1000. *The Formation and Consumption of Acetaldehyde and Formaldehyde in the Oxidation of Cyclopentane.*

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The total amounts of acetaldehyde and formaldehyde formed in the oxidation of cyclopentane have been measured by a radioactive-tracer technique. Thence the amount of paraffin consumed by way of these intermediates in both a high- and a low-temperature reaction has been calculated. The results are compatible with current oxidation theories. Whatever their importance in chain-branching reactions, neither formaldehyde nor acetaldehyde provides a principal reaction path for the oxidation of cyclopentane to its major products.

OXIDATION of hydrocarbons is a very complex process and, although much work has been done on elucidating the kinetics of the various chain-branching processes involved, less has been published on the routes by which the principal products may be formed.

Carbon monoxide, carbon dioxide, and water can account for some 90% of the products from a gas-phase hydrocarbon oxidation. It is of interest whether this large fraction of the products is formed directly from the parent hydrocarbon by fast radical reactions or indirectly by further oxidation of reactive intermediates such as peroxides or aldehydes. These reactive materials have long been prominent as candidates for the role of branching intermediates in the type of kinetic scheme first put forward by Semenov.[1] Although the measured pressure of aldehydes and peroxides may only amount to some 5% of the total products, it is possible that, if they were formed and consumed rapidly, they might be responsible for a large proportion of the products even though never present themselves in more than a small concentration in the reaction vessel. An analogy may be drawn with a radioactive decay series. When the decay of a parent takes place wholly through a daughter of short half-life, then the daughter is present only in low concentration in the equilibrium mixture.

There are various suggestions in the literature on the source of water, carbon monoxide, and carbon dioxide formed on oxidation of hydrocarbons. McGowan and Tipper [2] suggested

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[1] Semenov, " Chemical Kinetics and Chain Reactions," Oxford Univ. Press, 1935.

[2] McGowan and Tipper, *Proc. Roy. Soc.*, 1958, *A*, **246**, 64.

that the production of carbon dioxide from cyclopentane occurs largely through the direct decomposition of a cyclic $RO_2\cdot$ radical, and that water is produced by hydroxyl radicals that abstract hydrogen from the parent hydrocarbon. Bailey and Norrish [3] suggested that in the oxidation of hexane, aldehydes from C_6 to C_1 are formed in order:

$$C_6H_{14} \longrightarrow C_5H_{11}\cdot CHO \longrightarrow C_4H_9\cdot CHO \longrightarrow C_3H_7\cdot CHO \longrightarrow$$
$$C_2H_5\cdot CHO \longrightarrow CH_3\cdot CHO \longrightarrow H\cdot CHO$$

Several of Semenov's [4] oxidation schemes imply that large amounts of carbon monoxide and carbon dioxide are derived by oxidation of aldehydes.

In the present paper, an attempt is made to elucidate some of these points in the oxidation of cyclopentane. A tracer technique due to Neiman [5] is used to find the total amount of acetaldehyde and formaldehyde produced in the oxidation of cyclopentane, in both the low- and the high-temperature region of reaction.

EXPERIMENTAL

A conventional manometric apparatus was used. It consisted essentially of a 307-ml. Pyrex reaction vessel maintained at a constant temperature and fitted with a manometer, evacuation system, and storage globes. Cyclopentane and oxygen were admitted separately, and the course of the reaction was followed by the pressure change (Δp) measured on a mercury manometer. The validity of this procedure had been previously established.[6]

Materials.—Cyclopentane of 99% purity was obtained from Sherman Chemicals Ltd., and oxygen from the British Oxygen Company. Acetaldehyde and formaldehyde labelled with carbon-14 were prepared from labelled ethyl alcohol and labelled paraformaldehyde, obtained from the Radiochemical Centre, Amersham.

[2-^{14}C]Acetaldehyde was prepared by the oxidation of labelled ethyl alcohol over a copper chromium oxide catalyst prepared by the method of Connor *et al.*[7] The alcohol vapour was passed over the catalyst at 140° and the resulting acetaldehyde separated from hydrogen, water, and ethylene by gas chromatography. A column packing of dinonyl phthalate on Celite was used at 50°, nitrogen was the carrier gas, and the thermal conducivity detector was kept at 50°. To avoid problems associated with storage of acetaldehyde, only small amounts (about 0·5 ml. of vapour) were prepared at any one time and these were used in the course of a few hours. Acetaldehyde was admitted to the reaction vessel before the other reactants, its pressure being measured on a silicone oil U-tube manometer. The activity of the acetaldehyde used was about 0·5 μc ml.$^{-1}$.

