Anal. Calcd. for $C_{21}H_{34}O_2$: C, 79.2; H, 10.8. Found: C, 79.5; H, 11.1.

Acetate of Pregnanol-3-one-20.—A solution of 100 mg. of pregnanolone in 5 cc. of acetic anhydride was refluxed for thirty minutes. The product was crystallized from alcohol-water, m. p. 121°. A mixture of this compound with the acetate of *epi*-pregnanolone, m. p. 112°, gave a 20° depression in melting point.

Anal. Calcd. for $C_{23}H_{36}O_3$: C, 76.8; H, 10.1. Found: C, 76.4; H, 10.1.

Semicarbazone of Pregnanol-3-one-20.—Pregnanolone gave a semicarbazone of m. p. 245°.

Anal. Calcd. for $C_{22}H_{37}N_3O_2$: C, 70.3; H, 9.9. Found: C, 69.8; H, 9.8.

Androsterone from Androstanedione.—A solution of 100 mg. of androstanedione in 50 cc. of glacial acetic acid containing 1 cc. of constant boiling hydrobromic acid was added to 50 cc. of glacial acetic acid containing 25 mg. of previously reduced platinum oxide catalyst. The solution was shaken with hydrogen at 45 pounds (3 atm.) pressure for fifteen minutes. The product was isolated and purified by means of Girard's reagent and the half succinic ester. A small amount of isoandrosterone was removed by means of digitonin precipitation. The androsterone was crystallized from dilute alcohol, m. p. 184°; mixing with an authentic sample of androsterone gave no depression in melting point.

Anal. Calcd. for $C_{19}H_{30}O_2$: C, 78.6; H, 10.4. Found: C, 79.0; H, 10.3.

Summary

epi-Pregnanol-3-one-20, a natural product of human pregnancy urine, was prepared from pregnandione by partial catalytic reduction in alcohol and from pregnandiol by partial acetylation, followed by oxidation. Pregnanol-3-one-20 was prepared by catalytic reduction of pregnandione in acid solution. Androsterone was prepared by partial catalytic reduction of androstanedione in acid solution.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF STANFORD UNIVERSITY]

The Photolysis of the Aliphatic Aldehydes. IV. *n*- and Isobutyraldehydes

BY PHILIP A. LEIGHTON, LEO D. LEVANAS, FRANCIS E. BLACET AND ROBERT D. ROWE

Since the appearance of the first paper in this series,[1] new experimental data have been accumulated which are of importance in determining the nature of the processes involved in the photolysis of the aliphatic aldehydes. This work, which has dealt chiefly with acetaldehyde, includes a study of the effects of wave length and pressure on quantum yields[2] and of the effect of wave length on the yield of hydrogen,[3] a demonstration of the production of free raidcals during the reaction,[4] and the discovery of a high temperature chain reaction apparently propagated by radicals.[5] As a result, the originally divergent hypotheses of Norrish and Kirkbride[6] and the authors' have become modified[3,7] until they are in agreement that the decomposition may involve two possibilities: (A) an effective splitting of the aldehyde molecule into a hydrocarbon and carbon monoxide, and (B) a dissociation into independent free radicals. While process A predominates at longer wave lengths, the importance of B would appear to increase at shorter wave lengths.[3,8] From this point of view the low yield of free radicals observed by Pearson and Purcell[4] is not surprising since, in the source they used, the greater part of the effective radiation was at wave lengths above 3000 Å.

The photochemical behavior of *n*- and isobutyraldehydes, here reported, is in the main analogous to that of the lighter aldehydes. In all cases both decomposition and apparent polymerization occur at room temperature, and in common with acetaldehyde the butyraldehydes show chain decompositions at higher temperatures. There are also marked differences in behavior, which we will attempt to bring out.

Experimental

1. Purification of Materials.—The middle fraction of a sample of Eastman *n*-butyraldehyde was distilled onto anhydrous copper sulfate in the first of a series of bulbs sealed to the reaction system. After evacuation, several additional first fractions and residues were removed by low temperature distillation. Isobutyraldehyde was treated in a similar manner in some cases and in others it was prepared by the acid catalyzed rearrangement of methallyl alcohol.

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(1) Leighton and Blacet, THIS JOURNAL. **54**, 3165 (1932).

(2) Leighton and Blacet, *ibid.*, **55**, 1766 (1933).

(3) Blacet and Roof, *ibid.*, **58**, 278 (1936).

(4) Pearson and Purcell, *J. Chem. Soc.*, 1151 (1935).

