781. *Benzyloxyl Radicals in Benzyl Nitrite Pyrolyses.*

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Thermal decomposition of benzyl nitrite has been studied at 100—215° in the liquid, the gas, and solution. Decomposition occurs by O–N bond fission: $Ph{\cdot}CH_2{\cdot}O{\cdot}NO \longrightarrow Ph{\cdot}CH_2{\cdot}O{\cdot} + NO$. In the gaseous phase and in solvents such as cumene, the kinetics are approximately first-order. In cumene solution, benzyl alcohol is the predominant product. In the gaseous phase, in inert solvents, and in the pure liquid, although the carbon skeleton survives, reaction is more extensive and benzaldehyde and benzoic acid are also formed. The nitric oxide is extensively reduced to nitrous oxide and nitrogen. Reaction in the pure liquid is autocatalytic and the benzoyl radical $Ph{\cdot}CO{\cdot}$, formed from benzaldehyde, plays an important part.

The benzyloxyl radical is compared with other primary radicals and other homologues. It is unusually stable; the thermochemical basis of this is discussed.

PYROLYSES of nitrites were first studied by Steacie [1] and by Rice and Rodowskas.[2] They worked on thermal decomposition in the gaseous phase, at less than 1 atmosphere and temperatures usually in the region of 170—240° C, studying the methyl, ethyl, n- and iso-propyl, and n-butyl esters. Decompositions were followed by measurements of pressure change. The reactions were homogeneous and obeyed first-order kinetics with activation energies near 37 kcal. mole^{-1} and pre-exponential factors near 10^{13} sec.$^{-1}$. Oxygen-nitrogen bond fission was written as the initiating and rate-determining step, and nitric oxide, alcohol, and aldehyde were postulated as the final products from a primary nitrite:

$$(1)\quad R{\cdot}CH_2{\cdot}O{\cdot}NO \longrightarrow R{\cdot}CH_2{\cdot}O{\cdot} + NO$$

$$(2)\quad 2R{\cdot}CH_2{\cdot}O{\cdot}NO \longrightarrow R{\cdot}CH_2{\cdot}OH + R{\cdot}CHO + 2NO$$

Interest is thus added to these nitrites as convenient sources of alkoxyl radicals.[3] The vapour-phase decomposition of the lower alkyl nitrite has continued to receive most attention [4,5] and less is known about the higher alkyl nitrites and about liquid-phase decompositions, although a small number of higher alkyl nitrites has been examined in the liquid phase. These include t-butyl nitrite in cumene,[6] (—)-octyl nitrite in a number of solvents,[7] (+)-1-methylheptyl nitrite as the pure liquid,[8] and both s-butyl and 1-ethylpropyl nitrite [9] in the presence of diacetyl peroxide. The high yields of alcohols formed in the presence of hydrogen-atom donors such as cumene, and the complete retention of configuration in the octanol from (+)-1-methylheptyl nitrite,[8] are in accord with the same initiating step of O–N bond fission. However, the stoicheiometry of the overall reactions has not been adequately established and kinetic data are not available which would establish whether O–N bond fission is also rate-determining. Even the best work [8] accounts for only 85% of the products. However, it is apparent that reaction does not end with the products of equation (2), even though it is initiated according to equation (1). First, some nitric oxide is reduced. Even in the low-temperature pyrolysis of methyl nitrite, 0·13 mole of nitrous oxide per mole of nitrite is produced; [10] the same reduction occurs with ethyl nitrite,[11] and higher alkyl nitrites [8,12] yield appreciable amounts of

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[1] Steacie, " Atomic and Free Radical Reactions," Reinhold Publ. Corpn., New York, 1946.
[2] Rice and Rodowskas, *J. Amer. Chem. Soc.*, 1935, **57**, 350.
[3] Gray and Williams, *Chem. Rev.*, 1959, **59**, 239.
[4] Adler, Gray, and Pratt, *Chem. and Ind.*, 1955, 1517.
[5] Gowenlock and Trotman, *J.*, 1955, 4190.
[6] Yoffe, *Research*, 1954, **7**, 44.
[7] Gingras and Waters, *J.*, 1954, 3508.
[8] Kornblum and Oliveto, *J. Amer. Chem. Soc.*, 1949, **71**, 226.
[9] Kharasch, Meltzer, and Nudenberg, *J. Org. Chem.*, 1957, **22**, 37.
[10] Williams, Ph.D. Diss., Leeds, 1959.
[11] Levy, *J. Amer. Chem. Soc.*, 1956, **78**, 1780.
[12] Rathbone, unpublished work, 1959.

nitrogen. Secondly, some of the alkoxyl radicals decompose [2,4] to alkyl radicals. Nitrite esters are, in fact, excellent indirect pyrolytic sources of hydrocarbon radicals and have been used [13] to prepare such unusual radicals as $\cdot CH_2\cdot CN$, cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl in addition to the commoner alkyls. In the presence of nitric oxide, alkyl radicals also yield the corresponding nitrosoalkanes and these are characteristic products of many nitrite pyrolyses.[5]

