the other from the hydrogen bound directly to carbon.

3. The quantum yield of the decomposition of ethyl alcohol is 0.8.

4. Isopropyl alcohol is decomposed according to

$$CH_3CH(OH)CH_3 \longrightarrow CH_3COCH_3 + H_2 \qquad (2)$$

the acetone being decomposed in a subsequent reaction.

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[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

On the Photochemical Decomposition of Aliphatic Aldehydes in Aqueous Solutions

BY Y. HIRSHBERG AND L. FARKAS

The photochemical decomposition of the aliphatic aldehydes in the gaseous state has been investigated thoroughly in the last few years.[1-5] It was found that under the influence of ultraviolet light absorbed below 3000 Å. the aldehydes are decomposed mainly according to

$$RCHO + h\nu \longrightarrow RH + CO \qquad (1)$$

yielding hydrocarbon and carbon monoxide (in the case of formaldehyde $CO + H_2$) as main products. Only a few per cent. of hydrogen and RR hydrocarbon is formed. The reactions

$$RCHO + h\nu \begin{array}{l} \nearrow RH + CO \qquad (1a) \\ \searrow R + H + CO \qquad (1b) \end{array}$$

were suggested as primary processes, (1a) being the more probable one. Reaction (1b) gives RH, H_2 and R–R in secondary reactions and is practically equivalent to another possible primary reaction

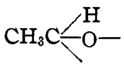
$$RCHO + h\nu \longrightarrow R + HCO \qquad (1c)$$

which gives in secondary reactions also $RH + H_2 + RR$; RH is the main product if the primary process is followed preferentially by the bimolecular reaction

$$R + HCO \longrightarrow RH + CO$$

Beside these reactions a polymerization was observed to some extent.[4-6] The formation of radicals as expressed in (1b) and (1c) by light absorption of the aldehydes follows from the experiments of Leermakers,[7] Akeroyd and Norrish[8] and Patat,[9,10] from the investigation of the thermal and photochemical autoxidation of the aldehydes. Leermakers and Akeroyd and Norrish found that above 80° the photolysis of acetaldehyde is a chain reaction and some radicals which are formed by the photochemical primary process initiate the chains. The formation of H atoms in the continuous absorption spectrum of formaldehyde was shown directly by Patat: the H atoms formed by the photochemical decomposition induce a para–ortho conversion of hydrogen which is added to the formaldehyde.

The thermal oxidation of acetaldehyde is also a chain reaction, in which, according to Bodenstein,[11] aldehyde molecules with unsaturated valences such as



$$CH_3C\begin{array}{l} \diagup H \\ \leftarrow O- \\ \diagdown \end{array}$$

initiate and carry the chain. Bowen and Tietz[12] and recently Carruthers and Norrish[13] investigated the photochemical oxidation of formaldehyde and acetaldehyde and found that light absorption in the presence of oxygen leads to chains similar to those of the thermal oxidation with an approximate chain length of 20. In the case of acetaldehyde the same sort of reaction occurs in gaseous state, in the pure liquid and in solutions of water, hexane and acetic acid. These experiments show not only that the light absorption of aldehydes must give a reactive compound or reactive radicals, but also indicate that in liquid and in solution intermediate products with long life-time are involved. In the case of benzaldehyde Baeckstroem[14,15] showed that the primary product of the

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[1] F. W. Kirkbridge and R. W. C. Norrish, *Trans. Faraday Soc.*, **27**, 404 (1931).

[2] F. W. Kirkbridge and R. W. C. Norrish, *ibid.*, **29**, 103 (1933).

[3] F. W. Kirkbridge and R. W. C. Norrish, *J. Chem. Soc.*, 1518 (1932).

[4] P. A. Leighton and F. E. Blacet, THIS JOURNAL, **54**, 3165 (1932).

[5] P. A. Leighton and F. E. Blacet, *ibid.*, **55**, 1766 (1933).

[6] J. E. Carruthers and R. G. W. Norrish, *Trans. Faraday Soc.*, **32**, 195 (1936).

[7] J. A. Leermakers, THIS JOURNAL, **56**, 1537 (1934).

[8] E. I. Akeroyd and R. G. W. Norrish, *J. Chem. Soc.*, 890 (1936).

[9] F. Patat, *Z. physik. Chem.*, **B25**, 208 (1934).

[10] F. Patat and T. Locker, *ibid.*, **B27**, 431 (1934).

[11] Bodenstein, *Berliner Ber.*, **111**, 18 (1931).

