

verted into quinones of the structural type of vitamin K₁.

Another observation of this work is that a typical 2-alkyl-1,4-naphthoquinone oxide is converted into a bromohydrin by the action of mag-

nesium bromide in ether. New methods are described for the preparation of such oxides and for carrying out the reductive acetylation of quinones.

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Quantum Yields and Kinetics of a Photosensitized Production of Reducing Sugars from Sucrose in Aqueous Solutions of Uranyl Sulfate by Visible and Ultraviolet Light

By LAWRENCE J. HEIDT

Aqueous solutions of sucrose are about as transparent as water in the visible and near ultraviolet to 200 $m\mu$, so light in this region has not been found to produce any measurable effect upon the stability of sucrose dissolved in water. When uranyl ions are added to these solutions, they absorb visible and ultraviolet light; but their extinction coefficients between 470 and 208 $m\mu$ are the same as if no sucrose was present. Neither does the uranyl sulfate greatly affect the specific rotation of sucrose, which remains within 0.2% of 66.5° for the D lines of sodium.

Illumination of these sucrose-uranyl solutions with light absorbed by the uranyl ion causes a decrease in their optical activity and the formation of products which reduce the alkaline cupric solutions of Shaffer, Hartmann and Somogyi.¹

Materials.—The sucrose was U. S. Bureau of Standards sample 17, lot 3650, and the fructose and glucose were recrystallized specimens with the correct rotations.² They were stored in vacuum over "Anhydron" and were kept in the dark as much as possible.

The uranyl salts, oxalic acid, and permanganate were recrystallized and centrifuged specimens like those used previously.³

The sodium oxalate used to standardize the permanganate solutions was U. S. Bureau of Standards sample 40c.

All the other chemicals were reagent quality.

Apparatus and Procedure.—Monochromatic light was obtained by means of a prism monochromator using crystal quartz lenses. The 60° cornu prism was 6.5 cm. high and had faces 8 cm. long. It was purchased with a grant from the Warren Fund of the American Academy of Arts and Sciences. The monochromator transmitted in air the

185 $m\mu$ line of aluminum and separated the 578 and 546 $m\mu$ lines of mercury. In combination with a zinc spark, the energies at 208, 254 and 280 $m\mu$ transmitted by the exit slit were about the same as those obtained elsewhere with similar apparatus.⁴

Two reaction cells were used with the monochromator ensemble. One was rectangular, 20 mm. wide and 40 mm. high and held 5 cc. of solution in a 5-mm. layer. The other cell was trapezoidal and held 12 cc. of solution in a 30-mm. layer between the parallel windows. The front window was 10 mm. wide and 20 mm. high and the back window, 20 mm. wide and 40 mm. high. The transparency of the windows of both cells agreed within 2% at 208 $m\mu$.

The source of light at 366 and 436 $m\mu$ was an inverted "U" type mercury vapor arc lamp.⁵ Its intensity at these wave lengths was increased by reducing to 5 mm. the internal diameter of the quartz tubing containing the arc. This made available behind the exit slit (1 mm. wide \times 10 mm. high) 7×10^{17} photons per minute at 366 $m\mu$ and 4×10^{17} at 436 $m\mu$, varying less than 1% in twenty hours when the lamp was properly operated.

The amount of monochromatic light at 254 $m\mu$ was increased over 200-fold, to 5×10^{19} photons per minute, as described elsewhere.⁶ Duplicate cells and stirrers used with this apparatus were made from the same pieces of transparent quartz. Quantum yields were the same whether obtained with this set-up or with the monochromator (see Table I, Expts. 12 and 13). The effectiveness of the light-proof aluminum tube that acted as a shutter was demonstrated in Expt. 9d, Table I, where the values in parentheses are directly proportional to the light flux which would have been incident on the sugar solution had the shutter been removed.

Analytical.—The light flux entering the actinic systems was measured with the uranyl oxalate solutions recommended for use as actinometers.^{3,7} The oxalate content of the solutions was determined by electrometric titration with permanganate after proof that the method gave the same values of ϕ as titration to a color end-point. The

(1) Heidt and Purves, *THIS JOURNAL*, **60**, 1206 (1938), give data when this reagent is used to follow the hydrolysis of sugars.

