ether and extracted with water, dilute hydrochloride acid, dilute sodium hydroxide and finally with water. The dried xylene–ether solutions were distilled and the residues fractionated. The residue from the three-hour treatment yielded an olefinic product (b. p., 80–95° at 20 mm.) and approximately twice as much undecomposed bromide, while the residue from the six-hour treatment yielded an olefinic product (b. p. 85–95° at 20 mm.), an analysis of which indicated the presence of 25% bromide. Oxidation of the former olefinic product with chromic anhydride (method b) gave approximately 25% yields each of propiophenone and benzoic acid while oxidation of the latter olefinic product gave 25 and 30% yields of propiophenone and benzoic acid, respectively.

Treatment of 2-Phenyl-1-bromobutane with Potassium Carbonate in Boiling Xylene.—A sample of 2-phenyl-1-bromobutane (which did not give an immediate precipitate with alcoholic silver nitrate) was refluxed for fifteen hours in purified xylene with a suspension of excess potassium carbonate. The solvent was distilled and a bromide (which gave an immediate precipitate with alcoholic silver nitrate) was recovered boiling at 120–125° at 20 mm. No lower boiling product was found. The recovered bromide on treatment with excess potassium amide in liquid ammonia yielded an olefinic product which on oxidation with chromic anhydride (method b) gave a 33% yield of acetophenone and a 16% yield of benzoic acid.

Summary

1. It has been shown that 2-phenyl-1-bromopropane and 2-phenyl-1-bromobutane react with potassium amide in liquid ammonia to form largely unrearranged olefins.
2. In the presence of excess potassium amide in liquid ammonia, 2-phenylbutene-1 undergoes a prototropic change to form 2-phenylbutene-2.
3. When 2-phenyl-1-bromobutane is refluxed in xylene with potassium amide approximately equal amounts of unrearranged and rearranged olefins are obtained.
4. When 2-phenyl-1-bromobutane is refluxed in xylene with potassium carbonate a portion of the bromide apparently undergoes rearrangement.

DURHAM, N. C.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES, CARBIDE AND CARBON CHEMICALS CORP.]

Deoxygenation of Certain Aldehydes and Ketones: Preparation of Butadiene and Styrene[1]

BY W. M. QUATTLEBAUM, W. J. TOUSSAINT AND J. T. DUNN

This paper reports some of the basic experimental work on the process used during the recent emergency for the manufacture of butadiene from ethanol; a common mechanism is proposed for the various syntheses of butadiene from ethanol; and a related synthesis for styrene is described.

For many years prior to the work reported here, it was known that butadiene could be made in low yield by passing ethanol over powdered aluminum metal,[2] or in fair yields from ethanol and acetaldehyde over an alumina or clay catalyst,[3] and from ethanol alone over a combined dehydrating and dehydrogenating catalyst.[4]

While the yields obtained in the latter two processes represented a marked improvement over those reported by Ipatiev, they were still low, and the butadiene was contaminated with at least 15% of butylenes.

At the outset of the present program it seemed reasonable to suppose that the efficiency of the Ostromisslensky process, and the quality of the resulting butadiene, might both be improved, if the reactions responsible for the formation of four-carbon material from two-carbon material could be determined. With this in mind, an investigation into the mechanism of the reaction was undertaken. This work led to the conclusion that the deoxygenation of crotonaldehyde is responsible for the formation of butadiene in the Ostromisslensky reaction. It also resulted in an extension of the deoxygenation reaction to certain other aldehydes and ketones.

Deoxygenation of Crotonaldehyde by Ethanol. Ostromisslensky[3] and later Maximoff[5] obtained butadiene from diethyl acetal, ethyl vinyl ether, acetaldol, crotonaldehyde, tetrahydrofuran, etc. These compounds, however, were investigated only as potential commercial sources of butadiene, and not as possible intermediates in the acetaldehyde–ethanol reaction. Indeed Ostromisslensky came to the conclusion that 1,3-butylene glycol was the intermediate from which the butadiene was formed, and that the butylene glycol was derived from an acetaldehyde–ethanol hemiacetal as follows

$$H_3CCH(OH)OC_2H_5 \longrightarrow H_3CCH(OH)CH_2CH_2OH$$

To prove that it was the methyl group, and not the methylene group of ethanol, which combined with the carbon of the aldehyde carbonyl group, Ostromisslensky adduced the evidence that substitution of *i*-propanol for ethanol led to the formation of piperylene

$$CH_3CHO + CH_3CH(OH)CH_3 \longrightarrow CH_3CH(OH)CH_2CH(OH)CH_3 \longrightarrow CH_3CH{=}CHCH{=}CH_2 + 2H_2O$$

instead of isoprene

$$CH_3CHO + CH_3CH(OH)CH_3 \longrightarrow CH_3CH(OH)C(CH_3)_2OH \longrightarrow H_2C{=}CHC(CH_3){=}CH_2 + 2H_2O$$

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[1] Publication of this paper has been withheld since 1942 because of Government secrecy orders.

