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DEPARTMENT OF CHEMISTRY
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Peroxide Formation in Propionaldehyde

BY F. E. MCKENNA,[1] E. C. LINGAFELTER AND H. V. TARTAR

During the purification of propionaldehyde for use in the study of hemiacetal formation,[2] it was found not possible to store a pure sample in the presence of air without absorption of oxygen and a simultaneous change in physical properties.

The propionaldehyde was Eastman White Label product with a boiling range of 47.8–50.5°. The fraction which distilled at 48.0 ± 0.05° (760 mm.) represented about 80% of the total material. During redistillation of such a fraction boiling 48.0 ± 0.05°, distillation began at 44.1°. When the temperature reached 46.0°, the boiling liquid frothed violently and the temperature rose abruptly to 48.0°; about 15% of the material had distilled between 44.1–46.0°.

Violent frothing of the propionaldehyde during distillation suggested the presence of peroxide. The several fractions were tested for the presence of peroxides by a spot test.[3] Fractions boiling below 48.0° gave dark red colorations with the indicator, while the fractions boiling at 48.0° or higher produced only a very light orange color. When the aldehyde was distilled and collected in a nitrogen atmosphere, no coloration was obtained with the peroxide indicator.

During each distillation, a light yellow oily substance, presumably a polymer, was formed. Buckler[4,5] reported sporadic spontaneous polymerization of his propionaldehyde samples. Polymerization may have been initiated by ozone or ultraviolet light from the occasional use of mercury lamps in his laboratory.

The refractive index for propionaldehyde has been reported to be n^{20}_{D} 1.3636.[6] When freshly distilled, propionaldehyde was found to have n^{25}_{D} 1.3601; this value increased rapidly over a period of minutes and then more slowly until a constant value of n^{25}_{D} 1.3630 was reached after twenty-four hours. The change in refractive index was found to be at least partially dependent on the previous treatment of the Pyrex flasks in which the aldehyde was collected. The effects of pre-treatment of the glass surfaces are indicated in Table I. Refractive indices were measured with an Abbe refractometer.

TABLE I

CHANGE IN REFRACTIVE INDEX OF PROPIONALDEHYDE WITH PREVIOUS TREATMENT OF THE GLASS CONTAINERS

Atmosphere	Treatment of glass containers	Period of time with constant $n = 1.3601$	Change[a] to $n = 1.3611$	Period of time with constant $n = 1.3611$	Change[a] to $n = 1.3630$
Air	No treatment	Immediate change from this value	45 min.	24 hr.	2–3 days
Air	Boiled out with water for 20 min.	35 min.	40 min.	27 hr.	10 days[b]
N_2	Boiled out with water for 20 min.	90 min.	After 3 hr., $n = 1.3603$ (no further measurements)		
Air	Boiled out with 6*N*-H_2SO_4 for 20 min.	Immediate change from this value	30 min.	45 min.	11 days[b]
Air	Boiled out with 6*N*-NaOH for 20 min.	5 min.	30 min.	40 min.	3 days[b]
Air	Super-heated steam (105–125°) for 20 min.	35 min.	55 min.	8 days	......[c]
		COLORATION OF PEROXIDE INDICATOR			
Air	No treatment	Light orange; constant shade	Gradual intensification of color	Red orange; constant shade	

[a] "Change" indicates the period of time during which the index changed from 1.3601 to 1.3611, or from 1.3611 to 1.3630. [b] The refractive index remained constant for nineteen days; no measurements were made after that period. [c] No further observations.

Change of refractive index and change in color of the peroxide indicator were simultaneously compared; a correlation between increase in refractive index and increase in peroxide content is evident from Table I. The change in refractive

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(1) Present address: Air Reduction Sales Company, Research Laboratories, Murray Hill, New Jersey.

(2) McKenna, Lingafelter and Tartar, THIS JOURNAL, **71**, 729 (1949).

(3) The presence of peroxides was detected by addition of a drop of a 10% ammonium thiocyanate solution (to which a crystal of ferrous ammonium sulfate, free of ferric, had been added) to a drop of the aldehyde. When peroxides are present, a red coloration is obtained whose intensity is roughly proportional to the peroxide content.

(4) Buckler, *J. Chem. Soc.*, 1036 (1937).

(5) Buckler, private communication.

(6) Brühl, *Ann.*, **200**, 139 (1880).

index must be at least partially due to peroxide formation.

As a result of the above observations, all propionaldehyde samples[2] were distilled and collected in a nitrogen atmosphere, and the Pyrex receivers were boiled out with water for twenty to thirty minutes and thoroughly dried in an oven. The boiling procedure may remove an adsorbed oxygen layer from the glass surface.

Carefully cleaned copper, zinc, aluminum, tin, and stainless steel surfaces showed reaction when immersed in the aldehyde. The evidence of reaction, surface corrosion, coloration of solution, and crystalline solids in the solution was less pronounced in the oxygen-free aldehyde samples than in those which gave positive peroxide tests. It has been assumed that these reactions were due to the formation of an acid.