(2) I am indebted to Professor C. B. Purves for supplying these sugars and to Drs. F. B. Cramer and D. H. Crangaard for recrystallizing the fructose and glucose.

(3) Forbes and Heidt, *THIS JOURNAL*, **56**, 2363 (1934), and research referred to therein.

(4) Forbes and Brackett, *ibid.*, **53**, 3973 (1931).

(5) Forbes and Heidt, *ibid.*, **53**, 4349 (1931).

(6) Heidt, *Science*, forthcoming publication.

(7) Daniels, *J. Phys. Chem.*, **42**, 701 (1938).

end-point by the electrometric method can be reproduced to 0.04 cc. of 0.0002 molar permanganate (4×10^{-8} equivalent) when the volume of the titrated solution is less than 10 cc. Titrations were made with solutions weighed to 1 mg.

The amount of reducing sugars formed was determined with the Shaffer-Hartmann-Somogyi (S.-H.-S.) reagent, whose composition is given in reference 1. The procedure was modified when the solutions containing reducing sugars were buffered. In the first place, accurately measured aliquots of the buffered sugar solutions were made up to 5 cc. by adding more buffer if necessary. Then they were neutralized with caustic soda solution, before adding 5 cc. of the S.-H.-S. reagent. Second, instead of 5, 10 cc. of 1 *N* sulfuric acid was added to liberate the iodine before titration with approximately 0.002 *M* sodium thiosulfate, hereafter called "hypo." This avoided a fading end-point which occurred when the *pH* of the titrated solution was not low enough.

The calibration plots of mg. reducing sugar vs. cc. hypo (equivalent to the cuprous oxide formed) showed that the acetate buffer, the uranyl sulfate, the concentrations of the reducing sugars and sucrose, the dark reaction, and the reoxidation of the cuprous oxide during the heating and at room temperature—all affected the S.-H.-S. titrations. These effects, however, altered less than 10% the estimations of the reducing sugars formed in photolysis, as calculated from the observed difference between the titrations on the samples photolyzed and on those kept in the dark under otherwise similar conditions. The acetate buffer and uranyl sulfate increased slightly the weight of reducing sugar equivalent to a cc. of hypo, and corrections made for these effects were less than 7%. A yellow precipitate formed sometimes when the uranyl sulfate solutions were neutralized, but this did not seem to interfere with the reproducibility of the titrations. The calibration plots of the S.-H.-S. reagents used agreed within 3%.

Both "dark" and illuminated solutions were analyzed at the same time and under the same conditions. In most cases, the dark reaction was less than 2% of the total, but at the highest concentrations of sucrose, the dark reaction and the presence of the sucrose caused a reduction of the S.-H.-S. reagent, equivalent to 0.6 cc. of hypo per cc. of sugar solution.

The range of *pH* was confined between 3 and 6. At lower values, the hydrolysis of sucrose in the dark becomes appreciable.¹ At higher values, the stability of fructose and glucose decreases—the former being most stable at *pH* 3.3.⁸ In addition, it was observed that as the *pH* was increased from 6 to 11, a 0.01 *M* solution of uranyl sulfate changed from green to yellow and finally produced a yellow precipitate.

The *pH* values were measured to 0.05 on a vacuum tube *pH* meter which used a glass electrode against a calomel half-cell saturated with potassium chloride.

Stock solutions of sugar always were made up less than an hour before withdrawing a sample and were not used a second day except in experiments covering more than a day. These solutions were made from tared samples of

dry sucrose, 0.04 *M* uranyl sulfate, and enough water or 1 or 0.1 molar acetate buffer to complete the solution. Other organic compounds used as buffers between *pH* 3 and 6 absorb light strongly at 254 *mμ*. Even acetate absorbs 208 *mμ* and was omitted when working at this wave length. It was omitted also at 366 and 436 *mμ* because extinction coefficients of the acetate solutions were not available to evaluate the light transmitted. Phosphate buffers precipitated the uranyl ion and left solutions which transmitted through 3 cm. both 254 and 208 *mμ*, accompanied by a green fluorescence.

