

of the solution, the residues varying in color from brown ($1/10$ mol.) to almost black (1 mol. of thymoquinone). The color of the residues of the NaHSO_3 experiments were much lighter, varying from a light yellow to a brown. However, before evaporation the acidity of the solutions was tested by titration with $N/2$ KOH V.S. using phenolphthalein as indicator. The results are herewith tabulated:

NaHSO ₃ .	Thymoquinone.	Cc. $N/2$ KOH used.	Difference.
10.4 Gm.	Blank	196.9	24.7 cc.
10.4 Gm.	1.6 Gm. 0.1 mole	172.2	23.5 cc.
10.4 Gm.	3.2 Gm. 0.2 mole	149.7	29.5 cc.
10.4 Gm.	4.8 Gm. 0.3 mole	120.2	38.0 cc.
10.4 Gm.	6.4 Gm. 0.4 mole	82.2	18.6 cc.
10.4 Gm.	8.0 Gm. 0.5 mole	63.6	12.3 cc.
10.4 Gm.	9.6 Gm. 0.6 mole	51.3	25.9 cc.
10.4 Gm.	11.2 Gm. 0.7 mole	25.4	3.7 cc.
10.4 Gm.	12.8 Gm. 0.8 mole	21.7	4.6 cc.
10.4 Gm.	14.4 Gm. 0.9 mole	17.1	2.7 cc.
10.4 Gm.	16.8 Gm. 1.0 mole	14.4	

It becomes apparent that with three exceptions the amount of alkali used diminishes with each increase in the thymoquinone added. Ignoring for the moment the three irregularities, one would expect that according to equation No. 1 the amount of KOH set free, *i. e.*, neutralizing the NaHSO_3 to Na_2SO_3 , would be the same. However, this does not appear to be the case.

THE ULTRAVIOLET TRANSMISSION OF LIQUIDS.*

BY ELLERY H. HARVEY.

INTRODUCTION.

This paper covers the development of a method for the measurement of the ultraviolet transmission (or absorption) of liquids, and records the results obtained on forty typical essential oils, seventeen fatty oils, sixteen representative crude oils and thirty miscellaneous liquids of cognate interest:

Briefly, the technic consists in determining the photochemical decomposition of an oxalic acid solution catalyzed with uranium acetate, by the ultraviolet radiation of a carbon arc, during two hours' exposure through a 3-mm. layer of water, and considering the amount of decomposition as 100%. The identical process is repeated, interposing each time between the source of light and the oxalic acid-uranium acetate solution a 3-mm. layer of the liquid under examination to act as a screen to the passage of the active rays. The more absorbent the liquid toward ultraviolet the less will be the amount of oxalic acid decomposed, hence the number of milligrams of oxalic acid decomposed in each instance when a screening liquid is used, referred to the amount decomposed when a transparent liquid like water is used as 100%, is a direct measure of the transmission (or conversely of the absorption) of the liquid under scrutiny.

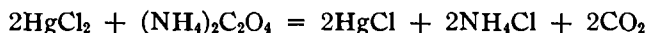
HISTORICAL.

The photochemical decomposition of aliphatic acids, particularly when catalyzed, has been known for many years. A brief history of the reaction with

* Scientific Section, A. Ph. A., Rapid City meeting, 1929.

which we are especially concerned, *i. e.*, oxalic acid and uranium salts, is given below. Recent interest in the chemical effects produced by ultraviolet radiation has shaped the reaction in the direction of making it a reliable chemical photometer.

The first person to find that uranium salts are sensitive to light was Bucholz¹ who described certain effects produced by the sulphate on alcohol. He also mentions that an ether solution of uranyl nitrate becomes green on exposure to sunlight, precipitating a black substance. Ebelman² confirmed the work of Bucholz and extended it by studying uranium oxalate, observing that it decomposed into a brown substance, carbon monoxide and carbon dioxide. Dobereiner³ proposed to use ferric oxalate as a photometer in which the ferrous oxalate or the carbon dioxide evolved could be measured. St. Victor and Corvissart⁴ noticed that if a solution of oxalic acid is exposed to light it will quickly reduce to a gold solution. They heated to boiling a 4% solution of oxalic acid and 1% uranium nitrate, finding it stable in the dark but decomposing at once when exposed to sunlight. Bonaparte⁵ obtained a decomposition of valeric acid by catalyzing with uranium salts. Eder⁶ used as a photometer a solution of ammonium oxalate and mercuric chloride which on exposure to sunlight gives off carbon dioxide and deposits mercurous chloride according to the reaction:



