

nickel found less than half the sorption at -191.5 and at -183° as at 0° . The probable explanation is that the greater solution taking place with massive nickel at 0° makes the differences in sorption at the higher temperature and at the lower temperatures greater with massive than with supported metal where solution is markedly less.

The rates of sorption at 0 and at -78.5° on the supported nickel were not so slow as many workers have found for activated adsorption. This leads to the question whether many cases of slow attainment of equilibrium in sorption measurements might not be due more to solution than to activated adsorption.

The final run in this series was one in which 0.039 cc. of carbon monoxide was introduced to the adsorbent at -78.5° a half an hour before hydrogen was admitted. Only three points were taken in this run and as seen in curve 5 they all fall slightly above the isotherm for the unpoisoned run. Thus at -78.5° , as at 0° ,⁶ where also activated adsorption takes place, carbon monoxide

used in very small quantity slightly increases the adsorption.

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Summary

Sorption measurements of hydrogen on supported nickel have been made at 0 , -78.5 and -196° . A step-wise increase of adsorption with pressure was found at -196° . Poisoning with carbon monoxide at -196° decreases the low-pressure adsorption by an amount approximately equal to the quantity of poison used. Experiments at -78.5 and at 0° indicate the process of solution takes place to a very slight extent at the latter temperature. A small amount of carbon monoxide causes a slight increase in hydrogen adsorption at -78.5° .

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The Photolysis of the Aliphatic Aldehydes. VII. Crotonaldehyde at Elevated Temperatures

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In view of the fact that crotonaldehyde is very stable at room temperature when exposed to ultra-violet light,¹ it has seemed advisable to continue the photochemical study of this compound at higher temperatures.

Experimental Methods

The quartz reaction tube was enclosed in an electric furnace in essentially the same manner as that described in a report on the photolysis of the butyraldehydes.² By using a single junction copper-constantan thermocouple and manually controlling the input of electrical energy, no difficulty was experienced in keeping the temperature of the furnace constant within 1° .

Since it is impossible to use a thermopile near a cell which is at the temperatures used in this study, the amount of radiant energy absorbed by the aldehyde was determined in the following way. After suitably protecting the thermopile from the furnace by a distilled water filter, it was found that for a given concentration of crotonaldehyde in the reaction cell the fraction of light of several different wave lengths absorbed by the vapors was independent of

temperature in the range 30 to 300° . Beer's law had been shown previously to apply to this compound at room temperature.³ In view of these facts it was assumed that the character of the absorption process did not change with temperature. Next, working at room temperature the fractions of light absorbed at several different concentrations were determined for all the wave lengths used in this study. A plot of these values gave the fraction absorbed at any concentration which might be used. Then from a series of measurements it was found that by manually controlling the amperage of the mercury arc the energy output could be kept constant to within about 2%. With these facts it was possible to get the energy absorbed during a given run simply by measuring the energy entering the cold, empty reaction tube. After this had been done the shutter was closed, the furnace brought to the desired temperature, the gas introduced and brought to the desired concentration and, finally, the exposure made.

Owing to fluctuation of the temperature of the system no attempt was made to follow the slight pressure change which took place during a run. The source of monochromatic radiation and the methods of analysis of the reaction products are adequately referred to in the previous articles of this series.

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

(2) Leighton, Levanas, Blacet and Rowe, *ibid.*, **59**, 1843 (1937).

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

In an attempt to detect fluorescence of crotonaldehyde a quartz tube and mercury arc were set up in the manner frequently employed in obtaining Raman spectra, and used with a Hilger E316 spectrograph. A resonance type cold mercury vapor arc⁴ was used in this case. The aldehyde was introduced in such a way that no mercury vapor could be present also in the tube.