Results

Extinction coefficients, *k*, were measured from 45,000 to 21,000 cm.^{-1} for aqueous solutions of uranyl sulfate at 0.04 and 0.0004 molar and for 0.0365 and 0.000365 *M* uranyl sulfate containing sucrose at 4.02 and 0.0402 *M*, respectively. The null photographic method was used. The presence of the sucrose had no effect upon *k* and Beer's law was obeyed. These facts strongly suggest that in this part of the spectrum the absorbing species in solutions of uranyl sulfate were not changed when 100 times as much sucrose was added or when concentrations were varied 100-fold.

The observed values of *k* agreed with the best values in the literature,⁹ but the dip in absorption at 366 *mμ* has a broader minimum on the long wave length side than the values previously obtained by extrapolation between 365 and 405 *mμ*. The smoothed values of $\log_{10} k$ are 0.6 at 450, 380 and 364 *mμ*; 0.7 at 445, 385 and 352 *mμ*; 0.8 at 443, 390 and 351 *mμ*; 0.9 at 440, 395 and 350 *mμ*; and 1.0 at 430, 405 and 349 *mμ*. $k = [\log_{10} (I_0/I)]/cd$ where *c* is in moles per liter and the depth *d* of the absorbing layer is in centimeters.

Pringsheim's photographs¹⁰ of the absorption spectrum of 0.05 *M* uranyl sulfate also show a broad minimum about 366 *mμ*.

No measurements of *k* were made on solutions containing acetate buffer because absorption of 254 *mμ* was complete whenever acetate buffer was used. It was observed, however, that the presence of acetate in uranyl sulfate solutions gave rise at 313 *mμ* and longer wave lengths to a green fluorescence which even defined the variations of the light intensity in the beam. At 254 *mμ*, the green fluorescence changed to blue. The oxalic acid-uranyl sulfate solutions gave only a very faint, visible fluorescence. An analysis of the visible and near ultraviolet absorption and fluores-

(8) Mathews and Jackson, *Bur. Standards J. Research*, **11**, 619 (1933).

(9) (a) Leighton and Forbes, *This Journal*, **52**, 3139 (1930); and (b) Brackett and Forbes, *ibid.*, **55**, 4459 (1933).

(10) Pringsheim, *Physica*, **4**, 733 (1937).

cent spectra of uranyl salts has been published.¹¹

Table I summarizes all the data obtained when reactions were followed with the copper reduction technique. This eliminated any corrections for the mutarotation of the liberated reducing sugars, and was many times more sensitive than following the accompanying change in the optical activity. Even in a 4-dm. tube, a change of 0.01° was equivalent per cc. of solution to nearly 0.5 cc. of hypo, which was reproduced within 0.1 cc.

Column II gives the average of two or more determinations of the reducing sugars formed by light in 1 cc. of the solutions photolyzed. These entries refer to the sensitivity of the S.-H.-S. reagent when reduced one-fourth by a solution containing invert sugar in the presence of 1 *M* acetate buffer and 0.008 *M* uranyl sulfate. Under these conditions 1 cc. of hypo was equivalent to 5.8×10^{-5} g. of invert sugar which represented the average of 5.74×10^{-5} g. for glucose alone, and 5.85×10^{-5} g. for fructose alone. This amount of invert sugar could be formed from $5.8 \times 6.06 \times 10^{18}/360 = 9.76 \times 10^{16}$ molecules of sucrose.

Column III gives the average of four or more determinations of the cc. of 0.00179 molar potassium permanganate equivalent to the oxalate particles which disappeared in 1 cc. of the actinometer solution each minute it was photolyzed. One-twentieth to one-fifth of the oxalate was decomposed. At the lowest intensities, the actinometer solutions were photolyzed immediately before and after illuminating the sugar solution; otherwise, the light intensities were determined at the beginning, middle, and end of a day. These values always agreed within 5% and showed no trend, so their average was taken for all experiments that day.

The actinometer was 0.001 *M* in uranyl sulfate and 0.0067 *M* in oxalic acid at 208 and 254 $m\mu$, and 0.01 *M* in uranyl sulfate and 0.067 *M* in oxalic acid at 366 and 436 $m\mu$. The fraction of an oxalate particle which disappeared per photon absorbed by these solutions at 25° was taken^{3,9} as 0.49 at 208 $m\mu$, 0.63 at 254 $m\mu$, 0.49 at 366 $m\mu$ and 0.58 at 436 $m\mu$ with a ten degree temperature coefficient of 1.03 at all these wave lengths.