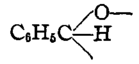
[12] E. J. Bowen and E. L. Tietz, *J. Chem. Soc.*, 234 (1930).

[13] J. E. Carruthers and R. G. W. Norrish, *ibid.*, 1036 (1936).

[14] Baeckstroem, *Z. physik. Chem.*, **B25**, 99 (1934).

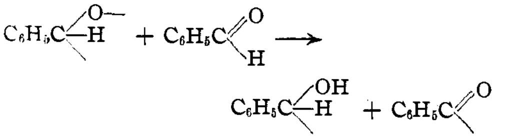
[15] *Cf.* Bonhoeffer, *Z. Elektrochem.*, **40**, 425 (1934).

light absorption is a benzaldehyde molecule with free valences



$$C_6H_5C\begin{array}{l}\diagup O- \\ -H \\ \diagdown\end{array}$$

which reacts with an ordinary aldehyde molecule according to



$$C_6H_5C\begin{array}{l}\diagup O- \\ -H \\ \diagdown\end{array} + C_6H_5C\begin{array}{l}\diagup O \\ \diagdown H\end{array} \longrightarrow C_6H_5C\begin{array}{l}\diagup OH \\ -H \\ \diagdown\end{array} + C_6H_5C\begin{array}{l}\diagup O \\ \diagdown\end{array} \qquad (2)$$

It seemed interesting to investigate the photochemical decomposition of aliphatic aldehyde in solution, in order to obtain some information about the primary products formed. As mentioned in the preceding paper[16] the photochemical decomposition of aldehydes in aqueous solution is distinctly different from that in the gaseous state, indicating that different primary processes are involved in solutions and in the gaseous state.

The following aliphatic aldehydes in aqueous solution were investigated: acetaldehyde, crotonaldehyde, acetaldol, propionaldehyde and formaldehyde.

The experimental technique was the same as in the preceding paper and the same mercury arc was used.[16] The aldehyde solutions were prepared from freshly distilled aldehyde and the concentration was determined before and after the illumination according to standard methods.

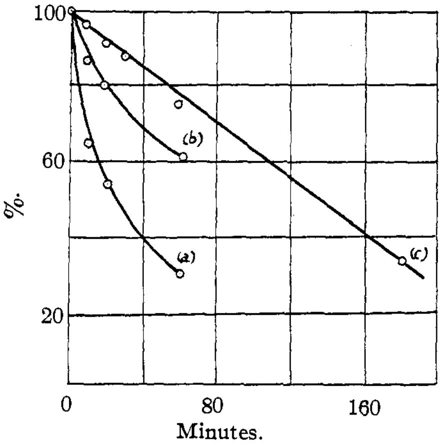


Fig. 1.—Acetaldehyde: (a), 0.05 *m;* (b), 0.135 *m;* (c), 0.5 *m*.

Experiments with Acetaldehyde

On illuminating acetaldehyde solution with the full light of the mercury arc the concentration of the aldehyde diminished rapidly. The intensity of the mercury arc was about the same in all these experiments and was measured by the photolysis of monochloroacetic acid. The quantum output was 4 × 10^{18} quanta per second according to this method. Of course the intensity of light active in the aldehyde reaction is not the same as in the photolysis of monochloroacetic acid, since acetaldehyde absorbs also in the region 3100–2600 Å. where the monochloroacetic acid does not.

TABLE I

Volume of the reaction vessel 200 cc.

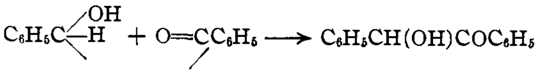
Time of illumination, min.	Aldehyde present in the solution in moles		
0	1.00×10^{-2}	2.10×10^{-2}	10.0×10^{-2}
10	0.65×10^{-2}	2.34×10^{-2}	9.7×10^{-2}
20	$.55 \times 10^{-2}$	2.20×10^{-2}	9.2×10^{-2}
30	$.45 \times 10^{-2}$		8.8×10^{-2}
60	$.30 \times 10^{-2}$	1.64×10^{-2}	7.5×10^{-2}
180			3.4×10^{-2}

In Fig. 1 the relative amounts of decomposed aldehyde are plotted at different concentrations. It will be seen that the decomposition is linearly dependent on the time, if the solution is concentrated enough. In this case the absorption of the active light is complete during the illumination, whereas such is not the case in the more dilute solutions.