Very little is known of benzyl nitrite and its homologues or of the benzyloxyl radical $Ph\cdot CH_2\cdot O\cdot$. Doubt has been expressed about the resemblance of this nitrite to other nitrites [5] and about the decomposition [13] of the radical to formaldehyde and free phenyl:

$$(3)\quad Ph\cdot CH_2\cdot O\cdot \longrightarrow Ph\cdot + CH_2O \qquad \Delta H = 16{\cdot}3 \text{ kcal. mole}^{-1}$$

This present paper reports a study of the rôle of the benzyloxyl radical in decomposition of benzyl nitrite in the gas phase, in the pure liquid, and in inert and active solvents. It aims to establish the stoicheiometry of decomposition, the overall reaction order, velocity constant, and approximate Arrhenius parameters, and the nature of the initial step, and to investigate the possible participation of alkoxyl radicals. While it in not possible to set up a unique detailed mechanism, an outline is suggested which is concordant with the results.

EXPERIMENTAL

Materials.—Benzyl nitrite was prepared by the slow addition of benzyl alcohol, dissolved in sulphuric acid, to ice-cold aqueous sodium nitrite. The crude product was washed successively with saturated sodium chloride solution and dilute sodium hydrogen carbonate solution. It was dried and stored over anhydrous magnesium oxide, and finally purified by vacuum-distillation; the middle fraction was retained. It was stored *in vacuo* in the dark, in a trap cooled by liquid nitrogen.

As full infrared and ultraviolet spectra of liquid benzyl nitrite have not been previously published they were recorded. A thin liquid film examined in a Grubb–Parsons double-beam recording infrared spectrometer showed absorption maxima at 3·30m, 3·40m, 6·05vs, 6·21s, 6·66m, 6·89m, 7·34vs, 8·00w, 8·25m, 9·27w, 9·75m, 10·21m, 11·01m, 12·25s, 12·72vs, 13·41vs, and 14·34vs cm.$^{-1}$. The characteristic doubling [14] due to the presence of rotational isomers was apparent.

Ultraviolet spectra of solutions in cumene and light petroleum recorded on an Optica double-beam absorption spectrometer showed absorption maxima at 318 (infl., ε 20·1), 327 (29·2), 337 (45·8), 348 (64·4), 359 (76·1), 371 (67·8), and 384 mμ (infl., 37·2), the figures in parentheses being absorption coefficients of light petroleum solutions. This is the familiar pattern of primary nitrite absorption bands.[15]

Benzyl alcohol, cumene, chlorobenzene, and benzaldehyde were purchased from B.D.H.; the benzaldehyde was thoroughly degassed and purified by fractional distillation *in vacuo*, before use.

Di-t-butyl peroxide was obtained from Laporte Chemical Industries. The nitric oxide was prepared by the action of acidified ferrous sulphate solution on sodium nitrite, in a nitrogen atmosphere. The crude gas was condensed out at $-196°$ and subsequently warmed to $-78°$, the nitric oxide boiling off from the impurities: this procedure was repeated three times. When necessary, the gas was freed from nitrous oxide by sublimation at 1 cm.

Cylinders of nitrous oxide and oxygen-free nitrogen were obtained from British Oxygen Gases Ltd., and of carbon dioxide from the Carbon Dioxide Campany Ltd.

Before use, the nitric oxide, nitrous oxide, and carbon dioxide were freed from traces of permanent gases by freezing and evacuation at $-196°$.

Procedure for Liquid-phase Decompositions.—The liquid-phase decompositions were carried out in the apparatus illustrated in Fig. 1. Reaction vessel *A* was used for the decompositions of benzyl nitrite in cumene, in which the benzyl alcohol yield was measured as a function of time. Reaction vessel *B* was used for all the other decompositions.

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[13] Lossing, personal communication, 1959.

[14] Tarte, *J. Chem. Phys.*, 1952, **20**, 1570.

[15] Ungnade and Smiley, *J. Org. Chem.*, 1956, **21**, 993; see also Gillam and Stern, " Electronic Absorption Spectroscopy," Arnold Ltd., London, 1957.

The reaction vessel containing a weighed sample of reactants was connected to the apparatus, cooled to $-78°$, and the system was evacuated through $T1$ and degassed for at least 15 min. The desired gaseous atmosphere was added to the system through tap $T2$. Residual air was removed from the gas-inlet tube by passing a stream of gas out through $T2$ for a short period before the experiment and following this by evacuation and flushing of the system with gas three times; $T5$ was kept closed during the latter operation. The pressure and volume of the gas were noted after the reaction vessel had been warmed to room temperature.

The reaction vessel was kept at a constant temperature by the vapour of a boiling liquid. When pure liquid benzyl nitrite was decomposed, the progress of the decomposition was followed by measurement of gas evolution, and also by analysis of the gaseous products at various stages of decompositions from 15 to 100%. The liquid products were weighed in some of the runs carried to complete decomposition in order to check the gas analysis. Decomposition in dilute solution in cumene was followed both by gas evolution and by benzyl alcohol production.