Labelled formaldehyde was prepared by gentle heating of labelled paraformaldehyde. It was mixed with the oxygen before admission to the reaction vessel.

Analysis.—Formaldehyde was determined spectrophotometrically by the chromotropic acid method.[8] Acetaldehyde and cyclopentane were determined gas chromatographically as above but with the detector at 80°. In all cases, samples were taken at Δp (and not Δt) intervals, so as to avoid inaccuracies due to variable induction periods. Δp- were converted into Δt- values by use of standard Δp–time curves.

Radioactive assay of formaldehyde and acetaldehyde was carried out with a gas-phase counter operating in the Geiger region with conventional electronic equipment. A filling of 12% of toluene in hydrogen to a total pressure of 15 cm. was used. The hydrogen was stored on pyrophoric uranium, from which it was released by heating.

Formaldehyde was extracted from an aqueous solution of the products by precipitation as the dimedone derivative; the acetaldehyde derivative was also precipitated but was shown to contain no activity in experiments where active formaldehyde was added. The dimedone derivative was filtered off and washed with water before being dissolved in 1 : 19 chloroform–ethyl alcohol. Weighed portions of this solution were evaporated to dryness and then burnt in a stream

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[3] Bailey and Norrish, *Proc. Roy. Soc.*, 1952, *A*, **212**, 311.

[4] Semenov, " Some Problems of Chemical Kinetics and Reactivity," Pergamon Press, 1958, Vol. I.

[5] Neiman, *Zhur. fiz. Khim.*, 1954, **28**, 1235; *Internat. J. Appl. Radiation Isotopes*, 1958, **3**, 20.

[6] Horscroft and Hinshelwood, *J.*, 1960, 3098.

[7] Connor, Folkers, and Adkins, *J. Amer. Chem. Soc.*, 1932, **54**, 1138; Adkins, Kommes, Struss, and Dasler, *ibid.*, 1933, **55**, 2992.

[8] Bricker and Johnson, *Ind. Eng. Chem. Analyt.*, 1945, **17**, 400.

of oxygen. The resulting carbon dioxide was collected, transferred to the counter, and assayed. Up to 3 cm. Hg pressure of carbon dioxide could be added to the toluene–hydrogen filling without serious effect on the counter plateau or characteristics.

Acetaldehyde, after being separated from the other products by gas chromatography, was added to the counter filling. It tended to shorten the counter plateau by raising the starting voltage, but up to 1·5 cm. Hg pressure could be added without trouble.

Full details of the tracer technique for kinetic investigations have been given by Neiman,[5] but a short account of it, as applied to this work, is as follows:

Let w_1 and w_2 be the rates of formation and consumption of some intermediate A; then the rate of accumulation of A, as measured by conventional analysis, at any time t in the reaction is given by:

$$\mathrm{d}[\mathrm{A}]/\mathrm{d}t = w_1 - w_2 \qquad (1)$$

To obtain the second equation needed to evaluate w_1 and w_2 separately a small amount of compound A labelled with a mass or radioactive isotope is added to the system, and the specific activity, α, is measured during the course of the reaction. Any isotope effect is neglected and the rate of change of specific activity will depend upon α, w_1, and [A], but not upon w_2. Thus $\mathrm{d}\alpha/\mathrm{d}t = \mathrm{f}(w_1, [\mathrm{A}], \alpha)$. From dimensional analysis it follows that

$$\mathrm{d}\alpha/\mathrm{d}t = k\alpha w_1/[\mathrm{A}] \qquad (2)$$

where k is a dimensionless factor, shown by Neiman[5] to be -1. From equation (2) we find the total amount of A formed, no account being taken of its subsequent removal, since it follows that

$$w_1 \,.\, \mathrm{d}t = -[\mathrm{A}]\,\mathrm{d}(\ln \alpha)$$

so that the total amount of A formed is

$$[\mathrm{A}]_{\mathrm{tot}} = \int_0^t w_1 \,.\, \mathrm{d}t = \int_\alpha^{\alpha 0} [\mathrm{A}] \,.\, \mathrm{d}(\ln \alpha)$$

A curve of $[\mathrm{A}] = \mathrm{f}(\ln \alpha)$ is constructed, and $[\mathrm{A}]_{\mathrm{tot}}$ found by graphical integration.

