products Obtained on Reduction of Crotonaldehyde.—The products of electrolytic reduction, obtained under varying experimental conditions, were found to consist of (*a*) a very small amount of unchanged crotonaldehyde; (*b*) a small amount (b. p., 110–125°) of a mixture of crotyl and butyl alcohols; and (*c*) a large fraction boiling above 125°, which proved to be a new compound, dimethyl cyclopentene aldehyde (III), the constitution of which has been definitely established by direct synthesis.[23] Little or no dipropenyl glycol is formed in this reaction.

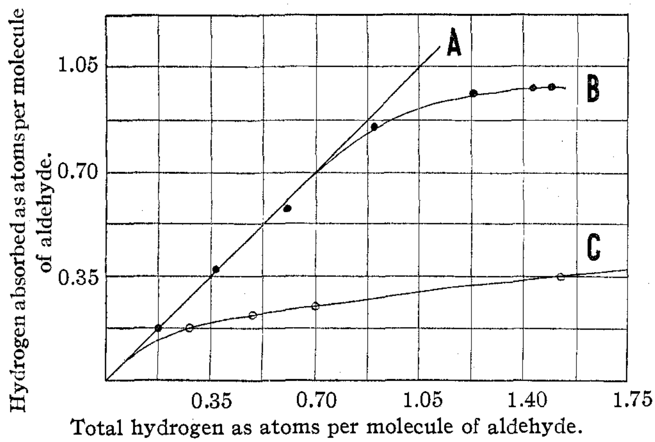

Fig. 2.—A, 100% efficiency; B, Crotonaldehyde; C, Butyraldehyde.

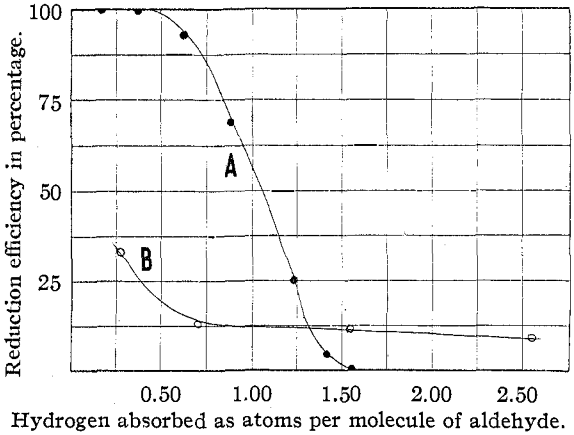

Fig. 3.—A, Crotonaldehyde; B, Butyraldehyde.

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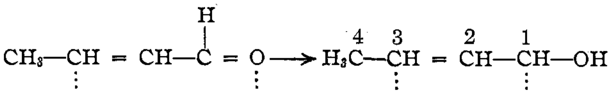
[23] To be reported in a later paper.

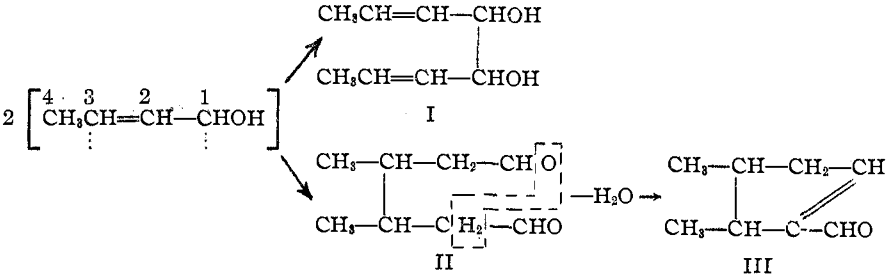
The change is thus analogous to the chemical reduction of mesityl oxide whereby a penta methylacetylcyclopentene is obtained.[24,25]

Mechanism of the Process.—It is not possible, as yet, to give any satisfactory explanation as to why dipropenyl glycol should be formed in the reduction of crotonaldehyde by chemical methods, and dimethyl cyclopentene aldehyde when an electrolytic process of reduction is employed. In both cases it would appear that the first stage of the reduction consists in the addition of one atom of hydrogen to the carbonyl group, whereby an unsaturated vinyl alcohol derivative is obtained.

