549. *The Gas-phase Oxidation of Crotonaldehyde.*

By A. D. Osborne and G. Skirrow.

The gas-phase reaction between crotonaldehyde and oxygen has been studied at temperatures between 150° and 350° c. Below 200° the reaction resembles the corresponding acetaldehyde–oxygen reaction. Peroxycrotonic acid is the main product and is responsible for chain-branching. The mechanism suggested by McDowell and Farmer for the oxidation of acetaldehyde has been adopted to explain the behaviour in this temperature range. Above 200° the reaction is more complex; acetaldehyde, which is produced in appreciable quantities from the terminal $CH_3{\cdot}CH$ group of the crotonaldehyde, contributes to the chain-branching. Probable reaction processes are discussed.

Aldehydes are almost invariably found as intermediates during the slow combustion of paraffins, and there has been much discussion about their mode of formation and the part they play in the overall mechanism. Because of the important functions of formaldehyde and acetaldehyde in the reactions in which they occur as intermediates, the oxidation of these compounds has been examined in considerable detail.[1–6] Although unsaturated aldehydes are produced during the oxidation of olefins,[7–9] published work dealing with their gaseous reactions is not yet extensive.

The photo-oxidation of crotonaldehyde at 30° has been described by Blacet and Volman,[10] but no general mechanism was suggested. Volman and Brinton[11] studied the decomposition of acetaldehyde and acraldehyde under the influence of methyl-radical attack, and showed that acraldehyde undergoes chain decomposition much less readily than acetaldehyde. More recently Pitts[12] *et al.* have sought to explain their observations on the interaction of methyl radicals with crotonaldehyde in terms of a displacement rather than an abstraction reaction. In the present work the slow combustion of crotonaldehyde has been investigated by kinetic and analytical methods.

Experimental

Materials.—Crotonaldehyde (B.D.H) was freed from traces of water and resin by fractional distillation in an atmosphere of oxygen-free nitrogen. The fraction of b. p. 102° was further purified by repeated bulb-to-bulb vacuum distillation, and the purified material transferred *in vacuo* to storage phials.

Cylinder oxygen was condensed at liquid-nitrogen temperature, and approximately 90% of the condensate removed by pumping. Most of the nitrogen-free fraction was allowed to evaporate into an evacuated storage bulb, water and carbon dioxide being retained in the remaining liquid oxygen.

Carbon dioxide, helium, and nitrogen were taken directly from cylinders. Acetaldehyde was prepared by bulb-to-bulb fractionation of B.D.H. "Pure" liquid, and formaldehyde was obtained by heating paraformaldehyde. Di-t-butyl peroxide (Laporte) was purified and freed from hydrogen peroxide by vacuum distillation.

Apparatus and Analysis.—The Pyrex reaction vessel (vol. 170 ml.; diam. 3 cm.) was washed with nitric acid and distilled water and allowed to drain before being sealed to the apparatus.

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[1] Scheer, Fifth Symposium on Combustion, Reinhold Publ. Corp., New York, 1954, p. 435.
[2] Axford and Norrish, *Proc. Roy. Soc.*, 1948, *A*, **192**, 518.
[3] Style and Summers, *Trans. Faraday Soc.*, 1946, **42**, 388.
[4] McDowell and Thomas, *J.*, 1949, 1462, 2208.
[5] Combe, Niclause, and Letort, *Rev. Inst. franç. Petrole*, 1955, **10**, 786.
[6] Small and Ubbelohde, *J.*, 1952, 4619; 1953, 637.
[7] Mullen and Skirrow, *Proc. Roy. Soc.*, 1958, *A*, **244**, 312.
[8] Blundell and Skirrow, *Proc. Roy. Soc.*, 1958, *A*, **244**, 331.
[9] Dobvinskaya and Neuman, *Doklady Akad. Nauk S.S.S.R.*, 1947, **58**, 1919.
[10] Blacet and Volman, *J. Amer. Chem. Soc.*, 1938, **60**, 1234; 1939, **61**, 582.
[11] Volman and Brinton, *J. Chem. Phys.*, 1952, **20**, 1764.
[12] Pitts, Thompson, and Woolfolk, *J. Amer. Chem. Soc.*, 1958, **80**, 66.

