limit of absorption detectable by the photocell-amplifier system, allowed calculation of 5×10^{-5} mm. as the lowest hydroxyl pressure detectable at 25° in the 120-cm. path length of the quartz reaction vessel.

All the above reactions were studied at 25° by introducing the reactants into the quartz tube at the following pressures: reaction 1, $CH_3I = 10$ mm., $O_2 = 1, 10, 100$ mm.; reactions 2 and 3, $H_2O_2 = 1.5$ mm.; reaction 4, $H_2O = 20$ mm.; reaction 5, $H_2 = 50, 140, 20$ mm., and $O_2 = 20, 140, 500$ mm., respectively; reaction 6, $CH_3OH = 10, 50, 100$ mm. In the processes where mercury was required, a few drops were scattered along the bottom of the quartz cell before introducing the reactants.

Results.—No absorption due to hydroxyl was detectable in any of the reactions studied. Hence, the steady-state concentration of hydroxyl, if any, was less than 5×10^{-5} mm. in processes 2, 3, 4, 5 and 6. In processes 3, 4, 5 and 6, the mercury surface became coated with oxide. In process 1, there was a slow increase in absorption due to formaldehyde formation. Any absorption due to intermediate formation had to be sought superimposed upon this drift. This decreased the sensitivity so that for this reaction it may only be said that the steady-state pressure of hydroxyl was less than 0.0003 mm.

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Photoöxidation of Methyl Iodide

BY W. J. BLAEDEL,[1] R. A. OGG, JR., AND P. A. LEIGHTON

Bates and Spence have postulated a mechanism[2] for the photoöxidation of methyl iodide which has a maximum quantum yield of two and involves the intermediate formation of free hydroxyl. This mechanism was based on a study of the products, which were iodine, paraformaldehyde, methylal and water, and on a measurement of the quantum yield as 2.3, using a chloroacetic acid actinometer, assuming its quantum yield to be unity. Since this work, experimental data from several sources indicate that this mechanism is not entirely correct.
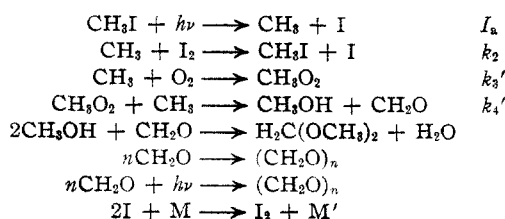
Iredale found the photodecomposition of methyl iodide to be greatly accelerated in the presence of nitric oxide.[3] His kinetic studies on this process and a comparison of his data with those of Bates and Spence permitted the inference that the quantum yield of photoöxidation should lie below a maximum possible value of 1.6.

In the hydroxyl mechanism,[2] hydroxyl radicals

(1) Present address, Northwestern University, Evanston, Illinois.
(2) Bates and Spence, THIS JOURNAL, **53**, 1689 (1931).
(3) Iredale, *Trans. Faraday Soc.*, **35**, 458 (1939).

disappear by the reaction $CH_3I + OH \longrightarrow CH_3OH + I$. This reaction probably has a high activation energy (15–20 kcal.) and, if the mechanism is correct, a high steady-state concentration of hydroxyl should be established. The failure to detect any hydroxyl[4] is an indication that this reaction is not an important one in the mechanism.

Lastly, the quantum yield of the chloroacetic acid actinometer has been shown to be greatly dependent on temperature,[5] being only 0.31 at 25°. Assuming that the photoöxidation quantum yield of 2.3 was measured at this temperature, the corrected value becomes only 0.71.

In the light of this evidence, suggestion of a new mechanism is possible, and the most likely is one involving the formation of a peroxide[2] as an intermediate.

$$CH_3I + h\nu \longrightarrow CH_3 + I \qquad I_a$$
$$CH_3 + I_2 \longrightarrow CH_3I + I \qquad k_2$$
$$CH_3 + O_2 \longrightarrow CH_3O_2 \qquad k_3'$$
$$CH_3O_2 + CH_3 \longrightarrow CH_3OH + CH_2O \qquad k_4'$$
$$2CH_3OH + CH_2O \longrightarrow H_2C(OCH_3)_2 + H_2O$$
$$nCH_2O \longrightarrow (CH_2O)_n$$
$$nCH_2O + h\nu \longrightarrow (CH_2O)_n$$
$$2I + M \longrightarrow I_2 + M'$$

This differs from the hydroxyl mechanism in reactions 3' and 4'.

The rate of formation of methyl iodide, as deduced from the new mechanism is

$$-\frac{d(CH_3I)}{dt} = \frac{I_a(O_2)}{\frac{k_2}{2k_3'}(I_2) + (O_2)}$$

This is identical in form to the experimental rate equation of Bates and Spence. The maximum quantum yield of unity is in accord with the previously conflicting data of Iredale and of Bates and Spence.

A recalculation of the data of the latter authors gives $k_2/k_3' = 820$, meaning that the activation energy of process 3' is 3.6 kcal. greater than that of process 2 at 0°.

