several times with a 4% solution of sodium hydroxide, washed twice with water, dried over sodium carbonate and fractionated. After three fractionations the fraction distilling between 190 and 195° (33–35 g.) was collected and analyzed; yield of *iso*-amyl *iso*-valerate, 45–48% of the alcohol taken.

Anal. Subs., 2.0247: required 59.40 cc. of 0.2 *N* KOH. Calcd. for $C_{10}H_{20}O_2$: 58.85 cc.

Besides *iso*-amyl *iso*valerate, *iso*valeric aldehyde, some unoxidized alcohol, small quantities of chlorinated products, acetone and carbon dioxide were identified.

When the washings from the ester layer were mixed with the aqueous layer and the mixture was treated with sulfuric acid, a layer of *iso*valeric acid separated out. The mixture was extracted with 300 cc. of ether and the ether extract dried over anhydrous sodium sulfate and subjected to fractionation. Most of the high-boiling liquid distilled between 175 and 177°. This was almost pure *iso*valeric acid; yield, 12–13 g. The acid had a very rancid odor and gave a gelatinous precipitate with a solution of zinc sulfate.

Summary

1. Vanadium pentoxide, in dilute sulfuric acid solution, induces the oxidation of methyl, ethyl, *n*-propyl, *n*-butyl, *iso*butyl and *iso*-amyl alcohols, acetal and mixtures of equimolecular proportions of paraldehyde and ethyl alcohol and paraldehyde and *n*-butyl alcohol with chlorates to give esters as the principal products.

2. Organic acids, small quantities of aldehydes and chlorinated products, acetone and carbon dioxide were isolated as by-products in the oxidation of some of the alcohols.

3. A tentative mechanism of the oxidation is presented.

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HEMIACETAL FORMATION AND THE REFRACTIVE INDICES AND DENSITIES OF MIXTURES OF CERTAIN ALCOHOLS AND ALDEHYDES

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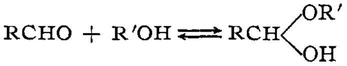
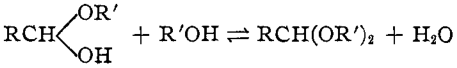
Heat is evolved when certain alcohols and aldehydes are mixed with each other. The addition of a catalyst such as hydrogen chloride or calcium chloride to the solution results in acetal formation. Presumably the pure alcohol and aldehyde react by addition according to the equation



$$RCHO + R'OH \rightleftharpoons RCH\begin{cases}OR'\\OH\end{cases}$$

The hemiacetal in the presence of a catalyst may then react with alcohol to form an acetal and water



$$RCH\begin{cases}OR'\\OH\end{cases} + R'OH \rightleftharpoons RCH(OR')_2 + H_2O$$

Our investigations of the reactivities of alcohols and aldehydes in acetal formation have led us to seek more precise evidence as to the justifiability of this hypothesis. We have therefore measured the refractive indices and the densities of mixtures of certain alcohols and aldehydes. A summary of the results is presented in the table.

TABLE I

REFRACTIVE INDICES OF MIXTURES OF VARIOUS ALCOHOLS AND ALDEHYDES[a]

Acetaldehyde and ethanol		Acetaldehyde and *iso*propanol		Heptaldehyde and *iso*propanol		Heptaldehyde and ethanol	
%	R. i.	%	R. i.	%	R. i.	%	R. i.
0	1.36424	0	1.38516	0	1.36994	0	1.35828
11.9	1.37134	13.3	1.38391	11.7	1.38113	11.3	1.36708
33.1	1.38266	33.6	1.38247	17.2	1.38381	20.5	1.37452
40.2	1.38583	42.6	1.38008	20.0	1.37640	30.8	1.38266
55.1	1.38506	52.6	1.37640	40.0	1.39318	40.4	1.38979
56.3	1.38612	64.4	1.37218	50.4	1.39699	51.2	1.39768
68.1	1.37762	70.6	1.36864	62.6	1.39945	61.1	1.40419
84.1	1.36424	74.2	1.36552	69.8	1.40350	71.1	1.40855
75.5	1.37480	81.0	1.36044	80.6	1.40577	81.0	1.41113
90.8	1.35686	92.1	1.35193	89.4	1.40765	90.1	1.41103
95.7	1.35097	95.8	1.34941	91.9	1.40835	95.5	1.41028
100	1.34445	100	1.34445	100	1.40884	100	1.40884

