THE PHOTOCHEMICAL OXIDATION OF AROMATIC HYDROCARBONS. I.

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The conversion of certain aromatic hydrocarbons into compounds with acidic properties, under the influence of light and air was first noticed by Weger,[1] who made experiments with hydrindene, cumenes and tetrahydronaphthalene under the following conditions :—(a) light and open to air : (b) dark and open to air : (c) light and glass-stoppered vessel : (d) dark and glass-stoppered vessel : (e) light and sealed tube : (f) dark and sealed tube, and all kept for 15 months.

Only the compounds kept under conditions (a) showed appreciable change, and the oxidation in these cases pointed to the formation of 3 to 5 per cent. of the corresponding monocarboxylic acid when measured by the acidity of the solutions. The oxygen content of the products was, however, much greater than this, pointing to the presence of oxidation products other than the carboxylic acids.

Nine years later Ciamician and Silber[2] confirmed the formation of acids from such hydrocarbons as toluene, the xylenes and cymene by sunlight in the presence of air and water. They worked with large glass flasks or bottles from 4·5 to 13 litres' capacity, and always used a quantity of water equal to or in excess of the hydrocarbon taken. They observed the formation of formic acid in addition to aromatic acids. The following figures give the percentage yields of monobasic acids after 6 or 12 months' exposure :—toluene, 12 ; p-xylene, 37 ; m-xylene, 31 ; o-xylene, 26·5 ; p-cymene, 25·3.[3] In the last case the acids include p-coumarinic, $C_3H_7 \cdot C_6H_4 \cdot CO_2H$; methovinylbenzoic, $CH_2 : CMe \cdot C_6H_4 \cdot CO_2H$ and p-a-hydroxyisopropylbenzoic $OH \cdot CMe_2 \cdot C_6H_4 \cdot CO_2H$. In most cases traces of aldehydes and small amounts of dibasic acids were also found. According to these authors, o-and p-nitrotoluenes and phenanthrene are practically unaltered under similar conditions.

In the same year Benrath and Meyer,[4] when studying the action of aromatic hydrocarbons on quinones in sunlight, found that phenanthraquinone is completely oxidised to diphenic acid, and the hydrocarbon partially to the corresponding monobasic acid. No phthalic
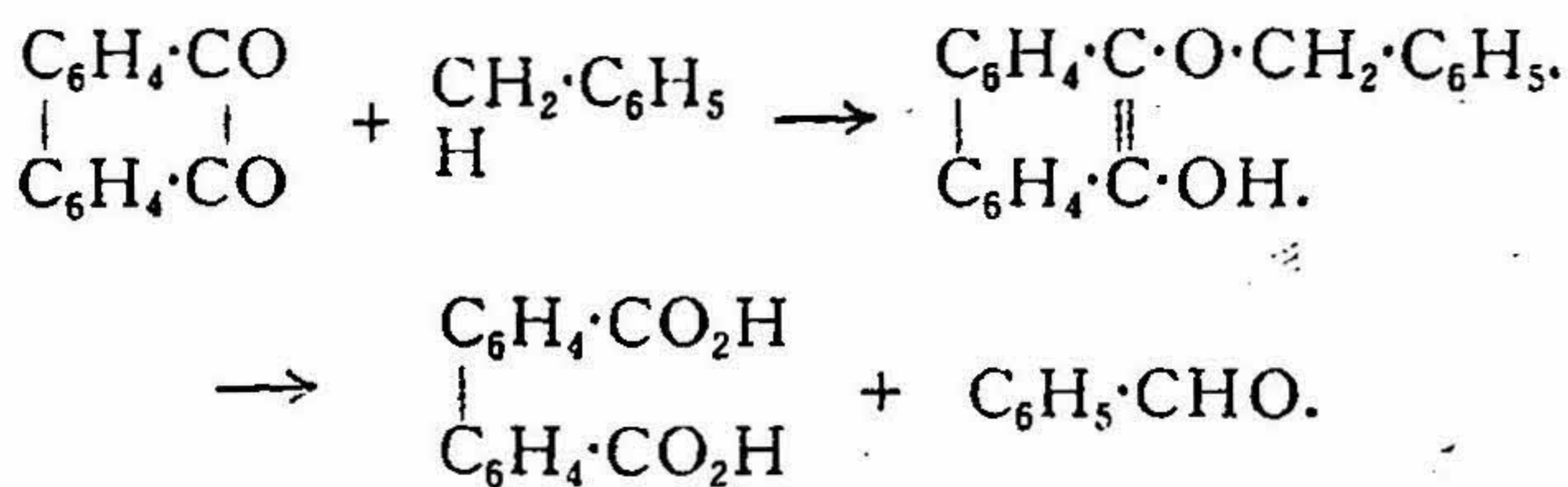
[1] *Ber.*, 1903, **36**, 309.
[2] *Ibid.*, 1912, **45**, 39.
[3] The values are calculated on the weight of the hydrocarbon.
[4] *Ber.*, 1912, **45**, 2707.