All the connecting tubes and taps and the glass spoon-type gauge were kept at a temperature high enough to prevent condensation of crotonaldehyde and reaction products. The vessel was heated in a furnace which controlled the temperature within ±1°. The reactants were admitted separately—crotonaldehyde first—to the reaction vessel and the reaction was followed manometrically. Samples were extracted for analysis by allowing the mixture to expand through a series of cooled traps into a Toepler pump. It was convenient to effect a preliminary separation by refrigerants so as to give the fractions: (*a*) gas not condensed at −215° (pumped out liquid-nitrogen trap); (*b*) fraction retained at −215°; (*c*) fraction retained at −120°; (*d*) fraction involatile at −78°.

Fraction (*a*), which contained oxygen, hydrogen (trace), carbon monoxide, and methane, was analysed by gas chromatography with a 4 ft. carbon column (Sutcliffe–Speakman, 80 mesh). Fraction (*b*), which contained ethylene, ethane, propene, C_4-hydrocarbons, carbon dioxide, and much of the formaldehyde, was similarly examined by using a 9 ft. dinonyl phthalate column. Fraction (*c*), which contained acetaldehyde and the rest of the formaldehyde, and (*d*), which contained unchanged crotonaldehyde, peroxides, water, and acids, were examined in the same manner as (*b*) or by conventional methods. Except for propionaldehyde and the permanent gases, the identity of each substance indicated by gas chromatography was confirmed by an independent method. It was not possible to determine formaldehyde, peroxides, acids, and water by gas chromatography, and these substances were analysed by the chromotropic acid method, iodometric titration, titration with barium hydroxide solution, and Karl Fischer titration, respectively. The total acid determinations included acid and per-acid.

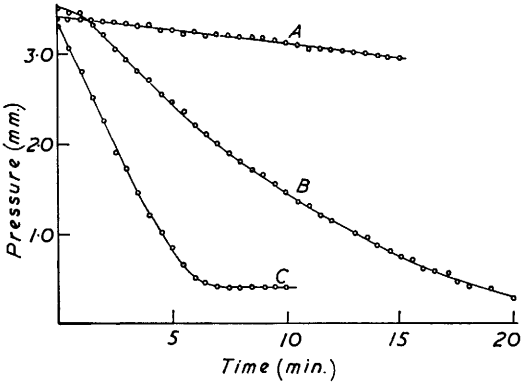


FIG. 1. *Pressure–time curves at* 166°.

A, Crotonaldehyde 98 mm., oxygen 100 mm.; *B*, crotonaldehyde 200 mm., oxygen 195 mm.; *C*, crotonaldehyde 300 mm., oxygen 140 mm.

Results

At temperatures below 200° the reaction was accompanied by a pressure decrease, but at higher temperatures the pressure increased throughout the reaction. In view of this change in character of the pressure–time curve with temperature, it is clearly not possible to compare reaction rates at different temperatures merely by comparing the maximum rates of pressure change ($\rho_{\text{max.}}$). However, it seems probable that at any one temperature $\rho_{\text{max.}}$ may be used as a measure of rate, since at both high and low temperatures a linear relation was observed between pressure change and oxygen consumption for most of the reaction.

Low-temperature Reaction (<200°).—A typical pressure–time curve for reaction at 166° is shown in Fig. 1. Following an initial acceleration, a steady rate of pressure decrease is attained and maintained over a considerable proportion of the reaction. In this respect the behaviour resembles that observed by McDowell and Farmer[13] for the oxidation of acetaldehyde at lower temperatures. These authors have pointed out that this constancy of rate despite consumption of reactants is a feature of branched-chain reactions in which a product functions as a degenerate branching agent, and termination is by interaction of chains as described by Semenov.[14] At this temperature the oxidation of crotonaldehyde proceeds with no increase in pressure towards the end of the reaction.

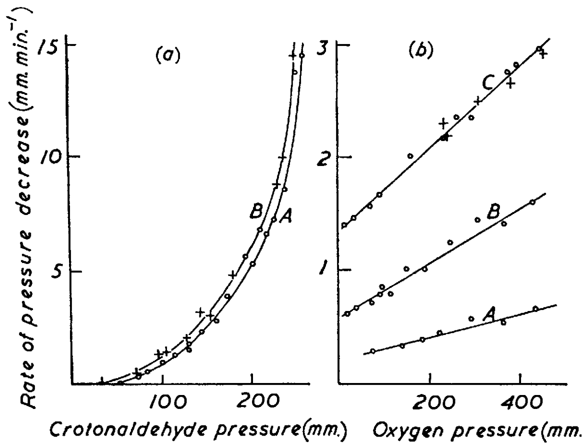
[13] McDowell and Farmer, Fifth Symposium on Combustion, Reinhold Publ. Corp., New York, 1954, p. 453.

