

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Evidence for Pentavalent Uranium as an Intermediate in the Reaction in Water between Photoactivated Uranyl Ions and Sucrose and Closely Related Substances, and Quantum Yields for these Reactions

BY LAWRENCE J. HEIDT AND KENNETH A. MOON^{1,2}

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It has been discovered that photoactivated uranyl ions react in water with sucrose and closely related substances to produce presumably the +5 state of uranium which subsequently disproportionates thermally into the +4 and +6 states. Quantum yields have been measured for the reduction of the uranyl ions and have been found to be independent of the concentration of uranyl ion but to increase with the concentration of carbohydrate. This behavior has been interpreted quantitatively in terms of simple reactions. The reactions were carried out at 25° with light of 2537 Å. Photoactivated uranyl ions do not appear to react with uranous ions to produce U(V) in perchlorate solutions at a pH between one and two. The carbohydrate materials employed were: sucrose, D-fructose, D-glucose, D-gluconic acid, and the methyl glycosides: β,L-arabinopyranoside, α,D-fructofuranoside, α,D-glucopyranoside and α,D-mannopyranoside. Complexes of uranous ion with glucose and the methyl glucoside have been identified and their association constants have been estimated.

The photochemical reaction between uranyl ions and sucrose has been shown by previous work in this Laboratory^{3a} to produce material which (a) produces cuprous oxide when heated together with the cupritartrate complex in mildly alkaline solution (b) decreases the optical activity of the solution and (c) browns the solution although the browning can be reduced by carrying out the reaction in the absence of air. In unbuffered solutions, it was found that the reaction produces eventually a pale green precipitate^{3a} which reduces cold permanganate and dichromate in acid,² so presumably contains uranium in the plus four state of oxidation, *i.e.*, U(IV). In solutions strongly buffered with acetate the reaction does not produce a precipitate and the results have been previously interpreted^{3a} in terms of a photosensitized hydrolysis of the glycosidic linkage of the non-reducing sugar, sucrose, into the reducing sugars, D-fructose and D-glucose the equimolar mixture of which is commonly known as invert sugar.

This article reports results indicating that the primary reaction in both buffered and unbuffered solutions reduces the uranium from the plus six, U(VI), to the plus five, U(V), state of oxidation and that the U(V) disproportionates by a thermal reaction into U(VI) and U(IV). Both U(V) and U(IV) have been found to be thermally oxidized slowly to U(VI) by oxygen dissolved in the solution,² so the work was carried out in an inert atmosphere. The concept of the reaction as mainly a photosensitized hydrolysis of the sugar is, therefore, no longer tenable.

Quantum yields have been measured for the reduction of the uranyl ion in an inert atmosphere of carbon dioxide as a function of the concentrations of the reactants cited in the abstract. These results can be interpreted in terms of simple reactions.

(1) The authors are indebted to the Sugar Research Foundation, Inc., under the scientific direction of Dr. R. C. Hockett, for a grant-in-aid in support of this work as part of an integrated program of research on fundamental physicochemical studies concerned with sucrose and closely related substances. The work was aided also by a grant from the Godfrey L. Cabot Fund of M.I.T.

(2) This article is based mostly on material presented in the thesis of Dr. Kenneth A. Moon in partial fulfillment of the requirements for the Ph.D. degree in Physical Chemistry at the Massachusetts Institute of Technology, June, 1952. The pertinent data will be found under the appropriate headings in this thesis.

(3) (a) L. J. Heidt, *THIS JOURNAL*, **61**, 3223 (1939); (b) see also C. Neuberger, *Biochem. Z.*, **13**, 305 (1908).

Materials.—Most chemicals were commercial reagents of C.P. or Analytical Reagent Grade or were obtained by recrystallization of these materials as described in the thesis.³

The "carbohydrate" materials were parts of samples purified previously in this Laboratory. They were all snow-white crystalline specimens whose m.p.'s and sp. rot. in water agreed with the accepted values.⁴

The uranyl oxalate was part of the very pure sample employed regularly for actinometry in this Laboratory.^{3a}

The basic uranous sulfate was prepared by the irradiation with sunlight of a solution of uranyl sulfate in a mixture of half water and half ethanol.⁵ The precipitate of the basic salt produced in this way was washed free of the mother liquor and air dried after a final washing with pure water. The uranous content of the salt corresponded within 0.4% to the formula $UOSO_4 \cdot 7H_2O$ as determined by titration with a standardized solution of ceric sulfate.

The uranous perchlorate stock solution was prepared by the electrolytic reduction of a well stirred solution of uranyl perchlorate. The reduction was carried out in a glass vessel with a cathode of platinum gauze; the solution was separated from the anode compartment by means of a Coors porous cup containing the anode of platinum gauze in perchloric acid.

The uranyl perchlorate stock solution, 0.1 M U(VI) and 0.8 M perchloric acid was prepared by dissolving the proper amount of uranium trioxide in perchloric acid. The trioxide was prepared by the method of Lebeau,⁶ although it was recognized later that the solution could have been prepared more easily by fuming uranyl nitrate with perchloric acid and subsequently adding the proper amount of water.

Experimental.—The apparatus employed to irradiate the solutions was similar to one previously described.⁷ Over 98% of the light incident upon the reaction vessels was of 2537 Å; none was of shorter wave length.

The reaction vessels were matched sets of cylindrical cells of fused quartz; one set of three had a capacity of 23 ml. each and the other set of three a capacity of 45 ml. each up to their necks.