During an illumination of one to three hours acetaldehyde solution did not evolve any gas and remained clear. In some experiments the change of acidity also was determined. It was found that during the illumination only a small amount of acid was formed, which did not correspond to more than 5% of the photochemically decomposed aldehyde. Thus it seemed that the formation of the acid was a side reaction, but it was still possible that the acetaldehyde underwent a photochemical Cannizzaro reaction and this reaction was responsible for the formation of acid, the main product being ethyl acetate. In order to test this possibility the illuminated solution was boiled with alkali (in nitrogen atmosphere) and distilled, but no appreciable amount of sodium acetate was found.

Another possible decomposition reaction was the formation of paraacetaldehyde. Although blind experiments showed that 0.3–0.5 molar aqueous solutions of paraacetaldehyde did not decompose in the dark or on illumination with ultraviolet light, it is certain that no appreciable amount of it is formed from acetaldehyde under the present conditions. After addition of sulfuric acid and distillation, the illuminated acetaldehyde solution had the same aldehyde content as before, whereas paraacetaldehyde added to acetaldehyde solutions was decomposed completely to acetaldehyde under the same conditions.[17] In view of these observations and the above-mentioned investigations on the thermal and photochemical oxidation of aldehydes, one had to look for other liquid or soluble reaction products.

Illuminating pure benzaldehyde Baeckstroem[14] found benzoin as the main product, formed according to



$$C_6H_5C\begin{array}{l}\diagup OH \\ -H \\ \diagdown\end{array} + O{=}\underset{\diagup}{C}C_6H_5 \longrightarrow C_6H_5CH(OH)COC_6H_5 \qquad (3)$$

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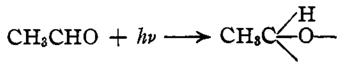
(16) L. Farkas and Y. Hirshberg, THIS JOURNAL, **59**, 2450 (1937).

(17) K. J. P. Orton and Ph. V. McKie, *J. Chem. Soc.*, **109**, 184 (1916).

The radicals figuring here are formed according to the reaction (2).

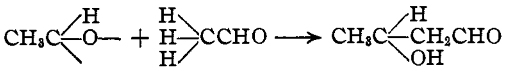
In analogy to this reaction one would expect the formation of acetoin $CH_3CH(OH)COCH_3$, of diacetyl and of butylene glycol, in the case of acetaldehyde. The quantitative estimation of these three substances carried out according to Kniphorst and Kruisher[18] yielded only traces of acetoin and none of the other two substances. Thus the main product of the decomposition of acetaldehyde is of a different type than that of benzaldehyde.

If we assume that the primary reaction in solution is



$$\mathrm{CH_3CHO} + h\nu \longrightarrow \mathrm{CH_3}\overset{\diagup\mathrm{H}}{\underset{\diagdown}{\mathrm{C}}}\mathrm{-O-} \qquad (4)$$

there is also a possibility for the formation of aldol according to



$$\mathrm{CH_3}\overset{\diagup\mathrm{H}}{\underset{\diagdown}{\mathrm{C}}}\mathrm{-O-} + \mathrm{H}\overset{\mathrm{H}\diagdown}{\underset{\mathrm{H}\diagup}{-}}\mathrm{CCHO} \longrightarrow \mathrm{CH_3}\overset{\diagup\mathrm{H}}{\underset{\diagdown\mathrm{OH}}{\mathrm{C}}}\mathrm{-CH_2CHO} \qquad (5)$$

The formation of acetaldol is the more probable, since acetaldehyde is to a great extent hydratized in aqueous solution, and thus it cannot react according to (2) and (3).

Since there are no direct methods of determining acetaldol in the presence of acetaldehyde, its determination was carried out in the following way: the greatest part of acetaldehyde of the illuminated solution was evaporated together with water in a nitrogen atmosphere at 50–60°. Most of the condensation products and some acetaldehyde remained in the residue, and they were precipitated with *p*-nitrophenylhydrazone in acetic acid solution. The precipitated crystals were fractionated from hot water and the most soluble fraction proved to be the *p*-nitrophenylhydrazone of crotonaldehyde, since it had a melting point of 187° in agreement with the value given in the literature. The precipitation of crotonaldehyde from the illuminated solution does not prove, however, that crotonaldehyde is formed primarily. If a diluted solution of acetaldol or a mixture of acetaldehyde and acetaldol was treated in the same way as the illuminated solution, we obtained the *p*-nitrophenylhydrazone of crotonaldehyde. Apparently in the presence of the acetic acid aldol splits off a water molecule and crotonaldehyde is formed.