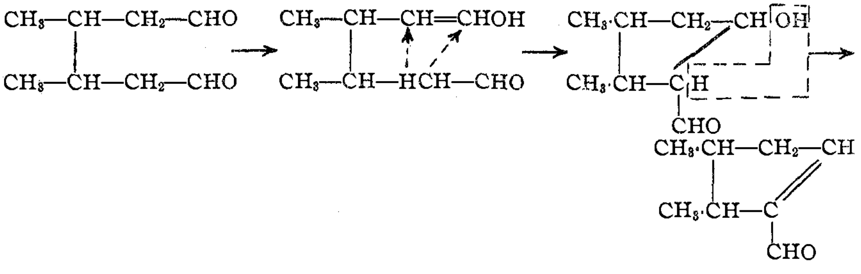


$$CH_3-CH=CH-\overset{H}{C}=O \longrightarrow H_3\overset{4}{C}-\overset{3}{C}H=\overset{2}{C}H-\overset{1}{C}H-OH$$

Union of two such molecules may occur at either C (1) or C (3), resulting in the first case (chemical reduction) in the formation of a molecule of dipropenyl glycol I; and in the second case (electrolytic reduction) in the formation of a dialdehyde II:



this 3,4-dimethyl hexane di-al then undergoing spontaneous dehydration to the dimethyl cyclopentene aldehyde III, the change possibly occurring through the medium of an "intramolecular aldol condensation" followed by a dehydration.



Other similar instances of dehydration and formation of cyclic pentene derivatives are (*a*) acetylcyclopentene from diacetylbutane;[26] (*b*) cyclo-

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[24] *Ann.*, **296**, 295 (1896).

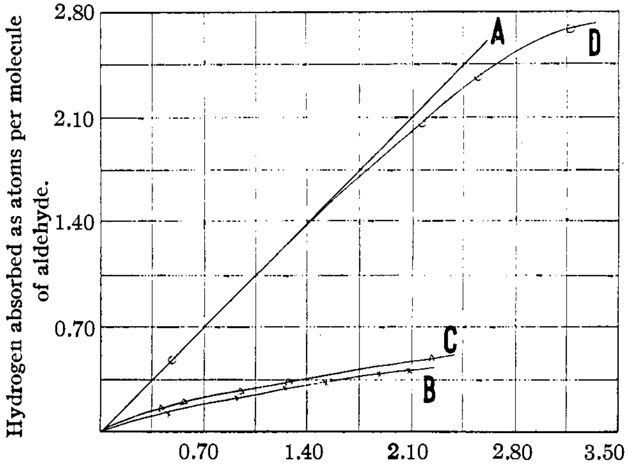
[25] Exception to this interpretation of the reduction of mesityl oxide is taken by Law, Ref. 16.

[26] Marshall and Perkin, Jr., *J. Chem. Soc.*, **57**, 204 (1890); **57**, 241 (1890).

pentene aldehyde from dihydroxysuberic acid;[27] and (*c*) pentamethylacetylcyclopentene from mesityl oxide.[24,28]

The electrolytic reduction of crotonaldehyde has been reported as giving a very good yield of *n*-butyl alcohol.[29] The conditions given were followed as closely as possible but the results claimed could not be duplicated. Calculations based on the ampere hours used indicated the improbability of obtaining results different from those found in the present investigation.

Ketones (saturated, unsaturated and substituted).—It is evident from Fig. 4 that the "current efficiency" of the ketones runs parallel to their values for the lowering of cathode potential and that both serve to indicate the much smaller reactivity of the carbonyl group in these compounds as compared with the corresponding aldehydes.



Total hydrogen as atoms per molecule of aldehyde.

Fig. 4.—A, 100% efficiency; B, Methylethyl ketone; C, Dimethyl ketone; D, Diacetone alcohol.

The introduction of an hydroxyl group (diacetone alcohol) increases the "current efficiency" in a marked manner.

Electrolytic Reduction of Glucose

The reduction of glucose produced results very similar to those reported by Findlay and Williams and by Loeb in that although the efficiency was high at the start it quickly fell to so low a value that the experiments were discontinued. Gunn's work could not be duplicated.

[27] Baeyer and von Liebig, *Ber.*, **31**, 2106 (1898).

[28] Further experiments are to be carried out by one of us (R.) on the electrolytic reduction of unsaturated aldehydes with a view to ascertaining how far the formation of cyclopentene derivatives may be considered to be a general reaction applicable not only to aldehydes but to other derivatives such as the esters of unsaturated acids.