(5) Leermakers, THIS JOURNAL, **56**, 1537 (1934); Akeroyd and Norrish, *J. Chem. Soc.*, 890 (1936).

(6) Kirkbride and Norrish. *Trans. Faraday Soc.*, **27**, 404 (1931).

(7) Norrish, *Cold Spring Harbor Symposia on Quantitative Biology*, **3**, 51 (1935); *Acta Physicochim. U. S. S. R.*, **3**, 171 (1935).

(8) Rollefson, *J. Phys. Chem.*, **41**, 259 (1937).

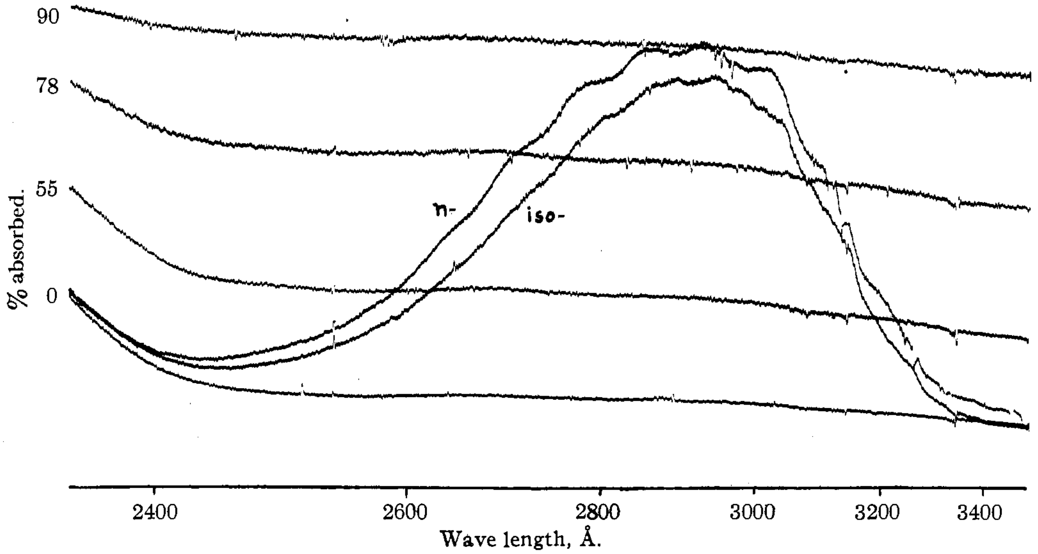

Fig. 1.—Absorption of *n*- and isobutyraldehyde vapors at 29 mm. and 27 mm. pressure, respectively. Path = 40 cm., T = 25°. Ordinates are absorptions of calibrated neutral screens.

2. Absorption Spectra.—Microphotometer tracings of the near ultraviolet absorption bands of the two compounds are shown in Fig. 1. The spectra from which the tracings were made were photographed on a Hilger E316 spectrograph and represent the continuum from a hydrogen discharge passed through an absorption path of 40 cm. of aldehyde vapor at a pressure of 29 mm. for *n*-butyraldehyde and 27 mm. for isobutyraldehyde. Included in the figure are tracings of the spectrum of the source alone (ordinate 0) and of the source reduced in intensity by calibrated screens of known absorption (ordinates 55, 78, and 90% absorbed). Both compounds show evidence of diffuse vibrational structure in absorption, although it is much less marked in iso- than in *n*-butyraldehyde, and the maxima are shifted slightly to longer wave lengths in the former.

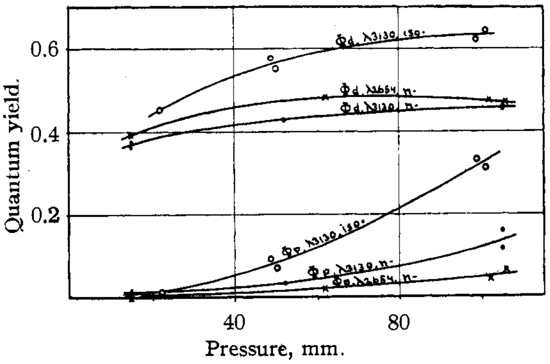

Fig. 2.—Variations of decomposition (Φ_d) and apparent polymerization (Φ_p) quantum yields with pressure at 30°.