The volumes of the actinometer and sugar solutions photolyzed were 11 cc. except when the change in optical activity of the sugar solution was followed; then they were 12 cc. However,

when the monochromator was used, the photolyzed samples were only large enough to intercept the diverging beam from the exit slit.

Quantum yields, ϕ , in Table I are equal to a constant, *A*, multiplied by column II divided by the product of columns I and III.

Light at 208 and 254 $m\mu$ was completely absorbed by the sugar and actinometer solutions, so at 25° for 208 $m\mu$, *A* equals 9.76×10^{16} divided by $(2.72 \times 10^{18}/0.49)$ to give 0.0176; and for 254 $m\mu$, *A* equals 0.0212 at 10° and 0.0288 at 35° .

Light at 366 and 436 $m\mu$ was not completely absorbed by the 30-mm. depths of either the (1) actinometer or (2) sugar solutions. Solution (1) absorbed 72% of the light incident at λ 366 $m\mu$ and 60% at λ 436 $m\mu$. Solution (2) absorbed 52% at 366 $m\mu$ and 82% at 436 $m\mu$. These percentages include the amount absorbed after reflection from the back window of the cell and were calculated from the data in reference 9a. Therefore, for 366 $m\mu$, *A* = 0.0248; and for 436 $m\mu$, *A* = 0.0155.

The reproducibility of the quantum yields for the sugar solutions was 3% as shown in Table I by Expts. 3 and 4 made six weeks apart, and by 19 and 20 made five weeks apart.

The products of the reaction which reduced the S.-H.-S. reagent were assumed to be equal weights of glucose and fructose commonly called invert sugar. This is, no doubt, too simple an hypothesis during the latter stages of the photolysis when much sucrose has been decomposed. Many attempts were made to test this hypothesis by following the decrease in the optical activity of the solution which accompanied the formation of the reducing sugars. It was impossible, however, to decompose by photolysis enough sucrose to decrease the observed rotations more than a fraction of a degree before the solutions became discolored or a precipitate appeared. Moreover, solutions could not be made alkaline to eliminate corrections for the mutarotation of the liberated reducing sugars because sucrose mutarotates in alkaline solutions containing uranyl salts.¹² Specific rotations, $\alpha^{21.5^\circ D}$, therefore, were obtained for glucose (52.0°), fructose (-91.0°), and sucrose (66.4°) at concentrations covering the range used in the photolysis. The fraction of *d*-glucose (starting at $\alpha > 100$) that underwent mutarotation each minute at 21.5° varied from 0.026 at *pH* 3.0 to 0.031 at *pH* 3.5 in these solutions. The

(11) Van Heel, *Comm. Phys. Lab., Univ. of Leiden*, Supplement No. 55B to Nos. 169-180, 7 (1925).

(12) Grossmann and Rothgiesser, *Ber.*, 43, 676 (1910).

TABLE I

Data giving the photochemical efficiency, ϕ , of the production by light of reducing sugars in aqueous solutions of sucrose and uranyl sulfate. $\phi = A$ multiplied by column (II)/(I)(III). The appropriate values of A are given in the text. The temperature was $10 \pm 1^\circ$ except as noted in column I. A starred ϕ indicates that the light was isolated by a prism monochromator and accompanying entries in columns II and III, marked "t," represent the amount photolyzed (per min. for III) in the total volume illuminated. In the pH column, the unmarked values represent solutions buffered with 1 M acetate, and values with one star those buffered with 0.1 M acetate. The barred w values are for unbuffered solutions and represent the average of the initial and final pH, which differed less than 0.1 except in Expt. 15 where the difference was 0.15. Solutions were placed only in glass vessels sterilized at 110° and then cooled to 25° just before being used.