Reaction 3' is postulated to be a two rather than a three body process. The evidence for this lies in the data of Bates and Spence, which show that k_2/k_3' remains constant as the total pressure varies over an eight-fold range from 25 mm. to 400 mm. This would not be expected if 3' were a three body process.

The agreement of this mechanism with the experimental data indicates that the recombination, $CH_3 + I \rightarrow CH_3I$, is negligible compared to reac-

(4) Blaedel, Ogg and Leighton, THIS JOURNAL, **64**, 2499 (1942).
(5) Smith, Leighton, Leighton, *ibid.*, **61**, 2299 (1939).

tion 2. This is contrary to the conclusions of Iredale,[3] who interpreted his data to mean that reaction 2 was negligible compared to the recombination. However, his data may be interpreted equally well in a second way; and in this case, the results are in accord with the findings on the photoöxidation. At present, work is in progress to determine which of the two processes is predominant in methyl iodide photolysis.

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Vapor Pressures of Indene, Styrene and Dicyclopentadiene

BY P. E. BURCHFIELD

The vapor pressures of indene, styrene and dicyclopentadiene were determined over temperature ranges. The pressure–temperature data were desired for the development of distillation procedure for the separation of the components of light oil solutions.

Experimental.—The compounds used in this investigation were purified by recrystallization. The process of purification and the physical properties of the purified compounds are described elsewhere.[1] The vapor pressures were determined by the method developed by Booth, Elsey, and Burchfield.[2] The temperature was measured by means of a calibrated thermometer graduated to 0.1°. The necessary stem corrections were calculated and applied.

Due to the reactive nature of the compounds studied, a time factor was imposed upon the vapor pressure measurements with the exception of those of styrene. Two pressure readings, separated by a ten-minute time interval, were taken at equal temperatures for each determination. The vapor pressures of styrene at the three highest temperatures were determined by employing a new sample for each measurement, thus reducing the possibility of error through polymerization. Depoly-

TABLE I

VAPOR PRESSURE DATA OF INDENE, STYRENE AND DICYCLOPENTADIENE

Compound	Clausius–Clapeyron constants A	B	No. 4 measurements	Temp. range of measurements, °C.	Average % deviation from mean
Indene	7.919	−2291	13	56.2 to 181.8	1.4
Styrene	7.929	−2103	7	33.5 to 116.3	1.1
Dichloropentadiene	7.925	−2218	6	40.1 to 90.8	0.6

(1) Smoker and Burchfield, "Cryoscopic Analysis of Light Oil Hydrocarbons," unpublished.

(2) Booth, Elsey and Burchfield, THIS JOURNAL, **57**, 2066 (1935).

merization was noticeable in the case of dicyclopentadiene at 100°.

The calculated constant, determined by methods of least squares, for the simplified, integrated Clausius–Clapeyron equation, and other pertinent data, are summarized in Table I.

RESEARCH DEPARTMENT
UNITED GAS IMPROVEMENT CO.
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A New Fructosan Isolated from *Yucca mohavensis*, Sarg.

BY KEENE P. DIMICK AND BERT E. CHRISTENSEN

Recently in connection with the chemical investigation of the *Yucca mohavensis*, Sarg. it was observed that its fructose content (3–5%) increased to as high as 60% on mild acid hydrolysis of the dried stem. This suggests the possibility of the presence of a considerable amount of fructosans which may be stored in the stem as a plant food. Further work on this material resulted in the isolation of a polyfructosan. This fructosan was first obtained from the 70% alcoholic extract of the stem of the *Yucca mohavensis* and comprised approximately 20% of the dry weight. It appeared to be similar to the compound Graminin, isolated from rye flour by Schlubach and Koenig,[1] in that it was a white hygroscopic powder, soluble in water and pyridine, and forms an addition product with ethyl alcohol.

Experimental

Isolation of the Fructosan.—The stem of the Yucca plant was stripped of its bark, cut into small pieces, dried at 60° and then ground in a small mill. The meal was then subjected to exhaustive and continuous extraction with petroleum ether, ether, absolute alcohol and 70% alcohol in the order given. The extract from the 70% alcohol, constituting 40% of the dry stem, was used in this study.

Twenty grams of the extract was dissolved in water and the solution made up to 100 ml. To this was added an equal volume of hot concentrated barium hydroxide suspension containing 20 g. of the hydrated base. When 200 ml. of 95% ethanol was added to this mixture, a heavy precipitate settled out. After cooling, the precipitate was removed and washed with 10% ethanol.

This material was suspended in 100 ml. of water, the barium removed with carbon dioxide, and the filtrate decolorized with 1 g. of charcoal. The compound was again precipitated with barium hydroxide and the treatment repeated.

To remove the last traces of barium the solution was treated with a small amount of dilute sulfuric acid until one drop would cause no further turbidity. By increasing the alcohol content of the aqueous solution the product was

(1) Schlubach and Koenig, *Ann.*, **514**, 182 (1934).