When the reaction was complete, the white crystalline solid, diethylamine hydrobromide, was filtered off, dried and weighed. The yield was practically theoretical.

The liquid product (filtrate) was distilled with a column. After the diethylamine was distilled off the product passed over at 90–100° (21 mm.). A considerable dark-colored residue remained in the flask. On redistillation the liquid boiled at 76–82° (5–6 mm.); n_D^{24}, 1.4385. There was again a dark-colored residue.

This redistilled product was shaken with dilute hydrochloric acid and the mixture, after being allowed to stand for an hour, was extracted with ether. The ether extract when dried and distilled yielded a liquid boiling at 155° which formed a phenylhydrazone melting at 117–117.5°. A mixed melting point with the phenylhydrazone of ethyl pyruvate gave no depression.

The aqueous layer was made alkaline and extracted with ether. The dried ether extract was found on distillation to contain a liquid boiling at 63–65° (4 mm.) which formed a methyl iodide derivative melting at 80–81°. By the method of mixed melting points this compound was identified as the methyl iodide derivative of ethyl β-diethylaminopropionate.

Summary

When diethyl α,α'-dibromo-adipate is treated with an excess of diethylamine the products are ethyl pyruvate and ethyl β-diethylaminopropionate.

It has been shown that ethyl α-diethylamino-acrylate is probably an intermediate in the formation of the pyruvic ester.

A mechanism involving the intermediate formation of a cyclobutane ring is suggested to explain these results.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE CATALYTIC OXIDATION WITH AIR OF ETHYL, ISOPROPYL AND *n*-BUTYL ALCOHOLS

BY ROBERT M. SIMINGTON[1] AND HOMER ADKINS

RECEIVED FEBRUARY 4, 1928 PUBLISHED MAY 5, 1928

In seeking information as to the role played by the catalyst in the oxidation of alcohols by air an extended experimental study has been made as to the relative amounts of reaction products obtained by the oxidation of ethyl, *iso*propyl and *n*-butyl alcohols over some 30 catalysts. The products of oxidation are carbon dioxide, carbon monoxide, saturated and unsaturated hydrocarbons, hydrogen, an aldehyde or ketone and an acid and its ester. The relative amounts of these products are determined by the nature of the alcohol, the alcohol–air ratio, and the chemical and physical properties of the catalyst.[2]

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[1] The authors are indebted to the E. I. DuPont de Nemours Co. for the support of a fellowship enjoyed by Dr. Simington during the academic year 1926–27.

[2] Orloff, *J. Russ. Phys.-Chem. Soc.*, **40**, 203 (1908), *C. A.*, **2**, 3346 (1908); also a footnote by Gibbs on p. 93 of Sabatier-Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, 1922.

The apparatus used is shown in the figure. Air from a compressed air line was passed through the alcohol, which had been dried by refluxing three times over lime. The outlet tube from the flask containing the alcohol was electrically heated to prevent the condensation of alcohol. The alcohol–air mixture was passed over the catalyst supported in the quartz tube C by means of a quartz rod. The catalyst tube was half a meter in length and had an internal diameter of seven millimeters. The catalyst was heated to the desired temperature by an electric furnace eleven centimeters in length, the temperature of which was controlled by means of a potentiometer temperature controller. In most cases the heat of reaction was sufficient to keep the catalyst at a red heat after the reaction had begun.

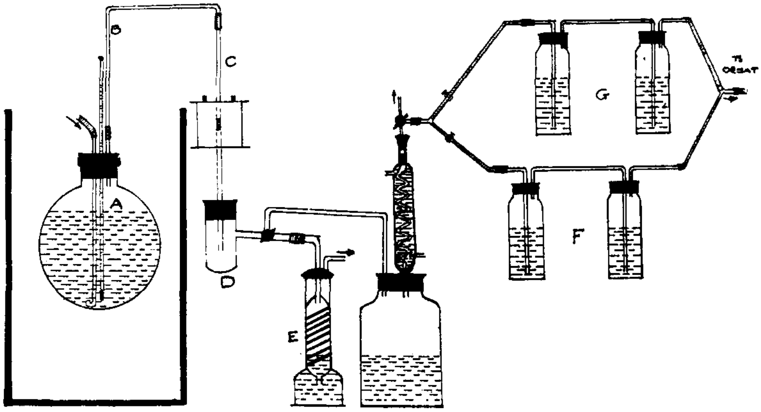

Fig. 1.

The gases from the reaction tube were passed through the tube D, which was heated by means of an electric hot-plate to prevent any liquid from condensing out of the gas stream. By means of a three-way stopcock attached to the tube D, the gas stream could be led either through the special wash bottles E, for aldehyde or ketone and acid determinations, or into the gas analysis apparatus, after passing through the cooling system and two wash bottles containing concentrated sulfuric acid or sodium bisulfite.