Expt.	G. sucrose in 50 cc.	Moles of UO ₂ SO ₄ per liter	pH	I	II	III	Av. quantum yields, ϕ
				Av. min. photolyzed	Av. reducing sugars formed measured as cc. hypo/cc.	Av. light absorbed per min. measured as cc. MnO ⁺ ₄ /cc.	
λ 254 m μ							
1	0.0000	0.008	3.5	102	0.00	0.050	0.000
2 a	.0306	.008	3.5	98	1.86	.048	.008
bcd				58	1.21	.048	.009
3 ab	.1396	.008	3.5	101	7.60	.050	.032
cd				24	2.14	.050	.038
4 abcd	.1406	.008	3.5	14.1	1.75	.075	.036
5 abcd	.1390	.0008	3.5	28.8	2.92	.049	.045
6 abcd	.1373	.008	6.0	30.4	2.74	.050	.039
7 abcd	.1397	.008	5.6*	26.2	2.46	.049	.040
8 abc	.1362	.008	6.0	1040	3.77	.0018	.042
9 ab	.1396	.008	6.0	7 at 35°	3.90	.43	.031
c				1 at 35°	0.70	.43	.037
d				(50) at 35°	.00	(.43)	...
10 ab	.1383	.008	6.0	77 at 35°	1.65	.0135	.037
11	.1405	.0008	$\overline{3.5w}$	3 at 20°	1.45	.137	.077
12 ab	.4173	.008	3.5	8	2.60	.076	.091
cd				4.1	1.44	.076	.098
13 ab	.4090	.008	6.0	68 at 27°	8.45t	.028t	.102*
14 ab	.4100	.008	$\overline{3.5w}$	3.5 at 20°	3.37	.125	.17
cd				1.5 at 20°	1.75	.125	.21
λ 208 m μ							
15	0.4162	0.008	$\overline{3.4w}$	81 at 27°	23.0t	0.0154t	0.32*
16 ab	.4072	.008	$\overline{3.5w}$	30 at 27°	7.45t	.0145t	.31*
λ 366 m μ							
17 ab	0.4080	0.0286	$\overline{3.0w}$	35 at 27°	37t	0.088t	0.30*
λ 436 m μ							
18 abc	0.4030	0.0286	$\overline{3.0w}$	38 at 27°	31t	0.043t	0.29*
λ 254 m μ							
19 ab	1.3944	0.008	3.5	104	29.5	0.050	0.12
cd				23	9.5	.050	.18
20 abcd	1.3983	.008	3.5	3.25	2.22	.072	.21
21 abcd	1.3909	.0008	3.5	7	3.43	.045	.23
22 abcd	1.3942	.0008	6.0	6.5	2.69	.042	.21

mutarotation of fructose was completed in less than ten minutes. Thus, the small decreases in the optical activities, when no discoloration was evident, were known only within 5% although the rotations were read to 0.02° in a 4-dm. tube. Despite this uncertainty combined with those in the S.-H.-S. method, the experiments showed that the reducing sugars—assuming them to have the same reducing power as invert sugar—produced by the photochemical decomposition of the sucrose had a combined *negative* rotation whose absolute

value was not greater than that of invert sugar.

The decreases in the optical activities of the samples kept in the *dark* agreed in every case to $\approx 0.02^\circ$, with the S.-H.-S. estimates of invert sugar, and no discoloration or precipitate occurred even when 13% of the sucrose had been inverted in a solution containing 4% sucrose in 0.016 M uranyl sulfate buffered with 1 M acetate at pH 3.0. The invert sugar derived from a gram of sucrose was taken to have an α of 360 ($52.0 - 91.0$)/2 \times 342 = -20.5° .

The dark rates for the inversion of sucrose at 21.5° and pH 3.0 to 3.5 were not changed in solutions partially inverted by photolysis.

Subsequent reactions in the early stages of the photolysis affected little the amount of reducing sugar formed. Quantum yields did not change more than corresponded to the depletion of the sucrose when 15% of the sucrose was decomposed in Expt. 2a, Table I, and the molar ratio of sucrose decomposed to uranyl sulfate initially present was less than one as in Expt. 21. Nevertheless, the decrease of 0.05 to 0.15 in the pH of the unbuffered solutions can be attributed to a minute amount of direct¹³ and also photosensitized decomposition of the reducing sugars initially formed.

Side reactions due to the deactivating effect of the acetate halved the efficiency of the measured reaction as shown by Expts. 12 and 14, Table I. Decreasing the acetate buffer from 1 *M* in Expt. 6 to 0.1 *M* in Expt. 7, however, had no effect, but in both experiments the concentration of the acetate was many times greater than the sucrose or uranyl sulfate. The deactivating effect of acetate, therefore, had reached a limit at 254 μ before its concentration was ten times greater than the uranyl sulfate.