The rate of formation may be found by graphical differentiation of the curve $[\mathrm{A}]_{\mathrm{tot}} = \mathrm{f}(t)$. The difference between the rates of formation and accumulation [the latter is found by graphical differentiation of the curve $[\mathrm{A}] = \mathrm{f}(t)$] gives the rate of consumption, as in equation (1).

RESULTS AND DISCUSSION

Two reaction mixtures were studied, each at two temperatures. Cyclopentane shows the usual anomalous type of Arrhenius plot common in hydrocarbon oxidations. Temperatures of 250° and 400° were chosen as representative of the low- and the high-temperature region.[9] Reaction mixtures containing (i) 50 and (ii) 100 mm. of cyclopentane with 100 mm. of oxygen were used. In the low-temperature region a trace of di-t-butyl peroxide was added to eliminate most of the induction period; it was established that this procedure had no effect upon the maximum rate of reaction.[10]

The details of a determination for formaldehyde with 50 mm. of cyclopentane and 100 mm. of oxygen at 400° are now given. The amount of formaldehyde vapour added was 0·04 ml. premixed with the oxygen. The results of the analysis for formaldehyde concentration and specific activity are shown in Fig. 1. Then as we have seen above, the total amount of formaldehyde formed, not accounting for its further oxidation, is $[\mathrm{A}]_{\mathrm{tot}} = \int_\alpha^{\alpha 0} [\mathrm{A}]\mathrm{d}(\ln \alpha)$, where α is the specific activity of the formaldehyde, and [A] is the formaldehyde concentration. A curve is drawn of $[\mathrm{A}] = \mathrm{f}(\ln \alpha)$, and $[\mathrm{A}]_{\mathrm{tot}}$ is found by graphical integration. The result is shown in Fig. 2. The graphical differentiation of this curve, $[\mathrm{A}] = \mathrm{f}(t)$, gives the rate of formation of formaldehyde. The difference between this and

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[9] Horscroft, *J.*, 1960, 3102.

[10] Seakins, *Proc. Roy. Soc.*, 1961, *A*, **261**, 281; Horscroft, Thesis, Oxford, 1959.

the rate of accumulation (found by graphical differentiation of curve A in Fig. 1) gives the rate of consumption. These rates are plotted in Fig. 3.

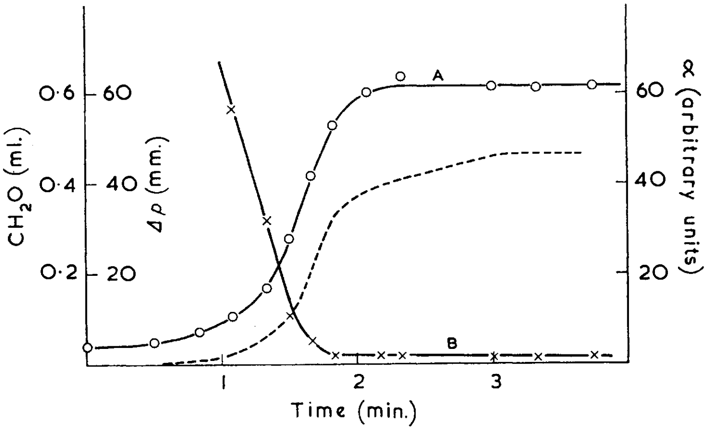

FIG. 1. Variation in formaldehyde concentration (A) and specific activity (B) during the oxidation of cyclopentane (50 mm.) in oxygen (100 mm.) at 400°. Broken line refers to Δp.