[14] Semenov, " Chemical Kinetics and Chain Reactions," Oxford, 1935.

The effect of reactant concentrations on the rate is summarised in Fig. 2. The rate increases rapidly with increasing pressure of crotonaldehyde; a logarithmic plot indicated an order of 2·6. Even at quite low oxygen pressures the rate was appreciable and showed a steady (almost linear) increase with further additions. That this increase was an inert-gas effect was shown by the influence of nitrogen, which produced precisely the same acceleration as that given by the equivalent amount of oxygen [Fig. 2(*b*)].

FIG. 2(*a*). $p_{\text{max.}}$ *as a function of crotonaldehyde pressure at* 166°.

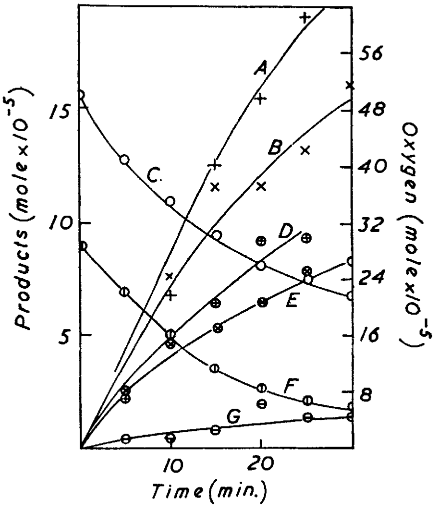
FIG. 2(*b*). $p_{\text{max.}}$ *as a function of oxygen pressure at* 166°



Oxygen pressure: (*A*) 144 mm.; (*B*) 289 mm.

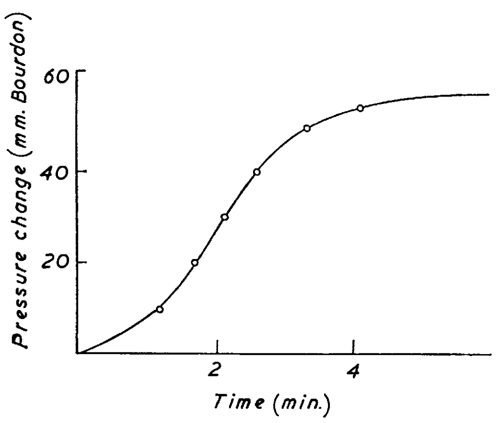
Crotonaldehyde pressures: (*A*) 72 mm.; (*B*) 101 mm.; (*C*) 137 mm. Crosses refer to total ($N_2 + O_2$) pressure in the reaction mixture containing 137 mm. of crotonaldehyde and 90 mm. of oxygen.

FIG. 3.—*Progress of the reaction at* 166°.



A, Acid; *B*, peroxide; *C*, oxygen; *D*, carbon dioxide; *E*, carbon monoxide; *F*, Δp; *G*, acetaldehyde.

FIG. 4.—*Pressure–time curve at* 260°.



Curve indicates experimental results. Circles calculated from: t (min.) $= 1{\cdot}5 \log_{10} (1 + 24x)/(1 - x)$, where

$$x = \frac{\text{pressure change at time } t}{\text{total pressure change at } t_{\infty}}$$

The true order of the reaction with respect to oxygen is thus zero. The order with respect to crotonaldehyde is difficult to determine, since at least part of the accelerating influence of additions of aldehyde must be an inert-gas effect. It is probable, however, that the order is very much less than 2·6, and for the purpose of the kinetic analysis an order of 2·0 is assumed.

Course of the reaction at 166°. The reaction products comprised mainly peroxides, acids, carbon dioxide, and carbon monoxide. Acetaldehyde and formaldehyde were produced in smaller amounts. The formation of water was not investigated. The results of a series of analyses made throughout the course of a reaction are shown in Fig. 3. The peroxide fraction was shown by paper chromatography to contain hydrogen peroxide and a per-acid having an R_F value similar to that expected for peroxycrotonic acid (*i.e.*, between the values for propionic and peroxybutyric acids [14a]). Since the total acid production somewhat exceeded the total peroxide, some breakdown of peroxycrotonic acid to crotonic acid probably occurs. Examination of the fraction accumulated at −78° by paper chromatography showed crotonic acid to be present.