The solutions were kept under controllable atmospheres by means of a device similar to one described elsewhere.⁸

The lamp, filter, reaction vessel and stirring ensemble were clamped to the same vertical shaft so the unit could be assembled conveniently and moved to the desired location without altering the alignment. The shutter consisted of a piece of copper tubing which fitted loosely between the filter and reaction vessel. Photolyses were begun by dropping the shutter after the intensity of the light had become constant.

The solutions were degassed before they were covered with an inert atmosphere of carbon dioxide. Care was taken to avoid loss of solution from the reaction vessel by the sudden release of gas during this operation. The photolyzed solutions also were kept in an inert atmosphere

(4) L. J. Heidt and C. B. Purves, *THIS JOURNAL*, **62**, 1006 (1940) and **66**, 1385 (1944).

(5) W. E. Harris and I. M. Kolthoff, *ibid.*, **67**, 1484 (1945).

(6) P. Lebeau, *Compt. rend.*, **154**, 1808 (1912).

(7) L. J. Heidt and H. B. Boyles, *ibid.*, **73**, 5728 (1951).

(8) L. J. Heidt and G. G. Palmer, *Science*, **114**, 467 (1951).

of carbon dioxide while samples were being withdrawn. The transfer pipets and the vessels which received the samples were filled with the same atmosphere.

The light flux reaching the solutions in the reaction vessel was determined by means of the uranyl oxalate actinometer in the manner previously described.^{2a} The actinometer was a water solution 0.0017 *M* in uranyl oxalate and 0.004 *M* in oxalic acid.

The value of the absorbency, $\log_{10} (I_0/I)$ per cm., of the actinometer solution and of the solutions under investigation were not always equal but both solutions always absorbed over 90% of the actinic light of 2537 Å. perpendicularly incident upon them before this light reached the center of the reaction vessel. The fraction of light of this wave length incident at all angles upon these solutions in the cylindrical reaction vessels but not absorbed by these solutions was always small. This was determined by changing the concentration of the uranyl oxalate solution so that its absorbency varied from 2.8 to 56.0 cm.⁻¹ for light of 2537 Å. compared to a value of 5.6 cm.⁻¹ for the actinometer solution regularly employed and by measuring the amount of oxalate destroyed in these solutions per unit time while the intensity of the light incident upon them and the volumes irradiated were held constant. The solutions whose absorbencies were 2.8 and 56 cm.⁻¹ were found to absorb, respectively, less than 1.5% less and less than 1.5% more of this light per unit time than the solution whose absorbency was 5.6 cm.⁻¹. None of our solutions exceeded this range of absorbency for this actinic light so our quantum yields are subject to an uncertainty of less than 1.5% because of the difference between their absorbencies and that of the actinometer solution employed to measure the light flux.

The photolyses were carried out in a thermostated water bath at 25°. In the acetate buffered solutions, the buffer was a mixture of sodium acetate and acetic acid at a total concentration of 0.2 *M*, the initial concentration of uranyl sulfate was 0.0077 *M* and the *pH* ranged from 3.3 to 3.6 except in some of the experiments carried out to check the earlier work,^{2a} which we were able to reproduce within the limits of error.

In the unbuffered solutions, the initial concentrations were mostly $U(VI) = 0.010 M$, $ClO_4^- = 0.50 M$, $Na^+ = 0.40 M$, ionic strength $\mu = 0.51$, $H_3O^+ = 0.08 M$, and *pH* = 1.1.

The spectrophotometric work was done with a calibrated Cary recording spectrophotometer, Model 11, Serial No. 69. All absorbencies are in terms of $\log_{10} (I_0/I)$ and were measured at 25°.

The *pH* values were read within 0.002 by means of a Cambridge Instrument Co. Model R *pH* Meter using their standard internal glass electrode ensemble. The instrument was standardized in the recommended way with solutions of potassium hydrogen phthalate and tartrate.

Optical rotatory powers were measured for the *D* lines of sodium within 0.02° at 25° by means of a Schmidt and Haensch Polarimeter.

Normax Brand glassware was employed for volumetric work requiring close tolerances.

Results and Discussion

Part I. Evidence for the Reduction of Uranyl, U(VI), to Uranous, U(IV) Ions by the Photochemical Reaction.—The photochemical reduction of the uranyl ions by the sugar was revealed to us first in buffered solutions like those previously studied.^{2a} The reduction of the uranium became evident when we compared the colors of the photolyzed and unphotolyzed portions of the same original solution and observed that the irradiation had produced a greenish tinge. Thereupon, a determination of the visible absorption spectra of the solutions showed that the tinge was due to the development of a strong absorption peak near 6500 Å., which is characteristic of uranous ions. This was demonstrated by determining the absorption spectrum of a synthetic solution of uranous acetate in nearly the same environment and comparing its spectrum with that of the photolyzed solution. These

spectra are displayed in Fig. 1; their striking similarity leaves little doubt that U(IV) is produced by the photolysis. Similar spectra did not develop in the unphotolyzed portions of the solutions even after standing in the dark for several weeks nor were such spectra developed by the irradiation of similar solutions lacking only the sugar.