Niepcę de St. Victor⁷ studied the effect of solar radiation in transforming a number of animal and vegetable materials. He reports in the same article that oxalic acid and uranium salts were heated to 50° C. in the dark for thirty hours without decomposition but that decomposition accompanied by evolution of carbon dioxide began at once when exposed to sunlight. Seekamp⁸ repeated the work of St. Victor and Corvissart identifying in the products of decomposition formic acid. Bolton⁹ reviewed the previous work and added a number of personal observations. Chastaing¹⁰ studied the effect of red and violet rays on a solution of alcohol and uranium nitrate, getting a strong odor of aldehyde. Wisbar¹¹ verified the work of Seekamp and showed that butyric acid in the presence of uranium salts and sunlight broke up into propane and carbon dioxide. Fay¹² in his thesis reviews the work done to date and adds new information on the action of sunlight on organic acids in the presence of uranium salts. He mentions that prior to 1896, H. C. Jones at the suggestion of Remsen, verified the work of Seekamp and amplified it.

Bacon¹³ reported the photochemical decomposition of aliphatic acids when

¹ *Ann. chim. phys.*, [1], 56 (1806), 142.

² *Ann. Chem.* (Liebig), 43 (1831), 294.

³ *Schweigger's Journ.*, 62 (1831), 90.

⁴ *Ann. Chem.* (Liebig), 43 (1842), 114.

⁵ *J. prakt. Chem.*, 30 (1843), 308.

⁶ *Wein. Acad. Ber.*, 2 (1849), 1879.

⁷ *Compt. rend.*, 49 (1859), 368-371.

⁸ *Ann. Chem.* (Liebig), 122 (1862), 113.

⁹ *Am. J. Sci.*, [2], 48 (1869), 206.

¹⁰ *Ann. chim. phys.*, [5], 11 (1877), 145.

¹¹ *Ann. Chem.* (Liebig), 232 (1886), 262.

¹² *Amer. Chem. Journ.*, 18 (1896), 269-289.

¹³ *Phillipine J. Sci.*, 2 (1907), 129.

catalyzed by uranium salts. Neuberg¹ found later that ferric sulphate could be substituted for the salts of uranium. Bacon² utilized the oxalic acid-uranium salt reaction as an ultraviolet radiometer in connection with solar radiation. He found that the action of uranium acetate was quite similar to the nitrate, that the decomposition was proportional to the amount of uranium salt present and that temperature changes exerted very little effect on the amount of oxalic acid decomposed. After studying the reaction Bruner and Kozak³ found that the decomposition occurred in two steps:



The speed of reaction is, contrary to the mass action law, independent of the concentration of the oxalic acid. The authors consider this fact a universal law of photocatalysis, analogous to the Faraday electrochemical law. Berthelot and Gaudechon⁴ studied the photolysis of complex acids by ultraviolet rays in the presence of uranium salts and found that the diabasic acids of a normal series split up into a monobasic acid and CO_2 . Fluorescent substances inhibited the photolysis. The accelerating action of uranium salts was held to be caused by photochemical resonance. Freer and Gibbs⁵ utilized the method of Bacon, after slight modifications, to study the solar radiation of the tropics. Boll⁶ found that the reaction was unimolecular when using 0.001 *N* solutions of oxalic acid and uranyl nitrate. Landau⁷ compared the photocatalytic activity of uranium salts with other agents. All uranium salts were found to possess marked photocatalytic power. The relative values of this power for six uranium salts and for thorium oxide were compared with the radioactive power as determined by Curie, but no relation was found to exist. The catalytic power of uranium salts is due alone to the cation. Mathews and Dewey⁸ made a quantitative study of some photochemical effects produced by the ultraviolet radiation of a quartz mercury vapor lamp, finding that solutions of oxalic acid were decomposed but very slowly; in the presence of uranium acetate, nitrate or sulphate, however, the decomposition was very marked, the rate varying directly with the amount of catalyst present. These authors suggested that the catalysis might be due to the radioactivity of the uranium salts. With the latter view Berthelot and Gaudechon⁹ took exception. Henri and Landau¹⁰ applied spectroscopy to the study of chemical equilibrium, using the system oxalic acid-uranyl salts. They found that the quantitative measurement of absorption in the ultraviolet might be used to follow the course of the reaction. The observed exaltation of the absorption constitutes a new proof of the general law that chemical lability causes an exaltation of the absorptive power in the ultraviolet. A direct relation exists between the photo-

¹ *Biochem. Z.*, 29 (1910), 279.

