514. *Alicyclic Alkoxyl Radicals in the Thermal Decompositions of Cyclohexyl and 1-Methylcyclohexyl Nitrite.*

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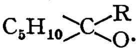
The thermal decompositions of cyclohexyl and 1-methylcyclohexyl nitrite have been studied in the liquid, gaseous, and dissolved states, at temperatures between 80° and 225°. Decomposition is initiated by fission of the oxygen–nitrogen bond, yielding nitric oxide and the oxygen radical,


$C_5H_{10}{>}C{<}^{R}_{O\cdot}$ (R = H or Me).

In solvents such as cumene, which contain readily abstractable hydrogen, conversion of the radical into the appropriate alcohol is essentially complete, and decomposition follows first-order kinetics. In inert solvents, in the pure liquid, and in the gaseous phase, decomposition is much more extensive. Only about half the carbon skeleton survives (as the cyclohexanol) and cyclohexanone is not a product. The nitric oxide produced in the initial step participates in several secondary reactions; part is incorporated in an intractable tar and part is reduced to nitrous oxide and nitrogen.

The chemistry of the cyclohexyloxyl radicals is compared with that of other alicyclic and heterocyclic oxygen radicals. Although decomposition might be expected to follow either of two paths it apparently occurs exclusively by ring fission. The thermochemical basis of this behaviour is examined and it is suggested that the alternative path to form cyclohexanone (or another cyclic ketone) and the free radical will occur if it is thermochemically favoured. Behaviour of this kind is to be expected of 1-t-butyl-, 1-allyl-, or 1-benzyl-cyclohexyl nitrite.

Studies of the thermal decomposition of a number of simple aliphatic nitrites have shown [1,2] that, in both liquid and gaseous phases, reaction is initiated by oxygen–nitrogen bond fission:

$$\text{(1A)}\quad RR'R''C{\cdot}O{\cdot}NO \longrightarrow RR'R''C{\cdot}O{\cdot} + NO$$

The same step has been found to account for the thermal decomposition of the aryl-substituted nitrites [3] (of which benzyl nitrite [4] is the simplest), and interest is thus added to these more complex nitrites for the information they give about complex alkoxyl radicals.

When the alkoxyl radical possesses an α-hydrogen atom, the " normal " course of reaction [1] is written:

$$\text{(2A)}\quad RR'CH{\cdot}O{\cdot}NO \longrightarrow 0{\cdot}5RR'CO + 0{\cdot}5RR'CH{\cdot}OH + NO$$

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[1] Steacie, " Atomic and Free Radical Reactions," 2nd edn., Reinhold, New York, 1955.

[2] Gray and Williams, *Chem. Rev.*, 1959, **59**, 239.

[3] Pearson and Rathbone, unpublished work, 1959; Rathbone, Ph.D. Diss., University of Leeds, 1961.

[4] Gray, Rathbone, and Williams, *J.*, 1960, 3932.

the alcohol and carbonyl compound arising by reactions of hydrogen abstraction or disproportionation. This (2A) is an oversimplification for it has been found that[5] considerable decomposition of the alkoxyl radicals generated can also occur; the alkyl radicals so formed associate with nitric oxide, yielding nitroso-compounds[6] or their decomposition products:

$$\text{(3A)}\quad \mathrm{RR'CH{\cdot}O{\cdot}} \longrightarrow \mathrm{R} + \mathrm{R'{\cdot}CHO} \text{ and } \mathrm{R'} + \mathrm{R{\cdot}CHO}$$

$$\text{(4A)}\quad \mathrm{R} \text{ (or } \mathrm{R'}) + \mathrm{NO} \longrightarrow \mathrm{R{\cdot}NO} \text{ (or } \mathrm{R'{\cdot}NO}\text{), etc.}$$

In addition, reduction of nitric oxide has proved to be commoner than originally thought. In the decomposition of the simplest nitrites, reduction proceeds as far as nitrous oxide;[7,8] in decomposition of the more complex nitrites, nitrogen is formed extensively.[3,4,8,9]

Previous work on the alkyl nitrites has been largely confined to the aliphatic esters. In particular, the alicyclic esters have received very little attention. In 1936, Hunter and Marriot[10] reported (briefly) that cyclohexyl nitrite decomposed spontaneously to adipic acid at room temperature; they did not find the cyclohexanol and cyclohexanone which would arise from reaction (2A). However, their decomposition was carried out with free access to the air. In 1937, Thompson and Dainton[11] reported that photolytic decomposition of cyclohexyl nitrite dissolved in carbon tetrachloride gave a complex mixture.

In 1955, Gowenlock and Trotman[6] pyrolysed a series of nitrites in a flow system in order to prepare nitroso-compounds (by reactions 1A, 3A, and 4A). They were unable to isolate nitroso-compounds from the decomposition products of cyclohexyl or 1-methylcyclohexyl nitrite and they raised doubts about the general resemblances between the cyclohexyl nitrites and other nitrite esters.