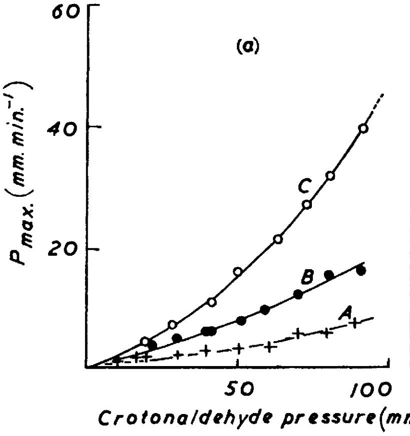


FIG. 5(*a*). $\rho_{max.}$ *as a function of aldehyde pressure at* 260°.

Oxygen pressure *A*, 14 mm.; *B*, 30 mm.; *C*, 60 mm.

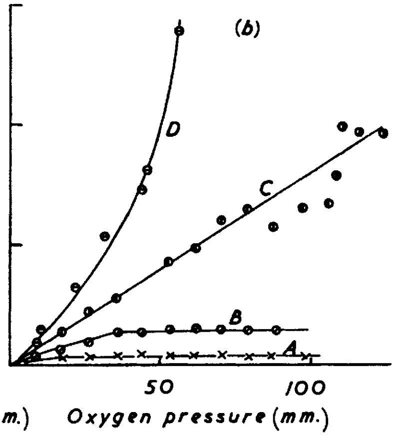


FIG. 5(*b*). $\rho_{max.}$ *as a function of oxygen pressure at* 260°.

Aldehyde pressures: *A*, 18 mm.; *B*, 36 mm.; *C*, 71 mm.; *D*, 88 mm.

Reaction above 200°.—At 260° the reaction showed a steady acceleration to a maximum rate (Fig. 4). There was no induction period, the reaction showing a small initial rate. The curve of Fig. 4 can be fitted to the equation:

$$t(\text{min.}) = 1{\cdot}50 \log_{10} (1 + 24x)/(1 - x)$$

where x is the fractional extent of reaction. An equation of this form was shown by Semenov [15] to be characteristic of autocatalytic and degenerately branched reactions which show a finite initial rate.

The maximum rate of pressure change at higher temperatures was not reached until comparatively late in the reaction when appreciable quantities of the reactants had been consumed. However, $\rho_{max.}$ values were reproducible and dependent solely on the initial reactant pressures, and were uninfluenced by addition of nitrogen, helium, or carbon dioxide. The variation of $\rho_{max.}$ with crotonaldehyde pressure for several values of initial oxygen pressure is shown in Fig. 5(*a*). Logarithmic plots gave an order with respect to crotonaldehyde of 1·5. The corresponding dependence on oxygen pressure can be seen from Fig. 5(*b*): $\rho_{max.}$ showed an initial linear increase with oxygen pressure, but tended ultimately to independence of oxygen except at high initial crotonaldehyde concentrations when explosion occurred before this independence was attained.

Analytical Data.—Analysis of products showed that the reaction was complex. The concentration of peroxides, although formed in the earlier stages of the reaction, had decayed to zero by the end. Acids were formed in much smaller quantities than at the lower temperature

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[14a] Cartlidge and Tipper, *Analyt. Chim. Acta*, 1960, **22**, 106.

[15] Semenov, *Compt. rend. Acad. Sci. U.R.S.S.*, 1944, **43**, 342.

(1·5 × 10^{-5} mole from a mixture of 21 × 10^{-5} mole of each of reactants compared with approximately 15 × 10^{-5} mole from a mixture of 63 × 10^{-5} mole of each of the reactants at 166°), but the acetaldehyde yield was much enhanced. Table 1 shows a material balance for a 1 : 1 mixture at 292°. A balance of over 90% for carbon, hydrogen, and oxygen shows that no major products were undetected.

Course of the Reaction at 292°.—By interrupting for analysis a number of experiments in which the amounts of crotonaldehyde and oxygen were each 21 × 10^{-5} mole, the data of Fig. 6 were obtained. Total peroxides reached the maximum concentration at a point coincident with $p_{\text{max.}}$. All other products either accumulated or showed ill-defined peaks.

