

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY,
No. 440]

PHOTOCHEMICAL REACTIONS IN SOLUTIONS OF THE ALKALI HALIDES IN ACETOPHENONE

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RECEIVED FEBRUARY 20, 1924

Introduction.—Dutoit¹ and Nicollier² have found that although the conductance of acetophenone does not change under the influence of light, under their experimental conditions, the conductance of solutions of sodium iodide and lithium bromide in this solvent decreases, when exposed to light, to a constant value, and then increases when these previously exposed solutions are placed in the dark. Furthermore, a yellow color which develops in the light disappears in the dark. From such observations, these investigators conclude that these reactions are *reversible*. Our preliminary experiments in the *sunlight*, for the short continuous period possible, have confirmed the results of Dutoit and Nicollier in *glass*. In *quartz*, however, the value of the conductance of a given solution, which had decreased to a constant value in glass, on further exposure to the light decreased enormously, continuing to decrease for several days.

In this work we have only attempted to study certain systems in Pyrex glass, using the controllable mercury-quartz lamp in place of sunlight, and employing precision methods and pure chemicals. Our main interest in this connection lay in the possible reversibility of the reaction in the solutions, and the absence of an effect of light on the pure solvent, both so strongly accentuated by Nicollier.

It may be said, here, to anticipate, that the behavior of these systems has been found to be far more complex than pictured by Nicollier. As we cannot go further with the work, we are now presenting our experimental results, with the obvious conclusions to be drawn from them, although necessarily the suggested explanation of the complicated mechanism of the photochemical reaction can only be tentative.

Experimental Part

Purification of Materials.—The acetophenone and sodium iodide were purified according to the method given in previous papers.³

For the iodine titrations commercial "Resublimed" iodine was further resublimed, once from potassium iodide and once without the salt; commercial c. p. thiosulfate, and commercial c. p. potassium dichromate, recrystallized once from conductivity water and dried in platinum at 160°, were used.

Apparatus and Manipulation.—The light used was a quartz mercury arc of the type manufactured by the Hanovia Chemical Company, operating on a 220-volt circuit

¹ Dutoit, *Z. Elektrochem.*, **12**, 640 (1906).

² Nicollier, *Thèse* (with Dutoit), Lausanne, 1907.

³ Morgan and Lammert, *THIS JOURNAL*, **46**, 881, 1117 (1924).

in a vertical position. The method of mounting the lamp and exposing the solutions to the light at a constant temperature can be seen in Fig. 1.

This apparatus is designed for use with two thermostats so that six samples, at each temperature, can be exposed at one time. By revolving the reaction flasks as we have done, in individual jackets through which clear distilled water from a thermostat passes, not only is the system in the flask well agitated, but the entire circumference of the flask is exposed uniformly to the light. These flasks were of clear Pyrex glass of such a diameter (3.5 cm.) that when placed within the jackets (20 cm. long) a layer of water 1.25 cm. thick surrounded them. The water was pumped back from the jackets through a block-tin coil into the bottle in the thermostat, by Brown and Sharpe pumps, not shown in the figure, especially packed on the water side with asbestos packing to prevent contamination which might destroy the clarity of the water.

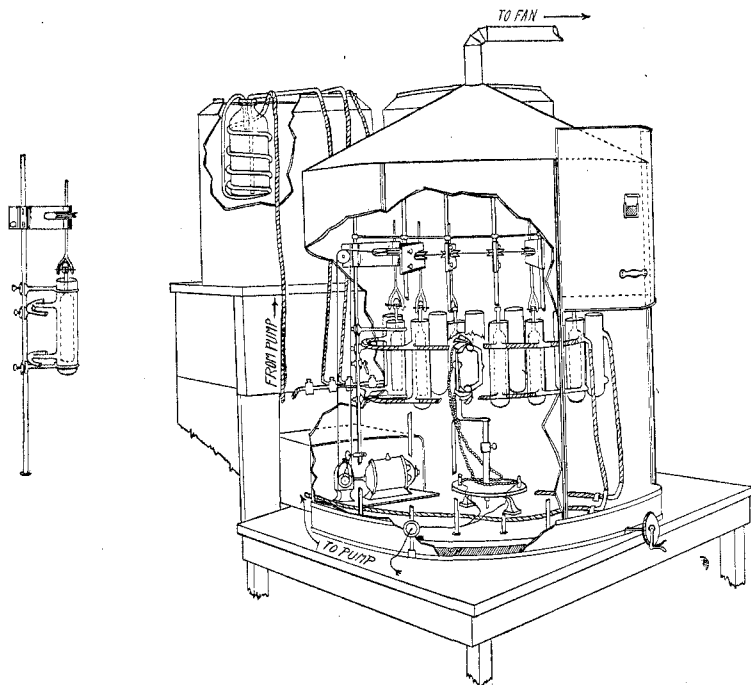


Fig. 1.