Part II. Evidence for the Production of Penta-valent Uranium, U(V), as an Intermediate in the Photochemical Reduction of Uranyl Ions and for the Subsequent Thermal Disproportionation of the U(V) into U(VI) and U(IV).—The role of U(V) in the photochemical reaction was revealed in the unbuffered perchlorate solutions at a *pH* between 1 and 2 under conditions where the equilibrium concentration of U(V), the hydrolysis of UO_2^{++} and UO_2^+ and the dimerization of UOH^{+3} are negligible^{9a} and any atmospheric oxidation of U(V) or U(IV) was kept negligible by employing an inert atmosphere of carbon dioxide. The key observation was the discovery that the irradiation of these solutions was followed by a transient increase in their visible absorbency. The increase was especially marked in the neighborhood of the 6500 Å. absorbency peak of U(IV) as is shown in Fig. 2. The results presented in this figure were observed through a ten-cm. depth of a photolyzed solution whose *pH* was 1.5 and whose initial composition was 0.01 *M* uranyl perchlorate, 0.011 *M* glucose and 0.029 *M* perchloric acid. The solution had been irradiated with light of 2537 Å. until about seven per cent. of the U(VI) had been reduced. The only species in the solution absorbing a significant fraction of light between 5000 and 7000 Å. are those containing U(IV)^{2,9}; so the transient dark reaction was due either to an increase in the absorbency per unit of U(IV) or in the concentration of U(IV). The former possibility requires large changes in the fractions of light absorbed by the various U(IV) complexes and this seems unlikely since the character of the visible absorbance curve of the solution did not change measurably throughout the after-effect and was essentially the same as that of synthetic solutions of U(IV) and glucose.² The kinetics of the reaction, moreover, can be attributed satisfactorily to the disproportionation of U(V).

Let D and D_0 represent the transient and final values of the absorbency per cm. of the freshly photolyzed solutions at the peak near 6500 Å. Also, let E_4 represent the absorbency per cm. per mole of U(IV) in all forms per liter and c_5 the concentration of U(V). Then $c_5 = 2(D_0 - D)/E_4$ since two U(V) produce one U(IV).

Let us now examine the rate equation for the disproportionation of U(V). This equation has been found^{9b} to be $-dc_5/dt = k(H^+)c_5^2$. Accordingly, plots of $1/c_5$ vs. time as determined from our absorbency measurements should fall on a line whose slope is $k(H^+)$. Such a plot appears in the

(9) (a) K. A. Kraus and F. Nelson, *THIS JOURNAL*, **71**, 2510 (1949); and **72**, 3901 (1950); (b) H. G. Heal and J. G. N. Thomas, *Trans. Faraday Soc.*, **45**, 11 (1949); (c) D. M. H. Kern and E. F. Orlemann, *THIS JOURNAL*, **71**, 2102 (1949); (d) F. R. Duke and R. C. Pinkerton, *ibid.*, **73**, 2361 (1949); (e) C. Voegtlin and H. C. Hodge, "National Nuclear Energy Series VI.1," Chapt. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

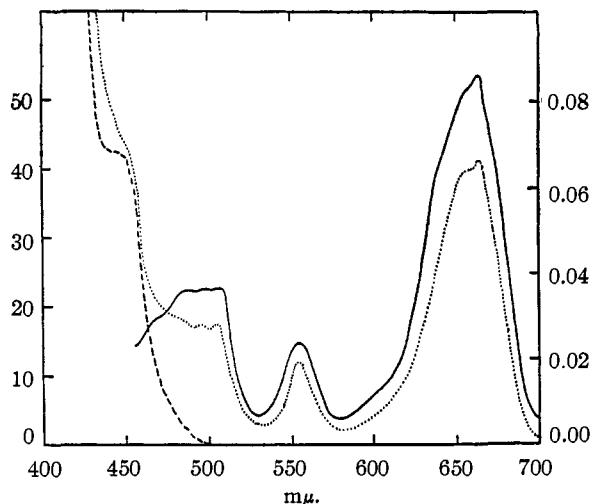


Fig. 1.—Spectroscopic evidence for the production of tetravalent uranium, U(IV), by the photolysis of aqueous solutions of sucrose and uranyl sulfate. The dotted and dashed lines represent, respectively, the visible absorption spectra of portions of the solutions which had and had not been photolyzed with light of 2537 Å.; the right hand ordinate gives the absorptivity values for these solutions. The solid line represents the absorption spectrum of a synthetic solution of uranous sulfate, the left hand ordinate gives for this solution the absorptivity values per mole of U(IV) per liter. All solutions contained nearly the same concentrations of sucrose and uranyl sulfate and were buffered at pH 3.6 with the same mixture of acetic acid and sodium acetate at a total concentration of 0.2 M. The temperature was 25°.

upper part of Fig. 2 where it will be seen that the results do fall rather well on the straight line whose equation is $1/c_5 = 1960 + 8.77t$; hence, the concentration of U(V), namely c_5^* , existing at the instant the irradiation was discontinued was $1/1960 = 5 \times 10^{-4}$ mole per liter and k is $8.77/0.029 = 300$.

The value of c_5^* can be evaluated also in another way. The rate of formation of U(V) is ϕI and the rate of destruction of U(V) is $k(H^+)c_5^2$; so c_5^* also equals $[\phi I/k(H^+)]^{0.5}$. The quantum efficiency for the production of U(IV) is $\phi/2$, and in this case, $\phi/2$ was about 0.1. The quanta absorbed by U(VI) per sec. per ml. of solution in the reaction vessel is I and this was 6.2×10^{-9} einstein of 2537 Å. These data, therefore, give a value for c_5^* nearly equal to $[0.2(6.2 \times 10^{-9})/8.77]^{0.5}$ or 4×10^{-4} which is in satisfactory agreement with the better value of 5×10^{-4} obtained for c_5^* by the extrapolation of the above plot to $t = 0$.