[29] Law, Ref. 16; also p. 1546.

It is evident from the above discussion that a determination of the two factors, (*a*) lowering of cathode potential, and (*b*) current efficiency, in the case of carbonyl derivatives such as the carbohydrates, anhydro-sugars and polysaccharides is unlikely—at least with the present technique—to yield results capable of serving as a means of distinguishing between the residual valences of their (free or latent) carbonyl groups. Even in the case of the ketones the values lie much too near together.

It is possible that by refinements in the method for determining the "change in cathode potential" some sharper differentiation of the several classes might be possible, but the outlook does not seem very hopeful when viewed from the limitations imposed by the non-reproducibility of the cathode. As a means of correlating "residual valence of the carbonyl group" with "tendency towards polymerization" it will presumably be necessary to measure some other property more sensitive to changes in structure.

The phenomenon of endosmosis is likely to give rise to considerable trouble in all processes of electrolytic reduction, and it is only by careful study of conditions that this can be controlled.

Experimental Part

The Electrolytic Reduction Apparatus

The apparatus used for the reduction consisted of the reduction cell, a gas coulometer, a hydrogen collection system with gas-control mechanism and apparatus for measuring the cathode potential.

The Reduction Cell (Fig. 5).—When in operation the reduction cell was placed in a glass jar 13 cm. in diameter and 20 cm. in height, which served as anode chamber and contained the anode, the latter consisting of a platinum spiral or series of lead strips according to the cathode in use. The cathode chamber consisted of a porous clay cell P, 7.5 by 18 cm., closed with a wooden stopper W. Fitted through this were a glass stirrer S of the propeller type, with an oil seal, a glass coil H for temperature control, a gas outlet fitted with an open manometer, the capillary extension N of the mercurous sulfate electrode and the cathode itself C. The stopper had a rubber sleeve R and fitted snugly into the cell, a gas, tight seal being effected by means of a pitch-shellac cement. This seal could be broken readily when it became necessary to open the cell. Preference was given to an oil seal rather than to one of mercury after it was discovered that the latter occasionally found its way into the cell. The stirrer was driven by a small motor connected by means of a belt and pulley permitting a high motor and low, uniform, propeller speed of 200–300 r.p.m. The metal tank surrounding the anode chamber was well insulated with felt so that the bath regulating the temperature could be held at any desired point.

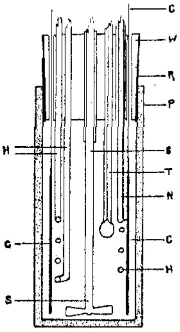


Fig. 5.

The Gas Coulometer.—This consisted of a large battery jar in which hung a bottomless bottle through the stopper of which a T-tube passed, permitting electrical connection with the carbon cathode which hung inside, as well as providing an exit for the hydrogen evolved. The anode (platinum foil) was suspended outside of the bottle in the electrolyte (dil. sulfuric acid). The coulometer was connected in series with the reduction cell.

Hydrogen Collection System and Gas Control Mechanism.—The hydrogen collection system consisted of two cylindrical galvanized iron tanks and a device permitting the outflow of water from them as the gas entered, thus maintaining atmospheric pressure in the reduction cell and collection tanks continuously and automatically. This insured the maintenance of the oil seal and prevented any pressure being exerted on the porous cell which would have resulted in considerable diffusion, since many of the experiments extended over considerable periods. The tanks were 13 cm. in diameter and 120 cm. in height, with a capacity of 14 liters, a glass water-gage backed by a scale making possible the determination of the gas volume in the tanks at any moment. The gas entered at the top and the water was withdrawn from the bottom.

The gas control mechanism (Fig. 6) regulating the outflow of water from the tank as the gas entered, consisted of a fine rubber diaphragm D, connected with the gas line L. This actuated a make and break K connected with an electromagnet E, which in turn controlled a needle valve U in the water outlet line. This apparatus was sensitive to pressure variations of less than 0.001 of an atmosphere. Since the make-and-break controlled a 110 volt d. c. circuit, considerable difficulty was experienced through arcking across the contacts, due to the inductance of the circuit. This was prevented by placing a condenser F of one microfarad capacity around the contacts and electromagnet.