So far as the saturated cyclic alkoxyl radicals are concerned, studies on peroxides or hydroperoxides afford some information about 1-methylcyclohexyloxyl[12,13] and 1-phenylcyclohexyloxyl,[14] but essentially none about cyclohexyloxyl itself. Accordingly, we have studied the thermal decompositions of cyclohexyl nitrite and 1-methylcyclohexyl nitrite in the liquid, gaseous, and dissolved states. The aims of the work have been to establish the stoicheiometry of decomposition and to determine whether its initial step is fission of the oxygen–nitrogen bond. Although the occurrence of the initial step (1A) has been proved, its immediate products do not react according to scheme (2A); reduction of nitric oxide is extensive, cyclohexanone is absent, and there is much tarry product. The implications of these results for alicyclic O-radicals may be further illuminated by the study of their thermochemistry.

EXPERIMENTAL

Materials.—Cyclohexanol, cumene, chlorobenzene, and benzaldehyde were purchased from Messrs. B.D.H. Ltd. The benzaldehyde was thoroughly degassed and purified by fractional distillation *in vacuo* before use. Freshly purified cyclohexanol is essential if all traces of cyclohexanone are to be absent.

Cyclohexyl nitrite was prepared by slow addition of freshly purified cyclohexanol (free from cyclohexanone) in sulphuric acid to an ice-cold aqueous solution of sodium nitrite. The crude product was washed successively with saturated sodium chloride solution and dilute sodium hydrogen carbonate solution. It was dried (MgO) and finally distilled in a vacuum. Cyclohexyl nitrite slowly decomposes under ordinary conditions of storage[3,10] (in light with

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[5] Adler, Gray, and Pratt, *Chem. and Ind.*, 1955, 1517.

[6] Gowenlock and Trotman, *J.*, 1955, 4190; *J.*, 1956, 1670.

[7] Levy, *J. Amer. Chem. Soc.*, 1956, **78**, 1780; *Ind. Eng. Chem.*, 1956, **48**, 762.

[8] Williams, Ph.D. Diss., University of Leeds, 1959.

[9] Kornblum and Oliveto, *J. Amer. Chem. Soc.*, 1948, **71**, 226.

[10] Hunter and Marriot, *J.*, 1936, 285.

[11] Thompson and Dainton, *Trans. Faraday Soc.*, 1937, **33**, 1546.

[12] Milas and Perry, *J. Amer. Chem. Soc.*, 1946, **68**, 1938.

[13] Hawkins, *J.*, 1950, 2801.

[14] Hey, Stirling, and Williams, *J.*, 1957, 1054.

access to air), crystals of adipic acid being deposited: it was stored *in vacuo* in the dark, in a trap cooled by liquid nitrogen.

1-Methylcyclohexyl nitrite was prepared in a similar manner to cyclohexyl nitrite, with 1-methylcyclohexanol in place of cyclohexanol; 1-methylcyclohexanol was prepared by the action of methylmagnesium iodide on cyclohexanone.

As infrared and ultraviolet spectra of pure liquid cyclohexyl and 1-methylcyclohexyl nitrite are not fully documented, we record here their salient features for comparison with other nitrites.[15] The infrared absorption spectra of thin films were recorded on a Grubb–Parsons double-beam recording infrared spectrometer. Ultraviolet spectra of solutions in cumene and light petroleum were recorded on an Optica double-beam absorption spectrometer.

Infrared absorption spectra: wavelengths in μ (and relative intensities). Cyclohexyl nitrite: 3·45s, 3·50s, 6·11vs, 6·26m, 6·84m, infl., 6·90s, 7·33m, 7·50w, 7·61vw, 7·93w, 7·98vw, 8·37vw, 8·64w, 8·83vw, 9·15vw, 9·44m, 9·76m, 10·26m, 10·56m, 10·70vw, 10·83vw, 11·11s, 11·46w, 11·56m, 11·74vw, 12·13vs, 12·94vs, 14·75s. 1-Methyl cyclohexyl nitrite: 3·41s, 3·47s, 6·14vs, 6·90m, 7·25w, 7·30w, 7·45vw, 7·51vw, 7·81vw, 7·95vw, 8·00w, 8·59m, 8·67m, 8·97w, 10·29w, 10·62m, 11·03vw, 11·11vw, 11·20vw, 11·68w, 11·83w, 12·13s, 12·7vs, 13·31s.

Ultraviolet spectra: wavelengths in mμ (extinction coefficients, ε, in parentheses). Cyclohexyl nitrite in light petroleum: 324 (24), 334 (36), 345 (54), 358 (72), 371 (71), 385 (infl., 42).

1-Methylcyclohexyl nitrite in the same solvent: 331 (24), 342 (35), 354 (54), 367 (76), 382 (82), 399 (56).

Procedure for Liquid-phase Decomposition.—The liquid-phase decompositions were carried out in the apparatus [4] used for the decomposition of liquid benzyl nitrite. A weighed sample of reactants in a Pyrex reaction vessel was carefully freed from dissolved air. The inert gaseous atmosphere (nitrogen or carbon dioxide) was then admitted.

The reaction vessel was maintained at a constant temperature by the vapour of a boiling liquid. In some experiments the progress of the decomposition was followed by measurement of the gas evolution.

Procedure for Gas-phase Decomposition.—The gas-phase decomposition of cyclohexyl nitrite was studied in both a static and a flow system.