The Becquerel effect exhibited by mixtures of U(VI) and U(IV) in dilute sulfuric acid and some other acids is due to the formation of U(V) by a reaction between photoactivated uranyl ions and U(IV).^{9a} This reaction does not take place in chloride solutions.^{9b} Nevertheless, a similar reaction may be responsible for the production of U(V) in our perchlorate solutions. Experiments, therefore, were carried out to test this possibility; they were identical in every respect to the experiment cited above except that glucose was omitted from the solution and instead of starting with all the uranium in the U(VI) state, the solution was made

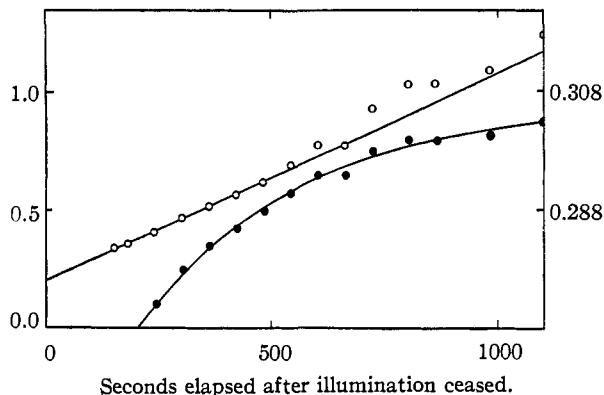


Fig. 2.—Evidence for the production of pentavalent uranium, UO_2^+ , when photoactivated uranyl ion reacts with sugar in water. The lower curve depicts the increase in absorbance, D^1 , at the 6500 Å. peak of uranous ion following the photolysis of a uranyl-sugar solution. The absorbance in this case reached a final value of 0.318 for the ten cm. depth of solution. The upper curve depicts the increase with time in the reciprocal of the difference between the final and observed values of this absorbency. The linear character of this increase is attributable to the thermal disproportionation of U(V) into U(IV) and U(VI). The right and left hand ordinates represent, respectively, the values of D^1 and $0.021/(0.318 - D^1)$.

up of equal parts of uranyl and uranous perchlorates. In these experiments, the absorptivity of the U(IV) peak near 6500 Å. remained constant from the instant the irradiation was discontinued until more than one thousand seconds later; hence, the concentration of U(V) produced by any reaction between photoactivated uranyl ions and U(IV) in these perchlorate solutions is negligible and the after-effect observed in the carbohydrate solutions is produced entirely by the photochemical production of U(V) from U(VI) by the carbohydrate.

Values reported for the rate constant, k , for the disproportionation of U(V) at 25° are: 97 in hydrochloric acid^{9a} at an ionic strength, μ , of 0.15 M; 130^{9c} and 156^{9a} in perchloric acid at μ equal to 0.4 and 0.5, respectively; and 8000 in sulfuric acid^{9c} at μ equal to 1.5. Our value of 300 in perchloric acid at μ equal to 0.5 is about twice as large as the above value, but it would be surprising if the organic material in our photolyzed solutions did not exert a catalytic effect in view of the strong catalytic effect exerted by sulfuric acid.

Similar results regarding the production of U(V) were obtained with D-gluconic acid and methyl α ,D-glucopyranoside. Sucrose and methyl α ,D-fructofuranoside were not employed in solutions at a pH below 3 because they are too rapidly hydrolyzed thermally, the half-life of sucrose being about eight minutes at pH 1 and 25°, and it is even less for the other fructoside.⁴ Sucrose is α ,D-glucopyranosido- β ,D-fructofuranoside. The methyl glucoside could be employed because the half-life of its acid hydrolysis is about ten thousand times longer than that of sucrose.⁴ D-Glucose was employed because it is the product of the hydrolysis of both the methyl glucoside and sucrose and D-gluconic acid was employed because it is the first product of the oxidation of glucose at carbon atom one.