A comparison of the near ultraviolet absorption of isobutyraldehyde with that of propionaldehyde and acetaldehyde has been published.[9]

3. Low Temperature Reactions.—The photodecomposition and polymerization of these compounds at 30° were studied by the methods described in earlier papers.[1,2] Quantum yields of decomposition and polymerization at various pressures and wave lengths are given in Figs. 2 and 3, while Table I gives the experimental data for a few typical runs. Additional results on isobutyraldehyde, not shown on the figures, were: at λ 2654, Φ_d = 0.78 at 74 mm. and 0.81 at 151 mm. and at λ 2537, Φ_p = 1.0 at 150 mm. pressure. Calculation of Φ_d was based on the number of CO molecules produced; calculation of Φ_p on the difference between the observed pressure change and the estimated pressure change due to decomposition. The amounts of decomposition and polymerization were kept small, usually over 97% of the aldehyde remaining unchanged at the end of a run.

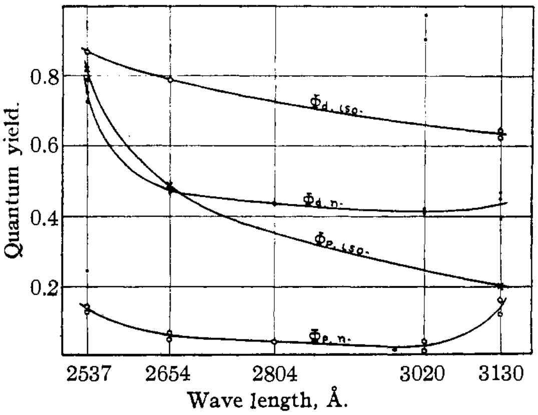

Fig. 3.—Variations of decomposition (Φ_d) and apparent polymerization (Φ_p) quantum yields with wave length, at 30° and 100 mm. pressure except Φ_p for isobutyraldehyde, which is at 75 mm.

Improvements in the method of micro gas analysis[10] used in the earlier work made possible a more complete

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(9) Leighton, *Chem. Rev.*, **17**, 393 (1935).

(10) Blacet and Macdonald, *Ind. Eng. Chem., Anal. Ed.*, **6**, 334 (1934).

TABLE I

EXPERIMENTAL DATA FOR TYPICAL RUNS AT 30°

Aldehyde	λ	Pressure, mm.	ΔP, mm.	Vol. CO, cu. mm.	Mean incident intensity, quanta/sec. $\times 10^{-15}$	Mean fraction absorbed, Q_m	Total quanta absorbed $\times 10^{18}$	Φ_d	Φ_p
n-	3130	52	+1.21	323	2.58	0.605	20.1	0.434	0.029
		105	1.34	539	3.52	.814	31.2	.467	.165
	3020	102	1.06	302	1.22	.880	19.3	.422	.039
	2654	15	0.24	42.8	0.617	.218	2.94	.394	− .01
		102	.41	115	0.644	.718	6.67	.477	.047
Iso-	3130	50	.88	260	2.08	.598	12.7	.555	.074
		101	.87	442	2.16	.779	18.5	.645	.315
	2537	151	− .12	189	0.478	.560	5.85	.875	1.01

determination of the reaction products. Experimental results are summarized in Table II. For each run separate analyses were made of the two fractions of gas pumped from a trap first at liquid air temperature, then at the temperature of a carbon dioxide–acetone refrigerant. In the case of *n*-butyraldehyde, after exposure to 3130 Å., the majority of the unsaturated hydrocarbons came off at the lower temperature, while in the samples exposed to 2537 Å. practically all of the unsaturated substances were retained in the trap surrounded by liquid air, but came off at the higher temperature.

TABLE II

RELATIVE NUMBERS OF MOLECULES OF GASEOUS PRODUCTS, TO NEAREST 5%, FROM PHOTODECOMPOSITION AT 30°

	n-Butyraldehyde			Isobutyraldehyde	
Wave length	3130	2654	2537	3130	2537
CO	100	100	100	100	100
C_3H_8	85	75	65	90	55
H_2	5	20	25	5	15
$C_2H_4 + C_3H_6$	15	15	15	10	5

n-Butyraldehyde showed weak fluorescence when exposed to 3130 Å. and none at shorter wave lengths, while isobutyraldehyde under our experimental conditions showed no observable fluorescence at any wave length.