When sucrose was omitted from an acetate buffered uranyl sulfate solution as in Expt. 1, no substances were produced which reduced the S.-H.-S. reagent¹⁴ nor were they produced when 0.008 *M* uranyl sulfate alone in water absorbed per cc. of solution 3×10^{19} photons of λ 254 μ . The depletion of uranyl particles¹⁵ also did not change the pH of this solution, which remained at 3.5.

In a preliminary experiment, a solution containing 0.14 g. of sucrose in 50 cc. of 0.0008 *M* uranyl sulfate without buffer was photolyzed under its own vapor pressure, and the results showed that the production of the reducing sugars was affected less than 20% by dissolved oxygen from the air which enters the photosensitized oxidation of iodide by uranyl sulfate.¹⁶

Kinetics of the Photosensitized Reaction.—The primary act is the capture of a photon by a uranyl particle. Part of the activated uranyl particles are sufficiently close to sucrose and the other reactants and properly oriented to initiate the hydrolysis. The fraction of the activated

particles so disposed is proportional to ϕ , whereupon

$$\phi = B[\text{UO}_2\text{SO}_4]^n[\text{sucrose}]^m[\text{H}_3\text{O}^+]^p \dots / [\text{UO}_2\text{SO}_4] \quad (1)$$

where *B* is the proportionality constant and the sum of the exponents in the numerator equals the number of reactant particles entering the photochemically active cluster. When ϕ cannot exceed a finite value *a*

$$\phi = a[1 - \exp(-gx)] \quad (2)$$

where *x* is directly proportional to the right side of (1) and *g* includes *B*. At small values of *gx* equation (2) becomes

$$\phi = agx \quad (3)$$

In this range of values, each exponent except that of the photosensitizer, uranyl sulfate, equals the slope of the plot of log ϕ against the logarithm of the concentration of the corresponding reactant when other variables are fixed. For the photosensitizer, however, *n* equals one plus the slope. The independence of ϕ upon the concentration of uranyl sulfate between 0.008 and 0.0008 *M* in Expts. 4 and 5, and in 19, 20 and 21, therefore, shows that only one uranyl particle enters the reactive complex. These results also confirm the observed independence of ϕ upon the light intensity, *I*, in Expts. 6 and 8, and 9 and 10, where *I* was changed over 200-fold, yet ϕ was not affected. They also show that the stirring adequately prevented the local depletion of reactants in the zones absorbing most of the actinic light, and that the transparent quartz stirrers did not alter the amount of light absorbed by the solutions even when there impinged on the stirrers possibly one-tenth of the light incident on the most dilute solutions of uranyl sulfate.

The points on a plot of log ϕ at 254 μ . in the buffered solutions against log (sucrose) fell on a curved line that approached unit slope, within experimental error,¹⁷ only when ϕ was less than 0.1. Therefore, the largest observed values of ϕ are too near the maximum value for equation (3) to hold. The approach of the plot to unit slope when ϕ is small, however, shows that *m* = 1. Thus, one molecule of sucrose enters the reaction with each uranyl particle.

In Fig. 1, the equation for the curve is

$$\phi = 0.3 [1 - \exp(-g[\text{sucrose}])] \quad (4)$$

g = 1 when, as plotted [sucrose] equals grams in 50 cc. of solution, but for [sucrose] in moles per liter of solution, *g* = 0.585.

(17) A straight line through all the points had a slope of 0.77 calculated by the method of least squares.

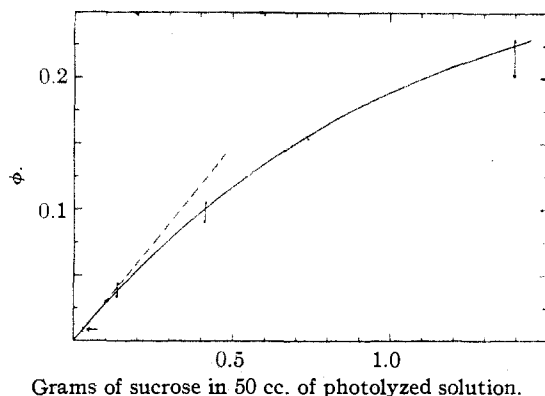
(13) Cantieni, *Helv. Chim. Acta*, **18**, 808 (1935).