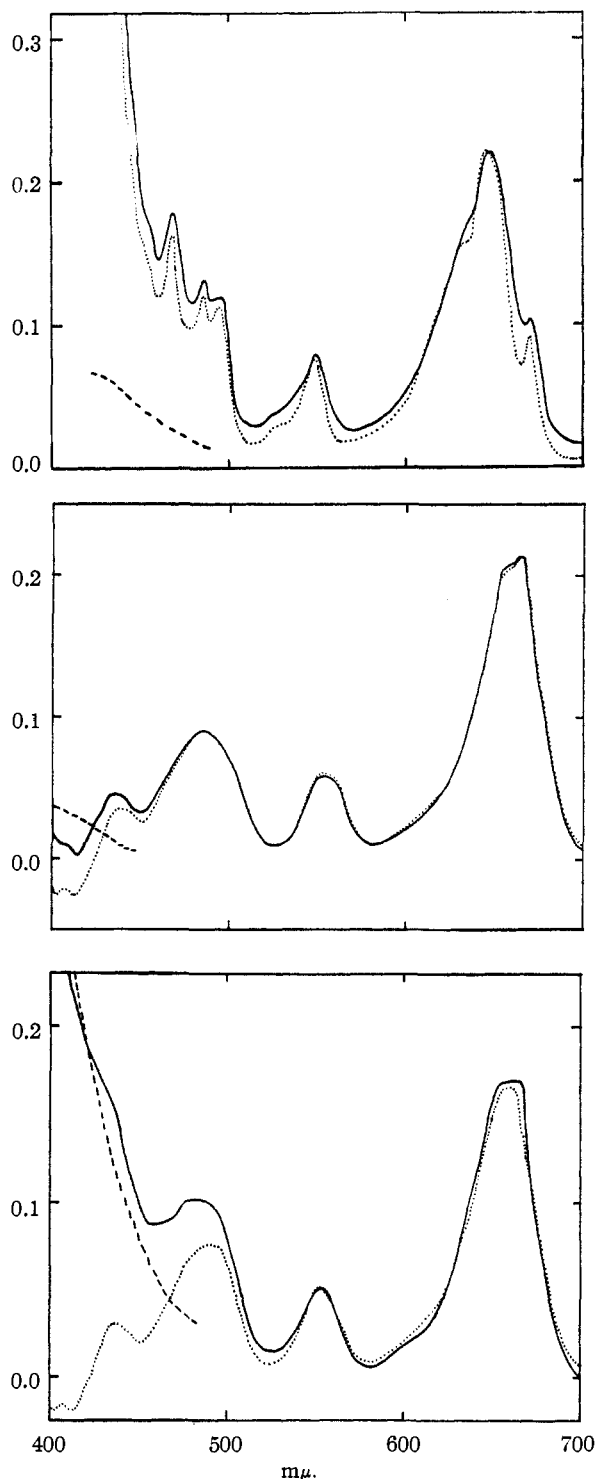


Fig. 3.—Absorbance curves produced by the photolysis of unbuffered solutions of uranyl perchlorate and sugar (solid lines) and of unphotolyzed synthetic solutions containing also uranous perchlorate (dotted lines). The other lines represent the difference between the solid and dotted curves. Absorbance values are given by the ordinates and are for a depth of ten cm. of the respective solution compared to portions of the uranyl solution which had not been irradiated. In every case, the initial concentration of the uranyl perchlorate was 0.01 *M*, the temperature was 25° and the *pH* and ionic strength were adjusted to 1.1 and 0.51, respectively. The uppermost set of curves is for 0.1 *M* glucose solutions in

which 6.5% of the U(VI) had been converted into U(IV). The middle and lowermost sets of curves are for 0.1 and 0.01 *M* gluconic acid solutions in which 9.2 and 8.2%, respectively, of the U(VI) had been converted to U(IV). In every case, there is close agreement between the absorbencies of the photolyzed and synthetic solutions at the peak near 6500 Å. but it can be seen that this is not always the case in the blue range of the spectrum where the organic products enhance the absorbance.

Our evidence for the production of U(V) in the photochemical reaction suggests that the primary photochemical process involves the transfer of one electron from the carbohydrate material to the uranyl ion and thereby lends support to the hypothesis¹⁰ that perhaps all photochemical reactions initiated by photoactivated uranyl ions involve the reduction of the uranium from U(VI) to U(V) even in cases where the uranyl ion appears to act as a photosensitizer such as in the decomposition of oxalic acid or one of its ions in the system employed for actinometry.

The equilibrium between U(VI), U(IV) and U(V) in the acetate-buffered solutions appears to be shifted completely to the side of U(VI) and U(IV) which presumably exist largely as acetate complexes. The evidence for this is that the optical density between 5000 and 7000 Å. of synthetic solutions of U(IV) at (9.5 to 62.2) 10^{-4} *M* and U(VI) at (11.4 to 21.4) 10^{-4} *M* in 0.2 *M* acetate buffer at *pH* 3.5 ± 0.1 was found to be independent of the value of the ratio of U(IV)/U(VI) between 0.8 and 2.9 but this would not have been the case if the U(IV) had reacted with the U(VI) to produce U(V) to the same extent as in the absence of the acetate.⁹

Part III. Determination of Quantum Yields for the Reduction of U(VI) to U(IV) in an Inert Atmosphere.—Quantum yields, ϕ , during the initial stage of the reaction have been calculated for the production of U(IV) on the basis that the light of 2537 Å., employed to produce the reaction, was absorbed mainly by U(VI) and that the visible light employed to determine U(IV) at its absorbency peak near 6500 Å. was absorbed to the same extent per unit of U(IV) as in synthetic solutions of U(IV) in the same initial environment. Some error results from this simplification but the error is not large. In the first place, the absorbency per unit of uranium at 2537 Å. is greater for U(VI) than for any of its other valence states,^{2,9} and in these experiments the concentration of the U(VI) state was always greater than any of the other valence states. In the second place, the character of the absorbance curves of all the photolyzed solutions were essentially the same between 5000 and 7000 Å. as those of corresponding synthetic solutions containing the reactants and U(IV) as is shown in Figs. 1 and 3. In the third place, although the organic products of the reaction do complex with the U(IV) as revealed by the greater absorbency of the photolyzed than of the synthetic solutions in the blue end of the spectrum even after correction for the absorbency of the U(VI) species, this effect, we believe, is due largely to complexing

(10) J. Weiss, *Trans. Faraday Soc.*, **34**, 451 (1938).

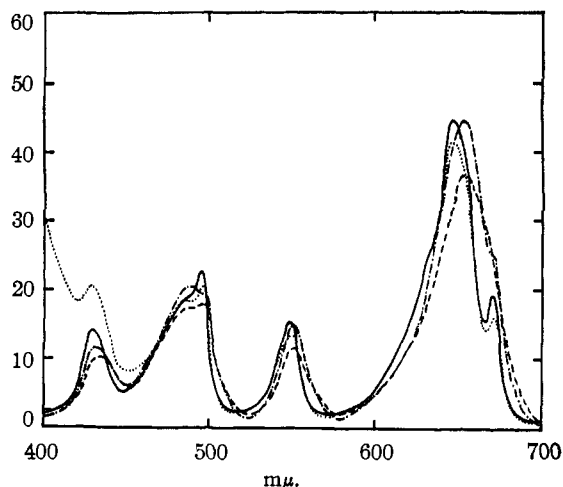


Fig. 4.—The enhancement produced by the enediol, ascorbic acid, upon the blue absorbency of uranous perchlorate solutions at 0.005 to 0.006 *M* and *pH* 1.1. The solid line is for uranous perchlorate alone. The dotted line is for a similar solution containing also the enediol, ascorbic acid, at 0.0057 *M*. The other lines show that *D*-gluconic acid at 0.0056 *M* (dashed line), and citric acid at 0.0047 *M* do not produce this effect. The ordinate represents the absorbency per mole of U(IV) per liter at 25°.