Butyraldehyde and *tert.*-butanol		Anisaldehyde and ethanol		Benzaldehyde and ethanol		
%	R. i.	%	R. i.	%	R. i.	d_4^{25}
0	1.38458	0	1.35828	0	1.35828	0.7839
4.8	1.38360	12.5	1.38008	7.8	1.37050	.8020
13.1	1.38333	23.5	1.39876	16.7	1.38448	.8251
21.3	1.38237	34.1	1.41782	36.3	1.41702	.8728
30.9	1.38094	45.3	1.44012	46.7	1.43770	.8933
41.1	1.38018	54.5	1.45956	56.5	1.45567	.9225
51.1	1.37932	61.9	1.47518	62.7	1.46562	.9391
66.9	1.39837	77.0	1.51040	67.3	1.47429	.9499
79.9	1.37772	84.7	1.52992	84.0	1.50774	.9935
81.6	1.37861	92.2	1.54966	83.9	1.52387	1.0155
92.5	1.37743	95.4	1.55733	96.1	1.53423	1.0300
100	1.37875	100	1.57004	100	1.54254	1.0403

[a] The readings of refractive indices are believed to be reproducible to within less than 0.0001. The concentration of the aldehyde was accurate to within less than 1% for all mixtures except those having a high content of acetaldehyde, for which an accuracy of less than 2% is claimed.

The percentages given in the table represent the per cent. by weight of aldehyde contained in the aldehyde-alcohol mixture. All measurements were made at 25° except for those mixtures containing acetaldehyde, which were made at 8°. The densities ($d_4^{25°}$) for the benzaldehyde-ethanol mixtures are also given in the table. The results of a few significant determinations on mixtures other than the seven noted in the table are as follows.

74.4% Anisaldehyde, 25.6% ethanol: d_4^{25}, 1.0135; n_D^{25}, 1.50432.
60.7% Butyraldehyde, 39.3% ethanol: d_4^{25}, 0.8442; n_D^{25}, 1.39134.
100% Anisaldehyde: d_4^{25}, 1.1192; n_D^{25}, 1.57031.
50% Acetaldehyde, 50% *tert.*-butyl alcohol: n_D^8, 1.37470.
100% *tert.*-butyl alcohol: n_D^8, 1.38684.

The refractive indices were determined by means of a Pulfrich refractometer. The densities were determined by the use of a pycnometer. The alcohols and the acetaldehyde were purified as described elsewhere;[1] ethanol, b. p. 77.8–78.0°; *iso*propyl alcohol, b. p. 82.1–82.5°; *tert.*-butyl alcohol, b. p. 82.5–82.7°, m. p. 25°. The bisulfite derivative of butyraldehyde was made from the liquid products of the air oxidation of butanol over copper. The aldehyde was liberated from the bisulfite compound by sodium carbonate and steam distilled. The aqueous mixture was repeatedly dried over calcium chloride and then fractionated. The portion boiling between 73 and 74° was collected and used within two or three days. All samples of butyraldehyde recovered from the commercial product or allowed to stand for a time in the laboratory boiled 6 or 7° too high. The benzaldehyde was fractionated and had a boiling point of 168.4° and $d_4^{20°}$, 1.04885. The heptaldehyde was fractionated from the product of the Eastman Kodak Company; b. p. 175.0–175.5°. The anisaldehyde was similarly obtained and distilled at 130–131° at 15 mm. No cinnamic aldehyde could be obtained sufficiently colorless so that it could be used in this work, although the compound is usually so described.

The refractive indices of mixtures of ethanol and acetaldehyde, ethanol and heptaldehyde and *iso*propanol and acetaldehyde have been plotted in Fig. 1. The curved lines pass through the experimentally determined points, while the straight lines represent what would be the refractive indices if the alcohol and aldehyde did not react. It is obvious that reaction has taken place between the alcohols and aldehydes. The curve for heptaldehyde and *iso*propanol is similar to that for *iso*propanol and acetaldehyde, although the divergence of the curve from the straight line is not so great. The single mixture of butyraldehyde and ethanol whose constants were measured shows a divergence similar to that of acetaldehyde and ethanol.

The refractive indices of mixtures of benzaldehyde and ethanol, anisaldehyde and ethanol and of tertiary butanol and butyraldehyde are quite different from what they would be if the alcohol and aldehyde did not react with each other. However, in the case of these pairs the experimental curve is below the straight line rather than above it, as is the case with the data shown in Fig. 1.

The refractive index is, of course, a function of the density of the liquid as well as of the constitution of the compound or compounds which com-

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[1] Adkins and Broderick, THIS JOURNAL, **50**, 178 (1928).

pose the liquid. The densities of all of the benzaldehyde-ethanol mixtures, of a single mixture of butyraldehyde-ethanol and of an anisaldehyde-ethanol mixture have been determined. These data have a relationship to the densities of the corresponding alcohols and aldehydes similar to that found to exist between the index of refraction of the mixtures and of the corresponding alcohol and aldehyde. However, the change in refractive index is not due solely to the change in density. This is evidenced by the fact that if one calculates the refractive index of a mixture of 74.4% anisaldehyde and 25.6% ethanol upon the assumption that these compounds are present as such, but that the mixture has the observed density of 1.0333, the value 1.51605 is obtained. The experimental value for this mixture is 1.50432, indicating that a constitutional change has taken place. However, in the case of butyraldehyde and ethanol, the change in refractive index parallels the density change. The molecular refraction based upon the observed indices of refraction of an equimolecular mixture of the alcohol and aldehyde was 33.24. The value calculated upon the assumption that the alcohol and aldehyde are present but have the observed density (0.8044) is 33.22. The calculated value for the molecular refraction of the hemiacetal is 32.92, the value 2.501 being taken for each carbon, 1.051 for each hydrogen, 1.521 for the hydroxyl oxygen and 1.603 for the ether oxygen.

