The conversion was practically quantitative. The pure product melted at 114° (uncor.).

Anal. Calcd. for $C_{25}H_{32}O_2$: C, 82.42; H, 8.79. Found: C, 82.48; H, 8.92.

Tetra-nitro Derivative.—About 1 g. of the crystals was dissolved in an excess of concentrated nitric acid in an Erlenmeyer flask, warmed on a steam-bath until no more fumes were given off, and then the flask was heated directly with a small Bunsen flame until a clear solution had resulted. Water was added to the cold solution, precipitating a yellow crystalline mass, which was filtered and recrystallized from 95% ethyl alcohol. The yellow crystals melted between 246–248° (uncor.). They were not analyzed, but a mixed melting point determination showed them to be identical with those obtained from the phorone–*m*-ethylphenol condensation product.

Phorone-*m*-Ethylphenol

4,4,4',4'-Tetramethyl-7,7'-di-ethyl-bis-2,2'-spirochroman.—Three-tenths of a mole (46 g.) of phorone and 0.6 mole (82 g.) of *m*-ethylphenol were placed in a 1-liter 3-neck round-bottomed flask and dry hydrogen chloride gas was passed into the reaction mixture for six hours, the flask was stoppered tightly and allowed to stand at room temperature for one week. An excess of Claisen solution was added, precipitating a brown gelatinous mass which was filtered through a large fluted filter. The residue was washed with distilled water and dissolved in hot 50% ethyl alcohol, and on cooling white plates crystallized out. These crystals could also be obtained, though not so readily, from 95% ethyl alcohol. The crystals are insoluble in Claisen solution and melt at 146° (uncor.).

Anal. Calcd. for $C_{25}H_{32}O_2$: C, 82.42; H, 8.79. Found: C, 82.43; H, 8.68.

Tetra-nitro Derivative.—One gram of the spirochroman was heated on the water-bath in an Erlenmeyer flask with an excess of concentrated nitric acid till no more brown fumes were evolved, then heated directly with a small Bunsen flame until a clear solution resulted. On cooling, yellow needles separated, which were filtered off on a sintered glass filter funnel, and recrystallized from 95% ethyl alcohol. The melting point was 246–248° (uncor.). A mixed melting point with the nitro compound prepared from the acetone condensation product produced no depression.

Anal. Calcd. for $C_{25}H_{28}O_{10}N_4$: C, 55.15; H, 5.15. Found: C, 54.96; H, 5.13.

Summary

The condensation of acetone with meta alkylated phenols was extended to include *m*-ethylphenol. Experimental results were obtained which are in full harmony with previously advanced postulations.

WASHINGTON SQUARE COLLEGE
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[CONTRIBUTION FROM THE WILLIAM ALBERT NOYES LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

Change of the Ultraviolet Absorption Spectrum of Acrolein with Time

BY A. M. BUSWELL, E. C. DUNLOP, W. H. RODEBUSH AND J. B. SWARTZ

During a study of the ultraviolet absorption spectra of solutions of pure organic compounds, we observed that in the case of acrolein the data were sometimes inconsistent. In one case a solution of a given strength showed less absorption than a solution of half the concentration had shown in a previous test. A check of the records showed that the weaker solution had been examined when freshly prepared, while the stronger solution was a few days old when its absorption was determined. This suggested a systematic study of the change of the absorption spectrum of acrolein with time to determine whether this effect was due to polymerization or some other reaction.

There are several articles in the literature[1] discussing the absorption spectrum of acrolein in the vapor phase, and in solution in alcohol, water and other solvents. They report a weak absorption band at about 3200 Å. and a very strong one extending from a sharp limit at 2500 Å. toward shorter wave lengths. There are no data showing what happens to the spectra of these solutions over a period of time. This point has been investigated and is reported herewith.

Experimental

The instrument used was a Bausch and Lomb medium quartz spectrograph with a sectorphotometer. The light source was a condensed iron-tungsten alloy spark. The cells were of glass with quartz windows and were 5.14 cm. in length.

