Reactions of Ozone with Saturated Hydrocarbons. Photochemistry of Ozone–Hydrocarbon Complexes

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Summary Irradiation of solutions of O_3 in saturated hydrocarbons with visible light results in products derived from the rearrangement of O_3–hydrocarbon complexes, while irradiation with u.v. light leads to products derived from both the rearrangement of the complexes and the attack of $O(^1D)$ atoms on the hydrocarbon.

Ozone absorbs in the u.v. (λ_{max} 255 nm) and visible (λ_{max} 600 nm) spectral regions. In the primary step, the photolysis of O_3 at $\lambda < 302$ nm produces oxygen atoms in their excited state (^1D), while at $\lambda > 334$ nm, oxygen atoms in their ground state (^3P) are formed.[1] Irradiation of O_3 and saturated hydrocarbons with u.v. light in the gas phase, or in dilute argon solutions, leads to a reaction between excited $O(^1D)$ atoms and the hydrocarbons while irradiation with visible light proves ineffective.[2]

We have found a different photochemical reaction of O_3 in saturated hydrocarbon solutions,[3] indicating the occurrence of different primary processes in the gas phase and the fluid phase.

Saturated solutions of ozone in methylcyclohexane† (containing *ca.* 0·1% by weight of ozone) were irradiated in the two absorption regions of ozone with visible and u.v. light in the absence of oxygen, at −78 °C. At this temperature no thermal reactions are observed, the ozone solutions being stable for prolonged periods. Irradiation with visible light (tungsten–iodine lamp and GWC filter) resulted in a mixture consisting of tertiary and secondary methylcyclo-

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† The hydrocarbons used were purified by conventional methods followed by passing through an $AgNO_3$–HNO_3–alumina column. Their purity, as determined by g.l.c., was > 99·99%.

Table

Product distribution from irradiation of O_3 and N_2O in saturated hydrocarbons.

Compound	Irradiation in the presence of	Product distribution (%)			Product distribution per C–H bonds			Retention of configuration (%)
		prim. alcohols and aldehydes	sec. alcohols and ketones	tert. alcohols	prim.	sec.	tert.	
Methylcyclohexane	O_3 (visible)	—	54·0	46·0		1·0	8·6	
	N_2O (185 nm)	19·2	71·7	9·1	1·0	1·1	1·4	
	O_3 (254 nm)	7·2	65·4	27·4	1·0	2·7(1·0)	11·4(4·2)	
2,3-Dimethylbutane	O_3 (254 nm)	43·0		57·0	1·0		8·1	
	N_2O(185 nm)	84·9		15·1	1·0		1·1	
cis-Decalin	O_3 (visible)		13·3	86·7		1·0	52·5	93·4
	N_2O (185 nm)		67·1	32·9		1·0	3·9	64·0
	O_3 (254 nm)		47·4	52·6		1·0	8·9	72·3
trans-Decalin	O_3 (visible)		18·5	81·5		1·0	35·3	96·0
	N_2O (185 nm)		85·2	14·8		1·0	1·4	92·0
	O_3 (254 nm)		60·7	39·3		1·0	5·2	96·5

hexanols and in the three isomeric methylcyclohexanones. The product distribution ratio indicated high regioselectivity for substitution of the tertiary C-atom. On irradiation with u.v. light (254 nm, low-pressure Hg lamp, Corex filter) the same alcohols and ketones were obtained but in different proportions with more of the secondary products as well as cyclohexylmethanol and cyclohexanecarbaldehyde.

These product distributions differ considerably from that formed on irradiation of solutions of N_2O in methylcyclohexane with 185 nm light.[4] In the latter case the near statistical ratio of primary : secondary : tertiary alcohols was taken as evidence for the indiscriminate attack of the excited $O(^1D)$ atoms on the C–H bonds, while the small excess of the secondary and tertiary products was ascribed to the concurrent reactions of $O(^3P)$ atoms present in small amounts in the solution.

A similar striking preference of attack at the more substituted C-atoms on irradiation of O_3 at 254 nm is evident from comparison of the relative amounts of the tertiary alcohols formed from 2,3-dimethylbutane with that obtained on the photolysis of N_2O solution in the same hydrocarbon. Since in the latter reaction the $O(^1D)$ atoms are responsible for the statistical distribution of products, it may be concluded that these $O(^1D)$ atoms cannot be the major reactants in the ozone irradiation at 254 nm.

We have also compared the results of all three photochemical reactions of *cis*- and *trans*-decalins in dilute pentane solutions (with O_3, visible; O_3, 254 nm; and N_2O, 185 nm light). It can be seen from the Table that for the irradiation of O_3 solution with 254 nm light, the values of the relative distribution of tertiary alcohols compared to secondary alcohols and ketones, and the percentage of the configurational retention at C-9 in the decalols are intermediate between the corresponding values of the other two photoreactions.

$$RH + O_3 \rightleftharpoons [RH{\cdot}O_3] \qquad (1)$$

$$[RH{\cdot}O_3] + h\nu \text{ (visible or 254 nm)} \rightarrow ROH + O_2 \qquad (2)$$

$$O_3 + h\nu(254 \text{ nm}) \rightarrow O(^1D) + O_2 \qquad (3)$$

$$O(^1D) + RH \rightarrow ROH \qquad (4)$$

We have previously suggested[3] that O_3 associates with saturated hydrocarbons in solution, preferentially with their tertiary C–H bonds (equation 1). These O_3-hydrocarbon complexes have charge-transfer character, as shown by spectral data.‡ Irradiation of solutions of O_3 in hydrocarbons with visible light leads to a rearrangement of these complexes, resulting in regioselective and stereoselective insertion of oxygen into the C–H bonds (equation 2). On irradiation with u.v. light these complexes react in the same manner (equation 2).§ However, u.v. irradiation of the nonassociated O_3 molecules producing excited $O(^1D)$ atoms (equation 3) which react indiscriminately with all the C–H bonds of the hydrocarbon (equation 4) may compete with the photolysis of the complex. Thus irradiation of O_3 solutions with u.v. light results in products derived from both the rearrangement of the complex, and from the attack of $O(^1D)$ atoms on the hydrocarbons.

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‡ Ozone solutions in methylcyclohexane show both enhancement of the symmetry-forbidden transition at λ 605 nm[3] when compared with the value in the gas phase and a red shift of the allowed transition (λ 262 nm) when compared with the value in pentane (λ 259 nm) and in the gas phase (λ 255·3 nm).

§ The molecular oxygen obtained upon u.v. irradiation (equation 2) is probably in its singlet state while that obtained by visible light irradiation is in its triplet state.

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