141. *The Syntheses and Reactions of Branched-chain Hydrocarbons. Part XIII.* The Course of the Oxidation of Saturated Hydrocarbons by Chromium*(VI) *Oxide.*

By G. Foster and W. J. Hickinbottom.

The rate of reduction of chromic(VI) oxide by a number of saturated hydrocarbons in acetic acid has been measured. The results permit an approximate assessment of the relative sensitivity of $\geqslant CH$, $> CH_2$, and $-CH_3$ groups towards oxidation. The methyl group is attacked about 10^3 times slower than $\geqslant CH$. Yet in paraffins having a methyl group adjacent to a tertiary carbon atom, it is the methyl group which is oxidised preferentially. This apparent paradox is discussed in relation to other observations and an explanation is offered.

It is now established[1] that oxidation of an isoalkane by chromic acid in acetic acid containing mineral acid proceeds through a tertiary alcohol which is dehydrated to an olefin by the mineral acid. Oxidation at the double bond then provides the final products.

When saturated hydrocarbons are oxidised under conditions which preclude the intermediate formation of alcohols,[1,2] there is evidence of dehydrogenation, and an unexpected feature is that a methyl group attached to a tertiary carbon atom is oxidised to carboxyl instead of there being the expected oxidative fission at the tertiary carbon atom. We have now studied the relative sensitivities of $\geqslant CH$, $> CH_2$, and $-CH_3$ towards oxidation by chromium(VI) oxide. No great accuracy is claimed for the resulting assessment, for it depends on the assumptions that the rate of reaction is determined by that of the most reactive centre, that oxidation at other points makes a relatively small contribution, and that the initial products are not sensibly more reactive than the hydrocarbons from which they are derived. These assumptions are based on qualitative examination of the products of a number of hydrocarbons. By using an excess of hydrocarbon in each of these measurements and considering the initial rate of disappearance of oxidant it has been possible to minimise the effect of any secondary reactions.

EXPERIMENTAL

Preparation and Purification of the Hydrocarbons.—As it was essential that the hydrocarbons should not contain oxidisable impurities, liquid hydrocarbons were purified by fractionation, followed by distillation from sodium and passage through activated silica. Before use, they were distilled from sodium to remove any peroxides. For aromatic hydrocarbons passage through silica was omitted. Materials used were:

n-Heptane, b. p. 98°, n_D^{20} 1·3878.

n-Octane, b. p. 126·5°, n_D^{20} 1·3976.

n-Dodecane, first crystallised from ether at —60°, b. p. 216°, n_D^{20} 1·4200.

n-Octadecane, crystallised from acetone and distilled from sodium; m. p. 18—18·5°, b. p. 280°.

2,2,4-Trimethylpentane, b. p. 99°, n_D^{20} 1·3920.

Cyclohexane, frozen and drained several times before the usual treatment, b. p. 81°, n_D^{20} 1·4262.

Methylcyclohexane, b. p. 100°, n_D^{20} 1·4225.

Isocamphane, prepared by the hydrogenation of camphene (platinum oxide in ether at 4 atm.) and crystallised from methyl alcohol; m. p. 63—64°, b. p. 164—164·5°.

t-Butylbenzene, prepared from t-butyl chloride, benzene, and ferric chloride, was purified by repeated treatment with 90% sulphuric acid followed by distillation from sodium; it had b. p. 167—168°, n_D^{20} 1·4930.

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* Part XII, *J.*, 1960, 215.

[1] Sager and Bradley, *J. Amer. Chem. Soc.*, 1956, **78**, 1187; Sager, *ibid.*, p. 4970; Roček, *Chem. Listy*, 1957, **51**, 1838.

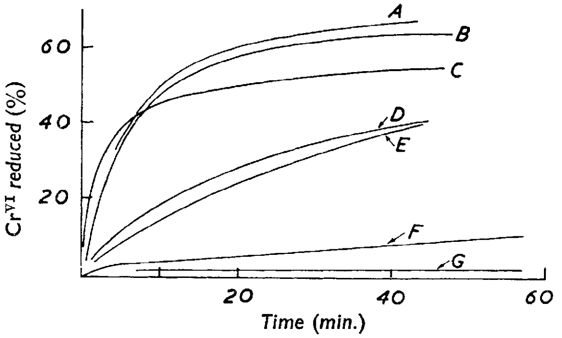
[2] Archer and Hickinbottom, *J.* 1954, 4197; Foster and Hickinbottom, *J.*, 1960, 215.