Experimental Results

Thermal Decomposition.—Preliminary experiments showed that some pyrolysis takes place in the temperature range over which photolysis occurs. In order to make the proper corrections in the photochemical study it was necessary, therefore, to investigate the thermal decomposition of crotonaldehyde to some extent. It was found that below 275° the rate of thermal decomposition is very slow and only small corrections were necessary in the photochemical runs. It is interesting to note, however, that at a temperature as low as 150° some decomposition occurs. For example, it was found with the aid of micro methods of analysis for carbon monoxide that crotonaldehyde at 30 mm. pressure in a fused silica container was 0.04% decomposed after being maintained at 150° for five hours.

Analyses of the thermal decomposition products of eight runs averaged 49% carbon monoxide and 47% unsaturated hydrocarbons. The remaining 4% appeared to consist of approximately equal amounts of hydrogen and methane.

Experiments carried out over a temperature range of from 150 to 400° and a pressure range of from 10 to 40 mm. indicated that the reaction was heterogeneous and between first and second order. Calculations of the approximate energies of activation gave 38,000 and 40,000 cal. for the assumption of first and second order reactions, respectively. These results are in substantial agreement with the work of Ure and co-workers.⁵

Photodecomposition.—Microanalysis of the gaseous decomposition products showed the following substances were formed in the percentages indicated, upon irradiation with λ 2380 at 245° and 38 mm. pressure.

	%
Carbon monoxide	60.0
Unsaturated hydrocarbons	27.0
Hydrogen	6.0
Methane	7.0

Evidence was obtained which indicated that the unsaturated hydrocarbons contained acetylene.

(4) Leighton and Leighton, *J. Chem. Ed.*, **12**, 139 (1935).

(5) DeLisle, Fowler, Lovell and Ure, *Trans. Roy. Soc. Canada*, 3d series, Sec. 111, **30**, 65 (1936),

However, some difficulty was experienced in the microchemical separation of carbon monoxide, acetylene and olefin hydrocarbons, and until this matter can be settled by further refinement of this separation it should not be stated positively that acetylene was a product of photolysis. The saturated hydrocarbon was found to be methane by the method recently described⁶ in a study of the decomposition products of acetaldehyde. Some evidence was obtained which indicates that the relative amounts of gaseous products vary with wave length and other experimental conditions but no systematic study of these variations was made.

In contrast to acrolein,⁷ crotonaldehyde does not polymerize rapidly on irradiation. Under the experimental conditions used it took many hours of exposure before any condensed material could be observed within the reaction cell. It was not possible to determine a polymerization quantum yield, but it seems certain that such a yield, if it were obtained, would be less than that reported for decomposition.

In Table I are summarized the experimental conditions and yields of the photochemical runs. Φ is the ratio of carbon monoxide molecules produced photochemically to the quanta absorbed.

TABLE I
SUMMARY OF PHOTOCHEMICAL DETERMINATIONS

Wave length, Å.	Temp., °C.	Press., mm.	Time, sec.	Quanta absorbed $\times 10^{-18}$	Photochem. CO, cu. mm.	Quantum yield, Φ
3130	245	36.4	14400	12.91	5.93	0.012
2804	245	37.6	14400	3.99	7.09	.048
2654	245	36.6	18000	1.67	7.73	.13
2537	245	36.8	21700	1.51	15.10	.27
2380	150	30.1	11400	5.53	15.55	.076
2380	200	33.5	18600	3.22	24.80	.21
2380	245	36.4	18000	4.22	73.20	.55
2380	245	26.1	18000	4.04	95.80	.65
2380	245	11.2	18000	2.69	82.50	.83
2380	265	36.3	4500	0.766	27.77	.99
2380	265	25.0	7200	1.03	40.68	1.08
2380	265	14.6	7200	0.528	18.18	0.93

No evidence of fluorescence of crotonaldehyde was found at room temperature over the spectral range 4000 to 9000 Å., even though exposures of fifteen hours were made using the Raman type of apparatus described above. The crotonaldehyde pressure was 37 mm. in the absorption tube. In these experiments in which the mercury arc was very close to the cell containing the aldehyde for

(6) Blacet and Volman, *THIS JOURNAL*, **60**, 1243 (1938).

(7) Blacet, Fielding and Roof, *ibid.*, **59**, 2375 (1937).