The acid was determined by allowing the gas to flow for eight minutes through the wash bottle E containing about two hundred cubic centimeters of water. The total sample was titrated with standard base and the amount of acid calculated.

Immediately after the acid determination another wash bottle containing exactly two hundred cubic centimeters of a 3% solution of sodium bisulfite was attached and the gases passed through for two minutes. The concentration of the bisulfite solution was determined by adding to an aliquot an excess of iodine and back-titrating with standard sodium thiosulfate. After the aldehyde was collected, a 10cc. aliquot of the bisulfite solution was titrated in a similar manner. The difference between the two titrations is a measure of the aldehyde or ketone present, since one molecule of sodium bisulfite combines with one molecule of aldehyde or ketone. In the ketone determination an excess of sodium bisulfite amounting to three or four times that needed was added and both the blank and run were permitted to stand for thirty hours as recommended by Jolles.[3]

A 100-cc. sample of gas was drawn during an interval of two to three minutes in order to obtain a uniform sample. The gases from the catalyst were washed through concentrated sulfuric acid G before all analyses except those for alkenes. Since concentrated sulfuric acid combines with or polymerizes alkenes, the gases were washed through sodium bisulfite F to remove the aldehyde or ketone for these determinations. Since the sodium bisulfite evolved sulfur dioxide, these samples could not be used for carbon dioxide determinations. The carbon dioxide was absorbed in potassium hydroxide, the unsaturated hydrocarbons in bromine water, the oxygen by phosphorus and the carbon monoxide by an acid solution of cuprous chloride. The hydrogen was estimated by contraction during combustion and the saturated hydrocarbon by absorption of carbon dioxide after combustion.

The amount of alcohol passed over the catalyst per hour was determined by weighing the flask A before and after the run. The rate of air flow was shown by a calibrated flowmeter and the pressure by a mercury manometer.

Copper and silver were used as the basic metals. Various forms of catalysts such as gauze, pellets, strips and wire were tried but no noticeable variations were found. The following were the chief catalysts used:

(1) Copper gauze; (2) copper wire; (3) brass plated on copper gauze; (4) 10% copper, 90% silver; (5) 50% copper, 50% silver; (6) 90% copper, 10% zinc; (7) 80% copper, 20% zinc; (8) 50% copper, 50% zinc; (9) 97.5% copper, 2.5% bismuth; (10) 90% copper, 10% cadmium; (11) 99% copper, 1% palladium; (12) 99% copper, 1% gold; (13) 99% copper, 1% platinum; (14) 99% copper, 1% nickel; (15) 50% copper, 50% nickel; (16) 50% copper, 50% manganese; (17) 90% copper, 10% silicon; (18) silver gauze; (19) silver pellets from Merck's precipitated silver and also from the reduction of ammoniacal silver nitrate with formaldehyde; (20) 99% silver, 1% gold; (21) 99% silver, 1% zinc; (22) 99% silver, 1% bismuth; (23) 99% silver, 1% palladium; (24) platinum gauze; (25) nickel gauze; (26) 50% copper oxide, 50% molybdenum oxide; (27) 50% copper oxide, 50% uranium oxide; (28) 50% copper oxide, 50% iron oxide; (29) 50% copper oxide, 50% vanadium oxide; (30) 50% copper oxide, 50% tungsten oxide.

The alloys were made by melting the two constituents together in a porcelain or graphite crucible for fifteen to thirty minutes, pouring into water and cutting into the desired size. The oxide mixtures were prepared by grinding the various oxides with copper oxide in a mortar and molding into pellets. Brass, copper and silver were

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[3] Jolles, *Ber.*, **39**, 1306 (1906).

plated on nickel and copper gauzes but gave unsatisfactory results because the high temperature caused the plated metal to diffuse quite rapidly into the base. The amount of catalyst used varied from two to six grams, depending upon its volume.