4. High Temperature Reactions.—For work at elevated temperatures the reaction cell was enclosed in an iron tube which projected 65 mm. beyond the front and 5 mm. beyond the back windows of the cell. This tube was wound with an asbestos insulated heating coil so spaced as to provide uniform temperature over its entire length. The tube was then enclosed in heavy asbestos–magnesia insulation, with the front end left open, while the rear end was provided with a removable insulating cap. Temperatures were determined by means of a calibrated thermocouple. Aldehyde samples were admitted with the tube at 30°, light intensity and absorption factor determined, the thermopile removed, the cap set in its place, and the tube heated to the desired temperature as quickly as possible. After exposure the decomposition products were pumped off immediately, through a trap at −80°. Calculations were essentially the same as at low temperatures, with the exception that Q_m, the fraction of light absorbed at 30°, was corrected to Q'_m, the fraction absorbed at the temperature of the run, by the following equation derived from Beer's law in which the assumption was made that the absorption coefficient does not change with temperature

$$\log(1 - Q'_m) = \frac{P'T}{PT'} \log(1 - Q_m)$$

Since the exposures were kept so short that around 99% of the aldehyde remained unchanged, it was assumed that the fraction absorbed remained constant during the run.

Table III summarizes the experimental data for typical runs. Observations were limited to the decomposition reactions and, in the main, the reaction products were analyzed for carbon monoxide only. A few analyses for hydrogen at λ 3130 and temperatures ranging from 500 to 550°K. gave averages of 6.4 and 9.8%, relative to carbon monoxide, for *n*- and isobutyraldehydes, respectively.

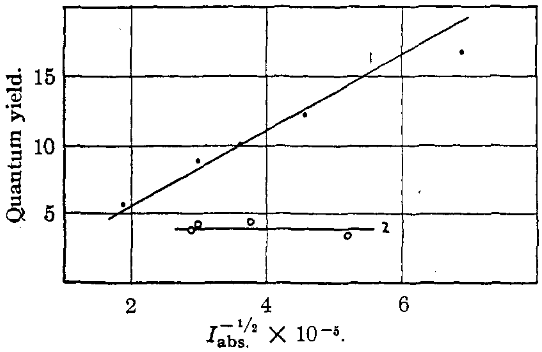


Fig. 4.—Quantum yields as a function of absorbed light intensity at 3130 Å., 549 °K. and 100–105 mm. pressure for *n*- (line 1) and iso- (line 2) butyraldehydes. Solid lines are for rates proportional to the square root (line 1) and to the first power (line 2) of the absorbed intensity.

Although the results are not as reproducible or as self-consistent as those at 30° and although they admittedly do not cover the range of conditions which might be desired, it appears (Fig. 4) that the quantum yield is approximately inversely proportional to the square root of the absorbed light intensity for *n*-, and independent of the absorbed light intensity for isobutyraldehyde. Accordingly, in observing the effects of temperature and pressure, for *n*-butyraldehyde the average quantity absorbed in einsteins cc.$^{-1}$ sec.$^{-1}$ for all the runs at λ 3130 was taken as a standard intensity and the quantum yields were corrected to this standard, assuming an inverse square relation. The corrected values (Φ'_d, Table III) are used in Figs. 5 and 6. No correction was made in the case of

TABLE III

DATA FOR TYPICAL EXPERIMENTS AT ELEVATED TEMPERATURES

Run	λ, Å.	T, °K	P, mm.	t, sec.	Total CO Cu. mm. at S.T.P.	CO Moles/cc. × 10^{-8}	(RCHO) Moles/cc. × 10^{-6}	I_0 einsteins/sec. × 10^{-10}	Q'_m fraction of I_0 absorbed	$I_{abs.}$, einsteins/cc. sec. × 10^{-12}	Φ_d	Φ'_d	k	k_c
						n-Butyraldehyde								
22	3660	572	103.1	1260	104	3.28	2.88	92.5	0.054	3.53	7.4	4.6		
57	3130	400	100.0	4200	175	5.52	4.00	24.8	.71	12.5	1.05	1.25	0.53	0.54
14	3130	448	92.5	930	97	3.06	3.30	26.6	.59	11.1	2.9	3.3	2.5	2.6
12	3130	498	101.6	900	199	6.28	3.27	28.0	.63	12.5	5.6	6.7	5.6	5.6
17	3130	549	28.4	1860	107	3.38	0.83	24.4	.24	4.1	4.4	3.0	9.7	9.7
20	3130	549	54.3	1200	161	5.08	1.59	25.4	.41	7.35	5.8	5.2	9.1	9.1
15	3130	549	79.6	1235	267	8.43	2.32	26.7	.52	9.85	7.0	7.4	8.8	8.8
56	3130	549	101.0	720	81	2.56	2.94	4.9	.60	2.1	16.9	8.2	8.1	8.2
10	3130	549	106.5	915	301	9.50	3.11	26.4	.58	10.8	9.6	10.5	9.7	9.8
9	3130	572	106.7	840	301	9.50	2.98	25.8	.55	10.0	11.3	11.9	11.5	11.5
54	2654	400	101.0	7200	118	3.72	4.03	18.8	.59	7.9	0.65	0.61	0.14	0.14
52	2654	500	101.0	1800	163	5.14	3.23	20.5	.51	7.4	3.9	3.5	2.9	2.9
51	2654	550	100.0	1800	211	6.66	2.91	21.5	.48	7.3	5.1	4.6	4.3	4.3
						Isobutyraldehyde								
45	3130	400	100.0	5880	193	6.09	4.00	15.1	0.71	7.6	1.4			
31	3130	498	100.6	1200	145	4.58	3.23	30.2	.61	13.1	2.9			
42	3130	549	22.0	3000	75	2.37	0.64	15.5	.18	2.0	3.9			
41	3130	549	68.0	1200	146	4.61	1.98	22.0	.48	7.5	5.1			
37	3130	549	100.9	1500	153	4.83	2.94	17.2	.58	7.1	4.5			
47	3130	653	102.0	900	255	8.05	2.50	15.0	.54	5.7	15.7			