[2] Ipatiev, *J. prakt. Chem.*, **2**, 67 (1903).

[3] Ostromisslensky, *J. Russ. Phys.-Chem. Soc.*, **47**, 1472–1506, 1491 (1915).

[4] Lebedev, British Patent 331,402.

[5] Maximoff, U. S. Patent 1,682,919.

The formation of piperylene thus showed that it was the carbon atom *beta* to the hydroxyl group in the alcohol which finally became attached to the carbon of the aldehyde group. But the alleged rearrangement of a hemiacetal or hemiketal to a 1,3-diol, so far as we are aware, does not have any experimental support. Similarly, in the case of the acetaldehyde–ethanol reaction, Ostromisslensky's mechanism failed to explain by known or demonstrable reactions how the two-carbon atom chains of the starting materials were joined together to form the four-carbon chain of butadiene.

Lebedev and his associates, the inventors of the ethanol process now used in Russia for the manufacture of butadiene, proposed a mechanism[6] for the formation of four-carbon products from ethanol. They suggested that $—CH_2-CH_2—$ and $—CH_2—CH(OH)—$radicals are first formed, and that these combine to produce a four-carbon radical which loses water to give butadiene. This explanation also seemed quite improbable. Among other things, it would lead one to predict larger quantities of ethylene and butylenes than are actually obtained, and ignores acetaldehyde, which is the normal dehydrogenation product of ethanol and is more reactive than ethanol in presence of a dehydrating catalyst.[7]

Consideration of the various reactions which could conceivably be responsible for the formation of four-carbon material in these processes led the authors to the conclusion that the butadiene is formed as follows: Acetaldehyde is condensed to acetaldol. This is dehydrated to crotonaldehyde. The crotonaldehyde is then converted to butadiene.

In a study of this mechanism, it was found that crotonaldehyde, passed with ethanol over an alumina catalyst, gave butadiene even more readily than did acetaldehyde, and that acetaldehyde was produced in the reaction. The crotonaldehyde had thus in effect been deoxygenated to butadiene by ethanol and the ethanol had undergone oxidation to acetaldehyde as shown in the following equation

$$CH_3—CH{=}CH—CHO + C_2H_5OH \longrightarrow$$
$$CH_2{=}CH—CH{=}CH_2 + CH_3—CHO + H_2O$$

These results, and the known ease of converting acetaldehyde to crotonaldehyde, indicated that the deoxygenation of crotonaldehyde (from acetaldehyde) was one of the essential steps in the conversion of acetaldehyde and ethanol to butadiene in both the Ostromisslensky and Lebedev processes, and that to improve yields an effort should be made to find optimum conditions for this reaction.

An investigation of various promoted alumina catalysts for the deoxygenation of crotonaldehyde with ethanol resulted in very little improvement in the quality of butadiene or in the efficiency of its production. It was then found that fuller's earth, which is chiefly an indefinite hydrated magnesium aluminum silicate, was a catalyst for the reaction. It gave a four-carbon fraction containing about 55% of butadiene, and produced a higher ratio of butadiene to acetaldehyde than had most of the alumina catalysts. When tried in the acetaldehyde–ethanol reaction (See expt. 3), it gave butadiene of higher purity (73%) in a higher efficiency[8] (49%) than had any of the alumina or promoted alumina catalysts. When purified silica gel was substituted for the aluminosilicate catalyst, a marked improvement in the efficiency of the reaction, and in the quality of butadiene resulted. In certain experiments, efficiencies as high as 80% based on crotonaldehyde were obtained.[9] The purity of the butadiene fraction, after removal of acetaldehyde, was increased from about 73% over the fuller's earth catalyst to about 98% over the purified silica gel catalyst.

When crotonaldehyde (1 mole) was passed with ethanol (3 moles) over the purified silica gel catalyst, butadiene was obtained in good yield (see expt. 4), and acetaldehyde was produced in approximately equivalent amount. But when acetaldehyde (1 mole) and ethanol (3 moles) were passed over the same catalyst under like conditions, butadiene was obtained in only a very low yield (see expt. 5). Obviously, in this case, acetaldehyde did not readily undergo aldol condensation with subsequent dehydration to crotonaldehyde—otherwise butadiene would have been produced in good yield as before. If in the first experiment, the crotonaldehyde had merely served as a source of acetaldehyde (by hydrolysis), it would not have given any more butadiene than was obtained from the acetaldehyde and ethanol. But since crotonaldehyde and ethanol did give a much higher yield of butadiene than acetaldehyde and ethanol, crotonaldehyde and not some hypothetical condensation product from acetaldehyde and ethanol—or from two-carbon free radicals—must have been responsible for the formation of butadiene when the crotonaldehyde and ethanol were passed over silica gel.