In the static system a Pyrex reaction vessel (volume *ca.* 80 ml.) was connected to a conventional vacuum-line. The reaction bulb was heated to the required temperature (*ca.* 200°) by means of an easily removable furnace. The pressure in the reaction vessel was measured by a heated capillary manometer. Cyclohexyl nitrite was distilled into the cold reaction vessel. The furnace was replaced in position and heated to 120°; the (initial) pressure at this temperature was taken. To study the decomposition, the furnace at 120° was quickly replaced by one at the required temperature. The condensable products were distilled into a small trap which was removed for the products to be analysed. The gaseous products were expanded into an infrared cell.

In the flow apparatus, a Pyrex reaction vessel (44 ml.) was kept at *ca.* 250° by means of an electric furnace. The nitrite vapour was carried through the reaction vessel (mean residence times *ca.* 10 sec.) by a stream of nitrogen at atmospheric pressure and the decomposition products were collected in a trap cooled to −78°. Samples of the gas were removed for infrared analysis.

Analysis of Gaseous Products.—The gaseous products (A) of decomposition of both nitrites contain nitrogen, nitric oxide, and nitrous oxide together with a small quantity of carbon dioxide; no carbon monoxide was detected. Similar analytical methods were applicable to the products of both gas and liquid-phase decompositions. Nitric and nitrous oxides and carbon dioxide were estimated quantitatively from infrared absorption spectra (maxima at 5·2, 4·5, and 4·3 μ, respectively). Nitrogen was determined by measuring the residual pressure when nitric and nitrous oxide and carbon dioxide were condensed out.

Analysis of Liquid Products.—The non-gaseous part (B) of the decomposition products is a dark, viscous liquid. Distillation yields a clear distillate (C) and an almost equal amount of an involatile oily residue (D).

The distillate (C) is almost wholly the appropriate cyclohexanol: other constituents were separated by fractionation and identified by ultraviolet and infrared spectroscopy, by vapour-phase chromatography, and by chemical or other physical tests where applicable.

Cyclohexanol was determined by both fractionation and weighing, and by comparison of

[15] Bellamy, " The Infrared Spectra of Complex Molecules," 2nd edn., Methuen, London, 1958.

its infrared spectrum in cumene solution (especially the peak at 2·65 μ) with those of standard solutions. In addition to cyclohexanol, water was found in small quantities in the volatile fraction (C); cyclohexene was identified as a very small fraction (b. p. 83°/760 mm.; decolorises bromine water). An aldehyde was detected by dimedone: a deep orange 2,4-dinitrophenylhydrazone, m. p. 135—140°, was prepared but not conclusively identified.

Element analysis of the oily residue (D) showed it to contain a considerable percentage of nitrogen; it was also acidic. The acidic component (possibly adipic acid) was estimated quantitatively by titration against standard sodium hydroxide.

Cyclohexanone was not present among the liquid products of normal decomposition of either pure nitrite. In the experiments on the influence of initially added cyclohexanone, the residual quantity was determined by comparing the vapour-phase chromatogram with that of standard comparison mixtures of similar composition. This proved more accurate than a gravimetric assay with 2,4-dinitrophenylhydrazine.

RESULTS

Decomposition of Cyclohexyl Nitrite in the Gas Phase.—Decomposition is slower in the gas phase than in the pure liquid, less than 2% of reaction occurring after 4 hr. at 100°. At higher temperatures, reaction is more rapid and may be followed analytically or by pressure measurements, the pressure increase accompanying complete decomposition being 50%. The gas-phase decomposition was studied in outline only; some product analyses are included in Table 1.

In the " static " apparatus at 224°, reaction is essentially complete in 30 min. The gases formed comprise (as 100 mole % of nitrite): NO 28·6; N_2 7; N_2O 2·6; the volatile liquids are water (*ca.* 10 mole %) and cyclohexanol (*ca.* 20 mole %); cyclohexanone is absent. A black tarry residue (41·4 g. per mole) remains in the reaction vessel after decomposition.

In a " flow " apparatus it is possible to handle larger amounts of reactants. The non-gaseous product of pyrolysis at 250° in a stream of nitrogen gas (contact time *ca.* 10 sec.) is again a dark, viscous liquid containing, in addition to the cyclohexanol and water (the main constituents), aliphatic aldehydes and showing infrared absorption bands at 6·13 7·25, 7·95, 9·4, and 10·85 μ ascribed to *C*-nitroso-derivatives or oximes.

TABLE 1. *Decomposition products of liquid and gaseous cyclohexyl nitrite. Yields are expressed as mole % of initial nitrite.*

Conditions	Temp.	Decompn. hr.	Decompn. min.	Cyclo-hexanol	Adipic acid	NO	N_2O	N_2	CO_2	Gas, total
Liquid-phase	100°	18	—	45	5					
decomp.	132	1	40	—	—	8·2	5·2	13	1·9	28
		3	55	50	4·1	11	10·5	17	3·1	42
		4	45	—	—	—	—	18	—	42
		6	40	—	—	10	10	16	3·9	40
	132	2	32		39 *	3·5	23	11	1·1	40
Gas.-phase	224	—	30	20	10 †	28·6	2·6	7·0	Trace	38
decomp.	250	—	(10 sec.)			30	3	*ca.* 15	Trace	*ca.* 48

* Equivs. of adipic plus benzoic acid; this run was carried out in presence of added benzaldehyde.
† Water.

Decomposition of Pure Liquid Cyclohexyl Nitrite.—The stoicheiometry and kinetics of decomposition (carried out under an inert atmosphere to prevent atmospheric oxidation) of liquid cyclohexyl nitrite have been studied at 100° and 132°.