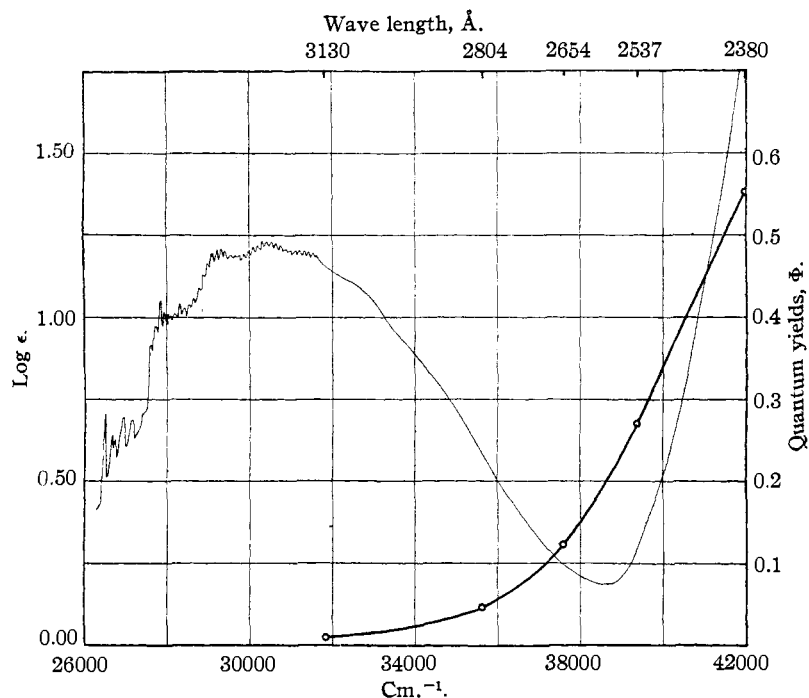


Fig. 1.—Showing the variations of the molecular extinction coefficients (irregular curve) and quantum yields of decomposition (smooth curve) with wave length. The quantum yields were obtained at 245° and 37 millimeters pressure.

long periods of time, it was observed that some resinous material and a small amount of gas was formed at room temperature. These products may have resulted from absorption of the mercury lines below $\lambda 2000$, which are present to some extent in radiation from the cold arc.

Discussion of Results

The predominance of propylene and carbon monoxide in almost equivalent amounts in the pyrolysis products indicates that the thermal dissociation consists for the most part of a splitting of the aldehyde directly into these two substances. Attention should be called to this method of studying thermal decompositions for since the amount of gas needed for an analysis is less than 0.1 cc., runs need not be carried ordinarily more than 1% of the way to completion and hence secondary processes are minimized and the concentration of reactants may be considered constant.

From Fig. 1 it may be seen that in the definitely banded region of absorption, above $\lambda 3130$, no photodecomposition occurs. For the remainder of the first electronic region, $\lambda 3130$ –2600, a small but definitely increasing yield has been found. Below $\lambda 2600$, where a second region of absorption

is apparent, the quantum yield increases rapidly with decreasing wave length. In spite of overlapping of the two regions, it is apparent from a study of the two curves that some decomposition results from both electronic absorption processes. Thus it appears that it is the amount of energy which is absorbed, and not the nature of the absorption process, which is important and that as the energy per quantum increases the probability of dissociation before the required energy is dissipated thermally, increases.

The variation of quantum yield with temperature, as shown in Fig. 2, is an indication that once dissociation has occurred, presumably into free radicals, a chain mechanism is set up similar to that found for the corresponding saturated

aldehydes.² In agreement with a previous report,¹ it is apparent from the figure that at room temperature no measurable decomposition yield for