Procedure for Gas-phase Decomposition.—Decomposition of benzyl nitrite in the gas-phase was carried out in a static decomposition apparatus. A " Pyrex " reaction vessel (volume *ca.* 80 ml.) was connected to a conventional vacuum-line. The reaction bulb was heated to a temperature of *ca.* 200° by means of an easily removable furnace, its temperature being measured by a mercury thermometer. The pressure in the reaction vessel was measured by a capillary mercury manometer heated to 80° to prevent condensation.

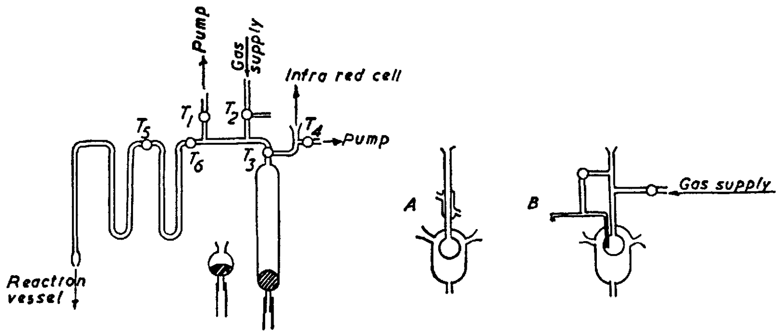

FIG. 1. *Apparatus used for studying liquid-phase decomposition. Vessel A used for cumene solutions; B for pure nitrite.*

Benzyl nitrite was distilled into the reaction vessel which was cooled in liquid nitrogen after removal of the furnace. The furnace was replaced, the apparatus heated to 120°, and the (initial) pressure at this temperature measured. Additives were admitted in a similar way. To study the decomposition, the furnace at 120° was quickly replaced by one at the required temperature. The time required for the reaction vessel to attain the required temperature was *ca.* 1 min.

The reaction was then followed by measuring the pressure change accompanying the reaction. The condensable products were distilled into a small trap which was removed for their analysis. The gaseous products were expanded into an infrared cell.

Analysis of Gaseous Products from Liquid- and Gas-phase Decompositions.—The gaseous products of decomposition contained nitrogen and nitric oxide together with small quantities of nitrous oxide and carbon dioxide. No carbon monoxide was detected. Similar analytical methods were used for the products of the gas- and liquid-phase decompositions. For the estimation of nitrogen, the two traps were cooled to $-196°$, at which temperature the nitric and nitrous oxides and carbon dioxide condensed. To facilitate condensation, the gases were circulated through cold traps by means of the gas burette. The non-condensable nitrogen was then measured. Experiments with artificial mixtures indicated that the method was satisfactory within 2% for the compositions encountered. Nitric and nitrous oxides and carbon dioxide were determined from infrared absorption spectra, by means of their maxima at 5·2, 4·5, and 4·3 μ, respectively. To minimise variable errors due to pressure broadening, all absorption spectra were recorded at a total pressure of one atmosphere, nitrogen being added if necessary.

Calibration curves of optical density against partial pressure (also at a *total* pressure of one atmosphere) were used. All infrared spectra were recorded by a Grubb–Parsons double-beam spectrophotometer.

The yields of nitrous oxide and nitric oxide calculated from the infrared spectra were found to be in fairly good agreement with the yields measured by the gas burette. However, where the yield of nitric oxide was small, the infrared analysis often gave a considerably lower value. In these cases, the error is assumed to be in the nitric oxide determination. The extinction coefficient for nitric oxide is much less than for nitrous oxide or carbon dioxide, and hence the accuracy of the nitric oxide estimation is much less than that for the other gases.

Analysis of Liquid Products of Liquid- and Gas-phase Decompositions.—The liquid products of decompositions contained benzaldehyde, benzoic acid, and benzyl alcohol, together with small amounts of benzyl benzoate. Different techniques were required for the quantitative estimation of products of gas- and liquid-phase decompositions because of the different amounts of material available.

(a) *Liquid-phase decomposition.* Benzaldehyde was characterised as its 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 234°, which was also used for the quantitative determination. Estimation on a standard equimolar mixture of benzyl alcohol and benzaldehyde was 94% efficient; a correction factor based on this was used for the actual determinations. Benzoic acid was isolated from the products by extraction with sodium hydroxide and acidification with hydrochloric acid, and, recrystallised from hot water, had m. p. and mixed m. p. 122°. It was estimated quantitatively by titration (phenolphthalein). Benzyl alcohol was identified by its b. p. and by comparison of the infrared spectrum of the products with that of an authentic sample. It was estimated quantitatively against standard solutions in cumene or chlorobenzene from the 2·65 μ peak (hydroxyl stretching frequency).