3,4-Dimethyl-3,4-diphenylhexane was prepared by the dimerisation of s-butylbenzene as described previously.[3] The hydrocarbon collected at 135—140°/0·5 mm. deposited a solid having m. p. 93—94° after three crystallisations from alcohol (Found: C, 90·2; H, 9·8%; *M*, 238, 245. Calc. for $C_{20}H_{26}$: C, 90·2; H, 9·8%; *M*, 266). The liquid portion of the distillate contained 3,4-dimethyl-3,4-diphenylhexane (Found: C, 90·2; H, 10·1%; *M*, 258).

Oxidations.—A solution of chromium(VI) oxide in a small amount of acetic anhydride was diluted with pure dry acetic acid to give a solution containing ~6—7 × 10^{-2} moles/litre. The concentration of this solution before and during an oxidation was determined by adding 2 c.c. samples to aqueous acid potassium iodide. The liberated iodine was titrated with thiosulphate.

It was established that <7% of acetic anhydride had little effect on the rate constants. Reduction of the oxide by the acetic acid–anhydride mixture is negligible if the oxidation of the hydrocarbon is rapid: for slow reductions a correction was applied.

Measurements were made on solutions at 25° ± 0·05° in long-necked flasks fitted with ground-glass stoppers and covered with tin foil.



Oxidation of (*A*) 2,2,4-*trimethylpentane*, (*B*) *methylcyclohexane*, (*C*) *iso-camphane*, (*D*) *cyclohexane*, (*E*) *n-heptane or n-octane*, (*F*) 2,2-*dimethylbutane*, (*G*) *neopentane*, *t-butylbenzene*, *or* 2,2,3,3-*tetramethyl-butane*.

The usual procedure was to add, to the oxidising solution, a known weight of the hydrocarbon (sufficient to give a ~0·7M-solution) in a sealed bulb. When the temperature of the system was judged to be that of the thermostat, the bulb was broken and the mixture shaken.

With hydrocarbons sparingly soluble in acetic acid, it was more satisfactory to mix previously prepared solutions of hydrocarbon and oxidising agent.

A typical oxidation is here recorded in detail, of n-octane (8·8 g.) in acetic anhydride (1·96 c.c.) and acetic acid (98·04 c.c.) containing 0·692 g. of chromic oxide.

Time (min.)	0	1	1·75	4·2	6·4	10·5	12·7	17·6	21·5	25·3	30·0	32·1	57·3	92·0	118
Cr^{VI} remaining (%)	100	98·8	98	94·2	90·8	84·1	77·2	75·7	71·5	68·2	64·7	63·2	57·4	46·9	45·2

The Figure shows some rates of reduction. The Table gives the initial rates of reduction.

Initial rates of reduction (10^{-5} mole $l.^{-1}$ $sec.^{-1}$).

Neopentane	2·9 × 10^{-3}	Methylcyclohexane	8·8
2,2,3,3-Tetramethylbutane	8·3 × 10^{-4}	2,2,4-Trimethylpentane	10·0
t-Butylbenzene	5·9 × 10^{-3}	Isocamphane	73·0
2,2-Dimethylbutane	2·9	3,4-Dimethyl-3,4-diphenylhexane	6·0
n-Heptane	1·4	s-Butylbenzene	Very fast
n-Octane	1·8	1,1,2,2-Tetraphenylethane	Very fast
n-Dodecane	8·0	Diphenylmethane	135
n-Octadecane	3·4		
Cyclohexane	5·5		

DISCUSSION

The results recorded show that chromic(VI) oxide is highly selective in its action on saturated hydrocarbons in an anhydrous solvent. As might be expected from other observations on aliphatic substitution,[4,5] the $\geqslant$CH group is the most sensitive and this

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[3] Ansell, Hickinbottom, and Holton, *J.*, 1955, 349.

[4] Hass *et al.*, *Ind. Eng. Chem.*, 1935, **27**, 1192; 1936, **28**, 333; 1937, **29**, 1337.