Further experiments showed that purified silica gel catalyst, when impregnated with tantalum oxide (zirconium oxide and columbium oxide are also very effective) gave higher yields of butadiene from crotonaldehyde and ethanol, and *less acetaldehyde* than the untreated catalyst (see expt. 7). In addition to catalyzing the deoxygenation of crotonaldehyde, this catalyst thus *seemed capable of converting some of the resulting acetaldehyde to butadiene.* The next step, therefore, was to try it as a catalyst for the acetaldehyde–ethanol reaction. When this was done (see expt. 8), excellent efficiencies, as high as 80%

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(6) Lebedev, *J. Gen. Chem.*, **3**, 698 (1933).

(7) For a further discussion of this and other possible mechanisms, see Egloff and Hulla. *Chem. Rev.*, **36** 63 (1945).

(8) For explanation of term "efficiency," see Experimental Section under "Calculations."

(9) In large scale experiments to be reported elsewhere, using a mixture of one mole of crotonaldehyde to six of ethanol.

on acetaldehyde and 64% on ethanol were obtained, and the quality of the butadiene was much higher than any hitherto reported for the Ostromisslensky or Lebedev processes.

It was observed that small concentrations of crotonaldehyde in ethanol could be deoxygenated in a single pass over the promoted silica gel catalyst. While only a small concentration of crotonaldehyde needs to be present in order to obtain rapid formation of butadiene, it is necessary, of course, that it be rapidly produced. This condition is met in the case of the promoted silica gel catalyst, where both condensation and deoxygenation reactions proceed at an accelerated rate. When acetaldehyde alone was passed over the tantalum oxide promoted silica gel catalyst, crotonaldehyde was produced (see expt. 6).

From the standpoint of the reaction mechanism the important facts are: (1), that crotonaldehyde is readily formed when acetaldehyde is passed over the tantalum oxide promoted silica gel catalyst; (2), that crotonaldehyde is not present in significant amounts in the products when acetaldehyde and ethanol are converted to butadiene over the same catalyst; and (3), that crotonaldehyde is readily converted to butadiene by ethanol over the same catalyst. These facts strongly support the view that crotonaldehyde is the principal intermediate in the acetaldehyde–ethanol reaction, but do not exclude the possibility that acetaldol is reduced by ethanol to 1,3-butylene glycol, which then undergoes dehydration to butadiene. To test this, 1,3-butylene glycol was passed over the tantalum oxide promoted silica gel catalyst under conditions similar to those used in the acetaldehyde–ethanol reaction (see expt. 9). Distillation of the products showed that propylene was produced in the ratio of one mole of propylene to 0.73 mole of butadiene. Since the ratio of propylene to butadiene obtained from acetaldehyde and ethanol over the same catalyst does not exceed about 1:25, 1,3-butylene glycol can be ruled out as an important intermediate in the reaction. The individual reactions may therefore be written as follows

$$2CH_3CHO \longrightarrow CH_3CH{=}CHCHO + H_2O$$

$$CH_3CH{=}CHCHO + C_2H_5OH \longrightarrow CH_2{=}CHCH{=}CH_2 + CH_3CHO + H_2O$$

and the over-all reaction is

$$CH_3CHO + C_2H_5OH \longrightarrow CH_2{=}CHCH{=}CH_2 + H_2O$$

The mechanism described above is considered to be applicable not only to the reaction catalyzed by tantalum oxide promoted silica gel but also to that over other catalysts, including those proposed by Ostromisslensky, for making butadiene from ethanol and acetaldehyde. Also it appears to apply to the catalysts, so far as they are known to the writers, which convert ethanol to butadiene, as proposed by Lebedev. These catalysts are capable of carrying out the Ostromisslensky reaction, and also have a dehydrogenating action which can supply the required acetaldehyde.

Having found a catalyst capable of converting acetaldehyde to crotonaldehyde, and of bringing about an efficient deoxygenation of the latter in the presence of ethanol, it was thought desirable to add substances to a promoted silica gel catalyst which would be capable of dehydrogenating some of the ethanol. The mixture of ethanol and acetaldehyde could then be converted to butadiene as outlined above by the tantalum oxide promoted silica gel catalyst. Among those dehydrogenating catalysts for ethanol which would not also catalyze the hydrogenation of butadiene, cadmium oxide seemed best. It was used with silica gel promoted with zirconium oxide, which is almost as effective as tantalum oxide. With a silica gel catalyst containing zirconium oxide (1.5%) and cadmium oxide (0.5%), ethanol was apparently dehydrogenated to acetaldehyde; the acetaldehyde was converted to crotonaldehyde; and the latter was deoxygenated in the same tube to give butadiene of at least 94% purity (see expt. 10). Under other conditions, copper could be used more advantageously for this purpose but a high concentration of acetaldehyde was apparently required to avoid hydrogenation of the butadiene. Experiments with the Lebedev catalysts gave less favorable results and required higher temperatures.