In order to establish whether acetaldol or crotonaldehyde are formed primarily we illuminated aqueous solutions of crotonaldehyde, acetaldol and mixtures of them with acetaldehyde.

TABLE II

115 cc. of crotonaldehyde solution illuminated for 30 min.

Concn., M	Amount decomposed, moles	% decomposed
0.25	7×10^{-4}	2.4
.05	4×10^{-4}	6.9
.025	3×10^{-4}	10.2

TABLE III

115 cc. of acetaldol solution illuminated for 60 min.

Concn., M	Amount decomposed, moles	% decomposed
0.141	2.8×10^{-3}	17.3
.070	3.0×10^{-3}	37.2
.057	1.9×10^{-3}	29.0

Tables II and III contain the data of the experiments with crotonaldehyde and acetaldol.[19]

On illumination these two solutions behave differently: (a) crotonaldehyde is decomposed under our conditions much more slowly than acetaldol;[20] (b) after a few minutes of illumination insoluble solid condensation products are formed in the crotonaldehyde solution, whereas the acetaldol solution remains completely clear during the experiment. The same was found with mixtures of acetaldehyde with crotonaldehyde and acetaldol, respectively. Crotonaldehyde gave also in this case insoluble reaction products on illumination; the mixture of acetaldehyde and acetaldol could be decomposed to 60% and more without any formation of insoluble compounds.

We can conclude, thus, that the photochemical decomposition of acetaldehyde gives primarily acetaldol, which subsequently decomposed yields also water-soluble reaction products. This conclusion is further supported by the observation that concentrated (1 normal) acetaldehyde solutions are decomposed at nearly the same rate at the beginning of the illumination as later, when 50% is already decomposed (see Fig. 1). Such a solution must contain commensurable amounts of acetaldehyde and the reaction product, and could only be decomposed further at a nearly constant rate of acetaldehyde and the reaction product are decomposed at similar rates. This is true for acetaldol, but not for crotonaldehyde (see Fig. 2).

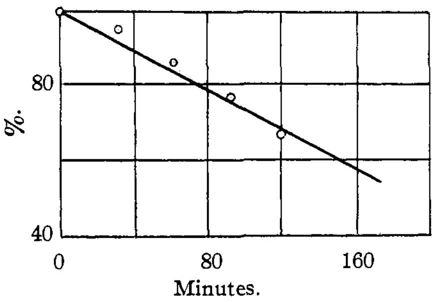


Fig. 2.—0.54 *m* acetaldol.

Since from two molecules of acetaldehyde one molecule of acetaldol is formed, the actual amount of acetaldehyde transformed is twice the amount of aldehyde which apparently disappears. (Acetaldol can be determined by titration with sodium bisulfite and iodine.) An exact estimation of the acetaldol formed during the illumination could not be carried out. Weighing the purified *p*-nitrophenylhydrazone of crotonaldehyde, which was precipitated in presence of acetic acid, gave nearly the same amount as expected from the disappearance of aldehyde estimated by titration.

It was interesting to determine the quantum yield of the acetaldehyde decomposition, since its photochemical oxidation is a chain reaction. The method of filtering the photochemically active light with a solution of mono-

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(18) L. C. E. Kniphorst and C. L. Kruisher, *Z. Untersuch. Lebensm.*, **73**, 1 (1937).

(19) Acetaldol was prepared according to C. Neuberg and E. Kerb, *Biochem. Z.*, **92**, 108 (1918).

(20) Also in gaseous state crotonaldehyde is very stable in ultraviolet light; see Blacet and Roof, THIS JOURNAL, **58**, 73 (1936).

chloroacetic acid was employed[21] and from the known quantum yield of its photolysis the quantum yield of the acetaldehyde decomposition determined. Table IV contains the data of two experiments on the estimation of the quantum yield.

TABLE IV

Time of illumination, 30 min.

Reaction vessel I	Reaction vessel II	Aldehyde disappeared, moles	Cl-ions formed, moles	Quantum yield
H_2O	0.8 *m* CH_3CHO	0.025	...	2.4
1 *m* $ClCH_2COOH$	.8 *m* CH_3CHO	.011	0.012	
H_2O	.75 *m* CH_3CHO	.029	...	2.7
1 *m* $ClCH_2COOH$	.75 *m* CH_3CHO	.009	.014	

The quantum yield 2.4–2.7 was calculated on the basis that the quantum yield of the monochloroacetic acid decomposition is 0.9,[21] and that from two aldehyde molecules one acetaldol is formed. From these figures it is clear that the acetaldehyde radical formed by the light absorption must have a comparatively long lifetime and it is not deactivated by collisions with the molecules of the solvent.