² *Phillipine J. Sci.*, 5 (1910), 281.

³ *Elektrochem. Z.*, 17 (1911), 354.

⁴ *Compt. rend.*, 152 (1911), 262.

⁵ "8th Inter. Cong. App. Chem.," 20 (1912), 160; *J. Phys. Chem.*, 16 (1912), 709.

⁶ *Compt. rend.*, 156 (1913), 1891.

⁷ *Ibid.*, 156 (1913), 1894.

⁸ *J. Phys. Chem.*, 17 (1913), 216.

⁹ *Compt. rend.*, 157 (1913), 333.

¹⁰ *Ibid.*, 158 (1914), 181.

catalytic power and exaltation of absorption for uranyl salts on oxalic acid. Berthelot¹ studied the products of photolysis of oxalic acid by ultraviolet rays of different wave-lengths, finding that the primary decomposition consisted of CO₂ and HCOOH, followed by a secondary decomposition of nascent HCOOH into CO and H₂O by rays of long wave-length, and into CO₂ and H₂ by waves of short length. These facts were held to verify the view that the radiant energy represents a lower form of energy than thermal energy, the frequency of vibration playing the same rôle in the first as does temperature in the second. Benrath² found that the greenish yellow powder deposited when uranyl chloride dissolved in ether is exposed to sunlight, to be UOCl₂, and a similar precipitate obtained by exposing an aqueous solution of uranyl nitrate containing alcohol to be UO₂(NO₃)₂. Baur³ states that insolated uranyl salt solutions act as if they contained both a higher and a lower state of oxidation in that when reacting with oxalic acid they are able both to oxidize to CO₂ and to reduce to CO; since the uranyl salt solution is fluorescent this indicates a dislocation or loosening of electrons, hence Baur assumes that the action of light is not a complementary oxidation and reduction of different uranyl atoms but is a rearrangement of the electrons within single molecules in such a manner that the molecules become electrically polarized, one terminal of the molecule being positive and the other negative. In the following year Baur⁴ advanced the idea that photolysis is analogous to a type of electrolysis. Glycolic acid in the presence of uranyl salts and light is converted into CH₂O and it is experimentally shown that electrolysis gives the same product. Oxalic acid and light with uranyl salts present produce an evolution of CO and CO₂ but it was impossible to find CO in the products of the electrolysis of oxalic acid. Dhar⁵ presented evidence to show that reactions which have a large temperature coefficient are sensitive to light, hence sensitiveness to temperature and to light radiations accompany each other. Salts of uranium function as general positive catalysts in photochemical reactions while salts of manganese as general negative catalysts in both the presence and absence of light. Baur and Haggénbacher⁶ found formic acid, carbon dioxide and carbon monoxide as the products of the reaction of sunlight on aqueous oxalic acid-uranyl sulphate solutions. Kailan⁷ was unable to detect any formic acid as a decomposition product of the irradiation of oxalic acid by a mercury vapor lamp; considerable formic acid developed, however, when uranium salts were added. Kunz-Krause and Manicke⁸ observed the lack of information on the subject of decomposition of oxalic acid by artificial light. Using electric arc irradiation on oxalic acid-uranyl acetate solutions they found what others had previously reported. Rideal and Norrish⁹ examined various substances for photoactivity by the potentiometer method. UO₂(NO₃)₂

¹ *Compt. rend.*, 158 (1914), 1791-1793.

² *Z. wiss. Photochem.*, 16 (1917), 253.

³ *Helvetica Chimica Acta*, 1 (1918), 186.

⁴ *Z. Elektrochem.*, 25 (1919), 102-109.

⁵ *Proc. Roy. Acad. Sci. (Amsterdam)*, 23 (1920), 308.

⁶ *Z. physik. Chem.*, 100 (1922), 36.

⁷ *Monatsh.*, 43 (1922), 1.

⁸ *Ber. deut. pharm. Ges.*, 32 (1922), 209.

⁹ *Proc. Roy. Soc. (London)*, 103A (1923), 342-366.

was among those tested and it gave definite positive results. Volmar¹ found that hydroxy acids and their salts underwent photolysis when exposed to ultraviolet, the decomposition being accelerated by the presence of such catalysts as uranyl acetate.