(b) *Gas-phase decompositions.*—The same substances were present among these products and were analysed by ultraviolet absorption spectroscopy. Optical densities of a methanolic solution of the products were measured at 5 mμ intervals from 250 to 280 mμ, and their individual contributions of acid, aldehyde, and alcohol deduced. In addition, chemical analyses were made for benzoic acid (by titration with N/200-alkali) and for benzaldehyde (by preliminary oxidation to acid followed by titration).

The products contained about 5% by weight of an involatile residue. This was principally a colourless liquid of high b. p., found by infrared absorption to contain benzyl benzoate (b. p. 321°) which was estimated by the absorption maxima at 7·85 and 9·0 μ. There was also a gum thought to be a nitroso-derivative.[10]

RESULTS

Decomposition of Pure Liquid Benzyl Nitrite.—Under ordinary conditions of storage, *i.e.*, exposure to light at room temperature, liquid benzyl nitrite decomposes slowly to benzaldehyde, benzoic acid, and, in the presence of air, nitrogen dioxide; after about a week, a pale yellow solid remains, consisting mainly of benzoic acid. Benzyl nitrite was therefore always stored *in vacuo* in the dark in a liquid nitrogen-cooled trap.

Stoicheiometry.—In the absence of air and in an inert atmosphere of, *e.g.*, nitrogen or carbon dioxide, decomposition is conveniently rapid at 100°. The pale yellow benzyl nitrite gradually deepens in colour, finally becoming dark brown. The products of decomposition are benzaldehyde, benzyl alcohol, benzoic acid, small quantities of benzyl benzoate, nitric oxide, nitrogen, small quantities of nitrous oxide, carbon dioxide, and water. Neither nitrosobenzene nor formaldehyde is obtained.

Pure liquid benzyl nitrite was decomposed at 100° and 132°; at the lower temperature, decomposition was practically complete after 5 hr., and at the higher temperature, after about 90 min. Some of the decompositions were carried to completion, and the remainder stopped after various times. The results are summarised in Table 1. Decompositions were carried out in inert atmospheres of nitrogen and carbon dioxide and also in nitric and nitrous oxide atmospheres, to see if these have any effect upon the decomposition. The yield of benzaldehyde is at least twice that of benzyl alcohol, and the benzoic acid yield is of the order of 10%. The yield of nitric oxide on decomposition at 132° is only about 36% of the value expected from the Steacie equation.[1] The composition of the gaseous products appeared to alter slowly during the decomposition; the percentage of both nitrous oxide and nitrogen appeared to increase slightly.

The detailed experimental results (cf. Table 1) of decomposition at 100° and 132° may be conveniently represented by the overall equations:

At 100°:

$$1{\cdot}00\mathrm{Ph{\cdot}CH_2{\cdot}O{\cdot}NO} \longrightarrow 0{\cdot}53\mathrm{Ph{\cdot}CHO} + 0{\cdot}22\mathrm{Ph{\cdot}CH_2{\cdot}OH} + 0{\cdot}15\mathrm{Ph{\cdot}CO_2H} + 0{\cdot}25\mathrm{NO} + 0{\cdot}26\mathrm{N_2} + 0{\cdot}018\mathrm{H_2O} + 0{\cdot}011\mathrm{CO_2} + \text{“}\,\mathrm{C_{0.69}H_{1.16}N_{0.19}O_{0.68}}\,\text{”}$$

At 132°:

$$1{\cdot}00\mathrm{Ph{\cdot}CH_2{\cdot}O{\cdot}NO} \longrightarrow 0{\cdot}44\mathrm{Ph{\cdot}CHO} + 0{\cdot}22\mathrm{Ph{\cdot}CH_2{\cdot}OH} + 0{\cdot}11\mathrm{Ph{\cdot}CO_2H} + 0{\cdot}36\mathrm{NO} + 0{\cdot}24\mathrm{N_2} + 0{\cdot}021\mathrm{N_2O} + 0{\cdot}025\mathrm{CO_2} + \text{“}\,\mathrm{C_{1.58}H_{1.94}N_{0.12}O_{0.69}}\,\text{”}$$

The decomposition temperature affects the product composition. At 100° about 90% of the phenyl groups are accounted for as Ph·CHO, Ph·CH$_2$·OH, or Ph·CO$_2$H; the remainder are in the residue. At 132°, the higher, condensed products account for a larger percentage of the phenyl groups and only 80% are accounted for as Ph·CHO, Ph·CH$_2$·OH, or Ph·CO$_2$H. Increasing the decomposition temperature decreases the yield of benzaldehyde from 0·53 to 0·44 mole per mole of initial nitrite, and that of benzoic acid from 0·15 to 0·11 mole: the yields of benzyl alcohol and nitrogen are unaffected, but that of nitric oxide is increased from 0·25 to 0·36 mole. Micro-analysis of the liquid products showed that the nitrogen content was 1·15%, corresponding to a further 0·10 atom of nitrogen per mole of initial nitrite, and therefore 98% of the total nitrogen is accounted for.