On the basis of reactions (4) and (5) one would expect the quantum yield 2. The experimental value is larger probably owing to errors which are generally great in such measurements.

The Decomposition of Propionaldehyde

The photochemical reactions in the solution of propionaldehyde are similar to those of acetaldehyde. Table V contains the results of a series of experiments.

TABLE V

200 cc. of a 1.5 molar solution of propionaldehyde

Time of illumination, min.	Aldehyde disappeared, mole	Acid formed, mole
5	0.0080	0.0009
15	.0186	.0013
30	.0330	.0016
60	.0630	.0041

Again the condensation of the aldehyde is the main photochemical reaction. The amount of aldehyde decomposed is not proportional to the time, at the beginning of the illumination the rate of decomposition being much greater than later. This is mainly due to the formation of insoluble substances, in consequence of which the intensity of the light is considerably diminished. For instance, after fifteen minutes of illumination a one molar propionaldehyde solution became opaque and when extracted with ether gave about 1 g. of an oil of aldehyde character. Although this amount of condensation product is only 30% of the theoretical yield, it seems that the reaction occurring here is analogous to that of acetaldehyde. Further analysis of the product of illumination has not yet been carried out.

Two other reactions also were observed: the formation of acid and the evolution of some gas during the illumination. The extent of the formation of acid can be seen from Table V. It is 5–10% of the main reaction. The amount of gas evolved was of the same order of magnitude and contained 20–25% carbon monoxide, 25% ethane and about 50% hydrogen. Both reactions are evidently side reactions; at present it is difficult to tell their mechanism.

The quantum yield of the decomposition was determined in the same way as in the case of acetaldehyde. Two experiments on the quantum yield of the propionaldehyde decomposition are listed in Table VI.[21] It may be seen that the quantum yield is approximately 2, which suggests a mechanism similar to that for the decomposition of acetaldehyde. It shows also that the activated propionaldehyde molecule is comparatively stable and is not deactivated by the solvent.

TABLE VI

Time of illumination, 30 min. Reaction vessel II containing 1 molar propionaldehyde.

In reaction vessel I	Aldehyde disappeared, mole	Chlor ions formed, mole	Quantum yield
H_2O	0.0170	....	1.9
$ClCH_2COOH$	.0056	0.0117	
H_2O	.0016	....	1.7
$ClCH_2COOH$	.0006	.0110	

Experiments with Formaldehyde

Table VII refers to experiments on the illumination of formaldehyde.

TABLE VII

200 cc. of 1 Molar Formaldehyde Solution

Time of illumination, min.	Aldehyde disappeared, mole	Acid formed, mole
120	3.5×10^{-3}	3.0×10^{-3}
180	9.0×10^{-3}	4.4×10^{-3}
300	23.0×10^{-3}	6.1×10^{-3}

Although the light intensity measured by the decomposition of monochloroacetic acid was about the same as in the previous experiments, the decomposition of the formaldehyde was one-fortieth as fast as that of acetaldehyde or propionaldehyde. The rate of decomposition in 0.02 to 10 molar solutions of formaldehyde was about the same.

This small rate of decomposition is due to the fact that formaldehyde solutions absorb only below 2350 Å.[22] and consequently are exposed to much less intense light than other aldehydes, which absorb all light below 3000 Å. The true rate of decomposition will be seen from Table VIII showing the quantum yields of the decomposition.

TABLE VIII

Reaction vessel II containing 1 molar monochloroacetic acid.

Time of illumination, min.	Vessel I containing	Aldehyde decomposed, mole	Chlor ions formed in vessel II, mole	Quantum yield
60	H_2O	....	0.0179	0.5
120	CH_2O	0.0063	2×0.0109	
30	H_2O	....	0.0112	.7
180	CH_2O	.0150	6×0.0073	
180	CH_2O	.0130	6×0.0103	.5
30	H_2O	....	0.0151	
30	H_2O	....	.0120	.5
180	CH_2O	.0138	.0311	

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[21] L. Farkas, *Z. physik. Chem.*, **B23**, 89 (1933). It was proved that in our arrangement all light below 2600 Å. was absorbed by acetaldehyde (propionaldehyde).

[22] Henry and Schou, *Z. Physik*, **49**, 774 (1928).