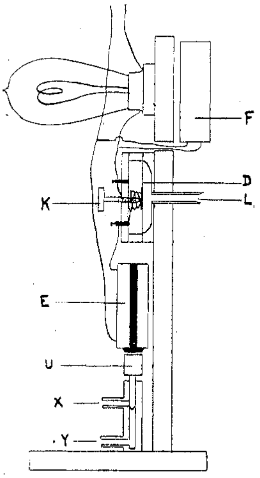


Fig. 6.

Apparatus for Measuring the Cathode Potential (Fig. 7).—The cathode C under observation was in contact with a glass capillary which widened rapidly to a tube of 0.5 cm. bore, closed at the upper end by a large ungreased stopcock. This tube was filled with *N* sulfuric acid and connected at the upper end with a mercurous sulfate electrode N. A slide-wire potentiometer M with a cadmium standard cell S, galvanometer G, and centivoltmeter V were used to determine the potential of this combination.

The voltage drop across the reduction cell was measured by a voltmeter V. The current through the reduction cell AC and coulometer B was measured by the ammeter I and controlled by a lamp-bank R.

The cathodes used were made of sheet metal and were 10.7 cm. by 17.5 cm., the metals being of high purity.

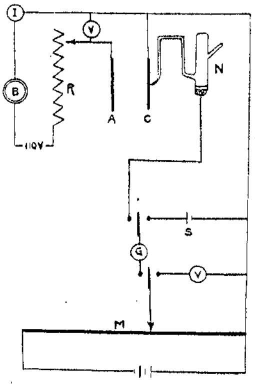


Fig. 7.

Procedure

As the various reductions were carried out in a similar manner a description of one typical run will suffice to illustrate the technique involved.

With the cathode in place, the top of the reduction cell was sealed to the porous cell and tested for leaks. The electrolyte was put into the cell and the latter transferred to the anode chamber. The connections for current, temperature control, coil and gas lines were made, the motor was attached, and the mercurous sulfate electrode connection established. When the potential of the cathode had become constant, the compound to be reduced was added, the gas vents were closed, and the gas collection system was put into operation. During the course of the reduction, readings were taken of the volumes of hydrogen from the reduction cell and coulometer, the temperature of the cathode solution, the voltage across the electrodes, and the cathode potential.[30] At the end of the reaction the contents of the cell were removed and the cell with inclosed apparatus was washed with a suitable solvent, the combined solutions being reserved for analysis.

Lowering of Cathode Potential by Various Carbonyl Compounds

The following data regarding the lowering of cathode potential by various carbonyl derivatives were obtained from a series of experiments carried out as just described. The values given below were those obtained immediately following the addition of the carbonyl compound and represent "maximum lowering."

TABLE I

THE LOWERING OF THE CATHODE POTENTIAL BY CARBONYL DERIVATIVES

The lowering of cathode potential with current density, 0.016 amp./cm.; temp., 12°; concn. of "depolarizer," 0.83 mole per liter; is shown in the fourth column.

Aldehyde	Formula	B. p. °C.	(Lead cathode) Volts	Catholyte
Acetaldehyde	CH_3CHO	21–26	0.30	2 *N* sulfuric acid
Propionaldehyde	CH_3CH_2CHO	48.5–51	.30	2 *N* sulfuric acid
iso-Butyraldehyde	$(CH_3)_2CHCHO$	62–64	.17	2 *N* sulfuric acid
			.24	2 *N* sulf. acid in 25% alco.
Butyraldehyde	$CH_3CH_2CH_2CHO$	72–76	.12	2 *N* sulfuric acid
			.15	2 *N* sulf. acid in 25% alco.
			.19	2 *N* sulf. acid in 70% alco.
Heptaldehyde	$CH_3(CH_2)_5CHO$	148–156	.22	2 *N* sulf. acid in 70% alco.
Acetaldol	$CH_3CHOHCH_2CHO$	78–85 (12 mm.)	.25	2 *N* sulfuric acid
Furfuraldehyde	C_4H_3OCHO	161–162	.58	2 *N* sulfuric acid
Crotonaldehyde	$CH_3CH = CHCHO$	102–104	.58	2 *N* sulfuric acid
Ketone				
Dimethyl ketone	CH_3COCH_3	56–57	.06	2 *N* sulfuric acid
Methylethyl ketone	$CH_3COC_2H_5$	78–81	.06	2 *N* sulfuric acid
Methylpropyl ketone	$CH_3COC_3H_7$	101–103	.04	2 *N* sulf. acid in 50% alco.
Diacetone alcohol	$(CH_3)_2COHCH_2COCH_3$	70–75 (25 mm.)	.15	2 *N* sulf. acid in 50% alco.