isobutyraldehyde, but the values plotted for this compound in Figs. 5 and 6 represent approximately equivalent intensities absorbed.

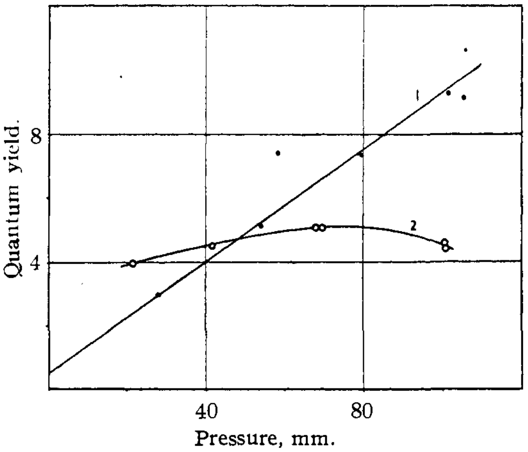


Fig. 5.—Variation of quantum yield of decomposition with pressure for *n*- (line 1) and iso- (line 2) butyraldehydes at 3130 Å. and 549 °K. Values for *n*-butyraldehyde are corrected to a standard intensity of $I_{abs.} = 9.0 \times 10^{-12}$ einsteins cc.$^{-1}$ sec.$^{-1}$.

Observations on *n*-butyraldehyde at different wave lengths showed variable behavior, with a maximum quantum efficiency for 3130 Å. One run at 3660 Å. and 572°K. showed measurable absorption, with definite decomposition. No dark reactions were observed at the temperatures employed in this study. No evidence of polymerization was obtained at the elevated temperatures.

Discussion

1. Low Temperature Reactions.—From the decrease in hydrogen and increase in propane yields with increasing wave length it appears necessary to assume, as in the case of acetaldehyde, that at longer wave lengths the predominating decomposition process is an effective splitting

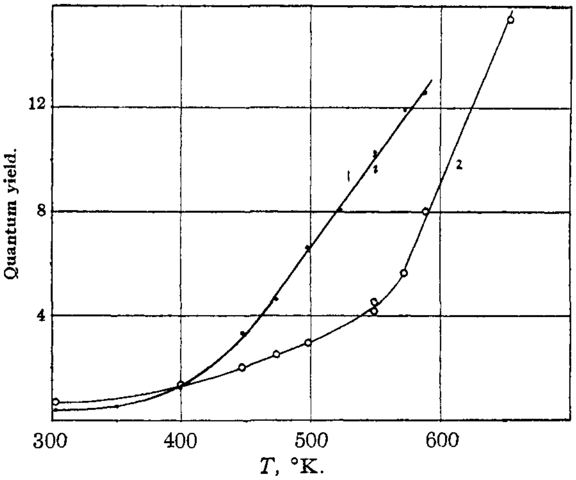


Fig. 6.—Quantum yields as a function of temperature for *n*- (line 1) and iso- (line 2) butyraldehydes at 3130 Å. and 100 mm. pressure. Values for *n*-butyraldehyde are corrected to a standard intensity of $I_{abs.} = 9.0 \times 10^{-12}$ einsteins cc.$^{-1}$ sec.$^{-1}$.