acids could be detected. They state that methyl derivatives of benzene are most readily oxidised, then ethyl and the more complex least readily, whilst benzene itself is not oxidised.

The view that the hydrocarbon is first oxidised to aldehyde and that the water so formed renders possible the oxidation of the quinone is not tenable, as the quinone appears to be stable in the presence of air, water and light. The authors conclude that the hydrocarbon unites with the quinone and that the resulting quinol ether is oxidised to diphenic acid and aldehyde and the latter to the monobasic acid.

$$
\begin{array}{c}
C_6H_4\cdot CO \\
| \qquad | \\
C_6H_4\cdot CO
\end{array}
+
\begin{array}{c}
CH_2\cdot C_6H_5 \\
H
\end{array}
\longrightarrow
\begin{array}{c}
C_6H_4\cdot C\cdot O\cdot CH_2\cdot C_6H_5. \\
| \qquad \| \\
C_6H_4\cdot C\cdot OH.
\end{array}
$$

$$
\longrightarrow
\begin{array}{c}
C_6H_4\cdot CO_2H \\
| \\
C_6H_4\cdot CO_2H
\end{array}
+ C_6H_5\cdot CHO.
$$

Suida [1] claims that the first product is a peroxide formed by the union of the hydrocarbon with oxygen and estimates the amount of such peroxide by determining the amount of iodine liberated from acidified potassium iodide. He concludes that the carboxylic acids are formed from relatively unstable intermediate products, and that the amount of acid formed cannot be entirely due to the decomposition of peroxides. The source of light was a mercury lamp placed about 10 cm. from the specimen under examination and this raised the temperature to $70-80^{\circ}$: glass containers were found to be more efficient than quartz. The results obtained show that pure benzene is almost passive, but that commercial benzene forms peroxides probably owing to its thiophene-content. Methyl-substituted benzenes undergo autoxidation when illuminated, and the action is accelerated by the presence of small quantities of nitrobenzene or of one of the nitrotoluenes, although nitrobenzene itself is stable.

An increase in the number of methyl groups facilitates oxidation and p-xylene reacts four times as readily as toluene. The para position of the two methyl groups appears to produce the optimum effect.

The results in sunlight are not so good as those with the mercury lamp. The peroxides formed appear to be fairly stable when kept in the dark, and boiling produces a diminution in the amount of active oxygen and also in the acidity.

[1] *Monatsh.*, 1912, 33, 1255.

Kharichkov [1] obtained results similar to those of Ciamician and Silber using atmospheric oxygen in the presence of sodium hydroxide solution. From mesitylene he obtained the three acids and from cumene, cuminic acid.

Eckert in his patent specification [2] states that he can obtain a 40 per cent. yield of benzoic acid by the atmospheric oxidation of toluene exposed six weeks to sunlight in presence of anthraquinone as a catalyst, which remains unaltered at the end of the oxidation.

Apparently traces of phenols, iodine or metallic iodides act as poisons on the autoxidation of many substances, e.g., acraldehyde, and the iodine ion appears to be the most energetic negative catalyst. [3]

As it was thought possible that the tropical sunshine of India would act more rapidly than the light of more temperate regions several experiments were made under conditions similar to those described by Eckert and at the same time a similar series was carried out by exposure to the rays from a mercury lamp.

EXPERIMENTAL.

Practically all the experiments were made with the proportions of materials recommended by Eckert, with the exception that water equal to half the volume of the hydrocarbon—in the great majority of experiments toluene—was added. Anthraquinone equal to 5 per cent. of the weight of the hydrocarbon was used as catalyst. Quartz vessels, either tubes or flasks were used throughout. In a few experiments the quantity of water was reduced, with the result that the oxidation was diminished.

