

Experimental

The experimental procedures employed in studying these reactions have already been described in previous publications.^{2,3} The data presented in Table I constitute a summary of the results obtained using various electrolytes, and electrolytes plus definite additions of water, in *n*-butylamine. The essential data for the reaction between liquid ammonia and ethyl benzoate are given in Table II. For purposes of comparison some data are also included in both tables of results previously reported on the catalytic effect of the corresponding "onium" salts. In both cases the observed catalytic effects are emphasized in the last column in which are given the experimentally determined half time values (in hours) for each series of runs.

TABLE I
AMINOLYSIS OF ETHYL PHENYLACETATE IN *n*-BUTYL-AMINE AT 25°

a = concn. of amine in moles per liter; *b* = concn. of ester in moles per liter.

Catalyst	Concn. of catalyst in moles per liter	<i>a</i>	<i>b</i>	<i>K</i> × 10 ³	<i>t</i> ^{1/2} (exp.)
None ^a	...	5.45	2.80	0.87	158
NaClO ₄	0.1	5.38	2.80	1.55	92
C ₄ H ₉ NH ₂ ·HClO ₄ ^a	.1	5.40	2.80	2.09	70
NaI	.1	5.37	2.81	2.06	73
NaI	.2	5.30	2.81	2.50	59
C ₄ H ₉ NH ₂ ·HI ^a	.1	5.34	2.80	2.57	57
NaSCN	.1	5.37	2.81	2.07	73
NaSCN	.2	5.42	2.77	2.39	63
C ₄ H ₉ NH ₂ ·HSCN ^a	.1	5.36	2.80	2.81	53
NaSCN	.2	4.91	2.81	4.7	36
H ₂ O	2.0				
NaI	0.2	5.11	2.81	5.7	26
H ₂ O	2.0				

^a Taken from data summarized in ref. 3.

TABLE II
AMMONOLYSIS OF ETHYL BENZOATE IN LIQUID AMMONIA AT 0°

Moles C₆H₅COOC₂H₅ = 0.035; moles NH₃ = 0.082 ± 0.3; moles catalyst = 0.00935.

Catalyst	<i>K</i> × 10 ⁴	<i>t</i> ^{1/2} (exp.)
None	0.47	ca. 15000
NH ₄ Cl ^a	7.86	882
NaCl	2.52	2760
NaNO ₃	1.28	5420

^a Taken from data summarized in ref. 2.

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

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- (2) Fellingner and Audrieth, *THIS JOURNAL*, **60**, 579 (1938).
(3) Glasoe, Kleinberg and Audrieth, *ibid.*, **61**, 2387 (1939).

Attempt to Detect Free Hydroxyl as an Intermediate in Photochemical Reactions

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

Free hydroxyl has been proposed as an intermediate in several photochemical processes.^{2,3} The mechanisms of all the following processes might involve this substance (at 2537 Å.)

- (1) CH₃I + O₂ + *hν*
- (2) H₂O₂ + *hν*
- (3) H₂O₂ + Hg + *hν*
- (4) H₂O + Hg + *hν*
- (5) H₂ + O₂ + Hg + *hν*
- (6) CH₃OH + Hg + *hν*

In any of these processes, if the reactions by which hydroxyl disappears have low rates compared to those by which it is formed, it is conceivable that steady-state concentrations might be attained which are sufficient to be detectable by the absorption spectrum. The purpose of the following work was to detect such absorption if possible.

Experimental.—The photochemical reaction vessel was a cylindrical quartz tube, 120 cm. long, and 3.5 cm. in diameter, with plane quartz end windows. Irradiation was effected by placing two low pressure mercury arcs, each 120 cm. long and 0.7 cm. in diameter, parallel to and on opposite sides of this tube. A cylindrical aluminum reflector, open at the ends, enclosed the arcs and quartz tube.

