

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Photochemical Oxidation of Crotonaldehyde

BY FRANCIS E. BLACET AND DAVID H. VOLMAN

In a study of the effect of ultraviolet light on crotonaldehyde at room temperature it was observed that the oxidation by oxygen of this aldehyde in the vapor phase is promoted by radiation.¹ This article describes a more detailed photochemical study which has been made of this reaction.

Experimental Method

The apparatus, diagrammed in Fig. 1, was designed to provide for the introduction of measured quantities of aldehyde vapor and oxygen without the use of stopcocks in the gas train, for the measurement of small pressure differences at relatively high pressures, and for the circulation of gases in the system. By using capillary tubing this was done without the incorporation of an appreciable volume of dead space. In the figure all triple lines represent capillary tubing. Crotonaldehyde was stored in the

which would stop mercury when the pressure difference was half an atmosphere or less. The operation of this cut-off is evident from the figure. The circulatory system ABCD-EF provided for adequate mixing of the gases as well as for rapid condensation of the aldehyde in the trap F when this was desired. CDE was a magnetic pump similar to that described by Bacon and Duncan.² An intermittent switch activated the solenoid, D, which in turn raised and dropped the glass enclosed iron bar, C, thereby opening and closing the valve, E. The differential pressure gage, UVW, differed from the one which has been described³ only by the fact that provision was made to let air into W, through the cut-off L, so that the dead end in V could be eliminated, by forcing the mercury into the capillary, during the operation of the pump. One millimeter change in height of the mercury column in U corresponded to a pressure change of 0.00558 mm. in the reaction system. Radiant energy was measured with the aid of a thermopile, T.

The apparatus was built in an air thermostat which was maintained at 30° during all experiments.

Monochromatic light was obtained from a 'high pressure, direct current mercury arc and a crystal quartz monochromator. The method of preparing pure crotonaldehyde has been described.⁴ Oxygen was prepared from potassium chlorate.

Experiments were made by carrying out the following operations in the order given. Crotonaldehyde was introduced into the previously evacuated system and frozen in the trap, F. The total energy entering the empty reaction tube was measured. Oxygen was allowed to enter the system and its pressure recorded, taking into consideration the temperature gradient in the trap, F. The aldehyde was permitted to come to the temperature of the thermostat and thorough mixing of the gases was accomplished by means of the circulating pump. Total energy passing through the cell was again measured and the radiation begun. Pressure readings were made at frequent intervals and the amperage

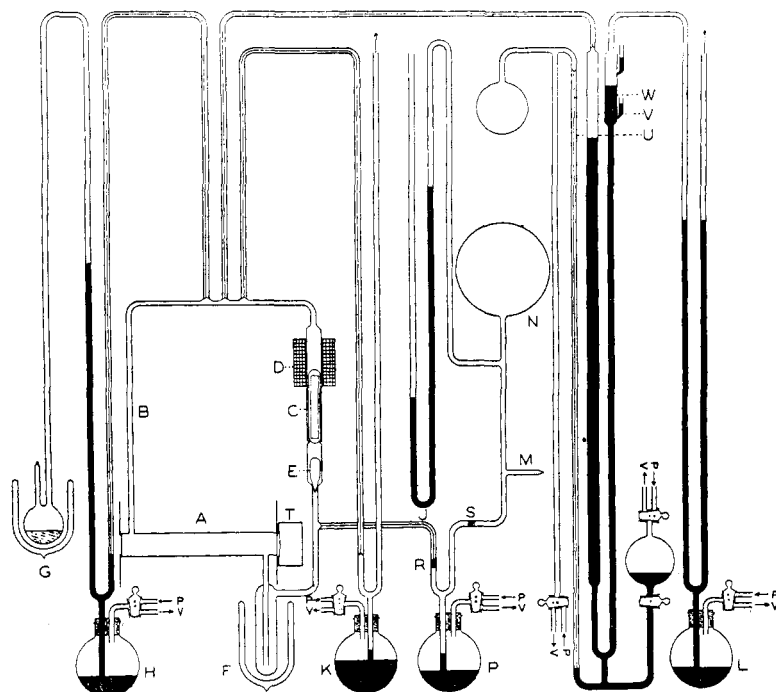


Fig. 1.—Diagram of the apparatus.

bulb G and the vapor was brought into the reaction cell, A, through the mercury cut-off, H. A, consisted of an all fused silica tube, 3 by 20 cm. with plane windows. Oxygen was stored in a 5-liter flask, N, from which it could be introduced into the reaction system through the cut-off P. R and S were sintered Pyrex glass plugs which would allow a gas to pass but would resist the flow of mercury. Using 7-mm. tubing, no difficulty was experienced in preparing plugs

of the arc was kept constant, since it was found that constant current ensures uniform intensity of radiation over long periods of time.