TABLE 1. *Product analysis of decomposition of liquid* (*runs* 1—20) *and gaseous* (*runs* 35—40) *benzyl nitrite.*

The products are expressed in moles per 100 moles of initial benzyl nitrite.

		Product yields							
Run no.	Decomp. time (min.)	Ph·CHO	Ph·CO$_2$H	Ph·CH$_2$·OH	NO	N$_2$O	N$_2$	CO$_2$	Gas (total)
				Decomp. at 100°					
1	81				7·9	0·05	7·4	0·2	15
2	145				18	1·3	18	0·7	38
3	198								47
4	210	51							53
5	220	52							54
6	400	53	15	22					
33	380				25	1·8	26	1·1	54
				Decomp. at 132°					
7	10				7·1	0·05	3·7		11
8	70		11				20		56
9	122				35	1·4	25	1·4	63
10	174	40	13		37	1·4	25	0·9	64
11	223	44	12	22	36	2·1	24	2·5	65
12	240	44	11	22					
13	15						5·6		14
14	20						9·3		29
15	10						5·0		16
16	15						7·8		28
17	174						21		62
18	180						23		61
19	20						48		23
20	20						7·8		31
				Decomp. at 205°					
35	4·5					0·14	1·96		
36	8·0				11·1	0·98	5·2	0·26	
37	30	59·3	12·1	26·6	47	4·5	19·0	1·5	
38	30	59	13	28			18·2		
39	30	58	13	26			18·6		
40		70							

The runs were carried out in nitrogen (1—12 and 33), nitric oxide (13—14), carbon dioxide (15—18), or nitrous oxide (19—20).

Entries 35 and 36 correspond to 14% and 26·5% decomposition of nitrite vapour and entries 37—40 to 100% decomposition. Each of these entries presents mean results of three or more runs.

Kinetics.—The measurement of gas evolution, and analysis of the gaseous products at various percentage decompositions, enables the rate of disappearance of benzyl nitrite to be inferred. In Fig. 2, curves of gas evolution with time for a number of runs are given; the results are expressed in terms of moles of gas produced from 100 moles of initial benzyl nitrite. The decomposition temperature was 132°, except for run 5 which was at 100°. The half life of benzyl nitrite at 100° is about 110 min., and at 132° is 20—25 min. When the benzyl nitrite is in dilute solution in cumene, the half life at 132° is about 150 min.

The decomposition is of first order only initially and is subsequently autocatalytic. This is particularly noticeable at the lower decomposition temperature. Experiments were therefore carried out in which reaction products were initially added to the system. No appreciable effect was observed when benzyl nitrite was decomposed in an atmosphere of nitric or nitrous oxide, but added benzaldehyde was found to accelerate markedly the rate of decomposition. The initial rate of decomposition in run 22, as measured by gas evolution, was found to be about a hundred times that of run 5, in which no benzaldehyde was added (see Fig. 2). Not only does added benzaldehyde accelerate the rate of decomposition, but it affects the yields of the products. Product analyses of runs 21 and 22 are shown in Table 2. There was a marked increase (at least five-fold) in the yield of nitrous oxide. The yields of benzyl alcohol and benzoic acid were also increased, but more benzaldehyde was consumed than was produced in the decomposition.

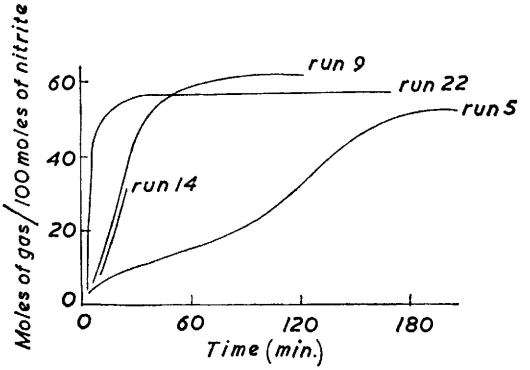

FIG. 2. *Gas evolution during decomposition of liquid benzyl nitrite (results for four selected runs). Runs 5, 9, 14: pure nitrite. Run 22: added benzaldehyde. Temp.,* 132°, *except for run* 5 (*at* 100°).

TABLE 2. *Analysis of decomposition products of benzyl nitrite in liquid benzaldehyde.*

The products are expressed in moles per 100 moles of initial benzyl nitrite.