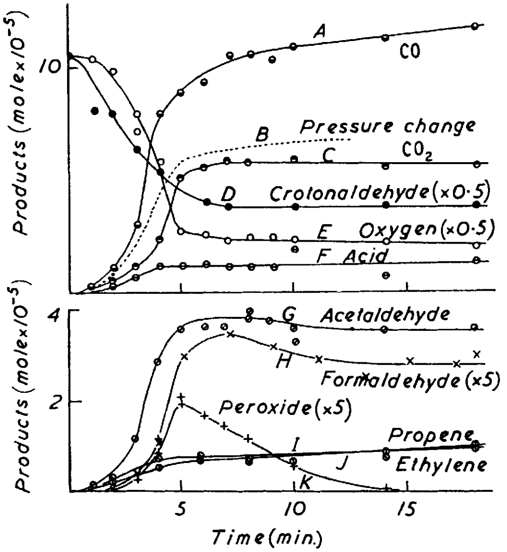

FIG. 6. *Progress of the reaction at* 292°.

A, CO; *B*, Δp; *C*, CO_2; *D*, crotonaldehyde (×0·5); *E*, O_2 (×0·5); *F*, acid; *G*, acetaldehyde; *H*, H·CHO (×5); *I*, propene; *J*, ethylene; *K*, peroxide (×5).

TABLE 1. *Material balance at* 292°.

Initial crotonaldehyde, 21 × 10^{-5} mole; initial oxygen, 21 × 10^{-5} mole.

	Products	C	O	H		Products	C	O	H
	(10^{-5} mole)	(10^{-5} g.-atom)				(10^{-5} mole)	(10^{-5} g.-atom)		
CO	12·0	12·0	12·0	—	C_2H_5·CHO ...	1·5	4·5	1·5	9·6
CO_2	6·0	6·0	12·0	—	Acraldehyde...	0·2	0·6	0·2	0·8
H_2O	7·2	—	7·2	14·4	H·CHO.........	0·7	0·7	0·7	1·4
CH_4	0·8	0·8	—	3·2	Crotonic acid	1·5	6·0	3·0	9·0
C_2H_4	1·0	2·0	—	4·0	Crotonaldehyde	8·0	32·0	8·0	48·0
C_3H_6	1·2	3·6	—	7·2					
CH_3·CHO	4·4	8·8	4·4	17·4	Oxygen	4·5	—	9·0	—

Increase = 7 × 10^{-5} mole = 2·6 cm. (Bourdon deflection).
Observed pressure increase = 3·0 cm. (Bourdon deflection).

Addition of Reaction Products.—Acetaldehyde and formaldehyde are known to act as degenerately branching agents in certain oxidation systems. Addition of formaldehyde in amounts up to several times that produced during the reaction between 37·7 mm. each of crotonaldehyde and oxygen was entirely without effect, showing it to make no contribution to chain-branching. Small additions of acetaldehyde had a pronounced effect on the reaction: the maximum rate increased and was attained earlier (Table 2).

TABLE 2. *Effect of additions of acetaldehyde on reaction rate at* 292°.

Initial pressures of reactants—each 37·7 mm.

Acetaldehyde (mm.)	0	0·9	3·8	9·9	19·3
Rate (mm./min.)	3·8	4·4	5·8	6·5	14·4

The failure of the acetaldehyde–time curve to show a clearly-defined peak is surprising in view of the contribution of this compound towards branching. Towards the end of the reaction small amounts of crotonaldehyde and acetaldehyde remained in the presence of unchanged oxygen. Separate experiments showed that, when these amounts of crotonaldehyde and oxygen were admitted to the vessel, any reaction was too slow to be observed. When amounts of acetaldehyde and oxygen identical with those remaining at the end of a reaction were admitted to the vessel in absence of crotonaldehyde, reaction occurred with the formation of carbon monoxide and methane. Progressive addition of crotonaldehyde to such a mixture of acetaldehyde and oxygen confirmed that it was responsible for partial inhibition of the degradation of the acetaldehyde, presumably by acting as a free-radical trap by replacing the more reactive radicals by the less reactive crotonoyl radical (Table 3).

TABLE 3. *Effect of crotonaldehyde on the oxidation of acetaldehyde at* 292°.