"Current Efficiency" of Various Carbonyl Derivatives

In addition to the determinations of lowering of cathode potential, measurements of the "current efficiency" were carried out in these, as well as in additional experiments.

Since the aliphatic ketones and aldehydes are not readily reduced (exceptions being those containing a negative group) it was found that

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[30] It was frequently found that at the conclusion of the experiment the cathode potential did not return to its initial value, and it was not always possible to account for this.

only cathodes of high over voltage could be effectively employed. For this reason the major part of the experimental work was carried out using lead cathodes.

It was necessary to provide a cathode that would be reproducible, as far as possible, pure lead being employed for this purpose.[31] The electrode cut from this sheet metal was placed in position in the reduction cell, repeatedly oxidized and reduced in 10% sulfuric acid. By this means the cathode potential was readily reproducible within the limits of ±0.02 volt (usually less). The potential of the cell, lead cathode $|$ 2 N H_2SO_4 $|$ N H_2SO_4 $|$ Hg_2SO_4Hg, was 1.99, volts the cathode potential being 1.03 volts and the overvoltage 1.31 volts.[32] In alcoholic sulfuric acid of the same concentration the cathode voltage was practically the same as in aqueous sulfuric acid.

The essential data concerning the conditions of reduction have been given in the discussion dealing with "lowering of cathode potential" so that only a consideration of the current efficiency of various carbonyl compounds is necessary.

Acetaldehyde.—This aldehyde reduced with maximum current efficiency up to a point that corresponded to an absorption of approximately two atoms of hydrogen per molecule. The efficiency then fell off rapidly to zero (Fig. 1).[33]

Propionaldehyde.—Reduction took place with very high efficiency until over half of the aldehyde was reduced, after which it fell off, slowly at first, then more rapidly until no more absorption took place, this occurring when over 80% of the hydrogen theoretically necessary to produce the alcohol had been absorbed (Fig. 1). Due to the high vapor pressure of the aldehyde in aqueous solutions, some of it is carried off by the hydrogen during the early stage of the reduction, thus accounting for the low value of the total hydrogen absorption. A determination of the propyl alcohol formed during reduction showed this view to be correct.

***iso*Butyraldehyde.**—*iso*Butyraldehyde was reduced in both aqueous and alcoholic solution. In the former, reduction started with moderate efficiency but rapidly decreased until, after 25% of the hydrogen necessary to produce alcohol had been absorbed, no further action occurred (Fig. 1). Due to the low initial current efficiency and consequent evolution of hydrogen it seems probable that the low total absorption was due to loss of aldehyde by volatilization, and that this was the case was shown by analysis of the reduction product and the presence of aldehyde in the hydrogen evolved. In 25% alcoholic solution the efficiency was higher for two reasons, (a) alcohol as a solvent increased the current efficiency in a manner parallel to its effect on the "lowering of cathode potential" and (b) the lower volatility of the aldehyde from this solvent prevented loss of aldehyde. Hydrogen absorption in the case of the alcoholic solution ceased when somewhat less than the theoretical amount required for the formation of the corresponding alcohol had been absorbed.

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[31] This was obtained through the kindness of the United Lead Co.

[32] With an acid concentration other than 2 N as electrolyte this value would be somewhat different.

[33] It should be noted that in the diagrams shown a 100% efficiency corresponds to a straight 45° line (A). Any "falling away" from this denotes a decrease in "current efficiency."

n-**Butyraldehyde.**—In aqueous solution the initial current efficiency was somewhat lower than that of *iso*butyraldehyde and fell off in an analogous manner (Fig. 1). It was found that alcohol was produced in quantity equivalent to the hydrogen utilized. In 25% alcoholic solution the initial efficiency was higher but decreased slowly; in 70%, a higher efficiency was maintained throughout. Due to the impossibility of separating small amounts of butyl alcohol from the large amount of solvent (ethyl alcohol) a complete analysis was not possible.