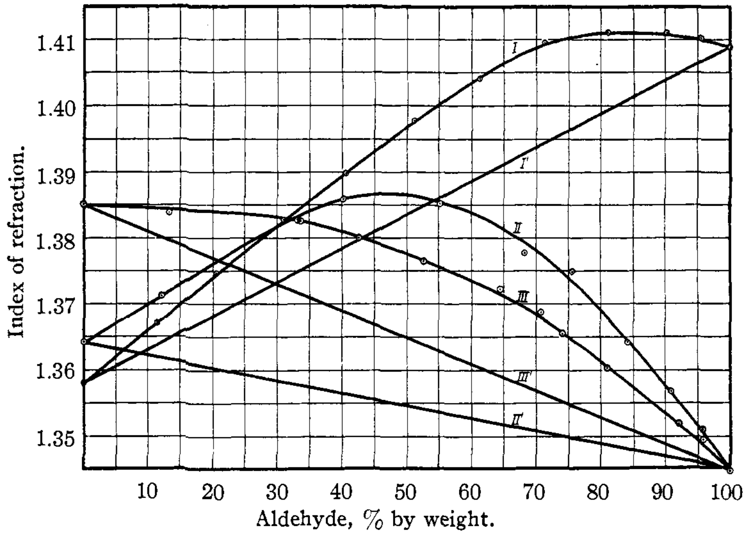

Fig. 1.—Refractive indices of mixtures of certain aldehydes and alcohols. The per cent. by weight of aldehyde in the mixture is plotted (abscissa) against the refractive index of the mixtures (ordinate). Curve I is for heptaldehyde and ethanol at 25°; Curve II, acetaldehyde and ethanol at 8°; Curve III, acetaldehyde and *iso*propanol at 8°. The straight lines show refractive indices of ideal solutions.

Success in detecting reaction between an alcohol and an aldehyde through determinations of the refractive indices of mixtures of the two is dependent upon whether or not the refractive index of the reaction product differs considerably from that of the ideal mixture. A small or even a total lack of difference of the constants from those of ideal mixtures does not prove that no reaction has taken place. It must also be kept in mind that two distinct questions may be asked with regard to the reaction under consideration. First, do certain aldehydes react with certain alcohols, and, second, how far to the right is the equilibrium point in those cases where reaction occurs? The first question is answered in the affirmative by the data for all nine of the pairs of compounds investigated. An answer to the second question can only be attempted in those cases where the observed values lie on a line having a *pronounced curvature.* This is true for only two or perhaps three of the seven complete sets of data, that is, for acetaldehyde-ethanol and heptaldehyde-ethanol and perhaps for acetaldehyde-*iso*propanol.

It should be emphasized that in a consideration of the experimental data from this point of view, the significant thing is not the point at which the refractive index is at a maximum but is the point at which there is the maximum *deviation* of the curve from the straight line representing the refractive indices of ideal solutions. For example the maximum deviation for heptaldehyde-*iso*propyl alcohol is for concentrations of between 60 and 70% heptaldehyde. These compounds are in molecular proportions when there is 65% heptaldehyde present. The maximum deviation for acetaldehyde-ethanol is for concentrations between 50 and 55% acetaldehyde. The equimolecular mixture contains 49% of acetaldehyde. The maximum deviation for acetaldehyde-*iso*propyl alcohol is almost constant over a wide range of concentrations from 35 to 60% aldehyde. The equimolecular mixture contains 42% of acetaldehyde. Thus it is seen that in the case of these three mixtures the maximum deviation of refractive indices from those of ideal solutions comes at approximately the concentration of reactants necessary for the formation of a hemiacetal, thus indicating that the equilibrium point of the reaction for these compounds is quite far to the hemiacetal side of the equation.

Summary

The refractive indices and densities of mixtures of several pairs of alcohols and aldehydes have been determined over the range from pure alcohol to pure aldehyde. All the data obtained indicate that chemical reactions took place and that, at least in some cases, one mole of alcohol and one mole of aldehyde reacted almost quantitatively to form what is presumably a hemiacetal.

MADISON, WISCONSIN