TABLE IV

NUMBER OF MOLECULES OF *n*-BUTYRALDEHYDE, PER 100 MOLECULES OF CO PRODUCED, DISSOCIATING BY PATHS A, B, AND C, TO GIVE OBSERVED PRODUCTS

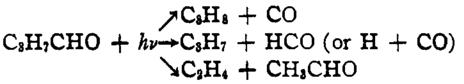
Relative rates assigned to secondary reactions	1 $R_1 = 0$			2 $R_1 = R_2$			3 $R_1 = 2R_2$		
Wave length, Å.	3130	2654	2537	3130	2654	2537	3130	2654	2537
Process A	85	60	50	80	40	25	70	20	0
Process B	15	40	50	20	60	75	30	80	100
Process C	10.5	3	0	11	3	0	11.5	3	0

of the aldehyde molecule into a hydrocarbon and carbon monoxide. This may occur, as suggested by Rollefson,[8] in a single step involving a different excited state from that producing free radicals, or it may result from a dissociation into radicals followed by a reaction between those radicals before they have become completely separated.[3,7,11] The net result is the same in either case and present data do not permit a decision to be made between the two postulated mechanisms of decomposition.

At shorter wave lengths the change in the nature of the products indicates that the direct splitting decreases in importance and a dissociation into independent radicals becomes predominant. It is debatable[8] as to which bond or bonds may be broken but, as with the simpler aldehydes, rupture of the C—C bond adjacent to the C═O bond seems best to account for the products observed. Supporting the formation of propyl radicals by such a process is the verification by Pearson[12] of the formation of mercury-*n*-propyl-iodide in a study of the photodecomposition of di-*n*-propyl ketone. The formyl radicals may retain their identity[3] or decompose immediately into H + CO.[7,11] Favoring the former are the low atomic hydrogen concentration observed by Patat and Sachsse[13] in the thermal decomposition of acetaldehyde, and the fact that the reaction HCO ⟶ H + CO not only appears to be somewhat endothermic, but since it involves an electronic rearrangement probably requires an appreciable activation energy. Favoring the latter view is the fact that formyl radicals, if produced, might be expected to yield some glyoxal,[14] resulting in a deficiency of carbon monoxide which has not been observed.[7]

A third mode of dissociation which must be considered, at least for *n*-butyraldehyde, is the splitting of the central C–C bond to form ethylene and acetaldehyde. Norrish[7] has found that for methyl ethyl ketone 20%, for dipropyl ketone 62%, and for both valeraldehyde and methyl butyl ketone 100% of the decomposition is of this type.

In accounting for the observed products, the relative importance assigned to the three dissociation processes



$$C_3H_7CHO + h\nu \rightarrow \begin{cases} C_3H_8 + CO & \text{A} \\ C_3H_7 + HCO \text{ (or H + CO)} & \text{B} \\ C_2H_4 + CH_3CHO & \text{C} \end{cases}$$

depends on the reactions assumed to follow process B and the relative importance assigned to these reactions. The simplest possibilities for these secondary reactions are

Assuming HCO radicals

1 $C_3H_7 + HCO \longrightarrow C_3H_8 + CO$ R_1

2 $HCO + HCO \longrightarrow H_2 + 2CO$ R_2

3 $C_3H_7 + C_3H_7 \longrightarrow C_3H_8 + C_3H_6$, $\searrow C_6H_{14}$

Assuming H + CO

1 $C_3H_7 + H(+m) \longrightarrow C_3H_8(+m)$ R_1

2 $H + H + m \longrightarrow H_2 + m$ R_2

3 $C_3H_7 + C_3H_7 \longrightarrow C_3H_8 + C_3H_6$, $\searrow C_6H_{14}$

As an illustration of the results obtainable, Table IV shows for *n*-butyraldehyde at 100 mm. pressure the relative numbers of molecules dissociating by processes A, B, and C per 100 molecules of carbon monoxide produced, using three provisional assignments of relative rates to reactions 1 and 2.

Reaction 3 is assumed to go 60% to give propane and propylene, 40% to form hexane.[15] $R_1 = 0$ would permit a maximum hydrogen yield of 50% relative to carbon monoxide, $R_1 = R_2$ would permit a hydrogen yield of 33%, and $R_1 = 2R_2$ a yield of 25%. As the experimental data indicate a hydrogen yield of more than 25% at wave lengths below 2537 A., assignment 3 appears improbable, therefore process A appears to be still appreciable even at 2537 Å. If process C decreases while B increases in importance at shorter wave lengths, the ratio of propylene to ethylene should increase. This is supported by our ob-

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[11] Norrish, *Trans. Faraday Soc.*, **30**, 103 (1934).

[12] Pearson, *Nature*, **136**, 221 (1935); Pearson and Purcell, *J. Chem. Soc.*, 253 (1936).

