619. *Influence of Structure on the Rate of Oxidation of Gaseous Cycloalkanes.*

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As in the paraffin series the rate of oxidation of gaseous cycloalkanes, in the region where the low temperature mechanism operates, increases rapidly with the number of carbon atoms in the molecule, and, for a given total number of carbon atoms, is markedly reduced by methyl-substitution.

The rate of oxidation in the gas phase of open-chain paraffins is known to depend in a most marked manner on the structure.[1] There has been less work on the slow combustion of cycloalkanes, though cyclopropane and cyclopentane have been studied in some detail by Tipper and others.[2] The oxidation of a series of cycloalkanes and methyl cycloalkanes, with special reference to structural effects, has therefore been investigated. Since the open-chain paraffins were compared in the so-called low-temperature region, the present work has been concerned with temperatures as near as possible to those used in the earlier comparisons.

Experimental

A conventional manometric apparatus was employed, the silica reaction vessel being 10 cm. long and 6 cm. in diameter. The criterion of ease of oxidation was the maximum rate of pressure increase, the validity of this having been established by mass-spectrometric analysis which showed that pressure changes were proportional to the consumption of the primary reactants.[3]

Commercial oxygen was passed through a liquid-air trap and drying-tube before use. 1,4-Dimethylcyclohexane and 1,3,5-trimethylcyclohexane were prepared by hydrogenation of *p*-xylene and mesitylene respectively, and cycloheptane by reduction of cycloheptanone. Cyclo-octane was prepared by hydrogenation of cyclo-octatetraene, its purity being established by its mass spectrum, b. p., f. p., and refractive index.

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[1] Cullis and Hinshelwood, *Discuss. Faraday Soc.*, 1947, **2**, 117.

[2] McEwan and Tipper, *Proc. Roy. Soc.*, 1953, *A*, **216**, 260, 266; Broatch, McEwan, and Tipper, *Trans. Faraday Soc.*, 1954, **50**, 576; McGowan and Tipper, *Proc. Roy. Soc.*, 1958, *A*, **246**, 52, 64.

[3] Cf. Parsons and Danby, *J.*, 1956, 1795.

KINETICS

Some preliminary experiments were made with n-pentane and with cyclopentane in order to ascertain the best methods of comparison for the remainder of the series. The kinetics were studied at 250° and the maximum rate ($\rho_{max.}$), taken from the pressure–time curve of each experiment, was used as the principal reaction parameter. The induction period (θ) was taken as the time between the admission of reactants and the attainment of a small arbitrary pressure increase (2·5 mm.). After this point the reaction rate rose rapidly to the maximum.

When the induction periods were inconveniently long, 0·4% of di-t-butyl peroxide was added with the oxygen. It abolished the induction period while leaving the maximum rate unchanged.

FIG. 1.

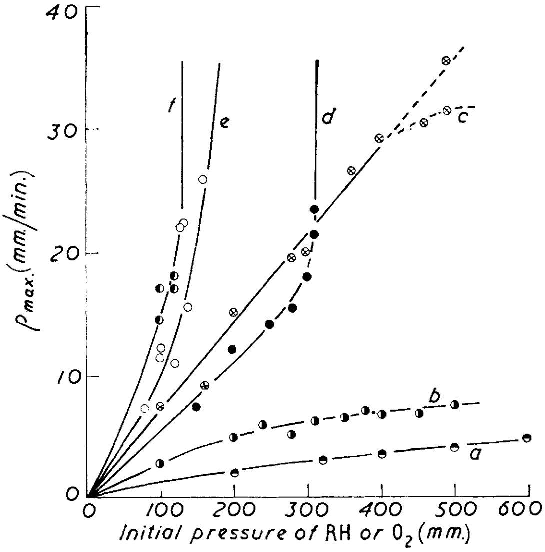

FIG. 2.