The data were read from the plates by visual comparison using a hand lens to find the matched lines. The percentage transmission was known from the sector setting and the molecular extinction coefficient was calculated from the Lam-

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[1] (a) Blacet, Young and Roof, THIS JOURNAL, **59**, 608 (1937); (b) Eastwood and Snow, *Proc. Roy. Soc.* (London), **A149**, 446 (1935); (c) Thompson and Linnett, *Nature*, **134**, 937 (1934); (d) Purvis, *J. Chem. Soc.*, **127**, 9 (1925); (e) Henri, *Compt. rend.*, **199**, 849 (1934); **178**, 844 (1924); (f) Luthy, *Z. physik. Chem.*, **107**, 284 (1923); (g) Purvis and McClelland, *J. Chem. Soc.*, **103**, 433 (1913); (h) Bielecki and Henri, *Ber.*, **46**, 3627 (1913).

bert–Beer equation $I = I_0\, 10^{-\epsilon c d}$ where $I_0 = 100$, I = relative per cent. of light transmitted, ϵ = molecular extension coefficient, c = concentration (molar), and d = length of the path of the absorbing media in centimeters.

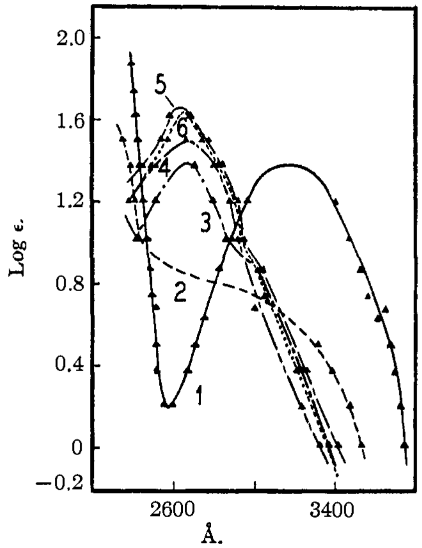

Fig. 1.—Acrolein in 50% ethyl alcohol solution: (1) immediately after making up solution; (2) after 7 days; (3) after 14 days; (4) after 21 days; (5) after 40 days; (6) after 60 days.

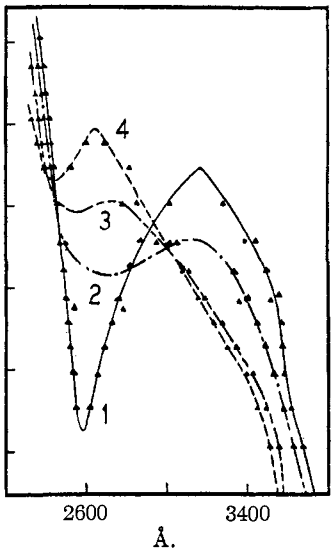

Fig. 2.—Acrolein in water: (1) immediately after making solution; (2) after 14 days; (3) after 30 days; (4) after 49 days.

The acrolein was purified and freshly distilled portions were used in making up all the solutions. The following solutions were made and tested: three solutions in 50% ethyl alcohol containing 1, 0.1 and 0.05 g. of acrolein per liter, respectively; two solutions in doubly distilled water containing 1 and 0.1 g. of acrolein per liter; and three solutions in doubly distilled water each containing 0.1 g. of acrolein per liter. To one of these last solutions a little hydroquinone was added, to another a little tannic acid and the third solution contained only acrolein and solvent. The ultraviolet absorption of each of the solutions was determined immediately after they were prepared. The solutions were then stored in glass-stoppered volumetric flasks and exposed to the diffuse light and temperature of the laboratory. Absorption tests were repeated at seven-day intervals on each of these solutions for periods up to eight weeks. In each test a small portion of the solution was removed, used for the absorption determination, and then discarded.