CH_3·CHO (mm.)	O_2 (mm.)	Crotonaldehyde (mm.)	CH_3·CHO left (mm.)	CH_3·CHO (mm.)	O_2 (mm.)	Crotonaldehyde (mm.)	CH_3·CHO left (mm.)
17	17	0	0·8	17	18	10	13·0
17	18	5	6·2	16	16	30	16·0

Production of Carbon Monoxide and Carbon Dioxide.—The ratio of CO : CO_2 produced during the reaction as a function of temperature and reactant concentrations is shown in Table 4. An eight-fold increase in the initial oxygen pressure decreases this ratio by approximately one half. Increasing the temperature increases the ratio somewhat, but the change is smaller than that observed in corresponding experiments with saturated aldehydes.[16]

TABLE 4. *Variation of carbon monoxide : carbon dioxide ratio with reaction conditions.*

	Pressure (mm.)				Pressure (mm.)		
Temp.	Oxygen	Crotonaldehyde	CO/CO_2	Temp.	Oxygen	Crotonaldehyde	CO/CO_2.
347°	4·6	24·6	4·2	292°	38	36·0	2·0
347	16·1	24·6	2·7	254	16·0	100·0	1·1
347	26·7	24·6	2·9	254	64·0	100·0	1·1
347	32·0	24·6	2·4	166	95·0	95·0	0·9

Attack of Methyl Radicals on Crotonaldehyde.—In the early stages of the reaction crotonaldehyde must be the major target for radicals. Information on the behaviour of crotonaldehyde under the influence of attack by methyl radicals in the absence of oxygen was sought by allowing the aldehyde and di-t-butyl peroxide, pre-mixed in a 5 l. bulb, to expand into the reaction vessel at 166°. The subsequent reaction was followed manometrically and the final products were removed for analysis by gas chromatography. The results are compared in Table 5 with an equivalent set obtained by replacing crotonaldehyde with acetaldehyde.

TABLE 5. *Reaction of* CH_3 *radicals from di-t-butyl peroxide with acetaldehyde and crotonaldehyde* (166°).

	10^{-5} Mole			10^{-5} Mole	
Crotonaldehyde	Acetaldehyde	Peroxide	CO	CH_4	C_3H_6
—	12·8	6·4	5·5	4·1	—
12·8	—	6·4	1·3	2·2	0·2
12·8	—	6·4	1·2	1·7	0·2
—	—	6·4	Not detectable		

Acetaldehyde–peroxide mixtures gave approximately equal amounts of methane and carbon monoxide, and the total pressure in the reaction vessel increased by about 50%. A much smaller amount of permanent gas was produced by the crotonaldehyde–peroxide mixture, and the amount of propene was about one-sixth of that of the carbon monoxide. Negligible pressure change occurred. Some C_4 hydrocarbon was produced, and, although not identified unambiguously, it is probable that this was but-2-ene. Since these experiments were performed, Pitts[12] *et al.* have described almost identical experiments and have obtained results with which ours are in close agreement. These authors showed the C_4 hydrocarbon to be but-2-ene.

Comparison with Methacraldehyde.—At 292° a mixture of 21 × 10^{-5} moles of methacraldehyde when allowed to react to completion gave 16 × 10^{-5} mole of formaldehyde and 0·2 × 10^{-5} mole of acetaldehyde. The corresponding experiment with crotonaldehyde gave 0·7 × 10^{-5}

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[16] Newitt and Baxt, *J.*, 1939, 1711.

mole of formaldehyde and $4{\cdot}4 \times 10^{-5}$ mole of acetaldehyde. This difference in behaviour indicates that the acetaldehyde formed during the oxidation originated from the terminal $CH_3{\cdot}CH$ group.

DISCUSSION

At both high and low temperatures peroxides are produced during the reaction, but whereas at the lower temperature these are comparatively stable and decompose only slowly, at higher temperature their instability leads to the formation of large amounts of products of low molecular weight. Since formation of acetaldehyde is greater at higher temperatures, it is reasonable to conclude that it is a decomposition product of either a peroxide or a peroxy-radical.

In the presence of oxygen, crotonoyl radicals produced by free-radical attack on crotonaldehyde can either peroxidise or decompose thermally, and it is of interest to examine more specifically the fate of the crotonoyl radical following such radical attack. The experiments with di-t-butyl peroxide gave convincing evidence for some hydrogen abstraction since methane is a reaction product. The amount formed is less than in the equivalent reaction with acetaldehyde for which

$$CH_3 + CH_3{\cdot}CHO \longrightarrow CH_4 + CH_3{\cdot}CO$$

is an established process, but the lower yield in itself is not evidence of a greater resistance of crotonaldehyde towards hydrogen abstraction since much of the methane from the acetaldehyde experiments is probably produced by further reaction of the acetyl-radical decomposition products. The aldehydic C–H bond energy in crotonaldehyde will be less than that in saturated aldehydes by virtue of the mesomeric structure of the crotonoyl radical, and the abstraction of the aldehydic hydrogen will occur more readily with crotonaldehyde. However, the low yields of carbon monoxide and (methane + propene) from crotonaldehyde show that the overall sequence

$$R{\cdot}CHO + CH_3 \longrightarrow CH_4 + R{\cdot}CO \quad \dots\dots\dots\dots \quad (1)$$

$$R{\cdot}CO \longrightarrow R + CO \quad \dots\dots\dots\dots \quad (2)$$

$$R + R{\cdot}CHO \longrightarrow RH + R{\cdot}CO \quad \dots\dots\dots\dots \quad (3)$$

occurs less readily with crotonaldehyde than with acetaldehyde and suggests that the rate of process (2) is low because of the stability of the crotonoyl radical.

