Reactions of Ozone with Saturated Hydrocarbons. Ozone–Hydrocarbon Complexes

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Summary The initial step in the ozonization of a hydrocarbon is formation of a complex between the two reactants; products are formed on warming, or under the action of reducing agents or visible light.

Saturated hydrocarbons are oxidized slowly by ozone, forming alcohols and ketones with a high regio- and stereospecificity. Although some aspects of these oxidations have been discussed, their mechanism still remains unclear.[1]

We report on results of ozonizations which suggest an initial formation of a complex between ozone and the saturated hydrocarbons.

When desorbed ozone from cold silica gel was passed through methylcyclohexane† at −110 and at −80 °C, saturated solutions of *ca.* 0·1 and 0·3% by weight of ozone, respectively, were obtained.‡ After sweeping at the same temperature with argon, the methylcyclohexane was warmed to room temperature and analysed by g.l.c., both directly and after treatment with reducing agents such as $NaHSO_3$ or Ph_3P but no products were detected.

Different results were obtained when the same cold ozone solution was treated with an excess of finely powdered $NaHSO_3$ or Ph_3P at −110 or −80 °C; ozone was not detected either in the cold reaction mixture or by sweeping with argon at the same low temperature. Analysis of this mixture by g.l.c. at room temperature revealed the formation of methylcyclohexanols and methylcyclohexanones in yields indicating reaction of all the dissolved ozone. On the other hand, no products were detected by g.l.c. when the reducing agent was present in the methylcyclohexane during the introduction of ozone. Similar behaviour was observed also with other saturated hydrocarbons.

Furthermore, when the solution of ozone in methylcyclohexane was warmed to −60 °C and the excess of ozone then driven off by argon, the same oxidation products were formed in lower yields than those obtained after treatment with reducing agents. However, hydrocarbons lacking tertiary C atoms, such as pentane and cyclopentane, were already oxidized at −80 °C§ at which temperature hydrocarbons possessing tertiary C atoms such as methylcyclohexane, 2,3-dimethylbutane, and *cis*- and *trans*-decalins were unreactive.

The yields of the oxidation products were increased by letting the ozone solutions warm up to higher temperatures.

These results can be accommodated by assuming formation of a complex between the ozone and the saturated hydrocarbon at low temperatures, which reacts with the reducing agents to give the oxidation products. When the ozone is driven off at these low temperatures by a stream of argon, the saturated hydrocarbon is regenerated. At higher temperatures, however, the complex decomposes to the oxidation products.

$$\text{hydrocarbon} + O_3 \rightleftarrows (\text{hydrocarbon–}O_3) \rightarrow \text{alcohols and ketones}$$

The Table summarizes the distribution and the relative distribution per ring H atom of the positional hydroxy- and oxo-isomers in the ozonization products of methylcyclohexane and *cis*- and *trans*-decalin as well as retention of configuration (%) in the epimeric decalins.

The comparative selectivity in the formation of the tertiary alcohols is consistent with the preference of the electrophilic ozone to form complexes with tertiary C atoms, while the high degree of configurational retention is indicative of an insertion reaction, which may occur by a concerted decomposition of the complex. Furthermore the lower temperatures at which hydrocarbons lacking tertiary C

Table

Isomer distribution from ozonization of saturated hydrocarbons

Compound	Temperature (*t*/°C)	Distribution (%) of tertiary alcohols	Distribution (%) of secondary alcohols and ketones	Ratio of the relative distribution of tertiary *vs.* secondary alcohols and ketones per H	Retention of configuration (%) in decalins
Methylcyclohexane	−110	48	52	9	
	−85	49	51	10	
	−60	53	47	11	
	0	56	44	13	
cis-Decalin	−80	91	9	76	93
	0	96	4	190	91
trans-Decalin	−80	62·5	37·5	13	94
	−20	73	27	21	91

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† The hydrocarbons used were of spectral grade and were purified by conventional methods followed by passing through an $AgNO_3$–HNO_3 alumina column (E. C. Murray and R. N. Keller, *J. Org. Chem.*, 1969, **34**, 2234); analysis by g.l.c. indicated less than 0·01% impurities.

‡ Halogenated solvents like CCl_4 or $CFCl_3$ could not be used in these studies since they react with ozone at low temperature.

§ Below this temperature saturated solutions of ozone tend to detonate on slight shaking, which is in contrast with stability of ozone in hydrocarbons possessing tertiary C atoms.

atoms react with ozone points to higher reactivity of complexes with these hydrocarbons.

The increase of the regiospecificity and the decrease of the stereospecificity with rising temperature (Table) may be explained by an additional mechanism which becomes more significant as the temperature increases and which may involve ionic or free-radical intermediates.

The *ca.* ten-fold increase in the extinction coefficient of the ozone bands at *ca.* 605 nm (the symmetry forbidden $^1A_1 \rightarrow {}^1B_1$ transition) in methylcyclohexane solution (ϵ, 14), as compared with its value in the gas phase (ϵ, 1·32) is also suggestive of an ozone hydrocarbon complex.¶

This enhanced absorption was used for the decomposition of the complex. Thus visible light irradiation at −80 °C of a solution of ozone in methylcyclohexane gave the same mixture of alcohols and ketones as obtained in the thermal reaction as well as on reduction at low temperatures.

Our suggestion of complex formation between ozone and saturated hydrocarbons is in accord with the polar nature of ozone,[2] whose tendency to form complexes with aromatic compounds,[3] olefins,[4] and hydrosilanes[5] is well known.

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¶ A charge-transfer interaction was suggested to explain a similar enhancement in the O_3 band in CCl_4 (G. W. Robinson, *J. Chem. Phys.*, 1967, **46**, 572.)

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