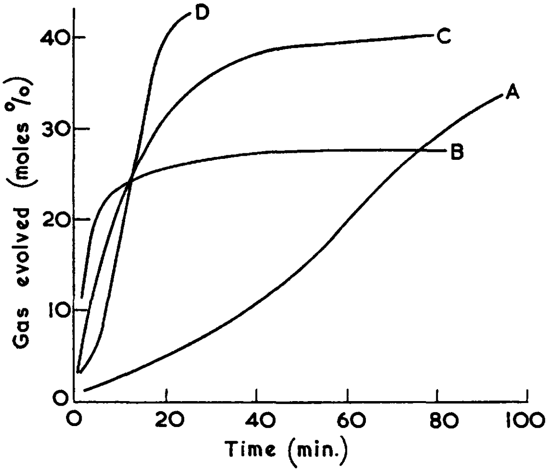
Stoicheiometry. The products of decomposition are a gas (A) and a dark, viscous liquid (B). The gas is a mixture of nitrogen, nitrous oxide, nitric oxide, and a little carbon dioxide; the total yield of gas at 132° is 0·42 mole per mole of nitrite; about 64% of the total nitrogen is accounted for by the gaseous constituents: N_2O 0·17, N_2 0·10, and NO 0·10 mole (cf. Table 1). The proportions of nitrous oxide and carbon dioxide in the gaseous products increase somewhat as reaction proceeds.

The non-gaseous fraction (B) was examined before and after fractionation. The principal identifiable constituent is cyclohexanol; cyclohexanone is absent. Fractionation yielded cyclohexene (b. p. 83°), a trace; water (b. p. 100°); cyclohexanol (b. p. 161°); and 60 g. per mole of nitrite of a black oil (D) (C, 63·45; H, 8·0; N, 5·7%). This (D) contained the adipic acid fraction; titration corresponded to 0·08 equiv. per mole of nitrite. It was fractionated with difficulty *in vacuo*, to yield a black liquid (E), b. p. >250°, and 19 g. of a black solid (F). The liquid (E) contained both carbonyl groups (strong infrared absorption at 5·81 μ) not attributable to cyclohexanone (b. p. 155°) and nitroso-groups. It was thought to be a nitrosocyclohexanone derivative. The evidence is, however, inconclusive, and the appropriate reference compounds are unknown. Infrared spectra of material (D) also demonstrated the absence of hydroxyl groups, and therefore the oxygen is probably present as carbonyl and nitroso-groups.

The course of decomposition may be represented by the equation:

$$1{\cdot}00C_6H_{11}{\cdot}O{\cdot}NO \longrightarrow 0{\cdot}45C_6H_{11}{\cdot}OH + 0{\cdot}17N_2 + 0{\cdot}14H_2O + 0{\cdot}11NO + 0{\cdot}10N_2O + 0{\cdot}04C_6H_{10}O_4 + 0{\cdot}035CO_2 + C_{3{\cdot}03}H_{4{\cdot}92}N_{0{\cdot}35}O_{0{\cdot}27}$$

That cyclohexanone is not present implies that it is not formed at all, or that it is formed but consumed. A solution containing cyclohexanone and cyclohexyl nitrite (molecular ratio 1 : 2) was kept at 132° for 12 hr. One half of the added cyclohexanone was still present at the end of this period.



The kinetic course of decomposition of liquid cyclohexyl nitrite at 132°. *Autocatalysis and the influence of added cyclohexanone.* (*Ordinates are moles of gas evolved per* 100 *moles of initial nitrite; abscissae are elapsed time, in minutes.*)

A, Pure nitrite (mean of three runs); B, Added cyclohexanone (50% ketone); C, Added cyclohexanone (33% ketone); D, Added benzaldehyde (33% nitrite).

Kinetics.—After 4 hr. at 100°, the liquid had become brown; infrared spectroscopy revealed that nitrite had been consumed and that hydroxyl groups had been formed. After complete decomposition the residue was black. At 132°, decomposition was essentially complete in less than 3 hr. Though the complex stoicheiometry prevents more than a superficial analysis, the progress of decomposition can be followed quantitatively by measurements of evolved gas or consumed nitrite. The Figure displays the amount of gas evolved at 132° in moles per 100 moles of initial nitrite as a function of time. One feature stands out: decomposition of the pure liquid is autocatalytic.

To investigate whether cyclohexanone might be a catalyst (as benzaldehyde is for decomposition of benzyl nitrite [4]) the decompositions of mixtures of cyclohexyl nitrite with equi- and semi-molecular proportions of added cyclohexanone were studied. The rate of reaction was considerably increased, and cyclohexanone is potentially the autocatalytic agent. The effect is not specific, however, for added benzaldehyde brings about the same result.

Decomposition of Cyclohexyl Nitrite in Cumene.—To discover if the cyclohexyloxyl radical $C_6H_{11}{\cdot}O{\cdot}$ is formed during decomposition, solutions of cyclohexyl nitrite in cumene were decomposed at 100° and 132° and the yields of cyclohexanol determined. At 132°, reaction was complete in a few hours. The final solutions were deep red-brown and this colour was retained in the last 1% of the involatile fraction when the liquid product was fractionated *in vacuo*.

The yield of cyclohexanol (see Table 2) was high, increasing from 90 to 97% as the solvent : nitrite ratio was increased. Bi-α-cumyl was not found.