An alternative scheme for the interaction of methyl radicals and crotonaldehyde has recently been put forward by Pitts and his co-workers, who suggest that the yields of but-2-ene and propene can be explained by the displacement reactions

$$R{\cdot}CHO + CH_3 \longrightarrow R{\cdot}CH_3 + CHO \quad \dots\dots\dots\dots \quad (4)$$

$$CHO \longrightarrow CO + H \quad \dots\dots\dots\dots \quad (5)$$

$$H + R{\cdot}CHO \longrightarrow RH + CHO \quad \dots\dots\dots\dots \quad (6)$$

It is not clear whether, or to what extent, such displacements do participate in the reaction, although it seems unlikely that they do so to the exclusion of abstractions. In particular, the probable activation energy for process (5), estimated at 26—28 kcal. by Tipper,[17] seems too high to allow much propene to be produced in this way. It is possible, however, that the high yields of but-2-ene are a consequence of the thermal stability of the crotonoyl radical which may have a lifetime sufficient to make important the reaction

$$CH_3{\cdot}CH{:}CH{\cdot}CO + CH_3 \longrightarrow CH_3{\cdot}CH{:}CH{\cdot}CH_3 + CO \quad \dots\dots\dots \quad (7)$$

Below 200° and in the presence of oxygen, the crotonoyl radical will peroxidise and continue the chain:

$$CH_3{\cdot}CH{:}CH{\cdot}CO + O_2 \longrightarrow CH_3{\cdot}CH{:}CH{\cdot}CO(O_2) \quad \dots\dots\dots \quad (8)$$

$$CH_3{\cdot}CH{:}CH{\cdot}CO(O_2) + R{\cdot}CHO \longrightarrow CH_3{\cdot}CH{:}CH{\cdot}CO(OOH) + R{\cdot}CO \quad \dots\dots \quad (9)$$

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[17] Tipper, *Quart. Reviews*, 1957, **11**, 313.

only a small proportion decomposing according to (2). The high yield of peroxides and acids and the decrease in overall pressure are consistent with this interpretation. Many features of the low-temperature oxidation of crotonaldehyde resemble those shown by the acetaldehyde–oxygen system, and it seems probable that the main reactions governing the kinetics in the two systems are analogous. Thus if the branching is

$$R{\cdot}CO(OOH) \longrightarrow R{\cdot}CO_2 + OH \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (10a)$$

or

$$R{\cdot}CO(OOH) \longrightarrow R + CO_2 + OH \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (10b)$$

and termination is by mutual destruction of peroxy-radicals, *viz.*,

$$R{\cdot}CO_3 + R{\cdot}CO_3 \longrightarrow \text{termination}$$

then, following the treatment outlined by McDowell and Farmer, the kinetic expression can be shown to be of the form:

$$d[O_2]/dt = k(\text{acetaldehyde})^2(\text{oxygen})^0$$

which is in agreement with our results when allowance is made for the inert-gas effect.

Additional processes must be introduced to account for the yield of carbon dioxide which accounts for some 25% of the oxygen consumed. There is evidence that in oxidation reactions formation of carbon dioxide follows from the dissociation of $R{\cdot}CO_2$ radicals[18] which are probably more unstable than the corresponding $R{\cdot}CO$ radicals.[19, 20] Although some carbon dioxide may be produced by branching reaction 10(*b*), this is unlikely to be the sole means of its formation, since peroxycrotonic acid decomposes only slowly under the experimental conditions, and an additional source may be non-termination reaction of the peroxy-radicals such as

$$R{\cdot}CO_3 + R{\cdot}CO_3 \longrightarrow 2R + O_2 + 2CO_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (11)$$