Since the absorption region of monochloroacetic acid reaches to longer waves than that of formaldehyde, in these experiments, the formaldehyde solution was illuminated in the reaction vessel I. It was proved that in the short wave region both monochloroacetic acid and formaldehyde absorbed completely in our arrangement all the emitted light.

In some of the experiments in Table VIII the decomposition of the monochloroacetic acid was calculated from the decomposition observed in thirty or sixty minutes in order to avoid inaccuracy due to the formation and light absorption of larger amounts of glycolic acid. The quantum yield in column 5 of Table VIII is the number of aldehyde groups disappearing per absorbed quanta. It is not yet possible to tell the mechanism of the decomposition. Since the amount of aldehyde disappearing and the amount of acid formed are of the same order of magnitude, it seems that in this case the formation of acid is one of the main reactions. According to Pribram and Franke[23] formic acid is one of the reaction products, beside the formation of glycolaldehyde.[24,25]

Although the formation of glycolaldehyde would suggest that the primary process is also in this case the formation of formaldehyde molecules with free valences, still further investigation of the photochemical reactions in the formaldehyde solution seems necessary. The distinct shift of the absorption spectra to short wave lengths in aqueous solution and the formation of acid make equally probable that in formaldehyde solution the primary process and the secondary reactions are of another type than those which we discussed for acetaldehyde and propionaldehyde.

A detailed investigation of the photochemistry of formaldehyde in monochromatic light and different solutions is planned.

Summary

1. The photochemical decomposition of formaldehyde, acetaldehyde, acetaldol, crotonaldehyde and of propionaldehyde has been investigated in aqueous solutions in the unfiltered light of a mercury arc.

2. The quantum yield, *i. e.*, the number of aldehyde molecules disappearing per absorbed quantum, is 0.5 for formaldehyde, 2.5 for acetaldehyde, 1.8 for propionaldehyde and very much smaller than unity for crotonaldehyde.

3. In the photolysis of acetaldehyde acetaldol is formed according to $2CH_3CHO = CH_3CH(OH)CH_2O$. It is suggested that the formation of an aldehyde molecule with free valences is the photochemical primary process.

4. When acetaldol is illuminated the reaction products formed are soluble in water, whereas from crotonaldehyde insoluble products are formed. In the photolysis of propionaldehyde and formaldehyde some acid is formed.

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[23] Pribram and Franke, *Ber.*, **44**, 1035 (1911).

[24] *Cf.* C. Neuberg, *ibid.*, **33**, 3207 (1900).

[25] *Cf.* Fischer and Landsheimer, *ibid.*, **25**, 2552 (1892).

[CONTRIBUTION FROM THE FLEISCHMANN LABORATORIES, STANDARD BRANDS INCORPORATED]

A Fermentation Test for Vitamin B. II

BY ALFRED S. SCHULTZ, LAWRENCE ATKIN AND CHARLES N. FREY

Introduction

It has long been known that certain naturally occurring substances cause a stimulation in the rate of alcoholic fermentation by yeast.[1] As recently reported,[2] we have discovered that crystalline vitamin B_1 and the synthetic product are powerful accelerators of fermentation. The importance of this accelerating action on the rate of fermentation was recognized immediately and an attempt made to devise a rapid method of vitamin assay. The short time required to carry out an assay makes the method a valuable tool to both research and industry.

We have accepted the terminology suggested at the Chapel Hill meeting (1937) and henceforth give the name thiamine to vitamin B_1.

Apparatus and Methods

The rate of fermentation is measured by the amount of gas evolved in a given time interval. The thermostat, shaker and gasometer system has been described.[3] To make a run we line up our six reaction bottles and place in them all the ingredients of the final reaction mixture except the yeast suspension. When all is ready, the yeast suspension is added to each by a fast pipet, the stoppers fixed in place, the bottles placed in the shaking cradle and connection promptly made to the gasometers. After two or three minutes have elapsed for temperature equilibration we make our initial or "zero" reading. This whole starting procedure is so timed as to give the same time interval (approximately four minutes) from the addition of the yeast to the "zero" reading.

In our preliminary work the reaction mixture was simply composed of yeast, sugar, ammonium phosphate buffer and distilled water. We now prefer to add a mixture of inorganic salts to the above so that no question of salt deficiency may interfere. The following standard control

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[1] Euler and Swartz, *Z. physiol. Chem.*, **140**, 146 (1924).

[2] Schultz, Atkin and Frey, THIS JOURNAL, **59**, 948 (1937).

[3] Schultz and Landis, *ibid.*, **54**, 211 (1932).