Space is not available to publish more than a small fraction of the data available, so that only a summary of the more significant experiments is given in the tables. The air flow in the experiments whose results are reported below was 83 (0°, 760 mm.) liters per hour, this flow being chosen because it gave the most satisfactory results in the preliminary runs. The figures of the gas analyses in Tables I and II are those taken after the analysis showed that a constant value had been reached. This was usually three or four hours after the oxidation was started. The figures in Col. C_1 represent the contraction due to the combustiom of the mixtures of hydrogen and hydrocarbons. It is thought advisable to report the contraction instead of assuming a certain hydrocarbon to be present. The figures under C_2 represent the contraction in volume which took place on absorption of carbon dioxide formed in the combustion. Table I shows the best yields of aldehyde or ketone obtained. The data from runs in which the 0.8 mole of alcohol per hour was passed over various catalysts have been collected in Table II. The figures under "A" represent the amount of alcohol in moles passed over the catalyst per hour. The figures under "B" represent the number of moles of alcohols converted to the

TABLE I

THE MAXIMUM YIELD OF ALDEHYDES AND KETONES

Catalyst	A	B	C	CO_2	C=C	O_2	CO	C_1	C_2	%
				Ethyl Alcohol						
Cu 90%, Ag 10%	1.31	0.98	0.016	3.7	..	1.9	0	2.3	1.2	76.0
				*Iso*propyl Alcohol						
Silver pellets	0.755	0.572	0.006	6.0	0.8	3.0	1.1	3.1	1.8	76.1
				n-Butyl Alcohol						
Copper 80%, Zinc 20%	0.811	0.586	0.015	5.6	1.2	3.6	1.4	2.8	1.8	72.5
Silver pellets	0.60	0.43	0.012	7.5	..	3.8	0.0	4.8	3.0	72.0

TABLE II

OXIDATION OF ALCOHOLS OVER VARIOUS CATALYSTS

Alcohol[a]	A	B	C	CO_2	C=C	O_2	CO	C_1	C_2	%
				Copper Gauze						
Ethyl	0.80	0.298	0.014	6.8	0.2	0.8	3.8	5.0	3.0	37.4
*Iso*propyl	.82	.404	.007	5.2	0.0	7.0	1.0	1.6	1.4	49.0
	.83	.416	.023	5.8	0.9	2.7	3.0	5.6	3.8	50.2
Butyl	.84	.482	.012	4.6	2.4	5.0	2.8	4.6	2.5	57.4
				Silver Gauze						
Ethyl	.82	.356	.017	6.2	0.0	3.0	2.8	3.5	2.0	43.7
*Iso*propyl	.79	.512	.006	6.2	0.6	4.6	1.4	0.8	0.4	64.6
Butyl	.80	.544	.015	4.0	2.4	5.4	2.6	3.3	1.0	68.3

TABLE II (*Concluded*)

Alcohol[a]	A	B	C	CO_2	C=C	O_2	CO	C_1	C_2	%
Copper 90%, Zinc 10%										
Ethyl	.79	.395	.016	8.3	0.2	1.2	2.0	9.2	3.1	51.6
*Iso*propyl	.80	.494	.008	7.7	0.6	1.2	1.8	5.3	1.8	61.5
Butyl	.831	.575	.015	5.8	1.8	2.4	2.0	3.4	2.4	69.1
Copper 80%, Zinc 20%										
Ethyl	.80	.248	.016	7.8	0.4	5.0	2.2	13.8	1.3	31.0
*Iso*propyl	.78	.532	.010	7.4	0.6	1.9	1.8	6.5	1.3	67.8
Butyl	.81	.586	.015	5.6	1.2	3.6	1.4	2.8	1.8	72.5
Copper 50%, Zinc 50%										
Ethyl	.80	.253	.020	8.3	0.8	3.8	3.5	26.8	2.4	33.0
*Iso*propyl	.80	.347	.029	6.4	2.2	2.2	3.4	14.0	2.0	43.5
Butyl	.77	.494	.010	6.2	1.5	5.0	1.4	12.0	1.5	63.9
Copper 97.5%, Bismuth 2.5%										
Ethyl	.82	.419	.012	8.0	0.2	1.0	2.5	4.0	1.8	51.0
*Iso*propyl	.77	.395	.007	7.1	0.2	2.4	2.0	2.0	1.4	51.5
Butyl	.80	.507	.006	5.0	5.4	1.2	4.4	10.1	6.3	63.6
Manganese 50%, Copper 50%										
Ethyl	.80	.286	.016	7.7	1.5	1.5	4.0	8.8	2.0	33.6
*Iso*propyl	.83	.195	.007	8.2	0.8	3.2	2.4	4.4	0.4	23.6
Butyl	.83	.371	.007	6.2	4.0	2.4	3.2	8.8	4.0	44.8
Copper Oxide 50%, Vanadium Pentoxide 50%										
Ethyl	.81	.240	.002	1.0	0.6	15.0	2.0	0.8	0.7	29.9
*Iso*propyl	.80	.082	.002	0.8	11.4	16.6	0.0	0.2	0.0	10.4
Butyl	.80	.223	.004	1.8	2.0	13.8	0.0	2.0	1.8	28.1
Copper Oxide 50%, Molybdenum Oxide 50%										
Ethyl	.80	.111		1.6	0.2	15.0	0.0	1.0	0.5	13.7
*Iso*propyl	.79	.120	.00	0.6	10.0	16.4	0.0	0.2	0.0	15.2
Butyl	.80	.315	.002	0.2	2.2	16.4	0.0	1.2	1.2	39.3
Copper Oxide 50%, Tungsten Oxide 50%										
Ethyl	.81	.193	.002	0.9	2.1	10.6	4.4	4.6	2.4	23.9
*Iso*propyl	.78	.167	.003	1.4	5.4	15.2	0.2	0.4	0.4	21.5
Butyl	.84	.422	.005	1.2	6.8	10.0	0.4	4.2	3.8	50.5
Copper Oxide 50%, Uranium Oxide 50%										
Ethyl	.81	.177	.008	7.8	1.0	3.4	2.8	8.8	1.8	21.9
*Iso*propyl	.81	.217	.010	8.4	1.4	3.6	2.4	4.4	0.4	26.3
Butyl	.82	.411	.008	6.2	5.4	1.2	2.2	10.2	6.4	50.0
Nickel 1%, Copper 99%										
Ethyl	.80	.354	.018	7.1	0.0	1.6	3.0	2.8	1.8	43.7
*Iso*propyl	.80	.397	.007	7.2	1.0	1.4	2.8	3.0	2.1	49.8