The kinetic course of hydrogen-abstraction was examined in outline by determining the

TABLE 2. *Formation of cyclohexyloxyl radicals in the decompositions of cyclohexyl and* 1-*methylcyclohexyl nitrites. The figures are yields of alcohol from decomposition in cumene at* 132° (*run* 18 *at* 100°).

Run	Nitrite	Initial nitrite concn. (mole l.$^{-1}$)	Duration (hr.)	Moles of alcohol per 100 moles of initial nitrite
9	Cyclohexyl	0·172	12	91
10		0·0980	8	95
11		0·0510	9	97
18		0·0741	6	95
22	1-Methylcyclohexyl	0·149	14	70
23		0·0507	12	90

yield of alcohol at intervals. 100 g. of a 0·07408m-solution were kept at 100°; the following yields were recorded:

Time (min.)	0	135	285	720
Yield (%) of alcohol	0	50	81	95

These figures are in accord with a first-order reaction velocity constant, $k = 1·7 \times 10^{-5}$ sec.$^{-1}$ at 100°.

Decomposition of Cyclohexyl Nitrite in Chlorobenzene.—Unlike cumene, chlorobenzene contains no readily extractable hydrogen. Since hydrogen abstraction leading to cyclohexanol is a competitor of decomposition by ring fission, chlorobenzene should favour the latter by removing the opportunities for the former.

TABLE 3. *Decomposition of cyclohexyl and* 1-*methylcyclohexyl nitrite in chlorobenzene at* 132°. *Figures are yields of alcohol expressed in terms of moles per* 100 *moles of initial nitrite.*

Run	Nitrite	Initial nitrite concn. (mole l.$^{-1}$)	Decompn. time (hr.)	Alcohol yield
27	Cyclohexyl	0·082	36	52
28	,,	0·0137	24	55
12	1-Methylcyclohexyl	0·038	43	54
13	,, ,,	0·076	30	59

Solutions containing about 0·3 g. of cyclohexyl nitrite in 10 ml. of chlorobenzene were heated at 100° for 18 hr. Cyclohexanol yields, determined by infrared analysis, are summarised in Table 3. They were much less than yields in cumene, and about the same as those obtained in the pure liquid.

An exploratory investigation of the other decomposition products was consistent with the presence of aliphatic aldehydes and *C*-nitroso-groups. The former were suggested by infrared spectra (5·78 μ) and by a dimedone test; the latter by infrared (6·9 μ) and ultraviolet (264, 272, 276 mμ) absorption maxima (in hexachloroethane and ethanol respectively).

Decomposition of Pure Liquid 1-*Methylcyclohexyl Nitrite.*—1-Methylcyclohexyl nitrite is considerably more stable than is cyclohexyl nitrite, though it also decomposes in the air at room temperature, eventually yielding a crystalline acid.

TABLE 4. *Analysis of decomposition products of pure liquid* 1-*methylcyclohexyl nitrite at* 132°. *Figures are yields expressed in moles per* 100 *moles of initial nitrite.*

Decompn. time							
hr.	min.	$C_7H_{14}·OH$	NO	N_2O	N_2	CO_2	Gas, total
8	40	64	8·9	4·8	21	5·7	41
18	30	—	9·1	3·5	22	3·8	39

Under a nitrogen atmosphere decomposition occurs conveniently rapidly at 132°. It was accompanied by darkening, and the viscous liquid finally produced was almost black. The gaseous products were nitric oxide, nitrogen, nitrous oxide, and carbon dioxide. Among the liquids, only 1-methylcyclohexanol was prominent. A small quantity of a ketone was indicated by the infrared spectrum and by the formation of a small quantity of a deep orange 2,4-dinitrophenylhydrazone; a negative iodoform test suggested that it was not a methyl ketone. Element analyses were made on the volatile and involatile fractions of the non-gaseous products. The volatile fraction contained: C, 70·3; H, 11·95; N, 1·55; and O, 16·2%. The tarry residue contained much more nitrogen: C, 59·75; H, 7·55; N, 8·05; and O, 24·65%). Table 3 summarises the results, which may be represented by the overall scheme:

$$1{\cdot}00C_7H_{13}{\cdot}O{\cdot}NO\ (144{\cdot}2\ \text{g.}) \longrightarrow 0{\cdot}64C_7H_{13}{\cdot}OH + 0{\cdot}21N_2 + 0{\cdot}09NO + 0{\cdot}05CO_2 + 0{\cdot}04N_2O + \text{Tar}\ (43\ \text{g.})$$

The rate of decomposition is somewhat irreproducible but autocatalysis is again present. In one run at 132°, reaction proceeded slowly for *ca.* 7 hr., then accelerated sufficiently to be essentially complete after 8 hr. 30 min.

Decomposition of 1-*Methylcyclohexyl Nitrite in Cumene.*—Solutions in cumene containing 0·149 and 0·507 mole of 1-methylcyclohexyl nitrite per l. were decomposed essentially to completion at 132°, and yields of alcohol determined. The results are summarised in Table 2. The yield was higher (*ca.* 90%) in the more dilute solution. Bi-α-cumyl was not found.