Deoxygenation of Other Aldehydes and Ketones

Deoxygenation of Butyraldehyde by Ethanol.—It seemed of interest to determine whether ketones and aldehydes other than crotonaldehyde are capable of undergoing deoxygenation in the presence of ethanol. The first one chosen was butyraldehyde. When one mole of this compound, in admixture with 2 moles of ethanol, was passed over an aluminum sulfate treated alumina catalyst at 270°, a 38% yield of mixed butylenes was obtained (see expt. 11). When a similar mixture was passed over silica gel (see expt. 12), butylenes were also obtained, but the chief product was butanol, indicating that in this case the chemi-sorbed intermediate is sufficiently stable toward dehydration to permit desorption of the alcohol.

In the crotonaldehyde deoxygenation, the possibility existed for hydrolysis of the crotonaldehyde, followed by resynthesis to four-carbon material by some other reaction. In the present reaction, however, butyraldehyde could *not* undergo such a change. Clearly, therefore, the four-carbon hydrocarbon was formed from butyraldehyde by a reaction which in effect amounted to a deoxygenation of the aldehyde.

Deoxygenation of Acetophenone by Ethanol.—Milligan and Reid[10] described the reduction of certain aldehydes to alcohols by ethanol over a ceria catalyst. Earlier, Sabatier and Murat[11] found that benzaldehyde, benzyl alcohol, acetophenone and benzophenone could be reduced completely to the hydrocarbons: toluene, ethyl-

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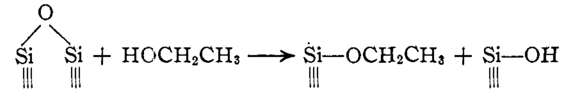
(10) Milligan and Reid, This Journal, **44**, 202 (1922).

(11) Sabatier and Murat, *Compt. rend.*, **157**, 1499 (1913); *Bull. soc. chim.*, (4) **15**, 227 (1914).

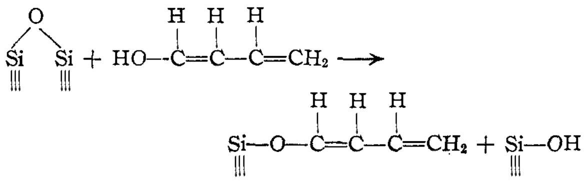
benzene and diphenylmethane, respectively, by passage with the vapors of alcohols over thoria at 420°. In the present experiments (13 and 14), reduction to ethylbenzene did not occur when acetophenone and ethanol were passed over the silica gel catalyst. Instead, styrene of high purity (n^{20}_{D} 1.5465) was obtained. Acetaldehyde was formed as co-product. Whether the reaction proceeds through a reduction of the acetophenone by ethanol to the carbinol, followed by dehydration of the latter is not known. In effect, however, the styrene is produced by a reaction which amounts to a deoxygenation of the acetophenone by ethanol.

Role of the Catalyst.—In this reaction the hydrocarbon formed has the empirical composition of the aldehyde or ketone from which it is derived, minus the oxygen atom. In some instances more than one isomer of the unsaturated hydrocarbon is obtained, which is explained by the known isomerizing action of the catalysts used. It seems likely that the hydrocarbon isomer is first formed which would result from the elimination of oxygen from the enol form of the aldehyde or ketone. This suggests that the reaction may consist of the hydrogenolysis of the adsorbed enol form of the aldehyde or ketone at the oxygen atom by hydrogen from the alcohol used. Any aldehyde or ketone possessing a loosely bound hydrogen atom may undergo such a reaction. Activated silica gel, which is the best material found for these deoxygenation reactions, is a porous mass in which each silicon atom is believed to be joined to four oxygen atoms, only the surface being more or less hydrated. Hence, points on the surface may be visualized as presenting the structures ≡Si–O–Si≡ and ≡SiOH, in which single bonds extend to oxygen atoms below the surface. Molecules of ethanol, and the enol form of the aldehyde, (crotonaldehyde in this example) could then react with the catalyst in the following manner



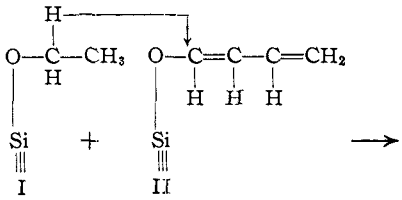
$$\underset{|||}{\mathrm{Si}}\overset{\mathrm{O}}{\wedge}\underset{|||}{\mathrm{Si}} + \mathrm{HOCH_2CH_3} \longrightarrow \underset{|||}{\mathrm{Si}}\text{—}\mathrm{OCH_2CH_3} + \underset{|||}{\mathrm{Si}}\text{—}\mathrm{OH}$$

and

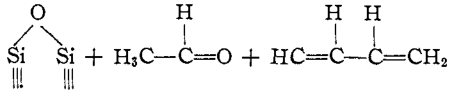


$$\underset{|||}{\mathrm{Si}}\overset{\mathrm{O}}{\wedge}\underset{|||}{\mathrm{Si}} + \mathrm{HO}\text{—}\overset{\mathrm{H}}{\mathrm{C}}=\overset{\mathrm{H}}{\mathrm{C}}\text{—}\overset{\mathrm{H}}{\mathrm{C}}=\mathrm{CH_2} \longrightarrow \underset{|||}{\mathrm{Si}}\text{—O—}\overset{\mathrm{H}}{\mathrm{C}}=\overset{\mathrm{H}}{\mathrm{C}}\text{—}\overset{\mathrm{H}}{\mathrm{C}}=\mathrm{CH_2} + \underset{|||}{\mathrm{Si}}\text{—}\mathrm{OH}$$