Experimental Results

It was found that oxygen and crotonaldehyde vapor in a clean system do not react at a meas-

(1) Blacet and Roof, *THIS JOURNAL*, **58**, 73 (1936).

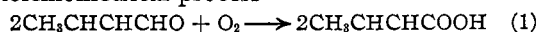
(2) Bacon and Duncan, *ibid.*, **56**, 336 (1934).

(3) Leighton and Blacet, *ibid.*, **54**, 3165 (1932).

(4) Blacet, Young and Roof, *ibid.*, **59**, 608 (1937).

urable rate in the dark. However, the products of oxidation initiated by light, catalyze a dark reaction which continues at a uniform rate after radiation is discontinued. At the beginning of a run the rate of pressure lowering would increase. After an hour or two, depending upon concentrations, etc., this rate became constant and runs were always continued thereafter until the slope of the straight ΔP versus time curve could be obtained accurately. The shutter was then closed and rate of the dark reaction followed until the slope of the ΔP curve for this reaction could be determined. From the over-all rate and the rate of the dark reaction the ΔP due to the photochemical reaction alone could be obtained. In most cases the thermal reaction rate was about one-third that of the photochemical reaction. The fractional change in concentration of reactants was small; even with oxygen pressures of one millimeter only about 20% of this gas was used.

Quantum yields were calculated as one-third of the pressure decrease due to the photochemical reaction, divided by the quanta absorbed. In the stoichiometrical process



presumably one activated crotonaldehyde molecule involves another aldehyde molecule plus an oxygen molecule to give two molecules of crotonic acid. During the time of linear decrease in pressure the acid (m. p. 72°) was condensing as fast as it was formed, hence three molecules left the gas phase for each quantum, which caused the reaction to occur. On this basis the quantum yield would be also the ratio of oxygen molecules used to quanta absorbed. Measuring the oxygen consumed involved an appreciable error since there were always small amounts of aldehyde in the capillary dead ends which could not be liquefied. However, as a check on the above over-all reaction the ratio of total pressure change to oxygen pressure change was determined in three cases and the following results obtained. For $\lambda 2804$ and 3.2 mm. O_2 , the ratio was 3.4; for $\lambda 2804$ and 1.0 mm. O_2 , the ratio was 2.9; and for $\lambda 3660$ and 1.0 mm. O_2 , the ratio was 3.3. Within the limits of error for measurement of oxygen decrease these ratios are 3, and oxygen react to give crotonic acid,⁵ no thus substantiating the above reaction.

The total pressure decrease during runs varied from 0.4 to 1 mm., producing as a combined result of the photochemical and thermal reactions a maximum of approximately 1 mg. of solid. This solid had the general characteristics of crotonic acid. Because of the ratios given above and because it is known that in solution crotonaldehyde

TABLE I
SUMMARY OF EXPERIMENTAL RESULTS

Expt.	Wave length, λ , Å.	Oxygen pressure, mm.	Crotonaldehyde pressure, mm.	Quantum yield, Φ
1	3660	1.03	39.0	0.026
2	3130	1.24	38.8	.076
3	3130	3.23	38.3	.086
4	3130	6.87	37.6	.12
5	2804	1.02	37.5	.21
6	2804	3.23	36.8	.35
7	2804	10.8	36.7	.40
8	2804	12.5	36.5	.39
9	2537	1.19	39.6	.39
10	2537	3.88	39.2	.45
11	2537	10.0	38.8	1.43
12	2537	10.7	36.5	1.20
13	2537	13.5	37.0	3.22
14	2537	13.8	37.2	3.16
15	2380	1.01	38.0	0.61
N_2 , 40 mm.	2537	10.2	38.0	.89
N_2 , 107 mm.	2537	11.5	37.0	.99