Run no.	Added Ph·CHO	Decomp. time (min.)	Ph·CHO	$Ph·CH_2·OH$	$Ph·CO_2H$	Gas	NO	N_2O	N_2	CO
21	270	3	240		27	38	17	7	13	0·7
22	250	170	200	45	20—40	36				

Decomposition of Gaseous Benzyl Nitrite.—Stoicheiometry. In the gaseous phase, decomposition is conveniently rapid between 150° and 220°; at 205°, decomposition (in a Pyrex reaction vessel) is essentially complete in 30 min. A 60% pressure increase accompanies complete decomposition. Product compositions vary only slowly throughout the course of the reaction. Analyses corresponding to partial and complete decompositions are summarised in Table 1. The liquid products are benzaldehyde, benzyl alcohol, and benzoic acid together with small quantities of benzyl benzoate and water; the gases consist principally of nitric oxide and nitrogen, with smaller amounts of nitrous oxide and carbon dioxide. No formaldehyde, carbon monoxide, or nitrosobenzene was identified. At 205° the normal course of gas-phase decomposition, taken to completion, may be represented by the equation: *

$$\begin{aligned}1{\cdot}00\mathrm{Ph{\cdot}CH_2{\cdot}O{\cdot}NO} \longrightarrow\ & 0{\cdot}59\mathrm{Ph{\cdot}CHO} + 0{\cdot}28\mathrm{Ph{\cdot}CH_2{\cdot}OH} + 0{\cdot}13\mathrm{Ph{\cdot}CO_2H} + \\ & 0{\cdot}02\mathrm{Ph{\cdot}CO_2{\cdot}CH_2Ph} + 0{\cdot}02\mathrm{CO_2} + 0{\cdot}50\mathrm{NO} + 0{\cdot}18\mathrm{N_2} + 0{\cdot}05\mathrm{N_2O}\end{aligned}$$

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* This equation refers to an initial nitrite pressure of up to 10 cm., the pressures commonly used. In a single experiment, with initial pressure *ca.* 30 cm., appreciable amounts of a rosin-like solid, possibly 1,2-diphenylethylene dibenzoate produced by the addition of benzoyl radicals to benzaldehyde, were obtained.[10] Waters (personal communication) has suggested that other products such as hydrobenzoin, benzoin, and benzil are also to be expected.

Thus, in contrast to Steacie's general equation for nitrite decompositions, the aldehyde: alcohol ratio is not 1 : 1 but 2 : 1, and the nitric oxide yield is only half the expected value.

The amounts of nitrogen and nitrous oxide and of benzoic acid are indications of the departure from Steacie's equation. The effect of initially added reaction products on the yields of these three has been examined. Added nitric oxide is reduced to nitrous oxide, though added nitrous oxide is not reduced to nitrogen; added benzaldehyde enhances the nitrogen yield at the expense of nitrous oxide. The hydrogen-donor, cumene, was also added. It led to reduction of nitric oxide.

Kinetics.—Since the product composition changes only slowly during reaction and the pressure change corresponding to complete decomposition is known, reaction rates may be followed by pressure measurement. Pressure–time curves showed that reaction was approximately of first order over the range of pressures and temperatures studied. Values of velocity constants k at different temperatures (calculated from times required for 25% decomposition, using the first-order law) are:

Temp.	175°	196°	205°	215°
10^5k (sec.$^{-1}$)	9·71	35·4	61·9	141·5

Arrhenius parameters corresponding to the linear variation of log k with $1/T$(°K) implied by these values have been derived. Though, in the absence of any very detailed investigation, they are subject to considerable uncertainty they may be set at $E = 34 \pm 2$ kcal. mole^{-1} and $A = 10^{12\cdot4 \pm 2}$ sec.$^{-1}$.

Decomposition of Benzyl Nitrite in Cumene.—Freshly prepared solutions of benzyl nitrite in cumene are colourless or pale green; when left at room temperature they become yellow within a few days. A measurable yield of benzyl alcohol is obtained with 24 hr. The decomposition is faster at higher temperatures, though it is considerably slower than that of the pure liquid at the same temperature.

TABLE 3. *Decomposition at* 132° *and* 151° *of benzyl nitrite in cumene.*

Yields of benzyl alcohol are expressed in terms of moles per 100 moles of initial nitrite.

Run no.*	Initial benzyl nitrite (mole l.$^{-1}$)	Decomp. time (hr.)	$Ph\cdot CH_2\cdot OH$ (%)	Run no.*	Initial benzyl nitrite (mole l.$^{-1}$)	Decomp. time (hr.)	$Ph\cdot CH_2\cdot OH$ (%)
23	0·0295	18	99	28	0·313	9	84
24	0·043	19	100	29	4·07	9	34
25	0·041	9	100	30	Pure	5	22
26	0·083	10	90	31	0·0905	26	85
27	0·1160	9	83	32	0·087	15	88

* Runs 23—30 at 132° and 31 and 32 at 151°.

Stoicheiometry. A series of solutions of benzyl nitrite, with concentrations ranging from 0·03 to 4·1 moles l.$^{-1}$, were decomposed to completion at 132° or 151°; progress of decomposition was followed by analysis of gaseous and liquid products. The time required for complete decomposition was of the order of 10 hr.; heating for longer periods did not increase the yield of benzyl alcohol. The final solutions obtained on complete decomposition were reddish-brown.

