

after the addition, the yield was slightly lower (324 g. or 86%). Substitution of sodium for potassium hydroxide in equivalent amount did not alter the results.

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RECEIVED OCTOBER 20, 1939

### A Photosensitized Production of Reducing Sugars from Starch

BY LAWRENCE J. HEIDT

Substances which reduce the Shaffer-Hartmann-Somogyi reagent are produced when light is absorbed by aqueous solutions containing uranyl sulfate and starch. The apparatus used to illuminate the solutions is described in *Science*, **90**, 473 (1939). The experimental procedure was the same as that given in *THIS JOURNAL*, **61**, 3223 (1939), for sucrose-uranyl solutions.

The ml. of hypo entered in Table I are calculated from the differences between S.-H.-S. estimations made simultaneously on the illuminated portions of a solution and on a portion kept in the dark, at the same temperature. When 5 ml. of water was added to 5 ml. of the S.-H.-S. reagent, the titration required 46.2 ml. of hypo, but 5 ml. of the unphotolyzed portions in Expts. 1, 2, 3, 4, 5 and 6 required 43.0, 45.5, 45.7, 42.8, 44.8 and 44.8 ml. of hypo, respectively. The potato starch, kindly supplied by Professor C. B. Purves, therefore contained very little reducing sugar, and both the illuminated and unphotolyzed solutions of starch in Expt. 4 appeared water-white.

Solutions were irradiated in quartz tubes at 21° with  $8.5 \times 10^{18}$  photons of  $\lambda$  254 m $\mu$  per minute incident on each 11 ml. sample. The starch solutions were 0.008 *M* in uranyl sulfate in Expts. 1, 2 and 3; 0.0004 *M* in quinine sulfate in Expt. 5; 0.0003 *M* in the sodium salt of fluorescein (Eastman Kodak Technical Grade) in Expt. 6 and contained only starch and water in Expt. 4. Each ml. of hypo entered in Table I was equivalent to  $5.7 \times 10^{-3}$  g. of glucose in the uranyl sulfate solutions and to  $5.5 \times 10^{-3}$  g. of glucose in the others.

The experiments with quinine and fluorescein were undertaken to discover for this reaction other photosensitizers—preferably dyes and natural products that absorb sunlight. The amount of reducing substances produced when quinine or fluorescein was present, however, was less or little

TABLE I

Expt.	Starch in 50 ml. g.	pH in soln. before photolysis	pH in soln. after photolysis	Min. photolyzed	Ml. of hypo	$\phi$
1a	0.5024	3.0	2.8	21.5	85	0.09
b			2.9	7.2	38	.12
c			2.9	5.0	29.5	.13
d			...	1.45	14.1	.22
2a	.1935	3.35	3.25	8.5	25.5	.07
b			...	4.0	18.0	.10
c			...	3.0	16.0	.12
d			...	2.0	12.1	.14
3a	.0658	3.5	3.4	24.0	26.0	.024
b			...	12.0	17.8	.033
c			...	6.0	13.2	.050
d			...	3.0	8.8	.066
4	.4894	4.35	3.55	860.0	34.5	...
5a	.1935	3.9	3.6	49.5	4.0	< .002
b			3.0	624.0	79.0	< .002
6a	.1956	6.2	6.2	94.5	2.5	
b			5.6	283.0	6.6	

more than when they were absent and very much less than when uranyl sulfate was used. The intense blue fluorescence initially present in Expt. 5b disappeared toward the end of this photolysis and a light straw solution was formed, but in Expt. 6b the yellow fluorescence was only diminished. This also occurred in parallel experiments with solutions of quinine and fluorescein without starch and the pH likewise decreased but in the quinine solution the amount of reducing substances produced was less than 10% of that formed in Expt. 5b and none was formed from the fluorescein or from the uranyl sulfate alone in water.

Quantum yields,  $\phi$ , represent the number of oxygen bridges (linking the glucose units) broken per photon of  $\lambda$  254 m $\mu$  absorbed by the system if the measured product is glucose and one bridge is broken per molecule of glucose produced. This may be too simple an hypothesis except, perhaps, for the initial reaction.

In Expts. 4 and 6,  $\phi$  is not given because the extinction coefficients of these solutions were not known at this wave length. Nevertheless, Expt. 4 shows that the measured reaction in Expts. 1, 2 and 3 is mainly a photosensitized reaction. Also in Expts. 1, 2 and 3,  $\phi$  is smaller and falls more rapidly than for the photosensitized decomposition of sucrose at the same concentration of oxygen bridges, if there is one bridge per sucrose molecule and one per glucose unit in starch. This decrease in  $\phi$  probably is due to the colloidal nature of starch solutions and the chain character of the starch molecule, both of which

protect some of the chemical bonds in starch that would otherwise enter the measured reaction.