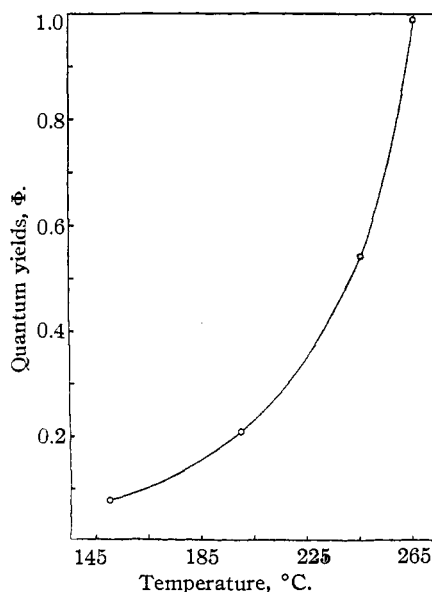


Fig. 2.—Quantum yields vs. temperature. Wave length, 2380 Å. and concentration of crotonaldehyde, 1.1×10^{-3} mole/liter. Corrections for thermal dissociation have been made in the calculation of quantum yields.

crotonaldehyde may be expected even at $\lambda 2380$. The curve leads one to suspect that above $265^\circ \Phi$ would be found to be greater than unity, but, unfortunately, above this temperature the thermal corrections become so large that photochemical calculations give erratic results.

The curves in Fig. 3 indicate that crotonaldehyde has a limiting quantum yield near unity as the pressure in the reaction system approaches zero. The facts that no fluorescence was observed and that no appreciable decomposition occurs at room temperature suggest a predissociation type of absorption in which the life of activation is sufficiently long so that under the experimental conditions which have been used, deactivation by collisions predominates. With decrease in pressure at a given temperature the primary dissociation quantum yield, ϕ , may increase.

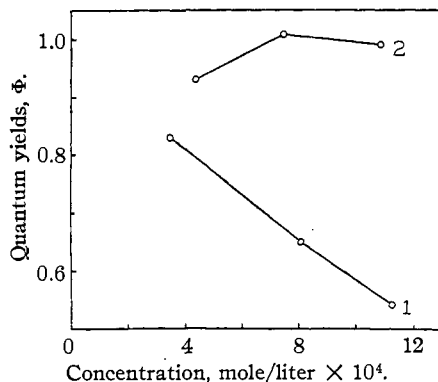


Fig. 3.—Quantum yields vs. molecular concentration of crotonaldehyde. Curve 1 at 245° , Curve 2 at 265° . Wave length 2380 \AA .

The variety of gaseous decomposition products and the fact that carbon monoxide predominates in these products indicate that the over-all photochemical process is complex and differs materially from the pyrolysis mechanism. The evidence is not sufficiently complete to warrant the postulation of a detailed photochemical mechanism at this time. However, the following observations

may be made. The presence of methane in the products is proof that the bond between the third and fourth carbon atoms is sometimes broken. This may be due to instability of the methyl vinyl radical or perhaps to splitting off of the methyl group in the primary act. In either case acetylene may be formed, leaving methyl and formyl groups to react with one another or with other molecules of crotonaldehyde. It is possible that acetylene will be difficult to identify since it is known to polymerize under similar experimental conditions. In agreement with results obtained in a study of acrolein, it seems that the high percentage of carbon monoxide in the gas can best be accounted for by assuming the formation of radicals and the subsequent reaction of these with more of the aldehyde to give carbon monoxide, hydrogen and substances of relatively high molecular weight which would not be collected in the vapor phase.

Summary

1. Crotonaldehyde has been found to decompose thermally over the temperature range 150 to 400° , to give carbon monoxide and unsaturated hydrocarbons as the principal products. The reaction is heterogeneous. The rate is slow at temperatures below 275° .

2. Photodecomposition was found to occur at 150° and to increase rapidly with increase of temperature. At constant temperature the decomposition increases with decrease in wave length, the quantum yield not being large except in the second electronic region of absorption. At constant temperature and wave length the quantum yield apparently approaches a value near unity with decrease in crotonaldehyde concentration.

3. The gaseous photodecomposition products were found to be 60% carbon monoxide, 27% unsaturated hydrocarbons, 6% hydrogen and 7% methane.

4. No attempt has been made to give a mechanism for the over-all photochemical process.

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