Heptaldehyde.—In order to bring this aldehyde into solution 70% alcohol was necessary. The current efficiency was high, being very close to that of butyraldehyde in the same solvent. The reduction was not carried to completion, as indicated by the cessation of hydrogen absorption, but it was found that after 70% of the hydrogen necessary to produce the alcohol had been utilized the efficiency was still 30%.[34]

Acetaldol.—Acetaldol was reduced with almost maximum efficiency at the beginning of the experiment, the efficiency then fell off slowly until complete reduction was attained, when approximately two atoms of hydrogen per molecule had been absorbed (Fig. 1). For purposes of comparison the efficiency curve for aldol is shown on the same graph with that for the simple aldehydes.

Crotonaldehyde.—Due to the interesting character of the products formed in the electrolytic reduction of crotonaldehyde numerous experiments were carried out under a wide range of conditions. In 2 *N* sulfuric acid, reduction was effected on platinum, copper, iron, zinc, lead (Figs. 2, 3)[35] and amalgamated lead; in *N* sulfuric acid, on platinum, zinc, copper and lead; in 20% acetic acid, on platinum, copper, zinc and lead; in 25% alcoholic 2 *N* sulfuric acid, on lead, platinum and amalgamated lead. The current density was varied between the limits 0.0055 and 0.016 amp./sq. cm., and in addition in the case of lead, between 0.0055 and 0.11 amp./sq. cm. With lead in 25% alcoholic 2 *N* sulfuric acid the temperature was also varied between 10° and 50°. The resulting absorption of hydrogen corresponded in each case to approximately one atom per molecule of crotonaldehyde.

Furfuraldehyde.—This absorbed between one and two atoms of hydrogen per molecule, the reduction commencing with high efficiency, which then fell off slowly.

Ketones

Dimethyl Ketone.—The current efficiency with this ketone (Fig. 4) under the conditions outlined previously, was low initially but did not fall off rapidly, as in the case of isobutyraldehyde and butyraldehyde. This may have been due in large measure to the lower volatility of this ketone as compared with the aldehydes.[36] The reduction was not carried out to completion due to the length of time required.

Methylethyl Ketone.—This ketone behaved very similarly to dimethyl ketone, but reduced with slightly lower efficiency (Fig. 4).

Methylpropyl Ketone.—This reduction was carried out in 50% alcohol due to insolubility in the usual electrolyte. The addition of alcohol increased the current-efficiency as was also found to be the case with dimethyl ketone, the latter reducing with slightly greater efficiency under the same conditions.

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[34] Further work on this reduction is to be undertaken by the authors.

[35] Figs. 2 and 3 show the relationship between crotonaldehyde and *n*-butyraldehyde when reduced on a lead electrode in 2 *N* sulfuric acid solution. In Fig. 2 total hydrogen is plotted against absorbed hydrogen, while in Fig. 3 "efficiency of reduction" is plotted against total hydrogen.

[36] It is possible this lower volatility is to be associated with a greater hydration of the CO group.

Diacetone Alcohol.—This hydroxy ketone reduced with almost maximum efficiency until approximately three atoms of hydrogen per molecule had been absorbed, and the efficiency then fell off rapidly to zero[37] (Fig. 4).

Products of Reduction[38]

Acetaldehyde.—15.3 g. was reduced with a hydrogen absorption equivalent to the formation of 14.4 g. of ethyl alcohol. The reduction product was neutralized and distilled, and the distillate found to contain 13.9 g. of ethyl alcohol. The liquid left from the distillation was evaporated on the water-bath under reduced pressure and the solid product remaining was extracted with alcohol. The latter left no residue on evaporation, indicating the absence of any glycol.[39]

Propionaldehyde.—20.1 g. of this aldehyde was reduced with a hydrogen absorption corresponding to 17.0 g. of *n*-propyl alcohol. The product was neutralized, distilled, the alcohol salted out with potassium carbonate and recovered by ether extraction; yield, 15.5 g. of *n*-propyl alcohol.

***iso*Butyraldehyde.**—25.0 g. of this aldehyde was reduced with a hydrogen absorption corresponding to 6.5 g. of alcohol; yield, 5.8 g. of *iso*butyl alcohol.

Butyraldehyde.—25 g. of this aldehyde was reduced with a hydrogen absorption corresponding to the production of 6.8 g. of alcohol. Yield, 7.0 g. of *n*-butyl alcohol.