CONTRIBUTION NO. 433 FROM THE  
RESEARCH LABORATORY OF PHYSICAL CHEMISTRY  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY  
CAMBRIDGE, MASS. RECEIVED OCTOBER 23, 1939

## A New Method for the Cleavage of Unsaturated Fatty Acids<sup>1</sup>

BY CHI-YI HSING AND KOU-JEN CHANG

The methods for the cleavage of unsaturated fatty acids reported in the literature are either by energetic oxidations or by ozonization. On account of the side reactions, the degradation products are usually complex mixtures and the yields are very low.

Lead tetraacetate has been introduced by Criegee<sup>2</sup> as a reagent for the cleavage of glycols with excellent results. This oxidizing agent should be equally effective in oxidizing polyhydroxy fatty acids which in turn can be prepared easily from the corresponding unsaturated fatty acids by means of oxidation with alkaline potassium permanganate. It was found that 9,10-dihydroxyoctadecanoic acid (from oleic acid) was oxidized completely in twenty-four hours by lead tetraacetate in glacial acetic acid. As reaction products, pelargonic aldehyde and azelaic semialdehyde were isolated in the form of semicarbazones, each in a yield of about 85%. By using benzene as a solvent, 9,10,12-trihydroxyoctadecanoic acid (from ricinoleic acid, m. p. 111–112°) oxidized in four hours and about 90% of azelaic semi-aldehyde semicarbazone and a product melting at 112–113°, the character of which has not yet been determined, were obtained. A mixed melting point with starting material indicated it was different. The supposition is it may be  $\beta$ -hydroxypelargonic aldehyde semicarbazone or a related compound.

A more extensive study of this method for cleavage of unsaturated fatty acids of known and unknown structure will be reported later.

### Experimental

In 10 cc. of glacial acetic acid which had been distilled over phosphorus pentoxide, was suspended 0.6740 g. of 9,10-dihydroxyoctadecanoic acid and to the mixture 0.95 g. of lead tetraacetate was added. This was shaken for twenty-four hours at room temperature. The solution was fil-

tered and heated in a water-bath at 45° for five minutes. It was then treated with 15 cc. of water and a concentrated aqueous solution of 0.5 g. of semicarbazide hydrochloride and 0.6 g. of sodium acetate was added. To the reaction mixture was now introduced a few drops of methanol and it was then vigorously shaken. After standing in an ice box for twenty hours, the semicarbazones separated as a white precipitate. The precipitate was filtered and shaken with cold dilute aqueous sodium hydroxide to dissolve the azelaic semialdehyde semicarbazone. Undissolved, impure pelargonic aldehyde semicarbazone was filtered and washed with water. The alkaline filtrate was acidified with 2% hydrochloric acid. The precipitated azelaic semialdehyde semicarbazone was filtered, washed and dried, yield 0.434 g. (90%). After purification by crystallization from ethanol it melted at 163–164° (Harries and Thieme<sup>3</sup> reported 163°).

The alkali insoluble part consisted of lead chloride and pelargonic aldehyde semicarbazone. It was dissolved in methanol and the lead chloride was filtered. On evaporating the solution to a small volume, the semicarbazone separated as fine crystals melting at 99–100.5° (Bagard and Harries and Turk<sup>4</sup> reported 100°). The yield was 0.348 g. (82%).

(3) C. Harries and C. Thieme, *Ann.*, **348**, 359 (1905).

(4) P. Bagard, *Bull. soc. chim.*, **4**, I, 346 (1907); C. Harries and H. O. Turk, *Ber.*, **40**, 2756 (1907).

NATIONAL RESEARCH INSTITUTE OF CHEMISTRY  
ACADEMIA SINICA  
KUNMING, CHINA RECEIVED NOVEMBER 2, 1939

## Dependence of Conductance on Field Strength

BY DARWIN J. MEAD AND RAYMOND M. FUOSS

We recently reported the field dependence of the conductance of tetrabutylammonium picrate in diphenyl ether at 50° [THIS JOURNAL, **61**, 2047 (1939)]. We are indebted to Dr. L. Tonks of this Laboratory for calling to our attention a correction which we neglected. The limit approached by the Wien coefficient at zero concentration now agrees with Onsager's theoretical value, when the correction factor of  $8/3\pi$  is applied.

Our measurements were made in a bridge circuit, in which balance is indicated by zero current in a detector circuit fed through a low-pass filter. Our solutions were non-linear impedances, and the detector showed balance for only the fundamental frequency. According to theory, the specific conductance  $\kappa$  is given by

$$\kappa(t) = \kappa_0 + A V_m |\sin \omega t| \quad (1)$$

where  $\kappa_0$  is the low voltage conductance,  $A$  is Onsager's coefficient and  $V_m$  is the peak voltage of the sinusoidal input at frequency  $f$ , with  $\omega = 2\pi f$ . The unit current then is

$$i(t) = \kappa_0 V_m \sin \omega t + A V_m^2 \sin \omega t |\sin \omega t| \quad (2)$$

(1) Presented at the 7th Anniversary Meeting of the Chinese Chemical Society, held at Kunming, China, August 29, 1939.

(2) R. Criegee, *Ber.*, **64**, 260 (1931); *Ann.*, **481**, 263 (1930); **507**, 159 (1933).