Decomposition of 1-*Methylcyclohexyl Nitrite in Chlorobenzene.*—Solutions in chlorobenzene containing 0·08 and 0·04 mole of 1-methylcyclohexyl nitrite per l. were decomposed to completion at 132°. Yields of 1-methylcyclohexanol were determined: the results are presented in Table 3. Alcohol yields (*ca.* 59% and 55%) are reduced from those obtained in cumene solution to values similar to those obtained in the pure liquid (*ca.* 65 moles %).

DISCUSSION

Formation of the Alkoxyl Radical.—The nature of the initial step in the thermal decomposition of these nitrites is revealed by the results obtained when decomposition is carried out in cumene. The alcohol yields rise to 100% in dilute solution. That this is a true chemical effect and not merely a physical consequence of dilution is proved by the much lower alcohol yields formed when decomposition is carried out in the inert solvent, chlorobenzene. The alcohol results from attack by the alkoxyl radical on the weakly bound tertiary hydrogen atom of cumene. Reaction is thus initiated by unimolecular oxygen–nitrogen bond fission to yield nitric oxide and the appropriate cyclohexyloxyl radical:

$$\begin{gathered} RO{\cdot}NO \longrightarrow RO{\cdot} + {\cdot}NO \\ RO{\cdot} + PhMe_2CH \longrightarrow ROH + PhMe_2C{\cdot} \\ (R = \text{cyclohexyl or 1-methylcyclohexyl}) \end{gathered}$$

These cyclic nitrites thus fall into line with other members of the family and, although previously attention has been drawn [6] to differences from other nitrites, these refer to subsequent reactions of the radicals and not to the initial step. The formation of a little cyclohexene may be evidence for the concurrent elimination: $C_6H_{11}{\cdot}O{\cdot}NO \longrightarrow C_6H_{10} + HO{\cdot}NO$. There is strong evidence for this in the isomeric family of nitroparaffins though it has not hitherto been reported for nitrites. The extent is very slight.

Bi-α-cumyl is not found as a product. The same absence of bicumyl has been noted (or its presence not reported [16]) in the decompositions in cumene solution of benzyl nitrite [4] and t-butyl nitrite; [16] it also has a parallel [17] in the absence of bibenzyl from the products of decomposition in toluene solution of n-octyl nitrite. Waters [18] has suggested that an alternative fate of the cumyl radical is oxidation to α-methylstyrene (b. p. 161°) by loss of hydrogen and that the stoicheiometry of hydrogen abstraction from cumene by alkoxyl radicals is the sum of the reactions:

$$\begin{array}{rcll} RO{\cdot} + PhMe_2CH & \longrightarrow & ROH + PhMe_2C{\cdot} & \\ X{\cdot} + PhMe_2C{\cdot} & \longrightarrow & XH + PhMeC{=}CH_2 & (X\ \text{may be RO}) \\ \hline 2RO{\cdot} + PhMe_2CH & \longrightarrow & 2ROH + PhMeC{=}CH_2 & \end{array}$$

In nitrite systems, nitric oxide also may take the rôle assigned to X, but in addition it may associate with cumyl radicals yielding a nitroso-compound.

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[16] Yoffe, *Research*, 1954, **7**, 44.

[17] Gingras and Waters, *J.*, 1954, 3508.

[18] Waters, personal communication, 1960.

As we pass from decompositions in dilute cumene solution to decomposition in the pure liquid or gas phase, the stoicheiometry alters; three features of the general pattern stand out. First, yields of alcohol fall to about 50% and this figure accounts for most of the intact cyclohexyl rings. Secondly, cyclohexanone is absent from both systems. Thirdly, there is considerable reduction of nitric oxide to nitrous oxide and nitrogen, and, although commonly [2,4,7] these gaseous constituents comprise all the nitrogen products, more than 35% of the total nitrogen here ends in the involatile tar. These are the observations to be explained in terms of reactions undergone by the nitric oxide and the alkoxyl radicals formed in the initial step.

Hydrogen-abstraction Reactions.—Hydrogen abstraction by the alkoxyl radicals is the origin of the two cyclohexanols. The substrates available are the parent nitrite, another alkoxyl radical (*i.e.*, disproportionation), and a product molecule. Although cyclohexyl nitrite (the ester of a secondary alcohol) offers a readily abstractable atom in its α-hydrogen, it is not exclusively this atom which is attacked here, for, if it were, cyclohexanone would be a major product. The possibility that some cyclohexanone is formed but is consumed in secondary reactions cannot be completely ruled out. It is reactive; cyclohexanone is readily oxidised by homolytic attack, much more so than is cyclohexanol; [15] and it can undergo [15] acid-catalysed condensation to β-unsaturated ketones. However, the survival of a considerable portion of initially added cyclohexanone and its complete absence on normal decomposition confirm that, if there is attack on this position, its extent is small.

Therefore, hydrogen abstraction is occurring (concurrently) from another position in the ring. All the hydrogen atoms of the cyclohexyl ring are relatively labile; even from cyclohexane itself, hydrogen abstraction by t-butoxyl [19] proceeds more readily than from isoparaffins, and at 135° is favoured even relatively to cumene. The activation energy of hydrogen abstraction by t-butoxyl from methylcyclohexane is only *ca.* 6 kcal. mole^{-1}. Hydrogen abstraction [20] from the methylene groups of cyclohexanone leads to higher ketones and to dicyclic 1,4-diketones.