Buchi² holds that the photochemical decomposition of oxalic acid in the presence of uranium salts is due to the decomposition of non-ionized molecules of uranyl oxalate ($\text{UO}_2\text{C}_2\text{O}_4$), or of complex ions $[\text{UO}_2(\text{C}_2\text{O}_4)_2]$, stressing the great stability of this complex. Holmes³ suggested the possibility of using the oxalic acid-uranyl salt reaction in connection with the study of the light fastness of colored fabrics. Anderson and Robinson⁴ studied the character of the photochemical reaction using a mercury vapor lamp and fused quartz apparatus. It was found that 0.1 *N* oxalic acid solutions through a thickness of 25 mm. absorbed all radiations below 3000 Å. and slightly up to 4050 Å.; oxalic acid solution 0.01 *M* plus uranyl sulphate 0.01 *M* absorbed all radiations below 3600 Å. and partially up to 4100 Å. The authors described a set-up that is satisfactory as an ultraviolet radiometer and showed that under the conditions of their experiment 1 mg. of oxalic acid, decomposed in 30 minutes, correspond to the following number of ergs absorbed at the respective wave-lengths:

Wave-length Å.	Ergs per second.
2550	4.18×10^6
3020	5.04×10^6
3650	5.27×10^6
Complete U. V.	4.84×10^6

Moss and Knapp⁵ developed a rather elaborate method for determining the ultraviolet intensity of various light sources, called the "Uroxameter" method, utilizing the oxalic acid-uranium salt photolysis and a specially constructed vessel that rotated on a mechanical stage. They concluded from their determinations that the Uroxameter value was:

1. Only slightly sensitive to temperature, amount of water present and speed of rotation, but that it was affected by,
2. Area of solution irradiated, presence of silica plate, distance from source of light, amount of catalyst present and age of uranium acetate solution.

Eidenow⁶ in discussing the various devices used for predicting relative efficiencies of light sources in producing erythema, does not include the oxalic acid-uranium salt reaction.

Sandonnini⁷ reported that while powdered carbon is a good absorber of many kinds of radiations it had no catalyzing effect on oxalic acid solutions when the latter were irradiated with an arc lamp.

Wobbe and Noyes⁸ used pressure measurements in studying the thermal

¹ *Compt. rend.*, 176 (1923), 742.

² *Z. physik. Chem.*, 111 (1924), 269.

³ *Am. Dyestuff Repr.*, 13 (1924), 188.

⁴ *J. Am. Chem. Soc.*, 47 (1925), 718.

⁵ *J. Soc. Chem. Ind.*, 44 (1925), 453T.

⁶ *Lancet*, 209, No. 5320 (1925).

⁷ *Atti accad. Lincei*, [6], 2 (1925), 427.

⁸ *J. Am. Chem. Soc.*, 48 (1926), 2856.

decomposition of anhydrous oxalic acid and its relation to photochemical decomposition. The latter was produced by using a monochromater and it was found that the effect was negligible for wave-lengths greater than 250 μ . Since the pressure increase continues after the light is shut off, it is presumed that its mechanism must be sought in physical diffusion through the crystal lattice.

Muller¹ determined the photochemical decomposition of lactic acid and sodium lactate to acetaldehyde, in the presence of uranyl sulphate, from the point of view of its quantum yield. Direct measurement of the radiation, assuming a wave-length of 4025 Å. as the center of the photochemical band, yields 1.05 quanta per mol. which corresponds with 0.99 quanta per mol. as determined from the light energy with the aid of oxalic acid-uranyl sulphate.

Allmand and Reeve² followed the photochemical decomposition of aqueous oxalic acid by microanalysis of the gaseous products, the cell having been evacuated previous to exposure to the mercury arc. The quantum efficiency increases with dilution of the solution. The primary reaction is photolysis to CO₂ and formic acid.

Dorcas and Forbes³ stated that the oxalic acid-uranium salt decomposition, among others, was not satisfactory for studying ultraviolet dosage and recommended the photolysis of *p*-benzoquinone in fifty per cent alcohol.

Gillam and Morton⁴ recommend the photolysis of potassium nitrate buffered at p_H 9.4 for a number of purposes but feel it is too slow for general use as an easy routine test for dosage in actino-therapy. These authors continued their study⁵ of various methods for determining the ultraviolet intensity of light sources and conclude that the nitrate and carbon tetrachloride methods are most suitable to measure bactericidal rays, while the oxalic acid-uranium salts' decomposition is more suitable for the middle ultraviolet.