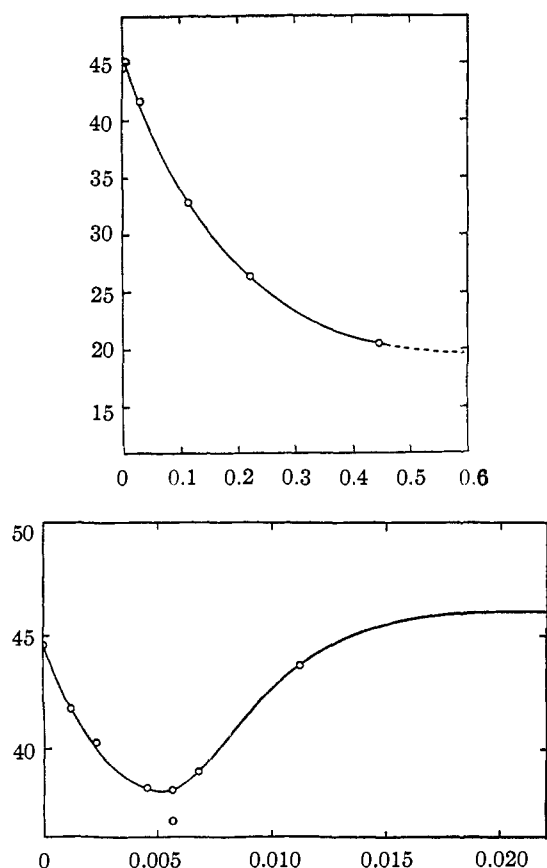


Fig. 5.—Calibration charts employed to determine spectrophotometrically the U(IV) in perchlorate solutions of glucose (upper curve), and of gluconic acid at *pH* 1.1, ionic strength 0.51, and 25°. The abscissa represent moles sugar per liter; the ordinates represent the absorbency per mole U(IV) per liter at the peak near 6500 Å.

of the U(IV) with enediolic products as shown in Fig. 4 and these complexes are seen to possess absorbency peaks near 6500 Å. which are of about the same magnitude per unit of U(IV) as the peaks of the other U(IV) complexes, so the error they introduced into our estimation of U(IV) is negligible.

The calibration charts for the spectrophotometric determinations of U(IV) in the unbuffered solutions appear in Fig. 5. The charts for U(IV) solutions containing glucose and methyl glucoside solutions are identical; their visible absorbency curves display nine isosbestic points between 4000 and 7000 Å. There is consequently only one kind of uranous complex of each of these compounds over the prevailing range of conditions and an analysis² of the data showed that each of these complexes contains only one U(IV) and one glucose or one glucoside unit and that the association constants of the complexes have about the same value, namely, 5. The visible absorbency curves for similar solutions of uranous perchlorate and gluconic acid displayed no isosbestic points although they crossed at several places,² so more than one kind of U(IV) complex is present in these solutions.

The visible absorbency curves for the acetate buffered solutions were not affected by the carbohydrate material in our photolyzed solutions, but the absorbency values change with the *pH* of the solution as shown in Fig. 6 and correction was made for this effect whenever necessary. The values for the first and second association constants of the uranous acetate complexes are 1300 and 320,

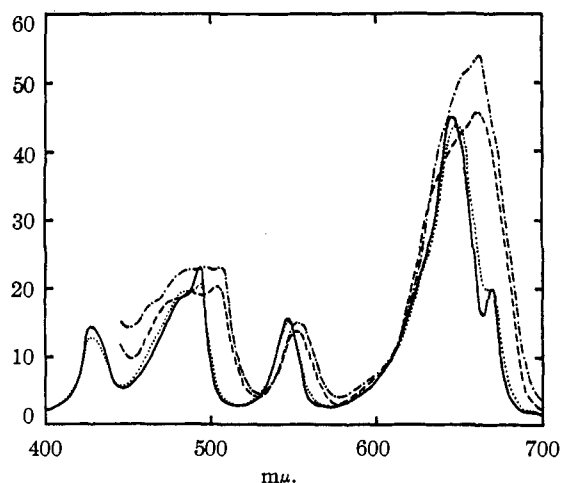


Fig. 6.—Influence of *pH* upon the absorbency at 25° of acetate buffered solutions of uranous perchlorate at 0.005 to 0.006 *M*. The ordinate represents absorbency values per mole U(IV) per liter. The solid line is for uranous perchlorate at *pH* 1.1 in the absence of any acetic acid or acetate. The dotted line is for a solution at *pH* 1.1 containing also acetic acid at 0.24 *M*. The dashed line is for a solution at *pH* 3.2 containing a mixture of acetic acid and sodium acetate at a total concentration of 0.2 *M*. The other line is for a solution similar to the last one mentioned except that the *pH* was 3.6. The absorbency peak in the vicinity of 6500 Å. moves toward longer wave lengths and is slightly enhanced as the *pH* is increased.