Light from a water discharge giving the 3064 Å. hydroxyl band in emission was passed lengthwise through the reaction cell and into the slit of a 21-ft. concave grating spectrograph. The intensity of the discharge in the region containing the Q₁ 1¹/₂ and Q₁ 2¹/₂ lines was measured in the focal plane of the spectrograph with a sensitive photocell-amplifier system. This region shows the highest absorption at room temperature. The absorption noted in this region when the low pressure arcs were turned on was taken as a measure of the steady-state hydroxyl concentration produced.

The limit of detection of hydroxyl was determined by a method similar to that of Oldenberg and Rieke,⁴ by measuring the absorption of water vapor dissociated at a high temperature. Here, the quartz cell was replaced by a cylindrical furnace with quartz end windows. Oxygen and water vapor at known pressures were passed through this furnace at about 1400° Å. The temperature distribution was measured along the furnace axis with a Pt/Pt-Rh thermocouple. Zeise's data⁵ on the dissociation constants of water at various temperatures enabled a calculation of the hydroxyl distribution along the furnace axis at the high temperature. From the rotational term levels of the hydroxyl molecule,⁴ the absorption of this same distribution at room temperature was calculated. This, with the

- (1) Present address, Northwestern University, Evanston, Illinois.
- (2) Urey, Dawsey and Rice, *THIS JOURNAL*, **51**, 1371 (1929).
- (3) Bates and Spence, *ibid.*, **53**, 1689 (1931).
- (4) Oldenberg and Rieke, *J. Chem. Phys.*, **6**, 439 (1938).
- (5) Zeise, *Z. Elektrochem.*, **43**, 704 (1937).

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, $\text{CH}_3\text{I} = 10$ mm., $\text{O}_2 = 1, 10, 100$ mm.; reactions 2 and 3, $\text{H}_2\text{O}_2 = 1.5$ mm.; reaction 4, $\text{H}_2\text{O} = 20$ mm.; reaction 5, $\text{H}_2 = 50, 140, 20$ mm., and $\text{O}_2 = 20, 140, 500$ mm., respectively; reaction 6, $\text{CH}_3\text{OH} = 10, 50, 100$ 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.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD UNIV., CALIF.

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Photooxidation of Methyl Iodide

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

Bates and Spence have postulated a mechanism² for the photooxidation 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.

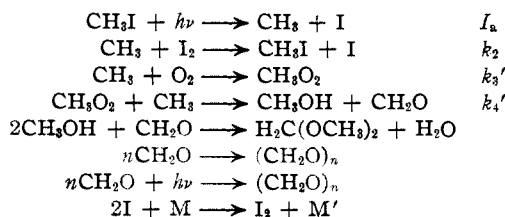
Iredale found the photodecomposition of methyl iodide to be greatly accelerated in the presence of nitric oxide.³ His kinetic studies on this process and a comparison of his data with those of Bates and Spence permitted the inference that the quantum yield of photooxidation should lie below a maximum possible value of 1.6.

In the hydroxyl mechanism,² hydroxyl radicals

disappear by the reaction $\text{CH}_3\text{I} + \text{OH} \rightarrow \text{CH}_3\text{OH} + \text{I}$. 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 hydroxyl⁴ 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 photooxidation 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 peroxide² as an intermediate.



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

$$-\frac{d(\text{CH}_3\text{I})}{dt} = \frac{I_a(\text{O}_2)}{2k_3'(\text{I}_2) + (\text{O}_2)}$$

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, $\text{CH}_3 + \text{I} \rightarrow \text{CH}_3\text{I}$, is negligible compared to reac-

(1) Present address, Northwestern University, Evanston, Illinois.

(2) Bates and Spence, *THIS JOURNAL*, **63**, 1689 (1931).

(3) Iredale, *Trans. Faraday Soc.*, **35**, 458 (1939).

(4) Blaedel, Ogg and Leighton, *THIS JOURNAL*, **64**, 2499 (1942).

(5) Smith, Leighton, Leighton, *ibid.*, **61**, 2299 (1939).