[13] Patat and Sachsse, *Naturwissenschaften*, **23**, 247 (1935).

[14] Bates, *Cold Spring Harbor Symposia on Quantitative Biology*, **3**, 49 (1935).

[15] Rice and Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Md., 1935.

servations on the retention in the liquid air trap of the unsaturated hydrocarbons produced by exposure to 2537 Å., and non-retention of these produced at 3130 Å. In spite of its more complicated behavior, an analogous change in the relative importance of processes A and B with wave length is indicated by the analytical results for isobutyraldehyde.

Following absorption, in addition to processes A, B, and C, other possibilities include fluorescence, polymerization, and collisional deactivation. The fact that Φ_d shows a tendency to *increase* with pressure at 3130 Å. suggests still other paths, such as dissociation induced by collision, for the absorbing molecules, and the increase in Φ_p at shorter wave lengths, particularly for isobutyraldehyde, indicates a reaction between the radicals from process B and aldehyde molecules to form non-volatile products. Finally, the possibility of a recombination of radicals must be recognized.

A comparison of Φ_d among the different aldehydes is of interest. At 3130 Å., for acetaldehyde it decreases markedly with increasing pressure (from 0.4 at 14 mm. to 0.2 at 200 mm.), for propionaldehyde it decreases but slightly, for *n*-butyraldehyde it increases slightly, and for isobutyraldehyde it increases markedly with pressure. One concludes that while in acetaldehyde Φ_d at this wave length is reduced by a pressure dependent process (collisional deactivation, polymerization, etc.), as one goes up the series to isobutyraldehyde this becomes progressively subordinated to a pressure dependent process increasing Φ_d. It may or may not be significant that the intensity of fluorescence and the amount of structure in absorption change in the same order.

At 2654 Å., in all cases Φ_d is essentially independent of pressure at pressures above *ca.* 50 to 100 mm., but drops off at lower pressures. Since this is in the region of continuous absorption, with process B predominating, a Φ_d independent of pressure, except as it may influence the secondary reactions, is to be expected. The drop in Φ_d at low pressures suggests a wall recombination. All the aldehydes show (Table V) a general increase in Φ_d with decreasing wave lengths, apparently approaching a value of unity at the limit of the absorption band.

TABLE V

QUANTUM YIELDS OF DECOMPOSITION, AT 30° AND 100 MM. PRESSURE

Values in parentheses are interpolated from runs at other pressures.

	Wave length, Å.				
Aldehydes	3130	3020	2804	2654	2537
CH_3CHO	0.28	(0.36)	(0.55)	0.77	0.91
C_2H_5CHO	.53	(.55)	(.68)	.78	(.82)
n-C_3HC_7HO	.44	.42	.44	.48	.75
iso-C_3H_7CHO	.63	.66	.72	.79	.87

2. High Temperature Reactions.—A chain decomposition becomes predominant in the photolysis of both butyraldehydes at elevated temperatures. For *n*-butyraldehyde the local rate is given by an equation identical in form to that found by Leermakers[5] for acetaldehyde. At 3130 Å., if the quantum yield for the non-chain part of the reaction equals 0.45

$$\frac{d(CO)}{dt} = 0.45\, I'_{abs.} + kI'^{1/2}_{abs.}\,(RCHO) \qquad (1)$$

Since the square root of the quantity of absorbed light is involved, this equation should give the over-all rate only in case the light absorption or the distribution of intermediate reactants (free radicals) involved in the chain is uniform throughout the cell. For non-uniform absorption and no diffusion of radicals from one element of volume to another in the cell one might expect the over-all rate to be given more exactly by the following expression in which Beer's law and a parallel light beam are assumed[16,17]

$$\left(\frac{d(CO)}{dt}\right)_{Av.} = 0.45\, I_{abs.} + \frac{2k'aI_0^{1/2}\,(RCHO)^{1/2}\,(1 - e^{-d(RCHO)l}}{Va^{1/2}} \qquad (2)$$

V is the volume of the cell, a is the cross section of the incident light beam. Since less than 2% of the aldehyde was consumed in each experiment, $(d(CO)/dt)_{Av.}$ may be replaced by $(CO)/t$ where (CO) equals moles of carbon monoxide produced per cc. of the reaction cell during the time, t, of the experiment. Taking $I_{abs.}$ in einsteins cc.$^{-1}$ sec.$^{-1}$ and (RCHO) in moles cc.$^{-1}$, the resulting values of k from the two equations, in einsteins$^{-1/2}$ sec.$^{-1/2}$ cc.$^{1/2}$, are given in Table III. It can be seen that for the gaseous system used in this study the rate constants are substantially the same for the two equations even though in some cases as much as 71% of the incident light was absorbed. However, it can be shown that as the fraction of the absorbed light becomes much greater than this value there is an increasing difference in the

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[16] Noyes, *Cold Spring Harbor Symposia on Quantitative Biology*, 3, 37 (1935).