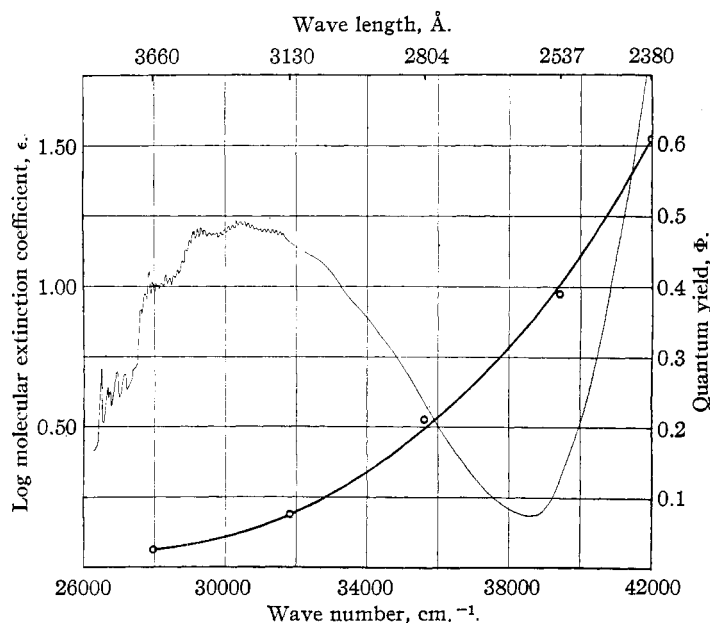


Fig. 2.—Showing relationship between the character of absorption (irregular curve) and quantum yields (smooth curve) obtained at 30° . Oxygen and crotonaldehyde pressures were 1 and 38 mm., respectively.

(5) Young, THIS JOURNAL, 54, 2498 (1932).

further attempt was made to identify the solid.

In Table I are given the quantum yields obtained at the wave lengths and pressures of reactants indicated. It may be noted that the crotonaldehyde pressure was kept substantially constant at 38 mm., while the oxygen pressure was varied from 1 to 14 mm. It was not practical to go to higher oxygen pressures, since the corrections for the dark reaction increased rapidly with increase in oxygen concentration. Nitrogen was added in the last two runs in order to test the effect of an inert gas on the reaction rate.

Discussion of Results

Figure 2 shows the variation of quantum yield with wave length and also, for comparison purposes, reproduces the logs of molecular extinction coefficients of crotonaldehyde.⁴ In spite of the apparent variation in types of absorption in the range of wave lengths covered in this study, the curve of oxidation quantum yields *vs.* wave length is very smooth. This is in good agreement with results previously reported⁶ on the photodecomposition of crotonaldehyde at elevated temperatures and leads one to believe either that there is actually no marked variation in the type

of absorption in this spectral range, or that it is the amount of energy absorbed and not the particular electronic excitation which is important in these reactions.

On the other hand, the curves in Fig. 3 suggest that the reaction mechanism is different at $\lambda 3130$ and 2804, where Φ is almost independent of oxygen concentration, from that at $\lambda 2537$ where Φ increases rapidly with pressure. The decrease in yield due to the presence of nitrogen indicates the formation of activated molecules as an important primary process at $\lambda 2537$. The rapid increase of Φ to 3.2, with the indication that it would go higher with additional oxygen, means that a chain process is involved. Bowen and Tietz⁷ have suggested a chain system involving the regeneration of activated aldehyde molecules to account for a high oxidation quantum yield of acetaldehyde. A similar postulate might be used to explain much of the data presented here. However, the authors have some misgivings in regard to such a mechanism and prefer to withhold further discussion until more information is available.

Summary

1. An apparatus suitable for the study of the photochemical reaction of a gas and an easily condensable vapor has been described.
2. The photochemical oxidation of crotonaldehyde vapor by oxygen gas has been investigated. With other conditions constant, the quantum yield of oxidation increased steadily over the wave length range $\lambda 3660$ to 2380, showing no apparent correlation between quantum yields and types of absorption.
3. With constant pressure of crotonaldehyde, the quantum yield remained substantially constant with increase of oxygen pressure at $\lambda 3130$ and 2804. At $\lambda 2537$, however, Φ increased rapidly with oxygen concentration, reaching a value of 3.2 at 13.5 mm. oxygen and 37.0 mm. crotonaldehyde. A chain mechanism is indicated. The introduction of nitrogen caused a marked decrease in Φ , indicating that activated molecules are involved.

LOS ANGELES, CALIF.

RECEIVED DECEMBER 27, 1938

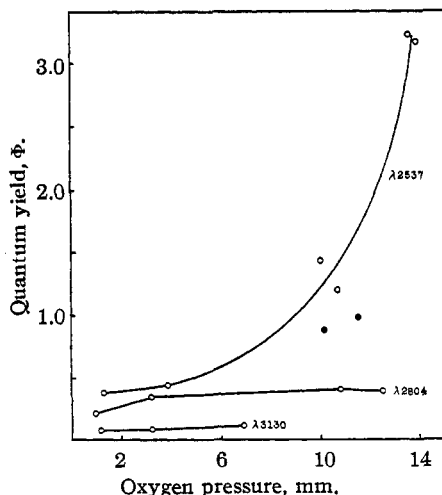


Fig. 3.—Showing variation of quantum yield of crotonaldehyde oxidation with oxygen pressure at wave lengths 3130, 2804 and 2537 Å. The shaded circles represent runs at $\lambda 2537$ in which nitrogen was added to the reaction system.

(6) Blacet and Lu Valle, *THIS JOURNAL*, **61**, 273 (1939).

(7) Bowen and Tietz, *J. Chem. Soc.*, 234 (1930).