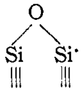
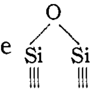
Then



$$\underset{\mathrm{I}}{\underset{|||}{\mathrm{Si}}}\text{—O—}\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}\text{—}\mathrm{CH_3} + \underset{\mathrm{II}}{\underset{|||}{\mathrm{Si}}}\text{—O—}\underset{\mathrm{H}}{\mathrm{C}}=\underset{\mathrm{H}}{\mathrm{C}}\text{—}\underset{\mathrm{H}}{\mathrm{C}}=\mathrm{CH_2} \longrightarrow$$



$$\underset{|||}{\mathrm{Si}}\overset{\mathrm{O}}{\wedge}\underset{|||}{\mathrm{Si}} + \mathrm{H_3C}\text{—}\overset{\mathrm{H}}{\mathrm{C}}=\mathrm{O} + \mathrm{HC}=\overset{\mathrm{H}}{\mathrm{C}}\text{—}\overset{\mathrm{H}}{\mathrm{C}}=\mathrm{CH_2}$$

A hydrogen atom is thus transferred as indicated by the dotted lines, and surface compounds I and II then yield acetaldehyde and butadiene, and regenerate the catalyst  $\underset{|||}{\mathrm{Si}}\overset{\mathrm{O}}{\wedge}\underset{|||}{\mathrm{Si}}$. Dehydration of ≡SiOH groups should regenerate  $\underset{|||}{\mathrm{Si}}\overset{\mathrm{O}}{\wedge}\underset{|||}{\mathrm{Si}}$.

By-Products Formed in the Butadiene Process.—In the reaction of acetaldehyde and ethanol over the tantalum-promoted silica gel catalyst, approximately one-third of all material reacting is converted to products other than butadiene. The more notable by-products found are ethylene, propylene, butylenes, ethyl ether, acetic acid, ethyl acetal, ethyl acetate, methyl ethyl ether, crotonaldehyde, crotyl alcohol, butyl alcohol, butyraldehyde, methyl ethyl ketone, pentadienes, pentenes, hexaldehyde, hexadienes and hexenes.[12] These by-products may be divided into two classes: one class is produced, or can be produced, by previously known effects of silica gel catalysts, such as simple dehydration and ester-forming disproportionation; the formation of the other class can best be explained by mechanisms analogous to that proposed above for butadiene. In the first class, dehydration of ethanol would account for ethylene and ethyl ether; reaction of ethanol with acetaldehyde, for ethyl acetal; disproportionation of acetaldehyde, for ethyl acetate; and hydrolysis of ethyl acetate, for acetic acid. In the second class, condensation of acetaldehyde to acetaldol, followed by dehydration, would account for crotonaldehyde. Deoxygenation of acetaldol (with subsequent rearrangement), would account for methyl ethyl ketone; reduction of crotonaldehyde, for crotyl alcohol; and isomerization of crotyl alcohol for butyraldehyde. Deoxygenation of butyraldehyde by ethanol would produce butylenes, and reduction without dehydration would give butanol, as shown in the experimental section. Furthermore, the condensation of crotonaldehyde with acetaldehyde would be expected to yield hexadienal, which by analogy with crotonaldehyde should be capable of undergoing reduction by ethanol to give hexenal and hexaldehyde. Deoxygenation of these aldehydes should give hexatrienes, hexadienes and hexenes. All of the above compounds, except the hexatrienes, have in fact been isolated from the products of the reaction. The three and five-carbon compounds such as propylene and the pentenes and pentadienes were somewhat more difficult to account

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[12] More detailed and quantitative data on the by-products of the reaction are given by Toussaint, Dunn and Jackson in *Ind. Eng. Chem.*, **39**, 120 (1947).