In a few of the earlier experiments the reaction liquid was sprayed on to the sides of a vertical quartz tube $23 \times 2\cdot5$ cm. exposed to bright sunlight. The tube was kept filled with oxygen by attachment to a gas-holder containing the gas so that the oxygen was replenished as fast as it was used. The liquid was placed in a reservoir some 85 cm. above the top of the quartz tube and was carried by means of a glass tube terminating in a fine jet to the bottom of the reaction-tube, which was closed by a cork through which the glass tube passed and the issuing liquid was thus made to spray the sides of the wider tube, and then run down and collected at the bottom,

[1] *Chem. Zeit.*, 1914, 36, 1250.
[2] Indian Patent 8425 of July 19, 1922.
[3] Moureu and Dufraise, *Compt. rend.*, 1922, 174, 258 ; 175, 127 ; 1923, 176, 797.

whence it was removed periodically to a bottle by opening the cock of a second glass tube passing through the cork. At intervals the liquid was transferred from the bottle to the main reservoir and in this way liquid was continuously being exposed to the sun's rays in an atmosphere of oxygen.

Had the experiment given satisfactory results, it was our intention to introduce a small centrifugal pump to lift the liquid back to the upper reservoir. After a few trials, however, the method was abandoned as there was appreciable loss of liquid and the nozzle frequently became choked by the catalyst.

For the great majority of experiments the reaction mixture was placed in a transparent quartz distillation flask (200 cc.) filled with oxygen and attached by the side-tube to an oxygen reservoir so that the gas was replenished as fast as it was absorbed. The flasks were placed in a cradle and rocked at such a rate that the liquid was continuously splashed over the upper part of the interior surface of the flask which was exposed to bright sunlight or to the light from a quartz mercury lamp. The lamp used was a new type working at atmospheric pressure manufactured by Messrs. Kelvin, Bottomley and Baird, consuming 2·5 amperes at 100 volts across terminals and the flasks were placed 25 cm. below the lamp. The exposure was usually from 9 a.m. to 9 p.m. and the temperature of the liquid in the flasks was 63–66°.

For exposure to the sun's rays the cradle and flasks were placed in the open during the bright weather, viz., December to May, and were thus exposed from 8 a.m. to 5 p.m. to bright tropical sunlight. The temperature of the liquid in these experiments ranged from 29–50° during the course of the day and in a few cases a maximum temperature of 53° was recorded.

The reservoirs containing the oxygen were graduated so that the volume of oxygen absorbed could be read from time to time.

In several experiments after exposure for a given time the whole reaction product was worked up and the acids isolated after titration with standard alkali to determine the total acid formed. The value found by titration was always in excess of the actual amount of acid isolated, and this is probably due to the presence of formic acid as pointed out by Ciamician and Silber. In other cases, where it was desired to study the reaction at intervals up to 600 hours, samples were taken from time to time and titrated with alkali, but the solid acid was only isolated at the termination of the full period. Before taking the sample the mixture was thoroughly shaken, allowed to stand and a portion of the clear upper liquid removed by means of a

pipette, weighed and finally titrated. Duplicate experiments gave an agreement to within 2 per cent., e.g., in one experiment the result was 0·0828 gram of benzoic acid per 2 grams of solution and in another 0·0838 gram.

The following was the method adopted for examining the reaction mixture at the end of the experiments :—

1. An aliquot part of the hydrocarbon layer was titrated with standard alkali using phenol-phthalein as indicator to ascertain the total acid present.

2. The hydrocarbon layer was filtered to remove catalyst, and the clear filtrate extracted with a 15 per cent. aqueous solution of sodium carbonate and then washed with water.

3. The solid residue was also washed several times with sodium carbonate solution and these washings were added to the sodium carbonate extract 2.

4. The combined sodium carbonate extracts and washings were extracted with ether and the extract added to the main hydrocarbon. After warming to expel ether, the alkaline liquid was acidified with concentrated hydrochloric acid, the precipitated acid removed and the filtrate saturated with common salt and extracted with ether. The weight and melting point of the crude acid were determined and the acid then crystallised from alcohol.