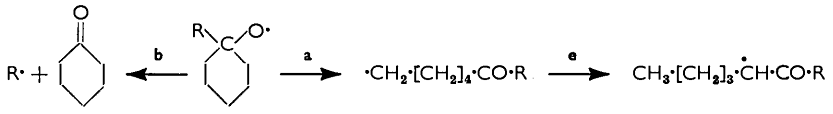
Moreover, in the decomposition of 1-methylcyclohexyl nitrite the yield of 1-methylcyclohexanol is no less than that of cyclohexanol from cyclohexyl nitrite; since 1-methylcyclohexyl nitrite does not possess any α-hydrogen, abstraction must there occur exclusively from elsewhere in the ring. The work of Hawkins,[13] which records the formation of 1-methylcyclohexanol in the decomposition of 1-methylcyclohexyl hydroperoxide, also requires this conclusion.

This behaviour contrasts with that observed in systems involving the cyclohexenyloxyl [21] and tetrahydropyranyloxyl [22] radicals. These yield considerable proportions of the parent alcohols and ketones, whether by disporportionation or attack on the parent. In each there is both the presence of an exceptionally weakly bound α-hydrogen atom and the possibility of an unusually stable ketone. The two factors owe their origin in the homocyclic system to the allylic configuration, and in the heterocyclic system to the influence of the oxygen atom.

Decomposition of the Alkoxyl Radicals and Reactions of the Nitric Oxide.—Radical decomposition is the normal competitor [2] of hydrogen abstraction and is the fate of nearly half the cyclic alkoxyl radicals produced here. Fission of the carbon–carbon bond in a cyclic alkoxyl radical (I) produces not separate fragments (*i.e.*, path b is not followed), but a single species (II) containing both carbonyl and alkyl radical groups (path a).[2] It is most striking that unimolecular decomposition by elimination of the group R leaving cyclohexanone (path b) has never been recorded In agreement with this general observation no methane, ethane, or nitrosomethane was formed from 1-methylcyclohexyl nitrite in our work. This step is the first on the path leading to aldehydic, ketonic, and acidic

[19] Brook, *Trans. Faraday Soc.*, 1957, **53**, 327.
[20] Farmer and Moore, *J.*, 1951, 131.
[21] Bateman and Hughes, *J.*, 1952, 4594.
[22] Milas, Peeler, and Mageli, *J. Amer. Chem. Soc.*, 1954, **76**, 2322.

products and to the polymeric, tarry residues characteristic [12-14] of alicyclic oxygen radical decompositions.



(I) (II) (III)

In the absence of nitric oxide, the radical (II) may react in three ways: (path c) it may abstract a hydrogen atom forming hexanal (when R = H) or heptan-2-one [12] (when R = Me); (path d) it may dimerise to a 1,12-dialdehyde (R = H) or diketone [12] (R = Me); or (path e) it may rearrange by an internal hydrogen abstraction. Rearrangement of the radical (II; R = Me) to (III) has been recognised in the decomposition [12] of t-butyl 1-methylcyclohexyl peroxide, 3,4-dibutylhexane-2,5-dione being the end-product of dimerisation of (III), and 3-methylheptan-2-one the end-product of association of (III) with methyl radicals from t-butoxyl.

In these nitrite decompositions, about 40% of the rings are ruptured in this way. The radical (II; R = H) is also the source of the adipic acid in decomposition of cyclohexyl nitrite:

$$\cdot CH_2\cdot[CH_2]_4\cdot CHO \xrightarrow{\text{Oxid.}} HO_2C\cdot[CH_2]_4\cdot CO_2H$$

In nitrite pyrolyses, formation of nitroso-compounds is well established [6,16] as another consequence of the decomposition [5] of an alkoxyl radical, the alkyl radical eliminated associating with nitric oxide. The same association here leads probably through nitroso-aldehydes and nitroso-ketones to complex decomposition products. The intractable tarry residues, characteristic of all cyclic alkoxyl radical decompositions,[12-14] are now further complicated by nitrogenous constituents. There is evidence for carbon–nitrogen bond formation (and for the presence of nitroso-groups), and Williams [8] has pointed out that the composition of the solid component of the tar * corresponds to an empirical formula near that of a C_6-nitroso-aldehyde.

The reduction of the nitric oxide which remains in the gas phase is also marked; about 50% ends as nitrous oxide and nitrogen. These figures are also in accord with the generalisation [4,23] that, though reduction of nitric oxide always occurs in pyrolyses of nitrites, yet with the simpler nitrites [23] it rarely proceeds beyond nitrous oxide while with the higher nitrites [3,4,8,9] nitrogen is formed and often predominates. The mechanism is by no means understood. The species HNO, formed [7] in a hydrogen-abstraction reaction by nitric oxide, is the most probable precursor of nitrous oxide. However, whether nitrogen in turn is wholly formed from nitrous oxide or whether there is a direct path [24] from nitric oxide to nitrogen is not known.

Energy Requirements of Ring Fission.—The strong preference for ring fission as against radical elimination is not confined to 6-membered rings with these simple substituents. Thus, 1-phenylcyclohexyloxyl radicals [14] split in the same way, forming pentyl phenyl ketone (37%) and 1,10-dibenzoyldecane (but not cyclohexanone and benzene). The original investigators [14] ascribed this preferential cleavage to the superior stability of the ketonic product originating in the conjugation of its carbonyl and phenyl groups. Although this is a contributory [25] factor, it is not a necessary one, since the same path is pursued when R = H, OH, or Me [12] as when R = Ph.