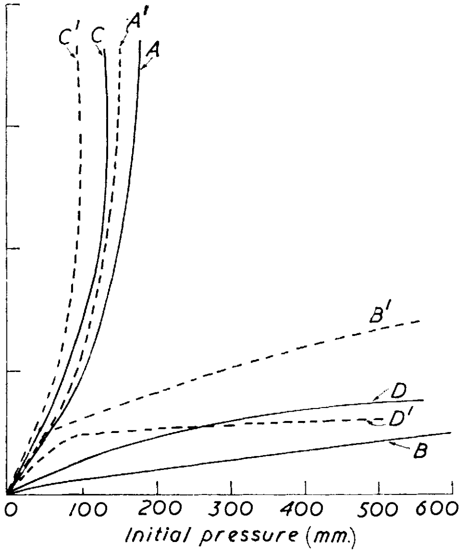

FIG. 1. *Oxidation of cyclopentane at* 250°.

	a	*b*	*c*	*d*	*e*	*f*
[RH] (mm.)	40	var.	var.	100	200	var.
$[O_2]$ (mm.)	var.	60	110	var.	var.	200

var. = variable.

FIG. 2. *Rate–pressure relations for cyclopentane.*

Full lines = experimental; broken lines = calculated from equation (1) *with* a = 132·9, b = 43·6, *and* c = 3·536.

	A,A'	*B,B'*	*C,C'*	*D,D'*
[RH] (mm.)	200	40	var.	var.
$[O_2]$ (mm.)	var.	var.	200	60

Four-fold and six-fold increases in the surface : volume ratio of the reaction vessel lengthened the induction period a little and slightly decreased the rate: higher pressures could be used without explosion, and sometimes with increasing reactant pressure the region of explosion was replaced by one of limiting rate.

The variation of $\rho_{max.}$ with reactant pressure is rather complex. The relations found for cyclopentane are shown in Figs. 1 and 2 and are expressed in a semiquantitative manner by the formula:

$$\rho_{max.} = \frac{c}{1 - \dfrac{[RH][O_2]}{a[RH] + b[O_2]}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where *a*, *b*, and *c* are constants, and [RH] and $[O_2]$ are the initial pressures of hydrocarbon and oxygen respectively.

This expression differs from that derived by Cullis and Hinshelwood for n-pentane, namely:

$$\rho_{\text{max.}} = \frac{c[\text{RH}][\text{O}_2]}{1 - \dfrac{a[\text{RH}]}{[\text{O}_2] + b[\text{RH}]}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

Experiments with the present apparatus and conditions showed, however, that n-pentane itself now gave results conforming better to eqn. (1) than to eqn. (2).

As exemplified in Fig. 2 the detailed fit is not very good, but the single expression (1) is useful in so far as it summarises the general form of a quite complex behaviour, in which there can, according to the pressure of one reactant, be two shapes of curve to represent the variation of rate with the pressure of the other.

The reason for the difference between the present results and those of Cullis and Hinshelwood must now be considered. In complex, branching, chain systems of this kind numerous factors are involved. On the one hand, self-heating may occur at high rates and distort the form of the curves. On the other hand, at the point of maximum rate there may have been enough depletion of reactant to lower the rate below the expected value. The one factor can cause the rate to rise rapidly to explosion when the pressure exceeds a critical value: the other may give an actual limiting rate to which no fundamental kinetic significance can be attached. If, with the vessels used in the present experiments, the limiting rate found in certain circumstances as [RH] increases is attributed to reactant consumption, and if the explosion limit found as $[O_2]$ increases at high values of [RH] is attributed to non-isothermal conditions, then the expression (2) could still be the expression of the true kinetics, and (1) would assume the character of a purely empirical expression.

For the present purpose it is not necessary to decide this problem, since expression (1) is to be used simply to provide the correct criteria for the comparison of the various hydrocarbons. In this connexion it is important to note that the relationships between pressure and maximum rate for 1,1,3-trimethylcyclopentane and for cycloheptane were found to resemble closely those for cyclopentane.