The yields of benzyl alcohol in the various runs are given in Table 3. They decrease as the initial concentration of nitrite increases. In dilute solution, there is 100% conversion into benzyl alcohol up to about 0·05 mole l.$^{-1}$ of initial nitrite; the alcohol yield slowly falls until at 4 moles l.$^{-1}$ (mole fraction of nitrite approx. 0·5) it is only 34%. In the limiting case of pure liquid benzyl nitrite, the yield has fallen still further to 22%. No bi-α-cumyl was obtained on removal of the cumene and volatile products *in vacuo*. The effect of temperature on the yields of benzyl alcohol appears to be very small or negligible. For a given initial concentration of benzyl nitrite, the alcohol yield at 151° is not appreciably different from that at 132°.

Kinetics. The kinetics were investigated by following the benzyl alcohol concentration as a function of time. Solutions of benzyl nitrite of initial concentration of ~0·085 mole l.$^{-1}$ were used in all cases. Under the experimental conditions (90% conversion according to stoicheiometry above) complete reaction corresponds to a final alcohol concentration of 0·0765 mole l.$^{-1}$. The results of several runs are shown in Fig. 3. Within any run, reaction is kinetically of the first order for most of the decomposition. Measurements of the initial rate, although less precise, indicate that it is somewhat higher. Velocity constants k obtained from the linear portion are shown below:

Temp.	101°	110·5°	131°	151°
10^5k (sec.$^{-1}$)	4·0	7·1	45	148

A plot of log k against reciprocal temperature (see Fig. 4) is linear within experimental error, and gives an activation energy of 20 kcal. mole^{-1}.

Decomposition of Benzyl Nitrite in Chlorobenzene.—In order to indicate that the high yield of benzyl alcohol produced when benzyl nitrite is decomposed in dilute solution in cumene is not simply a solvent effect, the decomposition in chlorobenzene was studied, for this is not a hydrogen-donor. A solution of benzyl nitrite (0·08 mole l.$^{-1}$) was decomposed to completion, and a 34% yield of benzyl alcohol was obtained; a solution of the same concentration in cumene gave a 90% yield of benzyl alcohol.

Reaction between Benzaldehyde and Nitrogen Oxides.—Benzaldehyde is readily oxidised and it might be expected to react when heated with nitrous and nitric oxide at temperatures and pressures similar to those of the actual benzyl nitrite decomposition. To establish the necessary conditions for these reactions some simple experiments have been made. They fall into two classes: (1) systems involving only benzaldehyde and nitrous or nitric oxide and (2) systems in which free radicals are also present.

FIG. 3. *The approach to first-order kinetics in the thermal decomposition of benzyl nitrite in cumene (results for runs at* 110·5°, 132°, *and* 151°).

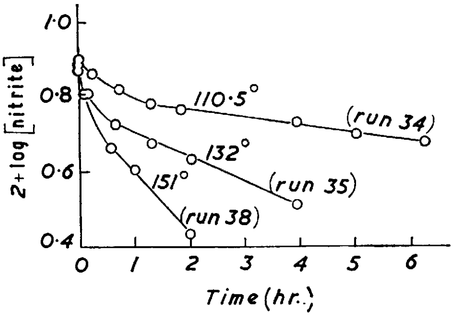
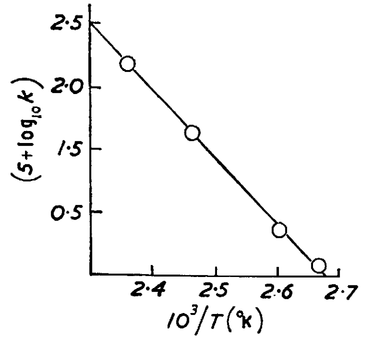


FIG. 4. *Arrhenius plot for first-order thermal decomposition of benzyl nitrite in cumene.* ($A \sim 10^{9\cdot4}$; $E \sim$ 20 kcal. mole^{-1}.)



Reaction between benzaldehyde and N_2O *or* NO. In the homogeneous gas phase, mixtures of benzaldehyde with nitric oxide alone or with nitrous and nitric oxides together were kept at 205° for 30 min. Pyrolysis was complete, but there was no pressure change and gas analysis showed that neither nitrogen nor extra nitrous oxide was produced.

In a heterogeneous (2 phase) system, liquid benzaldehyde was kept at 132° under a nitric oxide pressure of 1 atm. for 4 hr. No visible change occurred, no gas was evolved or absorbed, and analysis showed neither nitrous oxide nor nitrogen had been produced.

Reaction in the presence of free radicals between benzaldehyde and N_2O *or* NO. Nitrites are simultaneous sources of free radicals and nitric oxide. Conveniently for these experiments, methyl nitrite also yields considerable amounts of nitrous oxide [10] while t-butyl nitrite gives only nitric oxide.[6]

In the homogeneous gas phase, mixtures of benzaldehyde and methyl nitrite, at partial pressures of *ca.* 3 and 13 cm. respectively, were decomposed at 205°. Although the total pressure increase was equal to that expected from the nitrite decomposition alone, product analyses showed that 10% of the benzaldehyde had been oxidised to benzoic acid. The yield (expressed as moles/100 moles methyl nitrite decomposed) of nitrous oxide had fallen from 13 to 4 while that of nitrogen had risen from zero to 10.