[a] Ethyl alcohol was held at 46°, *iso*propyl alcohol at 41° and butyl alcohol at 80° in these experiments, the pressure being about 50 mm. above that of the atmosphere.

corresponding aldehyde or ketone per hour. The figures under "C" represent the number of moles of alcohol converted to acid, acetic acid being assumed to be formed from ethyl and *iso*propyl alcohols and butyric acid from butyl alcohol. The figures given in the last column of the table represent the percentage conversion of alcohol to aldehyde or ketone. The percentage yields would be increased if account were taken of the alcohol that did not react. A much more efficient oxidation of an alcohol may be attained if the percentage of alcohol entering into reaction is low. Catalysts 4 and 18 with ethyl, 5 and 22 with *iso*propyl and 2 and 18 with butyl alcohol gave better than a 70% yield of aldehyde or ketone.

The results as shown in Table II indicate that approximately three molecules of ethyl alcohol and two of *iso*propyl alcohol to one of butyl alcohol break down to form carbon dioxide. This ratio is independent of the kind of metal catalyst and of the mixed oxide catalysts which remained hot during the reaction. Those oxide catalysts which had to be externally heated—vanadium, tungsten and molybdenum—do not show this ratio.

Butyl alcohol produced more unsaturated hydrocarbons with the metallic catalysts than either ethyl or *iso*propyl alcohol. With the copper oxide–molybdenum oxide, copper oxide–vanadium oxide and copper oxide and tungsten oxide catalysts, *iso*propyl alcohol produced 10.0%, 5.4% and 11.4% of unsaturated hydrocarbon, respectively, while with the same catalysts under the same conditions of alcohol flow ethyl alcohol produced 0.2, 2.1 and 0.2%, respectively, and butyl alcohol 2.2, 5.4 and 2.0%, respectively.

That zinc brings about an increase in the production of hydrogen is shown by the fact that the contractions reported in column "C_1" increase very appreciably as the content of zinc is increased. This effect is most marked with ethyl alcohol and least with butyl alcohol, which indicates that under these conditions ethyl alcohol is more easily dehydrogenated than *iso*propyl or butyl alcohol.

Constable[4] has shown that there are practically no active points which cause dehydrogenation on the surface of copper gauze, foil, hammered or plated copper at temperatures above 400°. It is therefore probable that in our experiments the surface is being almost continuously reactivated. That a change of surface does take place is shown by the fact that a copper catalyst after use may vary from a golden yellow to black color. This color is due to a very thin layer of material, which is presumably an oxide.

If only a relatively few points on a catalyst be active, then these should be easily poisoned or their character changed by the addition of small amounts of foreign materials. Pease[5] has shown that 200 mg. of mercury per 100 g. of catalyst reduced the adsorption of hydrogen to $^1/_{20}$ of its former value. Mercury in much larger amounts than those described by Pease

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[4] Constable, *Proc. Roy. Soc.* (*London*), **110A,** 283 (1926).