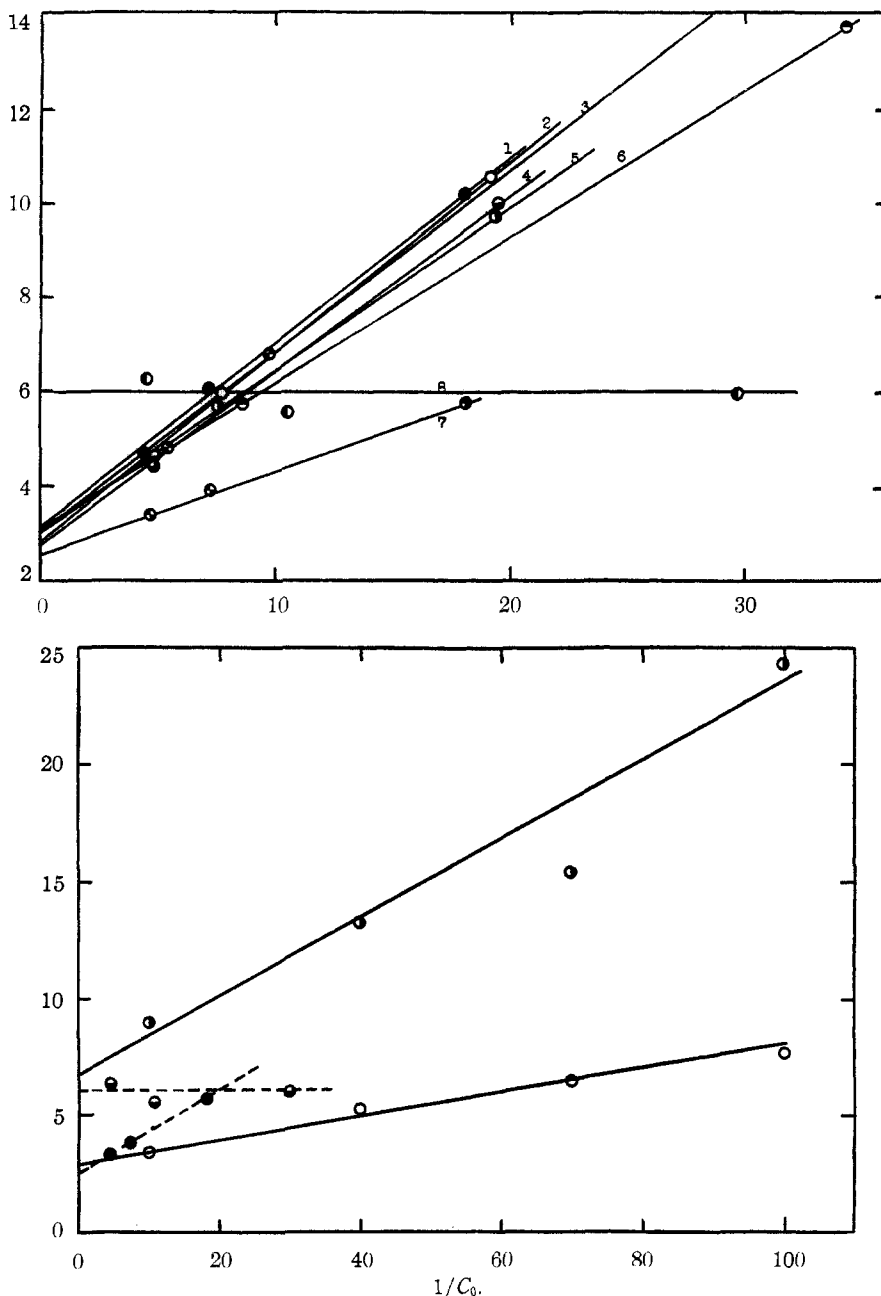


Fig. 7.—Influence of the initial sugar concentration, C_0 , upon the quantum yield, ϕ , for the production of U(IV) by light of 2537 Å. absorbed by uranyl-sugar solutions. The solutions were irradiated and stored under an inert atmosphere of carbon dioxide.

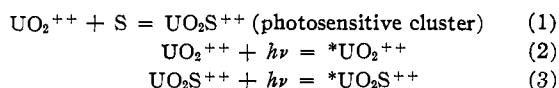
The upper set of curves is for 0.2 M acetate-buffered solutions at $pH\ 3.5 \pm 0.1$ and 25°. The initial concentration of uranyl sulfate was 0.0077 M, the fraction converted to U(IV) ranged from about 14 to 50% under conditions where ϕ is nearly independent of this fraction and of the light intensity. The numbers alongside the lines identify the compounds: 1, D-fructose; 2, methyl- α ,D-mannopyranoside; 3, methyl- α ,D-fructofuranoside; 4, methyl- α ,D-glucopyranoside; 5, methyl- α ,D-arabinopyranoside; 6, sucrose; 7, D-glucose and 8, D-gluconic acid. The structural relationship between these compounds is given in the text.