Acetaldol.—8.7 g. of aldol was reduced with a hydrogen absorption corresponding to 7.7 g. of glycol. Only 4.5 g. of the glycol was recovered, the relatively great loss being due, presumably, to insolubility of the glycol in ether.[34]

Crotonaldehyde.—This aldehyde was reduced under a wide range of conditions. The products discussed below were obtained by reduction on lead in 2 *N* sulfuric acid as well as on zinc in 25% acetic acid. The electrodes at the conclusion of these experiments had a somewhat oily appearance but were never discolored, although small amounts of a clear oil were found floating on the surface of the electrolyte. The solution, after neutralization, was ether-extracted and the extract dried over sodium sulfate. Fractionation of this yielded (A) a small amount of material boiling below 110°, possessing the penetrating odor of crotonaldehyde; (B) a fraction boiling at 110–125° containing a mixture of butyl alcohol and an unsaturated alcohol, presumably crotyl alcohol; (C) a large fraction boiling above 125°, which on direct distillation did not yield any product of definite boiling point. Usually small amounts of water were formed during this last distillation.

In view of the difficulty encountered in the isolation of pure products from Fraction C, resort was had to steam distillation of the neutralized electrolyte. This gave an aqueous distillate, together with a light oil, a small amount of viscous material remaining in the bottom of the flask. The oil was ether extracted, dried over sodium sulfate and fractionated, giving a product boiling at 170–175°. The latter had a strong but not unpleasant aromatic odor. It reduced potassium permanganate and ammoniacal silver solutions, decolorized a chloroform solution of bromine, but did not form an *insoluble* addition product with sodium bisulfite, in this last respect resembling other unsaturated aldehydes.

Mol. wt. Subs., 0.3323; benzene, 19.02 g.; f.-p. lowering, 0.689°. Calc. for $C_8H_{12}O$: mol. wt., 124. Found: 127.

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[37] The nature of the products is to be reported on in a separate communication by one of us (R).

[38] Unless otherwise noted the following reductions were carried out in 2 *N* sulfuric acid on a lead cathode.

[39] No glycol was obtained in any of the reductions of the saturated, unsubstituted aldehydes.

Analysis. Subs., 0.2102: CO_2, 0.5772; H_2O, 0.1816. Calc. for the saturated dialdehyde $C_8H_{14}O_2$: C, 67.5; H, 9.9; calc. for 2:3 dimethyl cyclopentene aldehyde $C_8H_{12}O$: C, 77.4; H, 9.7. Found: C, 75.0; H, 9.6.

The semicarbazone did not crystallize well from alcohol but separated from benzene as fine white needles; m. p., 185–187° (corr.).

Analyses. Subs., 0.1540: N, 31.3 cc. (over 30% KOH; 20°, 770 mm.). Calc. for $C_9H_{15}N_3O$: N, 23.2. Found: 23.6.

Subs., 0.1475: CO_2, 0.3225; H_2O, 0.1123. Calc. for $C_9H_{15}N_3O$: C, 59.7; H, 8.3. Found: C, 59.7; H, 8.5.

Furfuraldehyde.—This was reduced on a lead cathode in 70% alcoholic sulfuric acid. A yellow, gummy, deposit formed on the cathode which was not entirely soluble in alcohol or ether, and had a pleasant, peach-like odor. The cathode solution together with the alcoholic washings of the cathode were allowed to stand for 12 hours during which the solution darkened and a resinous mass separated. This was not further investigated.

Ketones

No attempt was made to isolate the reduction products of the ketones. After reduction, the electrolyte possessed, in general, a pungent odor and contained some insoluble oil. It was coated with a red, oily material (except in the case of diacetone alcohol) probably due to the formation of organic lead compounds as noted by previous investigators.[40] The product resulting from the reduction of diacetone alcohol was remarkable for its powerful but not unpleasant odor. In this case the cathode had a slightly oily appearance at the end of the experiment but was not discolored. The ease with which the reduction of this compound can be accomplished on a lead cathode and the absence of reaction with the metal of the cathode make it an interesting product for further investigation.

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Summary

1. The electrolytic reduction of a number of aliphatic aldehydes (saturated, unsaturated, and substituted) is described, and an account given of the technique employed.