TABLE I

REACTIONS CONCERNED IN BUTADIENE SYNTHESIS

Expt.	Reactants	Moles	Catalyst volume, cc.	Temp., °C.	Feed rate,[a] cc./hr.	Products	Yield		Efficiency, %[b]	Butadiene purity,[c] % by vol. (gas)
							Moles	% of theor.[b]		
						Alumina Catalyst				
1	Crotonaldehyde	2.5	400	380	110	Butadiene	1.02	41	...	60
	Ethanol	7.3				Butylenes	0.66	26	...	
						Acetaldehyde	0.27	...	...	
						Ether	1.2	...	...	
2	Acetaldehyde	4.0	100	420	400	Butadiene	0.26	3	...	54
	Ethanol	14.7				Butylenes	0.22	2	...	
						Ether	2.4	...	...	
						Fuller's Earth Catalyst				
3	Acetaldehyde	4.7	300	365	115	Butadiene	1.95	17	49[d]	73
	Ethanol	18.0				Butylenes	0.70	6	18[d]	
						Silica Gel Catalyst				
4[e]	Crotonaldehyde	9.8	335	365	330	Butadiene	1.9	19	...	98.5
	Ethanol	30.1				Butylenes	0.03	0.3	...	
						Acetaldehyde	2.6	...	...	
5	Acetaldehyde	5.1	300	365	175	Butadiene	0.21	2	...	..
	Ethanol	15.0				Butylenes	<0.04	...	...	
						Crotonaldehyde	Trace	...	...	
						Tantalum Oxide Promoted Silica Gel Catalyst				
6[f]	Acetaldehyde	12.5	300	320	170	Crotonaldehyde	1.0	16	45[h]	..
						Higher aldol products	1.1[g]	9	25[h]	
7[i]	Crotonaldehyde	4.0	280	325	200	Butadiene	4.9	123[j]	...	98
	Ethanol	24.1				Butylenes	0.1	3	...	
						Acetaldehyde	2.0	...	...	
8	Acetaldehyde	7.9	300	325	170	Butadiene	4.4	28	71[k]	97
	Ethanol	24.0				Butylenes	0.1	0.6	...	
						Crotonaldehyde	None detected			
9	1,3-Butylene glycol	4.5	300	350	100	Butadiene	0.73	16	...	77
						Butylenes	0.13	3	...	
						Propylene	1.0	22	...	
						Other[l]	..	...	...	
						Cadmium Oxide Zirconium Oxide Promoted Silica Gel Catalyst				
10	Ethanol	4.0	300	320	70	Butadiene	0.47	24	44[m]	>94
						Butylenes	<0.03	...	...	
						Acetaldehyde	0.28	7	...	
						Hydrogen	1.25	31	...	

[a] Includes any water present in feed mixture. [b] Where feed mixture consists of acetaldehyde and ethanol, both are used in calculating yield and efficiency; otherwise ethanol does not enter calculation, except of course in expt. 10. [c] Impurity is mixture of butylenes. [d] About 0.7 mole acetaldehyde and 14.0 moles ethanol recovered. [e] 24 moles water included in feed. [f] 25 mole water included in feed. [g] Equivalents, estimated. [h] 8.1 moles acetaldehyde recovered. [i] Less than 0.1 mole crotonaldehyde in products. [j] Yield of over 100% results from further reaction of acetaldehyde produced frrom ethanol. [k] 2.4 moles acetaldehyde and 17.1 moles ethanol recovered. [l] Small amounts of propane, acetaldehyde, and methyl vinyl ketone or crotonaldehyde. [m] 1.57 moles ethanol recovered. Credit taken for acetaldehyde.

for. Decarbonylation of the corresponding aldehydes was rejected because of an insufficient amount of carbon monoxide in the reaction products. Cleavage of 1,3-butylene glycol formed in small amount by reduction of acetaldol with ethanol appears to be the most probable source of by-product propylene. Experimental support for this was obtained in expt. 9, where propylene was produced in good yield from 1,3-butylene glycol in the presence of the promoted silica gel catalyst. In the cleavage of 1,3-butylene glycol to propylene, formaldehyde must be formed as a co-product. Condensation of this with other aldehydes and ketones present would give products capable of deoxygenation to propylene, pentenes, pentadienes, etc. Reduction of formaldehyde by ethanol would yield methanol; reaction of this with ethanol would account for methyl ethyl ether.

By-products obtained in the deoxygenation of other aldehydes and ketones probably are formed by reactions similar to those suggested above.

TABLE II

DEOXYGENATION OF BUTYRALDEHYDE AND ACETOPHENONE

Expt.	Reactants	Moles	Catalyst	Volume, cc.	Temp., °C.	Feed rate, cc./hr.	Products	Yield		Efficiency, %
								Moles	% of theor.	
11	Butyraldehyde	2.5	$Al_2(SO_4)_3$	120	270	100	Butylenes	0.95	38	...
	Ethanol	4.6	on alumina							
12	Butyraldehyde	4.8	Silica gel	300	360	100	Butene-1	.10	2	...
	Ethanol	9.7					Butene-2	.18	4	...
							Butadiene	.17	4	...
							Butanol	1.4	29	44[a]
13	Acetophenone	1.0	Silica gel	300	350	85	Styrene	0.29	29	...
	Ethanol	4.0								
14	Acetophenone[b]	5.8	Silica gel	1250	350	1200	Styrene	3.3	44[c]	92[d]
	Methylphenylcarbinol[b]	1.7								
	Ethanol	50.1								

[a] 1.6 moles of butyraldehyde recovered. [b] Acetophenone–methylphenylcarbinol mixture obtained by oxidizing ethylbenzene. [c] Based on the ketone–carbinol mixture. Carbinol underwent dehydration to styrene during reaction. [d] 3.5 moles acetophenone and 0.4 mole methylphenylcarbinol recovered.