From the curves, Figs. 1, 2 and 3, it is seen that a definite change has taken place in the period of time indicated. In the original curves the bands correspond to those reported by Luthy[1f] and verified by others. The broad band at 3200 Å. has been assigned as due to the carbonyl and the very intense band extending from 2590 Å. toward the shorter wave length as due to the ethylenic group. There has been no mention of the band at 2670 Å. which appears after a few days. As the age of the solution increased the band at 3200 Å. disappeared and the band at 2670 Å. appeared and increased up to a time of forty days. The shoulder of the peak toward the shorter wave length also is found to diminish with increasing time.

Discussion

The new band at 2670 Å. is due to some reaction that the acrolein has undergone. This new band cannot be due to an acetal form since the same results occur in both alcoholic and water solutions (Figs. 1 and 2). It has been reported by Herold and Wolf[2] that the formation of hemiacetals can be shown by the ultraviolet absorption spectra. We also have shown that this is true for propion-

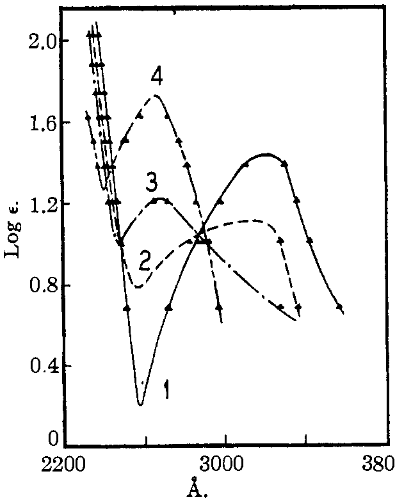

Fig. 3.—Acrolein in water: (1) immediately after making solution; (2) after 7 days; (3) after 14 days; (4) after 38 days. This solution was kept under identical conditions as those for Figs. 6 and 7.

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[2] Herold and Wolf, *Z. physik. Chem.*, **18**, 165 (1931).

aldehyde, Fig. 4, where a water solution of the propionaldehyde remained unchanged for forty-two days while in an alcohol solution the absorption of the carbonyl was gradually decreased with time. The absorption of acetal in water solution was determined and is shown in Fig. 5. From these data it is shown definitely that the acrolein does not form the hemiacetal.

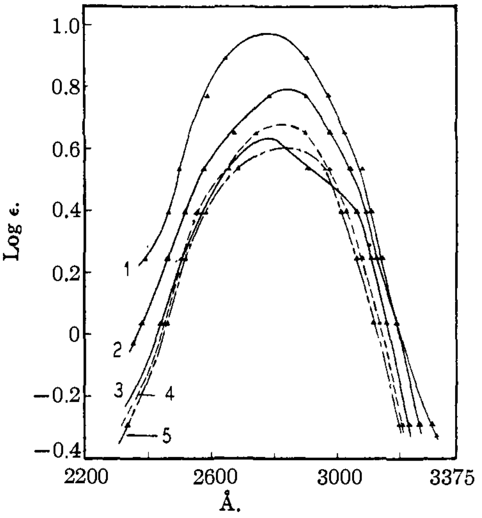


Fig. 4.—Propionaldehyde: (1) water solution remained unchanged for 42 days; (2) 50% ethyl alcohol solution immediately after making solution; (3) the alcohol solution after 9 days; (4) the alcohol solution after 16 days; (5) the alcohol solution after 42 days.

Paraldehyde has been reported as having no bands above 2500 Å. and we have verified this, Fig. 5. Comparing these data with the data for acrolein it is seen that the paraldehyde structure gives no absorption above 2500 Å. while in the aged acrolein solutions there was absorption at 2670 Å. Moreover, the aged solutions gave positive tests with fuchsin-aldehyde reagent and Tollens' reagent, thus indicating the presence of the aldehyde group. The solutions also gave a positive test with 2,4-dinitro-phenylhydrazine reagent but because of the small concentration the derivative was not isolated. This would indicate that the acrolein does not form a molecule of the paraldehyde structure.

No insoluble material formed in the solution, indicating that no long chain insoluble polymer was formed.

The absorption spectrum of allyl alcohol determined by Bielecki and Henri[3] shows that allyl alcohol is nearly transparent above 2400 Å. Since the aged acrolein solutions show absorption at 2670 Å., this eliminates the possibility of the formation of allyl alcohol.