[5] Pease, THIS JOURNAL, **45,** 1196 (1923).

was found to have no deleterious effects on the catalytic oxidation of alcohols. Lazier (unpublished data) has found that 1% of nickel in a copper catalyst produced a very marked effect in the dehydrogenation of ethyl alcohol but no appreciable differences were found when this catalyst was used for oxidation. Alloys of silver and of copper containing 1% of gold, platinum, palladium, nickel or bismuth did not differ markedly from the pure silver or copper. Larger amounts of material incorporated in the catalyst produced marked differences, as shown by the increase in hydrogen content of the gases with increase of the zinc content of the catalysts. Fifty per cent. of nickel incorporated into a copper catalyst caused a rapid decomposition with a heavy deposition of carbon. Ten per cent. of silicon in copper inhibited the reaction almost completely.

Several of the oxide mixtures differed from the alloys in the products formed and their relative amounts. The catalyst containing 50% of molybdenum oxide produced very noticeable amounts of formaldehyde from all three alcohols. The tungsten oxide–copper oxide mixture also produced formaldehyde but to a lesser extent. The oxide mixtures containing vanadium, tungsten and molybdenum oxides did not cause sufficient oxidation to maintain incandescence and had to be heated externally. The oxide mixtures of copper and iron and copper and uranium did not require external heating.

Summary and Conclusions

Ethyl, *iso*propyl and butyl alcohols have been mixed with air and passed over a number of catalysts with the production of aldehyde or ketone, acid, carbon dioxide, carbon monoxide, saturated and unsaturated hydrocarbons and hydrogen. The oxidation of butyl alcohol resulted in the formation of a small amount of ester with all catalysts and some formaldehyde with the mixed oxide catalysts. The following catalysts were used during the investigation: silver, nickel, copper and platinum gauzes; copper wire, silver pellets, pellets of alloys of copper and zinc, nickel, bismuth, palladium, platinum, gold and manganese, and silver alloys of copper palladium, platinum, gold and bismuth. Oxide mixtures of uranium and copper, tungsten and copper, molybdenum and copper, vanadium and iron and copper have been used. Silver and silver–copper alloys produced better than 70% yields of aldehyde or ketone. Ethyl alcohol has been found to produce approximately three times as much carbon dioxide as butyl alcohol and twice as much as *iso*propyl alcohol.

The amount of hydrogen in the effluent gases was found to be small except when brasses were used as catalysts. Large amounts of zinc apparently promote dehydrogenation but not oxidation of the hydrogen. Butyl alcohol was found to produce more unsaturated hydrocarbons than either ethyl or *iso*propyl alcohol except with oxide catalysts, which caused the production of 10 to 15% of unsaturated compounds with *iso*propyl alcohol. This latter fact indicates that the oxide catalysts were not completely reduced to the metals. The production of saturated hydrocarbons is rather small in all other cases. Acid production was found to be small and fairly constant for the same alcohols over different catalysts.

The plated catalysts were found to be unsatisfactory because the high temperature of reaction apparently caused solution of the plated metal into the supporting metal. It also seems likely that the reaction takes place throughout the catalyst. Evidence for this view is found in the change in mechanical properties of the gauzes, wire and pellets, and in the reduction of copper oxide to metallic copper in the center of pellets of a copper oxide–vanadium oxide mixture.

The temperature of the reaction varied with the alcohol–air ratios and with the catalysts employed. The copper–vanadium, copper–molybdenum and copper–tungsten oxide mixtures were comparatively inactive and external heating was necessary. Heat was also applied to maintain a reaction at the surface of the 50% zinc–copper alloy.

The fact that small amounts of material incorporated into the metallic catalysts produce no marked effect indicates that a larger portion of the surface of the catalyst is active in the catalytic oxidation of alcohols.

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[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

THE ADDITION OF SODIUM MALONIC ESTER TO ALIPHATIC MUSTARD OILS

BY DAVID E. WORRALL

RECEIVED FEBRUARY 6, 1928 PUBLISHED MAY 5, 1928

Phenylisothiocyanate reacts smoothly with substances containing an active methylene group, such as malonic ester, acetoacetic ester and acetylacetone, forming sulfur derivatives that have been shown[1] to be useful for the preparation of heterocyclics of the isoxazole and pyrazole series. Similar transformations might be expected starting with methylisothiocyanate; accordingly, with the hope of extending the scope of these reactions so as to include the aliphatic mustard oils, work has been resumed on the chemistry of the isothiocyanates. It first became necessary to synthesize the desired thio-amides, for methyl mustard oil, which is far more expensive and more difficult to prepare than phenyl mustard oil, has been much less studied. No such work has been done with it. This communication deals with the action of several alkyl mustard oils on dimethyl and diethyl malonate.

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[1] Worrall, THIS JOURNAL, **42**, 1055 (1920); **44**, 1551 (1922); **45**, 3092 (1923); **46**, 2832 (1924).