Abelous, Aloy and Valdiguie⁶ studied the effect of the insolation of the common sugars and found that it produced no appreciable change. Upon addition of a uranium salt, however, the solution changed in color and precipitated in a few minutes. Aldehydes were among the products.

METHOD.

Twenty-five cubic centimeters of a solution containing 6.3 Gm. of oxalic acid (COOH)₂·2H₂O, and 4.2 Gm. uranium acetate, UO₂(C₂H₃O₂)₂·2H₂O, per liter are exposed to ultraviolet radiation for two hours and the excess oxalic acid titrated with 0.1 *N* potassium permanganate. The reaction vessel is a 100-cc. clear quartz flask having an outside bulb diameter of 2¹/₄ inches, mounted behind an orifice of the same diameter in a dull black hard rubber box that is otherwise light tight. The flask is eleven inches from the source of light, the filter being mounted just in front of the flask so that no light can enter the flask that is not first passed

¹ *Biochem. Z.*, 178 (1926), 77.

² *J. Chem. Soc.*, 45 (1926), 2834.

³ *J. Am. Chem. Soc.*, 49 (1927), 3081.

⁴ *J. Soc. Chem. Ind.*, 46 (1927), 415T.

⁵ *Ibid.*, 46 (1927), 417T.

⁶ *Compt. rend. soc. biol.*, 96 (1927), 1385.

through the filter. The latter is a clear quartz cell $2\frac{3}{4}$ inches in diameter and has a thickness of 3 mm. between the inside walls. It is filled with the liquid under examination for its ultraviolet transmission by using a pipette, filling through a small neck on the top of the cell and permitting the air to escape through a similar opening several millimeters away.

The source of light is an enclosed type carbon arc operating on 220 volt D.C. at 13 amperes. The glass globe surrounding the arc is opaque to wavelengths below 3020 Å. This indicates that none of the very short wavelengths not found in sunlight are present. The electrodes are solid carbons of 12.7-mm. diameter. The total radiation at a distance of 11 inches, center to center, at 13 amperes, was found to be 0.1431 watt per sq. cm., the spectral distribution of the light being shown on the chart.

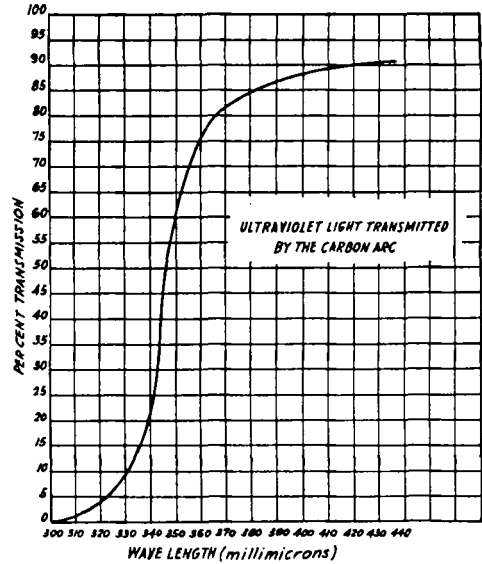


Fig. 1.—Ultraviolet light transmitted by carbon arc.

(To be continued)

A STUDY OF THE TOXIC PROPERTIES OF DIETHYLPHTHALATE.*

BY PHILIP BLICKENS DORFER AND LAWRENCE TEMPLETON.

During the past year there have been outbreaks of a peculiar form of paralysis in certain sections of the United States which have been traced directly to the drinking of a spurious form of Fluidextract of Ginger well known as "Jake" Ginger.

Various theories were at once advanced as to the cause of this paralysis. It has been blamed on diethylphthalate, iso-propyl alcohol, creosote, tri-cresyl phosphate, arsenic, vitamin deficiency and perhaps other causes.

The cause of the paralysis could be blamed on (1) the ginger, (2) the alcohol, and its denaturants or (3) a combination of the two. Diethylphthalate is one of the more common legalized denaturants for industrial alcohol and it seems probable that such a cheap form of alcohol has been used as the menstruum for the spurious "jake."

It is from this reasoning that we have studied the toxic properties of diethylphthalate.

A study of the toxic properties of diethylphthalate has been reported in this journal by Otto M. Smith (JOURNAL OF THE AMERICAN PHARMACEUTICAL ASSOCIATION, Vol. 13 (1924), page 812). In this short paper Smith reports that:

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