So far, however, no attempt has been made to identify the by-products obtained in the deoxygenation of butyraldehyde. In the case of acetophenone, only small quantities of by-products are produced.

Experimental

Experiments dealing with the synthesis of butadiene are presented in Table I; those concerned with the deoxygenation of butyraldehyde and acetophenone are given in Table II.

Calculations.—The term "efficiency," as used throughout the paper, is defined as the yield on *consumed* starting material. In all experiments involving more than one reactant (except where acetaldehyde–ethanol mixtures are used), the yields and efficiencies are based on the carbonyl compound. When the reactants are acetaldehyde and ethanol (expts. 2, 3, 5 and 8), the calculations are based on the mixture, since ethanol generates additional acetaldehyde in the reaction.

Catalysts.—Alumina was prepared from ammonium alum by calcining at about 680° and then crushing and screening before use. Aluminum sulfate–alumina was prepared by heating 100 g. of commercial alumina granules for eight hours at 80 to 90° with 30 g. of aluminum sulfate in just enough water to cover all of the granules. The aqueous layer was decanted, and the catalyst was washed once with distilled water and dried. Commercial fuller's earth was compressed into pellets for use as the catalyst in expt. 3. Silica gel for all of the experiments was obtained from the Davison Chemical Corporation under designation of no. 6953-80. For expts. 4 and 13 it was purified by digesting twice with equal parts by weight of nitric acid and water at the boiling point for about six hours. Following this it was washed nearly free of acid to litmus and dried of surface water. For the other experiments, the silica gel was water-saturated and purified as received from the manufacturer.

The preparation of promoted catalyst for expt. 8 illustrated the method and was as follows: 12.0 g. of potassium tantalum fluoride was dissolved in 160 cc. of water. The solution was filtered and added to 56 cc. of aqueous (1:1) ammonium hydroxide. The precipitate was washed five times with distilled water by decantation and then filtered by suction. The gelatinous material was mixed with a solution of 20 g. of oxalic acid dihydrate in 200 cc. of water and dissolved by heating one and one-half hours at 90°. The solution was added to 350 cc. of purified gel (about 316 g.), and heated on a steam bath with occasional stirring to apparent dryness. The catalyst was then heated gradually (four hours) from 150 to 350°. The final catalyst volume was 345 cc.; it weighed 246 g. and contained about 2.5% of tantalum oxide. The catalyst for expt. 6 contained about 0.8% of tantalum oxide, for expt. 7 about 1.9% of tantalum oxide, and for expt. 9, 2.0% of tantalum oxide.

Zirconium oxide catalysts may be prepared similarly. The catalyst for expt. 10 was prepared by evaporating an aqueous solution of zirconyl nitrate (6.9 g.) containing 3.1 g. of cadmium nitrate in the presence of 300 cc. of silica gel. The nitrates were decomposed by heating slowly to a temperature of 380°.

Apparatus.—In the various experiments, the reactants (under constant head) were added from a dropping funnel, or metered through a Zenith gear pump. The reactors were heated by an electrical winding. In some experiments glass reaction tubes were heated in an alundum core furnace; in others, steel tubes were heated with Dowtherm A in an outer pressure jacket bearing an electrical winding. The latter method provided a more uniform temperature in the catalyst bed. Control of heat was by 2KVA transformers. The receivers were either connected directly to the catalyst tube or through a water-cooled condenser and were usually cooled in a solid carbon dioxide–acetone mixture. Additional low temperature traps were provided as necessary and a wet test-meter completed the train. For fractionation of the low-boiling products, a Davis column or a conventional column was used. The still-head was cooled by brine or by circulating methanol through a coil in a solid carbon dioxide–acetone-bath. The columns were usually packed with glass helices.

Materials.—The materials, except as otherwise indicated, were plant refined, high purity commercial products. The acetaldehyde and butyraldehyde were at least 99% pure. Ethanol was denatured according to Formula SD-29 and a typical analysis is: ethanol, 91.2%; acetaldehyde, 0.92%; water, 7.5%; ethyl acetate, 0.3% and acetic acid, 0.01%. The crotonaldehyde was also plant refined material, consisting o 91.3% crotonaldehyde and 8.7% water.