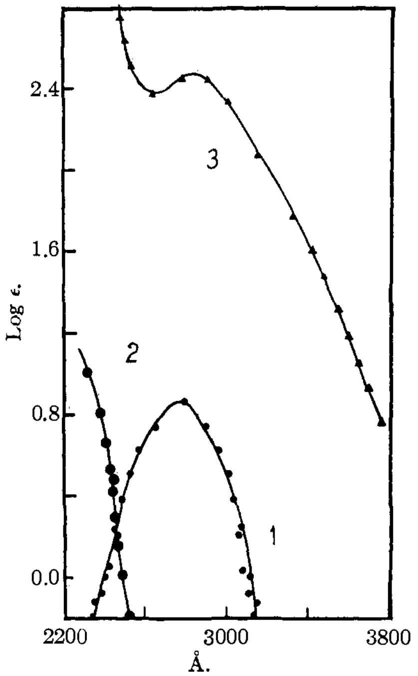


Fig. 5.—(1) Acetal in water; (2) paraldehyde in 50% ethyl alcohol; (3) aldol in 50% ethyl alcohol.

Backes[4] has shown that non-aqueous solutions of aldol show no peak above 2500 Å. while aqueous solutions have a peak at 2800 ± 10 Å. characteristic of the carbonyl group. We have verified the latter part of this statement as shown in Fig. 5 for aldol in 50% ethyl alcohol. The original carbonyl absorption of the acrolein in aqueous solution is changed completely while if the acrolein formed an aldol type of molecule the carbonyl would still be conjugated with the ethylenic linkage and should still absorb at the same wave length but should be diminished because of the disappearance of one-half the carbonyl groups. No one has ever suggested that acrolein would form the aldol and these data indicate no such formation.

From the results of the absorption spectra of the solutions to which a very minute amount of an antioxidant, either hydroquinone, Fig. 6, or tannic acid, Fig. 7, has been added, it is seen that the presence of the antioxidant has slowed down the reaction but has not stopped it. Compare Fig. 3 with Figs. 6 and 7 which show that the absorption at 3200 Å. is slower in disappearing

(3) Bielecki and Henri, *Ber.*, **46**, 2596 (1913).

(4) Backes, *Compt. rend.*, **200**, 1669 (1935).

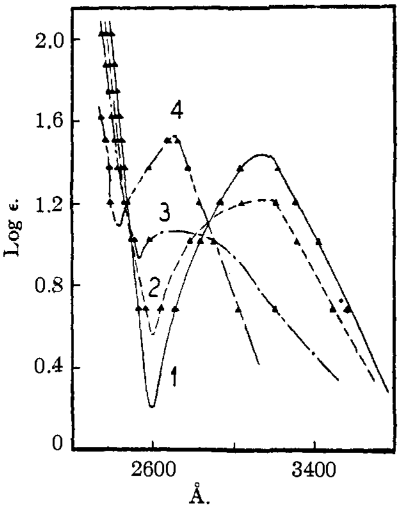


Fig. 6.—Acrolein in water plus a trace of hydroquinone: (1) immediately after making solution; (2) after 7 days; (3) after 14 days; (4) after 38 days.

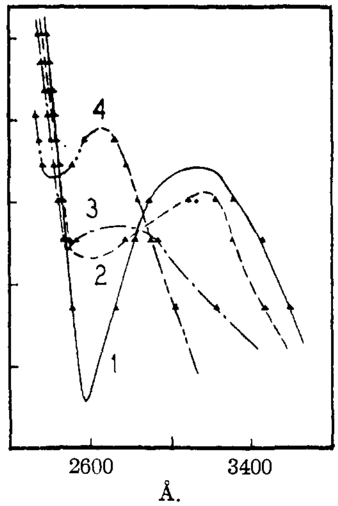


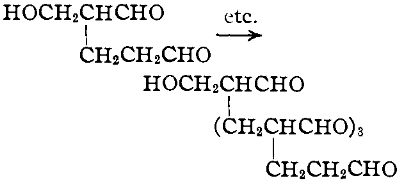
Fig. 7.—Acrolein in water plus a trace of tannic acid: (1) immediately after making solution; (2) after 7 days; (3) after 14 days; (4) after 38 days.