The lower set of curves extending to $1/C_0 = 100$ gives the results obtained in unbuffered solutions initially 0.01 M in uranyl perchlorate at $pH\ 1.1$. In these solutions 7% of the U(VI) had been converted photochemically to U(IV) by glucose, open circles, and by gluconic acid, half-filled circles. Also, included for comparison are the results obtained under about the same conditions with the same sugars, represented by

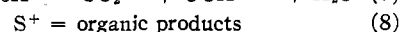
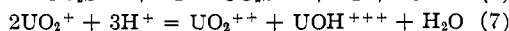
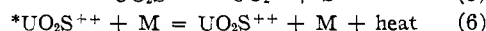
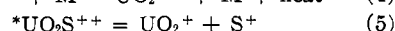
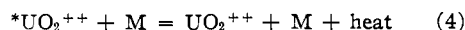
filled circles in the case of sucrose, in the acetate buffered solutions at $pH\ 3.4$. A simple interpretation of these results is given in the text.

respectively.^{9e} Photoreduction of uranyl ions by the acetate buffer is negligible.¹¹

Part IV. Dependence of the Quantum Yields upon the Concentrations of the Reactants and a Simple Quantitative Interpretation of These Results.—The dependence of ϕ upon the concentration of uranyl ion is negligible^{3a} but ϕ does depend upon the concentration, C , of the carbohydrate material as has been previously observed in the case of sucrose^{3a} and as can be seen in Fig. 7. In every case the values of $1/\phi$ in this fig. are seen to depend linearly upon $1/C$. This behavior is in accord with the following set of simple reactions



(11) K. Clusius and M. Geldmacher, *Z. Elektrochem.*, **53**, 197 (1949).



Fluorescence and secondary back reactions have been neglected. Accordingly, $\phi = K_5[{}^*\text{UO}_2\text{S}^{++}]/2I$ where I represents quanta of actinic light absorbed by U(VI) per unit volume per unit time. Also $+d[{}^*\text{UO}_2\text{S}^{++}]/dt = I[\text{UO}_2\text{S}^{++}]/([\text{UO}_2\text{S}^{++}] + [\text{UO}_2^{++}]) = I/(1 + 1/K_1C)$, where UO_2^{++} represents U(VI) in all forms except in the photosensitive cluster. Similarly, $-d[{}^*\text{UO}_2\text{S}^{++}]/dt =$

$K_6[*\text{UO}_2\text{S}^{++}] + K_6[*\text{UO}_2\text{S}^{++}][\text{M}]$. In the steady state, therefore, $[\text{*UO}_2\text{S}^{++}] = I/(1 + 1/K_1C)(K_5 + K_6[\text{M}])$ so $1/\phi = a + a/K_1C$ where $a = 2 + 2K_6[\text{M}]/K_5 = 1/\phi$ when $1/C = 0$, and where a/K_1 equals the slope of the plot of $1/\phi$ vs. $1/C$. The question as to whether a photoactivated uranyl ion reacts with any sucrose molecule within a given distance from it or if a certain combination of UO_2^{++} and S must be activated to produce the reaction as might be inferred from the above mechanism cannot be decided on the basis of our data. We have followed Weigert¹² in attempting to get around this dilemma by calling the combination of reactants potentially capable of bringing about the photochemical reaction upon the absorption of a photon, a photosensitive cluster. In the case of sucrose there is no evidence^{8a} that such a cluster containing UO_2^{++} and S differs in any way from any other pair of UO_2^{++} and S except as to the distance apart of the components. In the case of the anion of gluconic acid, however, an intimate association exists with UO_2^{++} giving rise to an absorption spectrum differing from the sum of the spectra of the two components in the absence of the other.³ In any case relative values of K_1 appear to be a measure of the relative concentrations of these clusters in these solutions.

Part V. The Photosensitive Clusters and their Relative "Association Constants" and Reactivities.—In the acetate-buffered solutions the photosensitive uranyl clusters of fructose, the four glycosides and sucrose and glucose, appear to have "association constants" K_1 which increase slightly in this order since the slopes of the corresponding lines in Fig. 7 decrease in this order. Nevertheless, these clusters all have about the same reactivity with respect to the measured reaction, since their lines all converge to about the same value at $1/C = 0$. Moreover, the point of convergence of the lines at $1/C = 0$ so nearly equals two that almost every photoactivated, $\text{*UO}_2\text{S}^{++}$, cluster produces the

measured reaction, namely, one UO_2^+ , two of which subsequently produce one U(IV) and one U(VI).

Gluconic acid appears to form a very stable photosensitive complex with uranyl ion at pH 3.5 since the line for it in Fig. 7 is nearly horizontal so K_1 is very large. The complex, however, is less often decomposed upon the absorption of the actinic light since the value of $1/\phi$ at $1/C = 0$ is significantly larger than in the case of the other carbohydrates.

The relationship between the structures of the carbohydrate materials is as follows: sucrose, the methyl glucoside, glucose and gluconic acid are related in the way already stated. D-Fructose is the product of the hydrolysis of the fructosides. The mannoside and glucoside are optical isomers. The arabinoside is similarly related to these glycosides except that the terminal CH_2OH group of the glucoside has been replaced by a hydrogen atom.

In the case of the unbuffered solutions at pH 1.1, the values of the intercepts are about the same as in the buffered solutions; hence, in the case of these substances the buffer does not decrease the production of U(IV) following the absorption of a photon by the cluster. The buffer, however, does decrease the concentrations of the clusters at least in the case of glucose, because the slope is less in the unbuffered solutions so K_1 is larger when glucose no longer is competing with acetate for UO_2^{++} . In the case of gluconic acid the slope in the unbuffered solutions is of the same order of magnitude as for glucose so the molecular form of the acid has no greater tendency than glucose to form photosensitive clusters with uranyl ions, and this implies that the more abundant clusters existing at pH 3.5 involve the anion of gluconic acid which nevertheless is as photochemically reactive as the cluster comprising the acid since the values of $1/\phi$ at pH 1 and 3.5 are seen to be about the same at $1/C = 0$.

(12) F. Weigert, *Z. physik. Chem.*, **102**, 416 (1922); **106**, 426 (1923).