During preliminary determinations of the density of propionaldehyde at $-64.2°$, it was observed that while the pycnometer was warming to room temperature, a relatively large volume of gas was evolved. A moderate quantity of a white solid, which melted near $-20°$, appeared to be the source of the gas bubbles. The pycnometer was closed with ground glass caps after filling, so continued absorption of oxygen from the atmosphere could not have occurred. When the pycnometer had been thoroughly flushed with dry nitrogen before it was filled with aldehyde, the solid and gas bubbles were not observed. The peroxide would be more stable at the lower temperatures and when warmed would decompose with liberation of oxygen.

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A Condensation Reaction of Thiols with Phenol Alcohols

BY I. W. RUDERMAN AND E. M. FETTES

We wish to report that thiols condense directly with phenol alcohols when treated with hydrogen chloride or boron trifluoride in the absence of water. This previously unrecorded reaction, which may be represented by the formula

$$o\text{- or } p\text{-(OH)RCH}_2\text{OH} + \text{R'SH} \longrightarrow \text{(OH)RCH}_2\text{SR'} + \text{H}_2\text{O}$$

where R is an aryl and R′ is an aryl or alkyl group, offers a convenient new synthesis of pure methylene thioethers of phenols in high yield. The preparation of such thioethers was recently reported[1] to be possible either through the reaction of a phenol, formaldehyde and a thiol (from which reaction it should be difficult to isolate a pure product because of isomer and polymer formation), or through the condensation of an o- or p-(dialkylaminomethyl)-phenol[2] with a thiol.

The synthesis of 2-hydroxy-α^1,α^3-bis-(butylmercapto)-mesitylene was accomplished as follows. One-half mole of 1-butanethiol and 0.05 mole of 2-hydroxy-α^1,α^3-mesitylenediol were dissolved in 125 ml. of glacial acetic acid, and dry hydrogen chloride gas was passed into the solution for two hours. The temperature rose seventeen degrees during the first fifteen minutes of the reaction, and then dropped gradually to room temperature. The reaction vessel was stoppered and set aside for two days. Water was added, and the oil which separated out was washed with water and then steam-distilled to remove unreacted thiol. A yellow oil remained, and it was distilled in a molecular still at a pressure of less than 1 micron. Ten and four-tenths grams (60% yield) of a clear, pale yellow liquid, $n^{20}\text{D}$ 1.5490, was collected when the pot temperature was 100-105°.

Anal. Calcd. for $C_{17}H_{28}OS_2$: C, 65.33; H, 9.03; S, 20.52. Found: C, 65.40; H, 9.00; S, 20.46.

The phenyl urethan derivative was prepared according to the method of Shriner and Fuson[3]; colorless crystals, m. p. 92.8-93.2°, were obtained after one recrystallization from petroleum ether-chloroform.

Anal. Calcd. for $C_{24}H_{33}NO_2S_2$: C, 66.78; H, 7.71; N, 3.25; S, 14.86. Found: C, 67.04; H, 7.67; N, 3.34; S, 15.43.

By analogy with the condensation of phenols with phenol alcohols under similar conditions,[4] the condensation of phenol di- or trialcohols with polythiols should yield polymers.

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[1] R. F. McCleary and S. M. Roberts, U. S. Patent 2,322,376, June 22, 1943. No preparation of a *pure* thioether is given.

[2] H. A. Bruson and C. W. MacMullen, THIS JOURNAL, **63**, 270 (1941).

[3] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1940, p. 136.

[4] J. B. Niederl and I. W. Ruderman, THIS JOURNAL, **67**, 1176 (1945).

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A Counter-Current Distribution System for the Separation and Determination of Streptomycin Types

BY G. W. E. PLAUT[1] AND R. B. MCCORMACK

As a means of extraction and purification of streptomycin, it was found that a 5% stearic acid solution in Pentasol[2] would extract streptomycin from an aqueous concentrate at pH 9. However, when a double extraction was made with this system, the distribution coefficient of this second extraction was appreciably lower than the first (Table I). The streptomycin content was determined by conversion to maltol.[3]

These observations indicated mixtures of streptomycin types in our original solution. A method of separation of these types into pure preparations or for analysis using counter-current procedures was suggested by these data.

For analytical purposes, applying the Craig counter-current technique,[4] the distribution co-

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[1] Present address: Dept. of Biochemistry, Univ. of Wisconsin, Madison, Wisconsin.

[2] A mixture of synthetic amyl alcohols made by Sharples Chemicals, Inc.

[3] J. R. Schenck and M. A. Spielman, THIS JOURNAL, **67**, 2276 (1945).

[4] L. C. Craig, *J. Biol. Chem.*, **155**, 519 (1944).