The lamp was turned through a definite interval a certain number of times during any continuous run, in case all twelve flasks were being exposed, to avoid shadows or unevenness of exposure. The presence of ozone made it necessary to wrap all rubber connecting tubes with friction tape.

The time of reaction was taken with a Warren Telechron Clock, synchronized with the alternating current supplied by the Edison Company.

The bridge assembly, the cell design and calibration, and the preparation of the solutions have been described in previous papers.⁴

For the iodine titrations, the method and conditions of acid concentra-

⁴ Morgan and Lammert, *THIS JOURNAL*, 45, 1623 (1923). Ref. 3.

tion described by Vosburgh⁵ were used. For the determination of iodine in the acetophenone solutions, special manipulation was necessary because in the acetophenone the usual blue color of the iodine and starch was masked. Accordingly a procedure was adopted which had for its principle the extraction of the iodine from the acetophenone layer in an excess of thiosulfate solution and the titration of an aliquot part of this with a standard iodine solution.

Results

Sodium iodide and lithium bromide, being the most soluble in acetophenone were selected in order to investigate more thoroughly the effect of concentration on the photochemical reaction. There is, however, a great difference between these two solutions in the depth of color developed during a given time of exposure to the light, the color in the sodium iodide solution being the deeper, and in the dark the color of the iodide solution seeming to disappear much more completely than that developed in the bromide solution. The deep yellow to red-brown color developed in the sodium iodide solution was found to be due to free iodine, since on shaking the solution with an aqueous solution of sodium thiosulfate the color disappeared; in the case of the bromide the color did not disappear. The color of free bromine added to pure acetophenone persists for only a few minutes, whereas that of the free iodine remains for a longer time. It was assumed that this reaction was similar to the one in aqueous solution ascribed by Dawson⁶ to a ketone-enolic change of the ketone and subsequent substitution of the halogen; this assumption is further corroborated by the fact that lithium bromide in benzophenone, in which one would expect no ketone-enolic change, becomes dark brown when exposed to the light, and this color does not fade, as in the case when in acetophenone. Consequently it seemed best to use first the sodium iodide solutions, since this secondary reaction, if it affects the other at all, does so more slowly than when bromine is one of the products; moreover, the iodine liberated can be titrated, this fact giving another method of following the reactions. All further work, then, was done upon solutions of sodium iodide in acetophenone.

The results given below in Table I are those, therefore, for the solutions exposed in the Pyrex flasks, in the way described in a previous section, all of the flasks being filled to a height of 11 cm. so that the surface exposed and the volume of the air above the solutions were constant. The flasks were sealed, and only one conductance value was taken from each flask.

The plot of the results is shown in Fig. 2, the ordinates representing specific resistance; the abscissas, time. The scale for the specific resist-

⁵ Vosburgh, *THIS JOURNAL*, **44**, 2120 (1922).

⁶ Dawson and Wheatley, *J. Chem. Soc.*, **97**, 2048 (1910).

TABLE I

DATA FOR THE CHANGE, UNDER THE INFLUENCE OF THE LIGHT TRANSMITTED BY PYREX GLASS FROM THE MERCURY ARC, IN THE SPECIFIC RESISTANCE OF SOLUTIONS OF SODIUM IODIDE IN ACETOPHENONE WITH TIME AT VARIOUS CONCENTRATIONS

Temp., 25° + 0.05°. Distance from the light, 20 cm. Diameter of electrodes, 38 to 50 mm.

Time Hours	Concn. 0.05051 M	Concn. 0.02704 M	Concn. 0.01654 M	Concn. 0.008130 M	Concn. 0.003660 M	Concn. 0.002194 M
0	1420.3	2265	3301	7240	11013	16367
1.5	1429.7	2286	..	7354	11277	16783
2	3339
3	1434.8	2297	3368	7472	11548	17027
6	1437.7	2319	3408	7794	12177	18025
12	1450.0	..	3451	..	13710	20301
18	3484
24	1457.2	2365	3545	9028	16084	24770
48	1471.7	2370	3595 (49 hr.)	9803	19833	38731
84	22600	...
96	1477.5	..	3732 (95 hr.)	44297
100	27223	...
144	28496	...
192	1523.3	..	3860