2. The "lowering of cathode potential" and "current efficiency" are found to run parallel.

3. Both of these factors are found to vary with (a) the nature of the aldehyde (saturated or unsaturated); (b) the length of the chain; (c) the spatial relations of the atoms in the molecule; (d) the nature of the groups comprising the molecule.

In general, the results found run parallel to those obtained on the reactivity of the carbonyl group as determined by the reaction velocity in such reactions as bisulfite, semicarbazide and hydrazone formation.

4. Unfortunately the values found for the "lowering of cathode poten-

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[40] Tafel, *Ber.*, **39**, 3626 (1906); Ref. 20; **44**, 323 (1911). Renger, *Ber.*, **44**, 337 (1911).

tial" and "current efficiency," in the case of closely related aldehydes and ketones, lie too close together to permit of the method of electrolytic reduction being used to distinguish between the small differences represented by their "residual valences." Further refinements in the measurement of both factors appear of little use in view of the limitations imposed by the non-reproducibility of the cathode.

5. It is thus improbable that such values are likely to be of much assistance in determining the "relative, residual valence" of carbohydrates, anhydro-sugars and polysaccharides. The relationship of this factor to "tendency towards polymerization" will thus have to be decided by the measurement of other properties more sensitive to slight changes in structure.

6. Crotonaldehyde on reduction gives as principal product, a new derivative, dimethylcyclopentene aldehyde.

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[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF WASHINGTON]

THE LABORATORY PREPARATION OF DIETHYL SULFATE

BY E. V. LYNN AND H. A. SHOEMAKER

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After a careful experimental check of the methods which have been proposed, we have arrived at the conclusion that no satisfactory one has yet been presented for the preparation of diethyl sulfate. Since this substance has recently achieved prominence as an ethylating agent[1] of considerable value, a convenient method of manufacture on a laboratory scale would undoubtedly be of great service to many of those pursuing research work with organic substances. Of the several general processes given in the literature,[2] we may reasonably reject most as unsuitable to laboratory practice, unless other methods should not prove efficient.

[1] Cade, *Chem. Met. Eng.*, **29**, 319 (1923).

[2] Wetherill, *Ann.*, **66**, 117 (1848). Baumstark, *ibid.*, **140**, 78 (1866). Claesson, *J. prakt. Chem.*, [2] **19**, 255 (1879). Mazurowska, *ibid.*, [2] **13**, 158 (1876). Orlowsky, *Ber.*, **8**, 332 (1875). Stempnewsky, *ibid.*, **11**, 514 (1878). Claesson and Lundvall, *ibid.*, **13**, 1699 (1880). Villiers, *Compt. rend.*, **90**, 1291 (1880). Damiens, *ibid.*, **175**, 585 (1923). Curme, G. O. and H. R., *Chem. Met. Eng.*, **25**, 957 (1922). Lilienfeld, U. S. pat. 1,074,633 [*C. A.*, **7**, 4046 (1913)]; Ger. pat. 272,339 [*C. A.*, **8**, 3100 (1914)]; Brit. pat. 143,260 [*C. A.*, **14**, 2802 (1920)]; U. S. pat. 1,427,215 [*C. A.*, **16**, 3665 (1922)]. Merck, Ger. pat. 133,542 (1902). Leproux, Fr. pat. 421, 628 [*C. A.*, **6**, 1981 (1912)]. Wolf, U. S. pat. 1,101,373 [*C. A.*, **8**, 2922 (1914)]; Aus. pat. 8,495, 9,624 [*C. A.*, **9**, 513 (1915)]. Curme, U. S. pat. 1,339,947 [*C. A.* **14**, 2001 (1920)]. Kuh, Brit. pat. 149,688 [*C. A.*, **15**, 374 (1921)]; U. S. pat. 1,411,215 [*C. A.*, **16**, 1781 (1922)]. Sidgwick and Plant, Brit. pat. 157,578 [*C. A.*, **15**, 1905 (1921)]. Bader, Brit. pat. 175,077 [*C. A.*, **16**, 2149 (1922)]. Engelhardt, Lommel and Ossenbeck, U. S. pat. 1,458,646 [*C. A.*, **17**, 2587 (1923)]. Dreyfus, Brit. pat. 177,189 [*C. A.*, **16**, 3094 (1922)].