(14) See also Baur and Rebmann, *ibid.*, **5**, 221 (1922).

(15) Pitzer, Gordon and Wilson, *THIS JOURNAL*, **58**, 67 (1936).

(16) Schneider, *Z. physik. Chem.*, **203**, 311 (1935).

The choice of 0.3 for a and of 1 for m was confirmed by a plot of $\log \log [(a - \phi)a]$ against $\log [\text{sucrose}]$ in which the points, within the limits of error, fell on a line with unit slope.



Grams of sucrose in 50 cc. of photolyzed solution.

Fig. 1 illustrates, for the initial reaction, the increase of quantum yields, ϕ , at 254 $m\mu$, with [sucrose] in acetate buffered solutions of uranyl sulfate. No other variables needed to be fixed because ϕ was independent of them. Vertical lines represent the spread of all the observed values at pH 3.5 to 6.0 and at 10 to 35°. The curve was calculated from theory. The dotted line gives the linear dependence of ϕ upon [sucrose] as both terms approach zero. The slope of this line equals ag where a is the maximum value of ϕ and g is also a constant.

The factor a equals the maximum value of ϕ at this wave length in these buffered solutions. It is a function of the transfer and utilization of energy within the complex.

The factor g includes the equilibrium constant K for the reaction defined in equation (1). As the stability of the cluster increases, g will increase. When more clusters are formed with increasing temperature, ϕ will approach a , and the temperature coefficient of ϕ will approach zero. The temperature coefficient will also be small for ϕ much less than a when $d(\ln K)/dT = -\Delta H/RT^2$ is small. In Expts. 6 and 10, ϕ remained unchanged while the temperature was increased from 10 to 35°, which shows that ΔH is small since these values of ϕ were not near $\phi = a$.

The independence of ϕ upon the pH in Expts. 4 and 6, and 21 and 22, shows that the catalytic effect of the hydrogen ions is replaced by the activated uranyl salts.

In Fig. 2, the plots of wave length against $\log \phi$ for the sugar and actinometer solutions have a dip in the ultraviolet at which ϕ is, roughly, 25% of ϕ at 436 $m\mu$. The values of ϕ for sucrose at 366 and 436 $m\mu$ may be slightly high because

absorption of light was incomplete and small increases in the concentration of the uranyl sulfate from the values given would increase ϕ measurably, but would hardly be detected in the measurements of the extinction coefficients by the null photographic method. The dip in ϕ at 208 $m\mu$ for the actinometer is due to absorption of this wave length by the oxalic acid.^{9b}

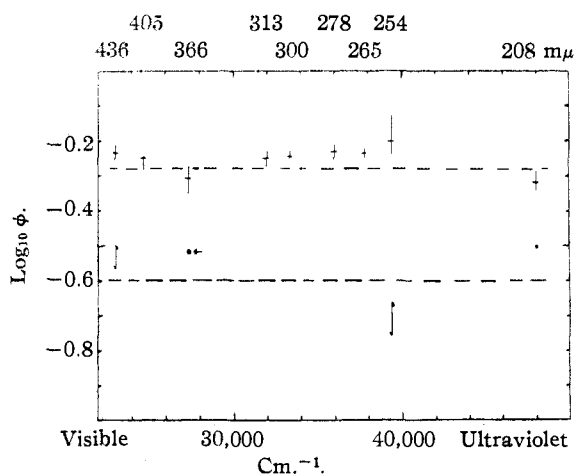


Fig. 2 illustrates the variations in quantum yields with wave length. The dotted lines only serve to emphasize these variations. Vertical lines of equal length give the same percentage spread of the separate, observed values of ϕ included in the average values tabulated. Lines with arrows represent the data for the photolysis of sucrose in the unbuffered solutions of uranyl sulfate given in Table I. Expt. 11 is not included. Lines without arrows represent the maximum values of ϕ at 25° for the oxalic acid-uranyl sulfate actinometer. The points where these lines are crossed give the logarithm of the weighted average values.⁹

It is also seen from Fig. 2 and Table I that blue light, at 436 $m\mu$, is just as efficient as the ultraviolet in the photosensitized production of reducing sugars from sucrose. This suggests that a part of the polysaccharides in plants is converted into simpler sugars by sunlight acting through naturally occurring photosensitizers.