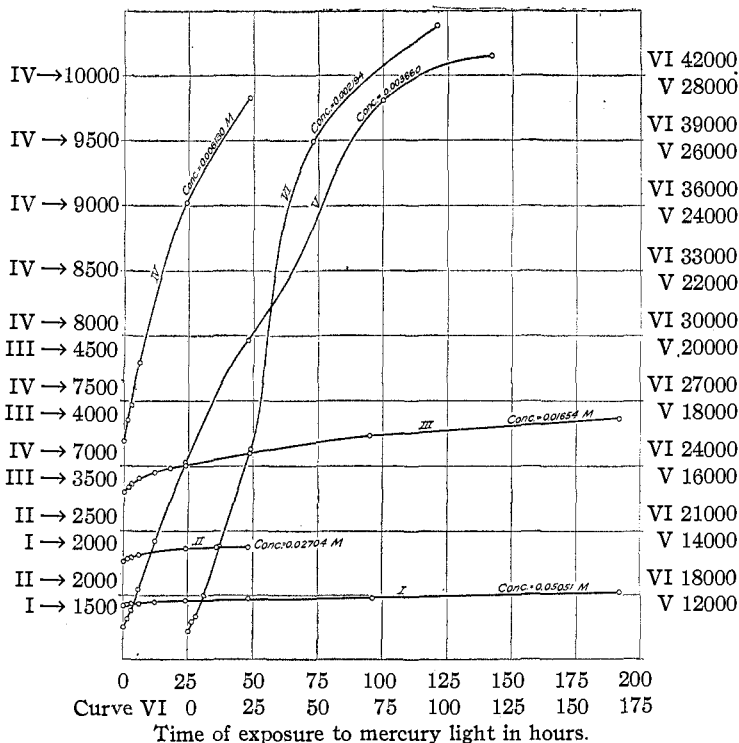


Fig. 2.—Effect of light radiation on the specific resistance of NaI solutions.

ance is the same for Curves I, II, III and IV; it is multiplied by four for Curve V, and by five for Curve VI.

The curves show that there is an enormous difference between the increase in the specific resistance, with the time of exposure to the light, in the concentrated and in the dilute solutions of sodium iodide; the more dilute the solution, the greater the relative change. Such a situation could be expected if the increase in resistance were due simply to the change of the same concentration of iodide ion to free iodine, since the removal of a definite quantity of iodide ion from a concentrated solution would not be expected to have as great an effect as from a dilute solution, the total concentration of conducting material being greater. But the curves do not indicate that any such simple reaction can account for all of the change. In the first place, at the time of exposure between 6 and 24 hours there is a definite break in the curve, the resistance suddenly increasing again after a slight tendency to become constant. At the same time, it was observed that a fine, white deposit was evenly distributed on the inside of the glass. The amount of this precipitate seemed to increase up to about 24 hours, after which there was no further precipitation. Such a change in state could of course account for a sudden break in the conductance curve. In the second place, another point is observable where the curves tend to change their direction, namely, after 48 hours, more noticeable in the dilute solutions. As the breaks are present in all of these runs, and were noted in a number of more qualitative determinations made earlier, it seemed quite evident that the reaction was not as simple as indicated by Nicollier, and that the failure to obtain curves of any regularity was due to the fact that the conductance measured not one reaction alone, but a number of concurrent or at least overlapping reactions. Furthermore, there was little tendency, as Nicollier had observed, and our earlier experiments in sunlight confirmed, for the systems when exposed in this way to come to any sort of equilibrium. Beyond the time to which these more quantitative experiments were carried, qualitative experiments indicated an even more complicated state of affairs. It was, therefore, with an idea of deriving some working hypothesis which would account for the anomalous behavior of these solutions, that the further experiments on the conditions affecting the reaction were performed.

The resistance of pure acetophenone, after being kept in the dark for 250 hours at 25°, was found to be unchanged in value.

The change of its specific resistance in the light with the time is shown in Table II and the plot of these values in Fig. 3.