Analyses.—Butadiene was determined by reaction of a one-liter gaseous sample with bromine in a previously evacuated flask. Excess bromine was removed by a stream of air, and volatile bromides by heating the flask at 60° and at 3 mm. pressure for one hour. Specific aldehydes and alcohols could be identified only by analysis of carefully fractionated samples. Aldehydes were determined by reaction with hydroxylamine hydrochloride, made alkaline with 0.5 *N* sodium hydroxide, and back-titrated with 0.5 *N* sulfuric acid, using brom phenol blue as indicator. Ethanol, in the 65–85° fraction, was determined by reaction with acetic anhydride–pyridine mixture, and titration at 0° of the unreacted reagent. About 200% excess of anhydride and one hour of heating at 95–100° was necessary to secure accurate results. Unsaturated hydrocarbons in expts. 9 and 12 were determined with a mass spectrometer by E. C. Kerr.

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Summary

The catalytic removal of oxygen from certain aldehydes and ketones by means of an alcohol is described. An olefin is produced from the aldehyde or ketone, water is formed, and an aldehyde or a ketone is obtained from the alcohol. Evidence is advanced to show that the deoxygenation of crotonaldehyde is responsible for the formation of butadiene from acetaldehyde and ethanol in the Ostromisslensky reaction. A new synthesis for styrene, involving the catalytic deoxygenation of acetophenone by ethanol, is also described.

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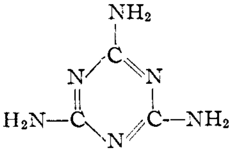
[CONTRIBUTION FROM STAMFORD RESEARCH LABORATORIES, AMERICAN CYANAMID COMPANY]

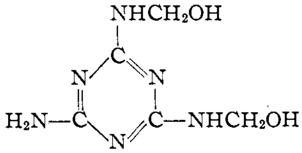
The Dissociation Constants of Melamine and Certain of its Compounds

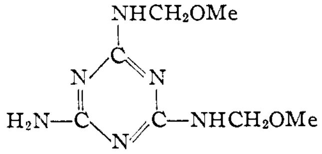
BY J. K. DIXON, N. T. WOODBERRY AND G. W. COSTA

Introduction

Melamine is a weak base which can be made up into several interesting series of condensation products also of basic character. Two of such series are the methylol melamines and methylated methylol compounds which are illustrated by the formulas







In connection with studies of the formation of polymeric materials from the methylol and methylated methylol melamines, it was of interest to determine the basic dissociation constants of several of these compounds so as to permit correlation of these data with their chemical structures and their properties as polymers. Unpublished information from this Laboratory[1] suggests qualitatively that an increase in the number of methylol groups or in the degree of etherification tends to decrease the rate of polymerization of the monomer. The hydrogen ion concentration is a factor in controlling the rate of polymerization and consequently the basicity of the polymerizing melamine compound affects the acidity of its solution, and, therefore, in turn influences the rate of polymer formation. Although the exact course and mechanism of polymerization are not known, it is expected that the information submitted below will be of help in future interpretations of other experimental data.

This paper presents measurements of the basic dissociation constants of melamine and certain of its related compounds as determined by electrometric titration and by ultraviolet absorption methods.

Experimental

Preparation of Materials.—The following preparation for methylated trimethylol melamine illustrates methods of preparing methylol and methylated methylol melamines. A mole of melamine was added to sufficient 37–40% formalin (adjusted to a *p*H 8 with sodium hydroxide) to contain 3.3 moles of formaldehyde. The mixture was heated to 75° with good agitation to complete solution and reaction with formaldehyde over a total time of around half an hour. The solution cleared up after reaction and was then cooled and poured out on shallow trays in order to "crystallize" the trimethylol melamine as a solid cake. The latter was dried at 50° for twelve hours, the low temperature being desirable to prevent extensive polymer formation. This solid product was essentially trimethylol melamine containing but a small fraction of polymerized product. Variations in the ratio of formaldehyde to melamine produced desired differences in the degree of methylolation.

In order to convert a methylol compound to its methyl ether, it was dispersed in two times its weight of anhydrous methanol. About 0.5% of oxalic acid, based on the weight of methylol melamine, was added to the slurry and the stirred mixture raised to reflux temperature over a period of twenty minutes. Refluxing was continued for about one hour to dissolve unreacted methylol melamine, after which the reaction mixture was clear and reaction was essentially complete. The *p*H was adjusted to 9, the solution filtered after the addition of filter aid, and the filtrate evaporated in vacuum at 85–90°. The sirup contained essentially monomeric methylated trimethylol melamine.

Crystalline types of methylol melamine are prepared by following the procedure outlined above, but in addition, working at slightly greater dilution. The crystalline product could be filtered off and washed with acetone. The procedure of Widmer[2] was followed in order to produce crystalline hexamethyl ether of hexamethylol melamine.

The melamine compounds were analyzed for combined formaldehyde, degree of methylation of the methylol groups, nitrogen and solid content. The nitrogen content determined agreed to within ±2% of that calculated from the molecular weight, using formaldehyde and meth-

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[1] J. R. Dudley and J. E. Lynn, *J. Soc. Dyers Colourists*, to be published.

[2] Gams, Widmer and Fisch, *Helv. Chim. Acta*, **24**, 302E (1941).