Reaction of Oxygen Atoms with Saturated Hydrocarbons in the Liquid State

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Summary Photolysis of N_2O in saturated hydrocarbon solution results mainly in alcohols whose distribution ratios indicate reactions of both excited $O(^1D)$ and ground state $O(^3P)$ atoms; the competitive reactions of $O(^1D)$ and $O(^3P)$ atoms were studied by photolysis of N_2O dissolved in mixtures of hydrocarbons.

N_2O is a convenient source for oxygen atoms. We report here on hydroxylation of saturated hydrocarbons in the liquid state by oxygen atoms, generated by N_2O photolysis.†

Solutions of N_2O in saturated hydrocarbons,‡ with O_2 excluded, were irradiated with a low pressure Hg immersion lamp§ (whose 184·9 nm radiation band is responsible for the photolysis) for 2–6 h. The main products of the reaction were alcohols accompanied by small amounts (*ca.* 5%) of monocarbonyl compounds, and dimeric hydrocarbons.¶ The conversions were between 0·3 and 2%, and increased linearly with irradiation time. The distribution ratios of oxidation products obtained by photolysis of N_2O in pentane, 2,3-dimethylbutane, methylcyclohexane, and *cis*-decalin are shown in Table 1. All the possible isomeric alcohols were formed in almost statistical distribution ratio, with only a small excess of the more substituted alcohols. We have also observed a high retention of configuration in the tertiary alcohols formed from *cis*-decalin.

We assume that the excited $O(^1D)$ atoms are the main reacting species in the liquid phase, since these atoms are highly energetic and are known to react indiscriminately in the gas phase with all the C–H bonds in a molecule.‡[1] The small preference for the more substituted C–H bond is ascribed to the concurrent reaction of $O(^3P)$ present in smaller amounts in the solution. The $O(^1D)$ atoms may react either by insertion or by H abstraction, while $O(^3P)$ atoms, for symmetry reasons, react only by H abstraction. The latter process leads to both alkyl and OH radicals whose recombination results in alcohols. The alkyl radicals which do not recombine in this manner form dimeric products.

Formation and reactions of oxygen atoms are described in the Scheme.

$$N_2O + h\nu \rightarrow N_2 + O(^1D)$$

$$N_2O + h\nu \rightarrow N_2 + O(^3P)$$

$$O(^1D) \rightarrow O(^3P)$$

$$\begin{array}{ll} & \nearrow \mathrm{ROH}\ \text{(insertion)} \\ \mathrm{RH} + O(^1D) & \rightarrow \mathrm{R}\cdot + \mathrm{OH}\cdot\ \text{(H abstraction)} \\ & \searrow \mathrm{R}^1{=}\mathrm{O} + \mathrm{H}_2\ (\mathrm{H}_2\ \text{elimination}) \end{array}$$

$$\mathrm{RH} + O(^3P) \rightarrow (\mathrm{R}\cdot + \mathrm{OH}\cdot) \rightarrow \mathrm{ROH}$$

$$\mathrm{R}\cdot + \mathrm{R}\cdot \rightarrow \mathrm{R{-}R}$$

SCHEME

The $O(^1D)$ atoms are formed directly by N_2O photolysis, and the $O(^3P)$ atoms either by collisional deactivation or by forbidden intersystem crossing in the excited N_2O molecule. The ketones (or aldehydes respectively) are not formed by oxidation of alcohols, but directly from hydrocarbons by $O(^1D)$ atoms with H_2 elimination in analogy with gas-phase reactions.[1] Irradiation of 1% solution of cyclohexanol in cyclohexane saturated with N_2O under the above conditions resulted in increased amounts of cyclohexanol, the sum of the amount of alcohol initially present

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† Reactions of oxygen atoms with saturated hydrocarbons in condensed phase previously reported were those performed in liquid argon: *cf.* W. B. DeMore, *J. Phys. Chem.*, 1969, **73**, 391.

‡ 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 greater than 99·99%.

§ Hanau TNN 15/32 Hg lamp was used throughout this work. Identical results were obtained with Philips 93106E zinc lamp, whose 213·9 nm radiation forms oxygen atoms.