Reaction above 200°.—The mode of branching operative at 166° will probably still operate at higher temperatures but will be reinforced by that due to the acetaldehyde oxidation. The pronounced effect of additions of acetaldehyde shows it to give more vigorous branching than crotonaldehyde despite the fact that radical attack takes place preferentially on the latter. At these temperatures the reaction is complex, and it is difficult to set up a mechanism which satisfies unambiguously all the observed facts. Propagation will be by reactions (8) and (9) and branching by (10) and the corresponding peracetic acid decomposition. The selection of a termination reaction poses a more difficult problem, since the form of the kinetic relationships indicates that it is unlikely to be a simple $R{\cdot}CO_3$–$R{\cdot}CO_3$ collision. This sort of termination would be surprising at higher temperatures since the product, dicrotonoyl peroxide, would be expected to be unstable and to behave as a source of reactive radicals. Dependence of the rate on oxygen pressure implies either a slow peroxidation step which occurs in competition with some non-branching process, or a termination collision involving oxygen. Although it is possible on the basis of these assumptions to derive kinetic expressions of form similar to those observed experimentally, this cannot readily be achieved without introducing steps the chemistry of which cannot be visualised in detail. Other factors—notably the appreciable consumption of reactants in the interval before the time of maximum rate—contribute to the difficulty in setting up a complete kinetic scheme.

Formation of Acetaldehyde.—The comparison experiments with methacraldehyde indicate that the acetaldehyde formed in the crotonaldehyde oxidation originates in the terminal $CH_3{\cdot}CH$ group. This may occur by oxidation of the $CH_3{\cdot}CH{:}CH$ fragment

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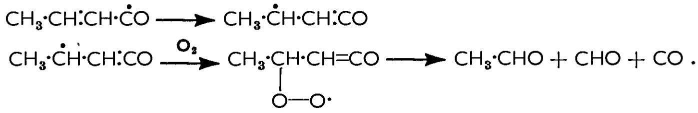
[18] Ferguson and Yokley, Seventh Symposium on Combustion, 1958, p. 113, London, Butterworths.

[19] Ausloos, *Canad. J. Chem.*, 1956, **34**, 1709.

[20] Skirrow and Tipper, Seventh Symposium on Combustion, 1958, p. 134, London, Butterworths.

produced on decomposition of peroxycrotonic acid, or it may follow from oxidation of the isomeric form of the crotonoyl radical according to



$$CH_3{\cdot}CH{:}CH{\cdot}\dot{C}O \longrightarrow CH_3{\cdot}\dot{C}H{\cdot}CH{:}CO$$

$$CH_3{\cdot}\dot{C}H{\cdot}CH{:}CO \xrightarrow{O_2} CH_3{\cdot}\underset{\substack{|\\ O-O\cdot}}{C}H{\cdot}CH{=}CO \longrightarrow CH_3{\cdot}CHO + CHO + CO \quad . \quad . \quad . \quad . \quad (12)$$

No decision can be made between these alternatives, but it is noteworthy that examination by paper chromatography showed five peroxides to be present. Two of these, peroxycrotonic acid and hydrogen peroxide, are explicable in terms of reactions (8) and (9) and direct oxygen attack on crotonaldehyde to give HO_2, while the remainder whose identity is unknown may include aldehyde–peroxide condensation products or hydroperoxides such as that formed from the isomeric crotonoyl radical and by direct attack on the olefinic link of the crotonaldehyde.

Change of the Carbon Monoxide : Carbon Dioxide Ratio with Conditions.—Skirrow and Tipper [20] have recently reviewed the processes leading to the formation of the oxides of carbon from a larger number of oxygen–fuel systems. They concluded that with saturated hydrocarbons and aldehydes the most important processes are R·CO radical decomposition for formation of carbon monoxide, and per-acid decomposition for formation of carbon dioxide. On this basis one would expect the carbon monoxide : carbon dioxide ratio to increase with increasing temperature which favours radical decomposition, and to decrease with increasing oxygen : fuel ratio. The data of Table 3 show this to be the case, although it is noteworthy that insofar as it is possible to make comparisons the change with temperature is much less than that observed in similar saturated aldehyde–oxygen systems. Thus, whereas with crotonaldehyde the ratio changed by a factor of 3 for a temperature increase from 166° to 347°, an approximately ten-fold increase for a similar temperature increase (240° to 360°) has been reported for acetaldehyde and propionaldehyde.[16] This provides support for the view that, although processes such as (2), (8), (9), and (10) are important in the oxidation of both saturated and unsaturated aldehydes, the latter oxidise in a more complex way, and processes such as (7), (11), or (12) contribute.

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