The decrease in resistance here is very rapid at first, the rate of change for the six-hour period being approximately one-half of what it was for the three-hour period, and a yellow color is developed. This color is

TABLE II

EFFECT OF LIGHT ON PURE ACETOPHENONE

The experimental conditions were the same as given in Table I

Time Hours	Sp. resistance in the presence of air	Sp. resistance in the presence of nitrogen
	$\times 10^3$ Mhos	$\times 10^4$ Mhos
0	164,420	164,420
3	17,501	29,911
6	11,381	15,404
12	10,762	14,897
24	8,533
48	7,120	7,159
96	5,249	7,215
192	3,997	8,445 (225 hrs.)

produced quite as rapidly in the dark, once the solution has been exposed to the light, as in the light. However, in the dark the resistance of the system again increases, but since such an increase was accompanied by a deepening of the yellow color, it could be considered in no wise indicative

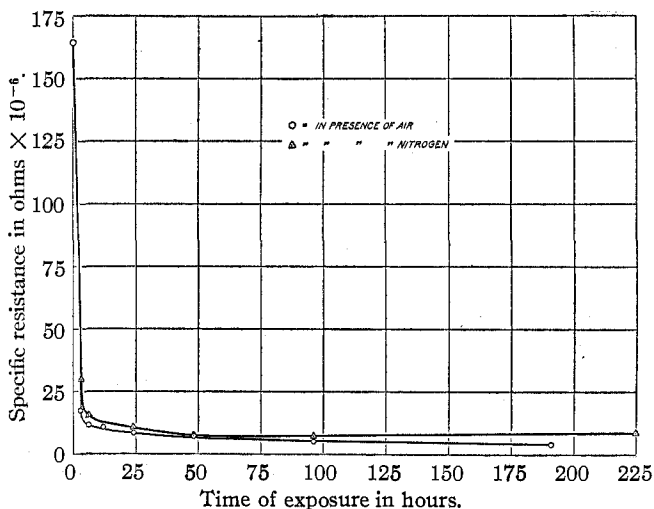


Fig. 3.—Effect of light radiation on acetophenone.

of a reversible reaction, but rather as of a secondary reaction taking place as the result of photochemical action. There was, further, a decided difference in the depth of color developed in a given time, when a small amount of water had been added to the solvent, showing that the formation of the yellow product was at least accelerated by the presence of the water; but no precipitate was formed. When the partial pressure of oxygen is reduced by displacing the air in the flasks by nitrogen, the change produced in Fig. 3 is observed, the data from which it is constructed being given in the third column of Table II. The curve follows the general

direction of that one representing the change of resistance with the time of exposure to the light in the presence of air up to about 24 hours, although the rate of change is not so great, but beyond this time the resistance tends to increase, as in the dark. Obviously, then, the photochemical reaction involves the oxidation of acetophenone.

The oxidation of acetophenone with potassium permanganate has been found to yield benzoic acid, carbon dioxide, etc. That benzoic acid is undoubtedly one of the products of the photochemical oxidation of acetophenone is indicated by the following experimental facts. A water extract of the acetophenone which has been exposed to the light reacts acid to litmus. This acidic substance can be extracted in a water layer in the form of its salt by shaking with potassium hydroxide and decreasing its solubility in the acetophenone layer by the addition of petroleum ether. The aqueous layer after being washed free from acetophenone with ethyl ether, acidified, and extracted again with ethyl ether, yields on evaporation of the ether extract a white substance which gives tests characteristic of benzoic acid. The first reaction, then, when acetophenone in the presence of oxygen is exposed to the light which results in a rapid decrease in resistance could quite conceivably be the formation of benzoic acid, or oxidation products such as benzaldehyde, intermediate between this and acetophenone. Secondly, the yellow color developed after a time could be due to the products of further reactions among these substances. The formation of condensation products in the light among types of substances such as these is well known.⁷ Experiment shows that the precipitate is formed by the action of light on the solution, and more readily in the presence of air and water.

The appearance and solubility of the substance indicated that the precipitate formed was probably sodium benzoate. In such a case the increased precipitation in the presence of water could be explained since the hydrolysis of acetophenone in the light yields benzoic acid as one of the products.⁷

Since the weight of iodine liberated (within the limits of error for the small quantities involved) per weight of acetophenone is the same for all concentrations, the reaction is dependent upon the quantity of acetophenone changed by the light.

Samples of pure acetophenone, *recently exposed to the light*, liberate iodine when added to a little of the mother solution of sodium iodide; samples which have been exposed for a long time, or samples which have been exposed for the same time as those which were found to liberate iodine, and then placed in the dark, do not liberate iodine. It seems evident, then, that the iodine is formed in a reaction taking place between the sodium iodide and a product of the photochemical oxidation of acetophenone.