[17] Dickinson and Nies, THIS JOURNAL, 57, 2382 (1935).

constants. For example, the difference between the two *k*'s ranges from 2 to 19% as the fraction absorbed is changed from 0.81 to 0.99. Neither equation will hold over large variations in light intensity since the rate (Fig. 4) increases somewhat more rapidly than $I_{\text{abs.}}^{1/2}$. Plotting log *k* against $1/T$ (at $T = 450°$K. and greater) gives a straight line with a slope corresponding to an apparent activation energy of 5600 cal.

The behavior of isobutyraldehyde is definitely more complicated (Figs. 5 and 6) and no correlation of the experimental data with a rate equation has been made. It may be said, however, that the close proportionality between rate and light intensity indicates removal of chain carriers by some other process than recombination of radicals. Under comparable conditions the chain lengths of decomposition for both butyraldehydes lie between those reported by Leermakers[18] for acetaldehyde ($\Phi_d = 10$ to 20 at 180°) and valeraldehyde ($\Phi_d < 1$ at 180°).

It appears unwise, without more detailed knowledge of the intermediates involved, to attempt construction of any mechanism for the high temperature reactions. That this mechanism is far from simple is indicated not only by the behavior of isobutyraldehyde, but also by the fact that for *n*-butyraldehyde the high temperature quantum yield is definitely lower at λ 2654 than at λ 3130 (Table III), whereas if the process consisted simply of chains initiated by a dissociation of type B, the increase in importance of this dissociation at shorter wave lengths, as indicated by the low temperature experiments, would require a higher yield.

Summary

The photochemical behavior of *n*- and isobutyraldehydes in the vapor phase, both at ordinary and at elevated temperatures, has been investigated. The room temperature reactions are analogous to those of the lighter aldehydes, consisting of both polymerization and decomposition, the variations of which with wave length and pressure have been studied. Analyses of the reaction products at different wave lengths are used as a basis for assigning relative importance to different dissociation possibilities.

Chain photolyses are found for both aldehydes at elevated temperatures. That for *n*-butyraldehyde resembles the chain photolysis of acetaldehyde, while that for isobutyraldehyde differs sharply from acetaldehyde in kinetic character.

LOS ANGELES, CALIF. RECEIVED JULY 6, 1937

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[18] Leermakers, *Cold Spring Harbor Symposia on Quantitative Biology*, **3**, 49 (1936).

[CONTRIBUTION NO. 37 FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Reactions in the Solid State. I. The Reactions between Barium Carbonate and Ferric Oxide in the Presence of Oxygen[1]

BY ROLAND WARD AND JAMES D. STRUTHERS[2]

A number of reactions of commercial importance depend upon absorption of oxygen from the air by solid compounds or by the products of solid phase reactions. The preparation of peroxides of the alkali and alkaline earth elements, the reactions of the oxides of the transition elements with alkali and alkaline earth oxides, and the preparation of several contact catalysts are reactions of this type. These reactions have not been subject to thorough quantitative investigation. This paper records an attempt to determine the mechanism of the reaction between barium carbonate and ferric oxide in an atmosphere of oxygen at atmospheric pressure.

Historical.—The reaction between barium carbonate and ferric oxide has been studied by J. Guillissen,[3] who prepared barium ferrite by heating the reactants in air at 830°. In a later paper, J. Guillissen and P. J. van Rysselberghe[4] showed that an appreciable yield of barium ferrite was obtained by heating an equimolecular mixture of barium carbonate and ferric oxide at 720°. They do not state that the reaction was carried out in the presence of oxygen. L. Moser and H. Brock[5] report obtaining barium perferrite

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[1] Abstracted from a thesis submitted in partial fulfilment of the degree of Bachelor of Science at the Polytechnic Institute of Brooklyn.

[2] Recipient of Sigma Xi "Certificate in Commendation of Research," 1936.

[3] J. Guillissen, *Acad. roy. Belg., Classe sci.*, **5**, XIII, 233 (1927).

[4] J. Guillissen and P. J. van Rysselberghe, *Trans. Am. Electrochem. Soc.*, **59**, 95 (1931).

[5] L. Moser and H. Brock, *Ber.*, **42**, 4279 (1909).