Summary

Reducing sugars have been produced from sucrose by visible and ultraviolet light acting through uranyl salts as photosensitizers.

The decrease in the optical activity which accompanied the formation of the reducing sugars was approximately equivalent to the Shaffer-Hartmann-Somogyi estimations of reducing sugars calculated as invert sugar.

Quantum yields, ϕ , were calculated as molecules

of sucrose decomposed per photon absorbed by the system. The variation in ϕ with the concentration of sucrose was given by $\phi = a[1 - \exp(-g[\text{sucrose}])]$. At 254 m μ , $a = 0.3$ and $g = 0.6$ when [sucrose] was expressed in moles per liter and solutions were buffered with acetate. ϕ increased when the solutions were not buffered, but the pH then decreased slightly due to subsequent reactions. ϕ was independent of (1) the light intensity over a 200-fold range, (2) the temperature between 10 and 35°, (3) the pH between

3 and 6, and (4) the concentration of uranyl sulfate between 0.0008 and 0.008 molar.

The kinetics of the reaction have been discussed.

Extinction coefficients of uranyl sulfate solutions were obtained at intervals of 0.1 in the logarithm and are given for the dip in absorption about 366 m μ . Beer's law was obeyed and sucrose concentrations up to 100 times those of uranyl sulfate did not affect the measurements.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Aquation of Carbonato Pentammine Cobaltic Bromide

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Carbonate tetrammine cobaltic salts undergo little or no aquation in pure aqueous solution at ordinary temperatures. In other words, the carbonate group is not readily displaced from the complex ion by molecules of water. This is explained by its firm attachment, presumably by two covalent links.

In carbonato pentammine salts the carbonato group appears to be held by one polar and one covalent link. While the former would permit dissociation, the latter holds the carbonato group firmly, so that it cannot function as a separate ion. In agreement with this, their freshly prepared solutions, like those of the corresponding carbonato tetrammine salts, do not give the characteristic tests for the carbonate ion and exhibit the conductance to be expected of uni-univalent electrolytes.

One might expect, however, that carbonato pentammine salts with but a single covalent link holding the carbonato group, would undergo aquation more readily than the carbonato tetrammine salts. Yet, Werner and Gosling,¹ to whom we owe most of our knowledge of the carbonato pentammines, appear never to have observed any aquation of these substances, and Schwartz and Tede² state that dilute solutions of the nitrate are stable both in the dark and when exposed to ultraviolet light, as shown by the constancy of their electrical conductance. Duff,³ to be sure, found that while dilute solutions of the nitrate showed

no change in conductance at 25° by themselves, an increase in conductance took place when the solutions were left in contact with platinum electrodes. Solely on the basis of this evidence he inferred that carbonato pentammine nitrate does not aquate spontaneously, but does so under the catalytic influence of the platinum. The latter part of this inference was and is quite unjustified, because no such catalytic effect on aquation has ever been observed by others, while it has long been recognized that the decomposition of cobalt ammines is markedly accelerated by contact with platinum electrodes.⁴

In this situation it appeared of interest to examine solutions of these carbonato pentammines more particularly for possible aquation, and this we have now done by means of measurements of the conductance of dilute solutions of the bromide at 25 and 0°.

The carbonato pentammine cobaltic bromide was prepared through the nitrate following the methods of Werner and Gosling.¹ The conductances were measured using "dip" electrodes following the procedure previously described in another connection.⁵ Duplicate readings were taken over an interval of more than an hour with and without the removal of the electrodes from the solution. Identical changes in conductance took place in each instance indicating that the platinum electrodes exerted no perceptible effect under the circumstances.

(1) Werner and Gosling, *Ber.*, **36**, 2380 (1903).

(2) Schwartz and Tede, *ibid.*, **60**, 65 (1927).

(3) Duff, *J. Chem. Soc.*, **123**, 573 (1923).

(4) Lamb and Larson, *This Journal*, **42**, 2025 (1920); Lamb and Yngve, *ibid.*, **43**, 2354 (1921); Brønsted, *ibid.*, **40**, 439 (1927).

(5) Lamb and Stevens, *ibid.*, **54**, 2643 (1932).