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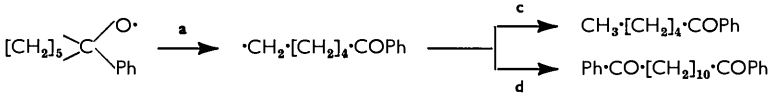
* A Referee has suggested that a polymer $-[-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}=N-O-]_n-$ could be formed by the polymerisation as a diene of a nitroso-compound of basic structure $>C=\underset{|}{C}-N=O$.

[23] Gray and Williams, *Nature*, 1960, **188**, 56; Eighth (International) Symposium on Combustion, Pasadena, 1960, in the press.

[24] Donaruma and Carmody, *J. Org. Chem.*, 1957, **22**, 635.

[25] Gray and Williams, *Trans. Faraday Soc.*, 1959, **55**, 760.



The same pattern is found in the hydroaromatic series: 1-tetralyloxyl,[27] 9-decalyloxyl,[28] and the tricyclic pinanoxyl [29] follow the same path. Among the five-membered rings, alkoxyl radicals have been examined [26] with R = Me, OMe, or OH, and the corresponding dimerised products of the initially ruptured ring have been found, often in high yield. The hydroxy- and methoxy-substituted radicals dimerise to dibasic acids and their methyl esters, respectively.

Some light is thrown on the preferential ring fission by an examination of the thermochemistry.[2,25] Table 5 summarises the enthalpies of unimolecular decomposition (strictly, in the gaseous phase) of some homocyclic alkoxyl radicals by the alternative paths available. Removing the hydrogen atom needs 16 kcal. mole^{-1}; removing the phenyl group, 9 kcal. mole^{-1}; removing the methyl group, 4 kcal. mole^{-1}. The difference between methyl and phenyl may be attributed to the conjugation in the products as suggested by Hey *et al.*[14]

TABLE 5. *Energy requirements of ring fission and radical* (*or atom*) *elimination from cyclic alkoxyl radicals* (6-*membered rings*).

Parent alkoxyl	Group eliminated	Carbonyl compound	ΔH (kcal. mole^{-1})
Cyclohexyloxyl	H	Cyclohexanone	16
	Ring fission	$\cdot CH_2\cdot[CH_2]_4\cdot CHO$	0
1-Methylcyclohexyloxyl	Me	Cyclohexanone	4
	Ring fission	$\cdot CH_2\cdot[CH_2]_4\cdot COMe$	2
1-Phenylcyclohexyloxyl	Ph	Cyclohexanone	9
	Ring fission	$\cdot CH_2\cdot[CH_2]_4\cdot COPh$	2
1-t-Butylcyclohexyloxyl	Bu^t	Cyclohexanone	−5
	Ring fission	$\cdot CH_2\cdot[CH_2]_4\cdot COBu^t$	+1·5
Decalyl-9-oxyl	1–9 Ring fission	Monocyclic radical	−1
	9–10 Ring fission	Monocyclic radical	0
Cyclohex-1-enyl hydroperoxide	H	Cyclohex-1-enone	−3
	Ring fission	$\cdot CH_2\cdot[CH_2]_2\cdot CH{=}CH\cdot CHO$	1
1-Hydroxycyclohexyloxyl	HO	Cyclohexanone	20
	Ring fission	$\cdot CH_2\cdot[CH_2]_2\cdot CH{=}CH\cdot CHO$	1
Tetrahydropyranyl-1-oxyl	H	Tetrahydro-1-oxopyran	16
	Ring fission	$\cdot CH_2\cdot[CH_2]_3\cdot O\cdot CHO$	0

In every case, ring fission required less energy than radical loss, and once again the kinetic features of reactivity have a reflection in the thermodynamic aspect. The extension of this principle suggests [25] that the alternative path (a) to liberate the radical and leave the cyclic ketone will occur when it is thermochemically favourable. On this basis, radical elimination and cyclohexanone formation are to be expected in the decomposition of the substituted cyclohexyloxyl derivatives $1\text{-}R\cdot C_6H_{10}\cdot O\cdot$ where R is, *e.g.*, t-butyl (see Table 5), allyl, or benzyl.

We express our warmest thanks to Drs. K. J. Ivin and M. W. T. Pratt for many valuable discussions, to Mr. M. J. Pearson for help with some of the experiments on cyclohexyl nitrite decomposition, and to Professor D. H. Hey and Dr. W. A. Waters for numerous useful comments. We are also grateful to the Merthyr Tydfil Education Committee and to the D.S.I.R. for postgraduate awards to A. W. and P. R. respectively.

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[*Received, January 24th,* 1961.]

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[26] Roedel, U.S.P. 2,601,224/1952; *Chem. Abs.*, 1953, **47**, 4363.

[27] Robertson and Waters, *Trans. Faraday Soc.*, 1946, **42**, 201; *J.*, 1948, 1574, 1578, 1585.

[28] Holmquist, Rothrock, Theobald, and Englund, *J. Amer. Chem. Soc.*, 1956, **78**, 5339.

[29] Schmidt and Fisher, *J. Amer. Chem. Soc.*, 1954, **76**, 5426.