[5] Geisler and Asinger, *Chem. Ber.*, 1957, **90**, 1790.

sensitivity is further increased by an adjacent phenyl group. A striking feature is the indifference of $^-CH_3$ oxidation compared with that of $>CH_2$ or $\geqslant CH$, the approximate relative sensitivities being 1 : 10^2 : 10^3.

(I) RR′CHMe. (a) R,R′ = C_9H_{14}. b) R = R′ = CH_2Bu^t. (c) R = Me, R′ = CH_2Bu^t. (d) R = Me, R′ = Pr

Examples are isocamphane (Ia) (which gives isocamphenilanic acid), and (Ib–d). In such systems, we assume that the main attack is at the tertiary carbon atom and that an intermediate $\geqslant C{\cdot}O{\cdot}CrO_2H$ results. Although it has not yet been possible to isolate any such intermediate, there is sound experimental evidence that it is formed. Thus, the observation that methylcyclohexanol is formed when methylcyclohexane in acetic anhydride–acetic acid containing chromium(VI) oxide is diluted with a large volume of water is compatible only with the hydrolysis of such an intermediate.

For the subsequent fate of such a complex—even if we include the possibility of its oxidation to a mono-ester of chromic acid—there are two probable routes (a) and (b) for its breakdown. Of these, (a) fits the experimental facts better: it explains the close resemblance between the products of the oxidation of olefins and of the corresponding saturated

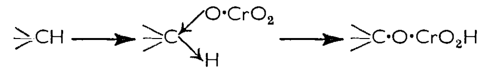
$$CrO(OH)_2 + R_2C{:}CH_2 \xleftarrow[a]{} R_2CMe{\cdot}O{\cdot}CrO_2H \xrightarrow[b]{} {}^+CMeR{\cdot}O{\cdot}CrO_2H + R^-$$

hydrocarbons. In one respect it may appear deficient: no epoxide has yet been isolated on the oxidation of a paraffin, but since the oxidation is associated with the formation of acids containing chromium, the formation of an epoxide is not to be expected, but rather the products derived from its reaction with a weak acid.

Oxidation at a methylene group may be expected to follow the same course, represented schematically as:

$$R_2CH{\cdot}O{\cdot}CrO_2H \longrightarrow {}^+CR_2{\cdot}O{\cdot}Cr(OH)_2 \longrightarrow R_2CO$$

The intermediate $\geqslant C{\cdot}O{\cdot}CrO_2H$ postulated as common to these oxidations can be assumed to arise (i) by abstraction of a hydride ion to give a carbonium ion capable of combining with CrO_3H, or (ii) by direct attack on the carbon by CrO_3 represented as:



$$\geqslant CH \longrightarrow \geqslant C\begin{matrix}\swarrow O{\cdot}CrO_2 \\ \searrow H\end{matrix} \longrightarrow \geqslant C{\cdot}O{\cdot}CrO_2H$$

The carbonium ion hypothesis (i) has the disadvantage that in the oxidation of isocamphane or of 2,3-dimethylbutane, a system would be set up favourable to rearrangement. No rearrangements have yet been observed in these oxidations, so it must be assumed that either the carbonium ion hypothesis is not valid or, if it is, the rearrangement of the carbonium ion is much slower than its combination with chromium(VI) oxide. The second hypothesis avoids this difficulty.

We also considered that oxidation might proceed by preliminary abstraction of a hydrogen atom to leave a free alkyl radical, as proposed by Slack and Waters [6] and by Wiberg.[7] This has the advantage that the similarity of products from the alkane and the related olefin can be explained if disproportionation of the free radical is assumed. Further, it avoids the disadvantages of the carbonium ion hypothesis and finds some support in the observations by Anson, Fredericks, and Tedder [8] on the free-radical halogenation of paraffins, where the ratio of tertiary to primary substitution is high—for bromination it is 1600 : 1, of the same order as that for oxidation by chromium(VI) oxide.

Against the free-radical hypothesis can be set that at no time do oxidations in acetic acid yield the products characteristic of free-radical reactions in acetic acid: and the

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[6] Slack and Waters, *J.*, 1948, 1666.

[7] Wiberg, personal communication.

[8] Anson, Fredericks, and Tedder, *J.*, 1959, 918.

advantages of the free-radical hypothesis are adequately covered by the alternative view of a bimolecular substitution.

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