VARIATION OF RATE WITH STRUCTURE

The procedure for comparison was as follows. When the initial oxygen pressure was 100 mm., the curves giving $\rho_{\text{max.}}$ as a function of [RH] were nearly linear, except for cycloheptane. The relative rates of oxidation were therefore taken from the ratios of the slopes of these lines. With cyclopropane a temperature extrapolation had to be made, and with cycloheptane there was no suitable linear portion to the rate–pressure curve, so that a different method was used. The limiting pressures at which the cycloalkanes tended to explode with 110 mm. oxygen were found to be approximately in the inverse ratio of the relative reaction rates as determined above. This relation, illustrated in Table 1, was considered close enough to allow the place of cycloheptane in the rate series to be inferred from the limiting pressure. Cyclo-octane is anomalous in its rate of oxidation. The experimental reproducibility was, however, not good, so that only a rough value for the relative rate can be given.

The collected results are shown in Table 2, from which it can be seen that structure has much the same effect in the cycloalkane series as in the open-chain series, and in particular that methyl-substitution lowers the rate in an analogous way. The logarithm of the maximum rate plotted against the number of carbon atoms in the molecule yields a smooth curve for the unsubstituted compounds similar to that found for the n-paraffins [1,3]

TABLE 1. *Rates of oxidation and limiting pressures for cycloalkanes;* 250°; *silica vessel.*

Compound	Slope	Relative slope (cyclohexane = 1)	Limiting pressure p (mm.)	Relative values of $1/p_c$ (cyclohexane = 1)
Cyclopentane	2·4	0·4	550	0·3
Methylcyclopentane	2·9	0·5	250	0·6
1,1,3-Trimethylcyclopentane	4·8	0·8	190	0·8
Cyclohexane	6·1	1·0	160	1·0
Methylcyclohexane	11·0	1·8	73	2·2
1,4-Dimethylcyclohexane	15·0	2·5	54	3·0
1,3,5-Trimethylcyclohexane	15·0	2·5	50	3·2
Cycloheptane	—	—	17	9·4

TABLE 2. *Rate and structure at* 250° *for cycloalkane series: relative rates (cyclohexane* = 1).

Cyclopropane	0·02	Methylcyclopentane	0·5
Cyclopentane	0·4	1,1,3-Trimethylcyclopentene	0·8
Cyclohexane	1·0	Methylcyclohexane	1·8
Cycloheptane	9·4	1,4-Dimethylcyclohexane	2·5
Cyclo-octane	0·6—0·8	1,3,5-Trimethylcyclohexane	2·5

(Fig. 3). The stabilising influence of the methyl group is also similar to that observed with the open-chain compounds.

The rate for cyclo-octane is lower than expected. Great care was taken to establish the authenticity of the material, and the result, if correct, may well be connected with an effect arising from the buckling of the ring. This will increase with ring size from cyclopentane and may reach a degree with cyclo-octane where the molecule, as a result of folding, resembles a substituted compound with a smaller ring.

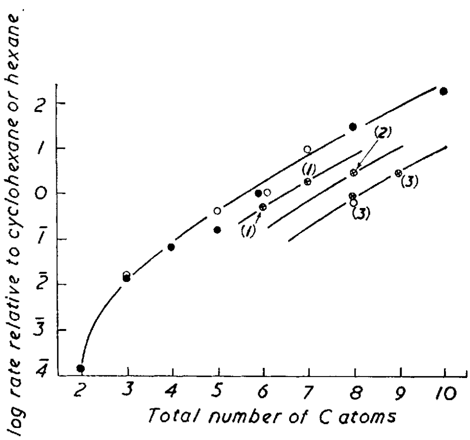

FIG. 3. *Rate and structure.*
● *n-Paraffins.* ○ *Cycloalkanes.* ⊗ *Substituted cycloalkanes. (Figures in parentheses indicate number of methyl groups).*

Apart from this anomalous example the addition of each successive methyl group causes the rate to fall by an approximately equal amount. Thus the effect is roughly additive. If r is the rate of oxidation of a cycloparaffin, r' that of one with x methyl groups and the same total number of carbon atoms, then, approximately, $\log r' = \log r - 0{\cdot}5x$.

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