¶ The reaction products were analysed by g.l.c. on a 6 m, 20% Carbowax 20M on Chromosorb W. column. All the products were identified by comparison with authentic samples.

TABLE 1

Product distributions from photolysis of N_2O in saturated hydrocarbons

Compound	Temp/°C	Product distribution/%			Product distribution per C–H bonds			
		prim. alcohols and aldehydes	sec. alcohols and ketones	tert. alcohols	prim.	sec.	tert.	Retention of configuration/%
Pentane	−78	47·2	52·8		1	1·11		
	−20	49·5	50·5		1	1·02		
2,3-Dimethylbutane	0	84·9		15·1	1		1·07	
Methylcyclohexane	−78	19·2	71·7	9·1	1	1·12	1·41	
	0	19·9	71·1	9·0	1	1·07	1·35	
cis-Decalin	−15		80·4	19·6		1	1·94	96
	0		80·9	19·1		1	1·89	95
	+50		82·6	17·4		1	1·68	93

and that formed in the reaction. In order to account for the high degree of the retention of configuration at the tertiary positions of *cis*-decalin, it must be assumed that the fraction of tertiary decalol derived from the reaction with $O(^3P)$ atoms is also formed with retention of configuration (Table 1). This leads us to assume that the very short-lived *cis*-decalyl radical formed by $O(^3P)$ atom reacts with OH radicals to give *cis*-9-decalol before it can isomerize to the more stable *trans*-decalyl radical, which would be expected to lead mainly to the *trans*-9-decalol.[2] Such a fast recombination may occur when the decalyl and the OH radicals are both contained in a solvent cage. Upon lowering the temperature, the reaction medium becomes more viscous and the solvent cage tighter, facilitating the recombination of the alkyl and OH radicals. The result is a decrease in *cis* to *trans* decalyl isomerization rate, *i.e.* an increase in the retention of configuration.

TABLE 2

Product distributions per C–H bonds in pentane solution

	Methylcyclohexane						*cis* Decalin			
	−78 °C			0 °C				−78 °C		
Conc.	prim.	sec.	tert.	prim.	sec.	tert.	Conc.	sec.	tert.	Retention of configuration/%
Neat	1	1·12	1·41	1	1·07	1·30	Neat[a]	1	1·94	96
50%	1	1·14	1·79	1	1·09	1·85	10%	1	3·75	76
20%	1	1·13	1·85	1	1·20	3·6	5%	1	3·92	64
4%	1	1·40	2·77							

[a] At −15°C

Competitive reactions of $O(^1D)$ and $O(^3P)$ were observed on photolysis of N_2O dissolved in mixtures of methylcyclohexane or *cis*-decalin in pentane. Although the overall yield of the alcohols derived from methylcyclohexane decreased by lowering its concentration in pentane, the relative ratio of the more substituted alcohols increased substantially (Table 2). A diminishing concentration of *cis*-decalin in pentane also led to an increase of the relative ratios of tertiary alcohols derived from *cis*-decalin, as well as to a dramatic decrease in the retention of configuration at its tertiary position (Table 2). Thus, upon lowering the relative concentration of methylcyclohexane or *cis*-decalin in pentane and keeping that of oyxgen atoms constant (which is very small relative to the decalin), the total amount of all the alcohols formed by an attack of $O(^1D)$ and $O(^3P)$ atoms decreases. Since $O(^1D)$ atoms react indiscriminately with all C–H bonds while $O(^3P)$ atoms react preferentially with tertiary C–H bonds, the proportion of the C–H bonds attacked by $O(^3P)$ atoms will increase.

Thermal decomposition of the vibrationally excited alcohols formed by $O(^1D)$ insertion in the gas phase[1] does not occur in condensed phase, probably owing to their fast collisional deactivation, which explains their higher proportion among the products of the liquid phase.

The fact that alcohols are the major products of the reaction of excited oxygen atoms in the liquid phase allows the use of photolysis of N_2O for the introduction of OH groups into highly unreactive hydrocarbons.

(*Received*, 19*th March* 1975; *Com.* 328.)

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