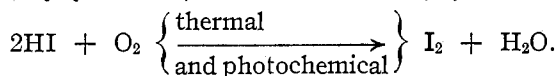
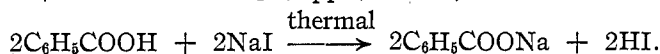
⁷ See Plotnikow, "Lehrbuch der Photochemie," W. de Gruyter and Co., Berlin and Leipzig, 1920.

In conclusion, then, from such experimental data as this, the following outline of a tentative theory for the reaction originally observed by Nicollier is proposed.

(1) Acetophenone + O₂ $\xrightarrow{\text{photochemical}}$ colorless substances, *A* + *B*.
A, acidic in nature, possibly benzoic acid, formic acid, etc.; *B*, aldehydic or ketonic, possibly benzaldehyde, etc.

(2) Acetophenone + *B* $\left\{ \begin{array}{l} \text{photochemical} \\ \text{and thermal} \end{array} \right\}$ colored condensation products.

(3) *A* + 2NaI $\xrightarrow{\text{thermal}}$ I₂ + ppt., that is,



The colorless products are substances which would be expected to form conducting solutions in acetophenone, whereas the condensation products would not. The decrease in the rate of the change of resistance with time might then be the result of these two contrasting effects, as well as the effect of the decreasing concentration of oxygen. In the case of the sodium iodide solutions the increase in resistance due to the liberation of iodine and the consumption of the colorless *A* will overbalance the decrease in resistance observed with the pure acetophenone. That Reactions 2 and 3 both take place in the sodium iodide solution is shown by the fact that all of the color developed in these solutions during the longer periods of exposure is not discharged by agitation with sodium thiosulfate. The acidic constituents *A* quite possibly decompose further with prolonged exposure to the light, since these solutions no longer liberate iodine from sodium iodide solution. Such photochemical decomposition of acids has been observed previously.⁷

Instead of this reaction being a simple reversible photochemical reaction, it is plainly made up of a number of photochemical and thermal reactions, so interrelated that the results obtained depend greatly upon the experimental conditions. The effective wave lengths for the reactions in glass were found to be between 300 $\mu\mu$ and 400 $\mu\mu$. Undoubtedly the difference observed in quartz is due to the fact that the shorter wave lengths are more effective for at least some of the reactions. Although no definite data are given here to indicate that the reaction is *not* reversible, it would seem, since this somewhat complicated series of reactions is markedly affected by oxygen, moisture, temperature and intensity and wave length of light, that the observations of Nicollier of apparent equilibrium were due to specific experimental conditions rather than to a true reversible reaction.

Summary

Pure acetophenone, contrary to the findings of Nicollier, is decomposed by light.

The reaction of sodium iodide on acetophenone is certainly not a simple reversible photochemical reaction.

The quantity of iodine liberated in such a solution is independent of the concentration of sodium iodide present, and apparently depends only upon the time and the intensity of the light and, consequently, upon the quantity of acetophenone decomposed.

The presence of water hastens the formation and increases the quantity of the flaky, white precipitate produced by light in acetophenone-sodium iodide solutions.

The tentative explanation offered for the photochemical reaction studied is that an acidic substance, such as benzoic acid, formed from acetophenone by the light, reacts with the sodium iodide—a thermal reaction—producing hydriodic acid and a precipitate of sodium benzoate, the hydriodic acid being further oxidized by the light into free iodine and water.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE SPECIFIC HEATS OF MAGNESIUM, CALCIUM, ZINC, ALUMINUM AND SILVER AT HIGH TEMPERATURES

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RECEIVED MARCH 4, 1924

In previous papers from this Laboratory^{1,2} accounts have been given of a study of the connection between the high specific heats and the electropositive character of certain metals. The present experiments were undertaken in order to extend this study to other metals and to higher temperatures. This paper will be confined to a description of the measurements and record of the results; the theoretical aspects will be discussed in the paper immediately following this.

The Experimental Measurements

The method adopted in this work for the specific-heat measurements is the ordinary one,³ in which a known mass of the desired substance at a known temperature is transferred to a calorimeter at a lower temperature, and the temperature rise in the latter noted, the heat capacity of the calorimeter being independently determined.

The heating of the metal was carried out in a tube resistance furnace, the working chamber of which was 20 cm. long and 3 cm. in diameter.

¹ Lewis, Eastman and Rodebush, *Proc. Nat. Acad. Sci.*, **4**, 25 (1918).

² Eastman and Rodebush, *THIS JOURNAL*, **40**, 489 (1918).

³ The method has been discussed at length by White, *Am. J. Sci.*, [4] **47**, 1 (1919).