This procedure was followed for the six sets of figures, for both acetaldehyde and formaldehyde, set out in the Table. The last line, giving the percentage of cyclopentane which is oxidised through the intermedate stated, shows that, whatever their importance in chain-branching reactions, neither formaldehyde nor acetaldehyde provides a principal path for the oxidation of cyclopentane in either temperature region. The most that they can account for is 16% of the cyclopentane at low temperature and slow reaction.

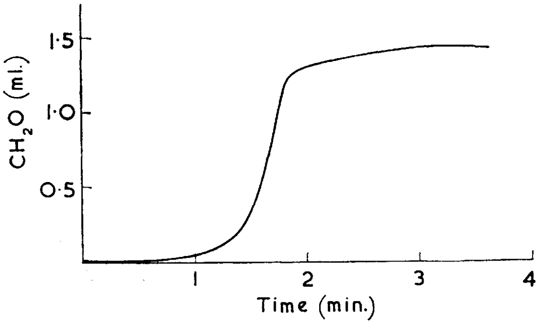

FIG. 2. Formation of formaldehyde during oxidation of cyclopentane (50 mm.) in oxygen (100 mm.) at 400°, no account being taken of its consumption.

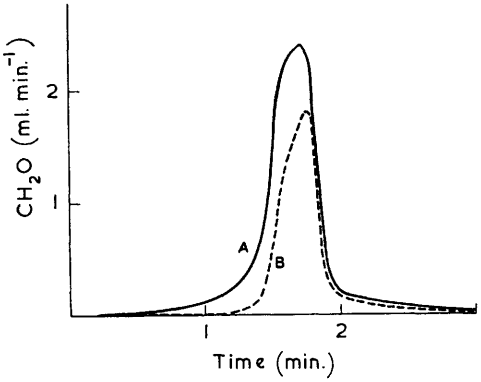

FIG. 3. Rates of formation (A) and consumption (B) of formaldehyde during the oxidation of cyclopentane (50 mm.) in oxygen (100 mm.) at 400°.

As might be expected, the fastest formation and consumption of formaldehyde and acetaldehyde follow the fastest pressure change in the reaction.

Less formaldehyde and acetaldehyde are formed at high than at low temperature, despite the faster reaction, probably because the high-temperature reaction proceeds more through primitive radical reactions than through the more complex labile intermediates formed at lower temperatures.

Intermediate formation and consumption in cyclopentane oxidation.

Intermediate	Formaldehyde			Acetaldehyde		
Temperature	400°	250°	250°	400°	250°	250°
Cyclopentane (mm. Hg)	50	50	200	50	50	200
Oxygen (mm. Hg.)	100	100	100	100	100	100
$\Delta p/\Delta t$ (mm. min.$^{-1}$)	40	5	9	40	5	9
Obs. concn. of intermediate (ml.)	0·62	1·18	1·70	0·20	0·70	0·77
Total intermediate formed (ml.)	1·15	2·90	2·50	0·30	1·45	1·68
Intermediate consumed (ml.)	0·53	1·72	0·80	0·10	0·75	0·91
Maximum rate of intermediate formation (ml. min.$^{-1}$)	2·4	0·6	1·15	0·30	0·19	0·38
Maximum rate of intermediate consumption (ml. min.$^{-1}$)	1·9	0·41	0·40	0·23	0·15	0·32
Cyclopentane consumed (ml.)	5·9	7·4	10·5	5·9	7·4	10·5
Cyclopentane consumed through intermediate	4%	8%	5%	2%	8%	6%

In the low-temperature region it is possible to compare the formaldehyde and acetaldehyde concentrations at two reaction rates given by the different mixtures. The Table shows that a little less cyclopentane is oxidised by way of these aldehydes at the higher rate. Although more formaldehyde is observed at the higher reaction rate by conventional analysis, the tracer technique shows that less is formed and that less is consumed. Acetaldehyde, on the other hand, is formed and consumed in larger quantities in the faster reaction. It thus appears that in the low-temperature mechanism formaldehyde plays little or no part in the chain-branching processes. While acetaldehyde probably does play some part in the chain-branching responsible for the observed pressure rise in the reaction, the increase in the total amount of acetaldehyde formed in the reaction at low temperature with increase in rate is not large, and it seems improbable that acetaldehyde is the principal intermediate responsible for the slow chain-branching characteristic of paraffin oxidation.

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