and that at the end of the thirty-eight-day period the new band at 2670 Å. is not as strong in the solutions which contained an antioxidant as it is in the other solution. These data suggest that the reaction may be an oxidation. In this case the product would be an acid, acrylic acid or perhaps a resin acid. The spectrum does not agree with that of acrylic acid as determined by Luthy[1f] and also the pH of the solution, which was 6.5 ± 0.3 when the solutions were made up and which remained constant, does not indicate any acid formation.

Nothing very definite can be said in regard to the ethylenic group since we have been unable to extend our working range of the spectrum below 2300 Å. In observing the results near 2350 Å., however, we notice that in every case the shoulder is diminished with time and this may be taken as an indication that the ethylenic group is disappearing.

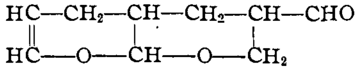
The new band which appears at 2670 Å. is undoubtedly due to a molecule formed by the polycondensation of the acrolein. Several investigators have described the formation of a white product from the polycondensation of acrolein but have made no attempt to characterize the polymer. Gilbert and Donleavy[5] have recently shown that the polycondensation is an equilibrium reaction which they represent by the equations

$$\overset{\text{I}}{\mathrm{CH_2{=}CHCHO}} + \mathrm{H_2O} = \mathrm{HOCH_2CH_2CHO} + \mathrm{I} =$$



$$\begin{array}{l}\mathrm{HOCH_2\underset{|}{C}HCHO} \quad \xrightarrow{\text{etc.}} \\ \quad\;\; \mathrm{CH_2CH_2CHO} \\ \qquad\qquad \mathrm{HOCH_2\underset{|}{C}HCHO} \\ \qquad\qquad\qquad \mathrm{(CH_2\underset{|}{C}HCHO)_3} \\ \qquad\qquad\qquad\qquad \mathrm{CH_2CH_2CHO}\end{array}$$

Sherlin, *et al.*,[6] have reported on the polymerization of acrolein in anhydrous condition at 170° and have proposed the formula



$$\begin{array}{l}\mathrm{HC{-}CH_2{-}CH{-}CH_2{-}CH{-}CHO} \\ \mathrm{HC{-}O{-}CH{-}O{-}CH_2}\end{array}$$

This molecule, with water added to the double bond, may be in equilibrium with the chain molecule as prepared by Gilbert and Donleavy.[5] The absorption data agree with the equilibrium reaction proposed by Gilbert and Donleavy[5] in which the ethylenic group disappears and the carbonyl group is changed, giving absorption at a shorter wave length. This would be expected since the conjugation disappears, causing the shift to the shorter wave length. The absorption data show that an antioxidant slows down the reaction, which is known to be the case for the above reaction. A sample of the polymer described by Gilbert and Donleavy[5] was prepared and its alcohol solution was found to give an absorption peak at the same wave length as that for the aged acrolein solutions.

Summary

The change in the absorption spectrum of acrolein in water and alcoholic solutions has been determined over a period of time. The effect of hydroquinone and tannic acid on the spectrum also has been determined.

The absorption due to the carbonyl of the acrolein changes with time, and the change is slowed down by the presence of an antioxidant. A band which appears at 2670 Å. is probably due to the carbonyl of the polymer since the product described by Gilbert and Donleavy[5] gives the same absorption band.

Curves for propionaldehyde in water and 50% alcohol solutions, for acetal in water, paraldehyde in 50% alcohol and aldol in 50% alcohol are also given for comparison.

Urbana, Illinois Received July 13, 1939

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[5] Gilbert and Donleavy, This Journal, 60, 1911 (1938).

[6] Sherlin, *et al.*, *J. Gen. Chem.* (*U. S. S. R.*), 8, 22 (1938); *C. A.*, 32, 5398 (1938).