

## Esterification in the Liquid Phase as Effected by Alumina and Ultraviolet Light<sup>1</sup>

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Bancroft (1) calls attention to the fact that sufficient data are available to show that ultraviolet light of suitable wavelength can produce the same results as catalysts in many instances. Berthelot and Gaudechon (2) studied the effect of ultraviolet light on various organic compounds, using a 110-volt lamp and employing temperatures of 50°-60° C. and 80°-90° C. Their work with alcohols led them to the conclusion that these compounds are decomposed by the action of ultraviolet light with the formation of gas mixtures. Pougnet (3) in 1911 found that ultraviolet rays accelerate the saponification of acetic ester by sodium hydroxide. Massol and Faucon (4) studied the absorption of ultraviolet rays by primary, secondary, and tertiary alcohols and found that the tertiary alcohols are more transparent to the rays than are the isomeric primary alcohols. Liquid-phase esterification, if sufficiently rapid, should be advantageous since lowering the reaction temperature in catalytic processes increases the yield in two ways (5): first, there is less decomposition at lower temperatures, and secondly, direct union of the two reactants occurs with the evolution of heat and hence, a lower temperature would be more favorable. The object of this investigation was to determine the effect of combinations of ultraviolet light, catalysts, and agitation on the liquid-phase esterification of various primary, secondary and tertiary alcohols with acetic acid.

### Experimental

**Materials.** Ordinary 95 per cent ethyl alcohol was dehydrated, using one pound of anhydrous calcium oxide per liter of alcohol, refluxed for a period of four hours, and finally triple distilled to remove all traces of the oxide. The final distillate was preserved in 300 ml. ground-glass stoppered bottles to insure its being absolute. Glacial acetic acid of analytical reagent quality was purified by recrystallization and stored in ground-glass stoppered bottles. The alumina (grade A, mesh 8-14) was weighed on an analytical balance, placed in test tubes, and activated by heating in an electric oven for ten hours at 145° C. The test tubes

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were then stoppered and placed in a calcium chloride desiccator until used. All alcohols except ethyl alcohol were obtained from the Eastman Kodak Company, and were used without further purification. The uranyl sulfate was obtained from A. Daigger and Company, alumina from the Aluminum Ore Company, thoria and titania from the City Chemical Corporation of New York, and Silica from Silica Gel Division, Davison Chemical Corporation, Baltimore, Maryland.

**Apparatus.** As a source of ultraviolet radiations, a Cooper-Hewitt mercury arc type of lamp (manufactured by the General Electric Vapor Lamp Company of Hoboken, New Jersey) was used, operating on a current strength of 2.25 amperes and 17 volts D.C. This lamp was suspended on the inside of an asbestos lined wooden box, the dimensions of which were 30 x 30 x 40 centimeters. The front of the box was covered by a removable glass plate which was also covered with asbestos except for a small circular spot in the middle through which the inside of the box could be viewed. To secure an elevated temperature in the box where the reaction chamber was located (just below the lamp), a nichrome heating coil was attached to the rear wall. A Cenco de-Khotinsky Thermo-Regulator maintained a constant (plus or minus 1° C.) temperature within the box. A 200 ml., wide-mouthed, quartz florence flask served as a reaction chamber. It was suspended directly beneath the mercury lamp by a glass rod, fastened into the stopper. The other end of this rod extended through the box and was connected on the outside to an electric motor through a system of gears. This furnished a means of agitating the chamber. The axis of rotation of the flask was about 5 cm. below the mercury arc and parallel to it. The reaction chamber was agitated by rotating at 30 r.p.m. The temperature was maintained at 47° C., plus or minus one degree.

**Determination of The Intensity of Ultraviolet Light.** The method of Anderson and Robinson (6) was used in the determination. The following procedure was used to determine the intensity of radiation: 25 ml. of the oxalic acid-uranyl sulfate solution was placed in a crystallizing dish having a diameter of 7.6 centimeters. The dish was suspended beneath the arc so that the surface of the liquid was 5 centimeters below it. After having been exposed to the light for three hours, the sample was removed from the box and titrated with the standard potassium permanganate solution. The average of three samples gave 68.7166 milligrams of oxalic acid decomposed for each square centimeter of surface exposed.

**Procedure.** The general method of procedure was to determine the amount of ester formed under the prevailing conditions of the experiment. The amount of acetic acid which had not reacted was determined by titration with standard barium hydroxide solution and the yield of ester calculated from these results.

## Results and Discussion

TABLE I.—Effect of Ultraviolet Light, Alumina, and Agitation on Equal Volumes of Alcohol and Acetic Acid at 47° C.

Catalyst	Ultraviolet Light	Agitation	Time (Hrs.)	Time			Sec. Butyl
				Methyl	Ethyl	Isopropyl	
.....	.....	.....	4	3.43	3.32%	1.49	1.50
.....	.....	Agitation	4	.....	3.59	1.50	1.66
.....	.....	Agitation	8	.....	7.63	2.23	1.95
Alumina	.....	.....	4	3.32	3.65	2.39	3.04
Alumina	.....	.....	8	4.37	3.77	3.08	3.47
Alumina	.....	Agitation	4	3.81	4.30	3.90	3.77
Alumina	.....	Agitation	8	6.47	7.15	4.89	4.88
.....	Light	Agitation	4	9.15	6.86	3.59	4.49
.....	Light	Agitation	8	15.30	13.21	6.34	9.11
Alumina	Light	Agitation	4	10.96	11.15	13.28	15.43
Alumina	Light	Agitation	8	14.85	13.42	14.13	16.44
Alumina	Light	Agitation	12	19.02	15.92	14.84	18.01
Alumina	Light	Agitation	24	27.50	22.26	16.98	19.88
Alumina	Light	Agitation	28	29.50	24.08	17.43	20.16
Alumina	Light	Agitation	31	30.50	25.21	17.72	20.31

Experiments were carried out with silica, thoria, titania, and alumina. Alumina was found to be the most effective.

Experiments performed with tertiary butyl and tertiary amyl alcohols gave data which were erratic. They showed no yield of ester at times, and, in some instances, a negative yield which indicates that the ratio of acid to alcohol in the mixture was increased. The reliability of esterification limits of tertiary alcohols is questionable, since these alcohols have a tendency to split off water and form unsaturated hydrocarbons.

There seems to be at least three processes involved in these esterifications: (1) the forward reaction of esterification; (2) the reverse hydrolytic reaction; and (3) the photochemical decomposition of the reactants and of the esters formed. The assumption is made that at the temperature of these reactions (47° C.) there is no thermal decomposition of any of the compounds present. If it is further assumed that photochemical decomposition occurs to an appreciable extent, the yields of ester in all instances represent a resultant of these three processes.

So far as could be learned from chemical literature, no data are available as to the comparative rate of decomposition of acetic acid and the various alcohols and esters by ultraviolet light. However, in the case of the tertiary alcohols, since at times a negative yield was obtained, it can be supposed that here the rate of esterification is slower than the rate of photochemical decomposition and that this decomposition acts to a greater extent on the alcohol, giving rise to a gaseous mixture of decomposition products and thus causing the reaction mixture to be richer in acid than it was originally.

## Summary

1. The effect of ultraviolet light, alumina, and agitation on the rate of esterification of equal volumes of acetic acid and various alcohols in the liquid phase has been studied.

2. With methyl, ethyl, isopropyl, and secondary butyl alcohols ultraviolet light increased the yield in nearly all instances.

3. Photochemical decomposition may be a significant factor, particularly with tertiary alcohols.

### Bibliography

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