5. The hydrocarbon layer was steam-distilled to remove unaltered hydrocarbon and aldehyde. The presence of small amounts of benzaldehyde in the toluene experiments was proved by the characteristic odour of better almonds and also by the formation of small amounts of a phenylhydrazone melting at 150–152°. As a rule it was not found possible to isolate definite products from the residue after steam distillation.

6. The solid obtained by filtering the original reaction product was crystallised from alcohol and finally sublimed, when pure anthraquinone was obtained. The solid in all but two experiments was nearly pure anthraquinone, but in these two, viz., numbers 10 and 11 the product contained appreciable amounts of anthracene, and in both these cases the oxidation of the hydrocarbon (toluene) has proceeded to a much smaller extent.

The results of the experiments in sunlight are given in Table I, and those in ultraviolet light in Table II.

In one experiment (No. 15) nitrobenzene was introduced as catalyst as suggested by Suida, but the effect produced was practically nil.

In experiment 16 nitrogen was used in place of oxygen but after 200 hours' exposure no reduction of anthraquinone to anthracene could be detected and no formation of acid occurred.

The solubility of pure anthraquinone in toluene was determined at several temperatures and the following values obtained per 100 grams of toluene :

Temperature	....	....	....	15°	27°	60°	100°.
Grams of anthraquinone		....		0·49	0·44	4·23	5·56.

A few experiments were made with *m*-xylene and mesitylene, but even after 200 hours the oxidation was not marked.

The results with ultraviolet light indicate that the oxidation proceeds at much the same rate as stated by Eckert although water was used in all experiments.

They also show that the oxidation is roughly proportional to the time of exposure and that the amount of water present has a marked effect on the rate of oxidation. A quantity of water equal to 20 or 50 per cent. of the weight of the hydrocarbon used produced more rapid oxidation than a 5 per cent. addition.

It is hoped to continue the experiments and extend them in several directions.

TABLE I.

Oxidation of toluene (50 grams) in sunlight with anthraquinone (5 per cent.) as catalyst.

No. of Expt.	Time in hours	Grams of water	Percentage of benzoic acid calculated from titration	Calculated percentage of toluene oxidised	Per cent. of acid actually isolated	REMARKS
1	60	25	2·03	1·49	2·0	Spraying.
2a	60	25	1·67	1·22	1·4	Stationary.
2b	60	2·5	0·76	0·55	...	
3a	100	25	7·40	5·58	6·8	
3b	100	2·5	3·75	2·80	3·0	
4a	100	25	4·27	3·20	...	The result is low compared with 3a.
4b	100	2·5	1·33	1·0	...	
4a	200	25	8·60	6·32	...	
4b	200	2·5	2·55	2·92	...	
4a	300	25	13·20	9·90	...	
4b	300	2·5	4·25	3·15	...	
4a	400	25	17·30	12·76	...	The volume of liquid left was small, so acid was not actually isolated.
4b	400	2·5	6·60	4·90	...	

TABLE II.

Oxidation in ultraviolet light (50 grams) : catalyst as above.

No. of Expt.	Time in hours	Grams of water	Percentage of benzoic acid calculated from titration	Calculated percentage of toluene oxidised	Per cent. of acid actually isolated	REMARKS
5	72	10	5·23	3·86	...	No shaking.
6	96	10	6·87	5·32	...	24 hours shaking and 72 hours stationary.
7	200	10	15·82	11·67	13·6	
8	100	10	4·10	3·02	3·4	
9	72	10	3·0	2·21	2·4	
10	200	10	0·37	0·27	...	Catalyst partly reduced to anthracene.
11	200	10	1·60	1·19	0·7	do.
12	600	10	30·1	22·68	27·0	
13	200	2·5	4·7	3·5	4·4	
14a	200	25	15·7	11·6	...	
14b	200	2·5	5·38	4·03	...	
14a	336	25	27·9	20·90	...	
14b	336	2·5	11·5	8·48	...	
14a	400	25	32·1	23·60	...	
14b	400	2·5	14·9	10·95	...	
14a	600	25	34·8	25·64	...	
14b	600	2·5	16·3	12·01	...	
14a	650	25	36·3	26·77	...	

Unless otherwise stated continuous rocking was adopted in all the experiments.

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