In the heterogeneous system, when free radicals are generated in liquid benzaldehyde exposed to a nitric oxide atmosphere, only slight reduction occurs. A liquid mixture of benzaldehyde and di-t-butyl peroxide (molar ratio 6 : 1) kept at 132° for *ca.* 48 hr. under a nitric oxide atmosphere afforded 1% of nitrous oxide. The products also contained t-butyl alcohol and methane (from the peroxide) and 1,2-diphenylethylene dibenzoate (from the benzaldehyde).

In the homogeneous liquid phase, when nitric oxide and free radicals are produced simultaneously in benzaldehyde solution by pyrolysis of a nitrite, reaction is extensive. 2 : 1 mixtures of benzaldehyde and t-butyl nitrite were kept at 132° under carbon dioxide; nitric oxide, nitrous oxide, nitrogen and benzoic acid were found among the products.

DISCUSSION

The Initial Step.—The products of decomposition in both the liquid and the gaseous phase, and the enhanced yields (up to 100% conversion) of benzyl alcohol obtained in the presence of the hydrogen-donor cumene, provide evidence that the decomposition in both phases begins by fission of the oxygen–nitrogen bond:

$$(1)\quad \mathrm{Ph{\cdot}CH_2{\cdot}O{\cdot}NO} \longrightarrow \mathrm{Ph{\cdot}CH_2{\cdot}O{\cdot}} + \mathrm{NO}$$

In this respect, benzyl nitrite falls into line with other nitrites, and in particular with with Kornblum and Weaver's [16] recent report on the slow thermal decomposition of 4-nitrobenzyl nitrite at room temperature where initial O–N fission, leading first to alcohol, aldehyde, and nitric oxide explains the nearly theoretical yield of aldehyde and acetal:

$$\begin{aligned}
\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}O{\cdot}NO} &\longrightarrow \mathrm{NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}O{\cdot}} + \mathrm{NO}\\
\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}O{\cdot}} &\longrightarrow 0{\cdot}5\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH} + 0{\cdot}5\mathrm{NO_2.C_6H_4{\cdot}CHO}\\
0{\cdot}5\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH} + 0{\cdot}25\mathrm{NO_2{\cdot}C_6H_4{\cdot}CHO} &\longrightarrow 0{\cdot}25\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH(O{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2)_2} + \mathrm{H_2O}
\end{aligned}$$

If this step 1 is rate-determining, then the " observed " activation energy of the first-order gas-phase reaction, $E_1 = ca.$ 34 kcal. mole^{-1}, is a measure of the O–N bond strength and equals the bond dissociation energy if the reverse reaction has $E_{-1} = 0$.

In dilute cumene (XH) solution, hydrogen abstraction occurs exclusively and 100% yields of alcohol are formed:

$$(4)\quad \mathrm{Ph{\cdot}CH_2{\cdot}O{\cdot}} + \mathrm{XH} \longrightarrow \mathrm{Ph{\cdot}CH_2{\cdot}OH} + \mathrm{X{\cdot}}$$

Dimerisation to bi-α-cumyl is not detected and the cumyl radicals must have been removed in other ways. Similar states of affairs are found in the absence [6] of bi-α-cumyl from cumene solutions in which t-butyl nitrite has been pyrolysed and of bibenzyl from toluene solutions in which n-octyl nitrite [7] has been decomposed. The cumyl radicals (like benzyl radicals [7]) are readily oxidised to α-methylstyrene. Waters (personal communication) has suggested that the net result would be: $2\mathrm{Ph{\cdot}CH_2{\cdot}O} + \mathrm{Ph{\cdot}CHMe_2} \longrightarrow 2\mathrm{Ph{\cdot}CH_2{\cdot}OH} + \mathrm{Ph{\cdot}CMe{:}CH_2}$. The cumyl radicals X are known to combine with free nitric oxide and they may also abstract nitric oxide from the parent nitrite. Reactions such as this have been established for methyl,[17] s-butyl and 1-ethylpropyl nitrite [9] and invoked in decomposition of t-butyl nitrite.[18]

$$\begin{aligned}
&(5) && \mathrm{X{\cdot}} + \mathrm{NO} \longrightarrow \mathrm{X{\cdot}NO}\\
&(6) && \mathrm{Ph{\cdot}CH_2{\cdot}O{\cdot}NO} + \mathrm{X{\cdot}} \longrightarrow \mathrm{Ph{\cdot}CH_2{\cdot}O{\cdot}} + \mathrm{X{\cdot}NO}\\
&(7) && 2\mathrm{X{\cdot}NO} \longrightarrow (\mathrm{X{\cdot}NO})_2 \text{ and decomposition products}
\end{aligned}$$

Reactions (1), (2), and (6) constitute the essentials of a chain reaction and their participation has been suggested [10] as the reason for the greater speed of liquid-phase decomposition. The decomposition of benzyl nitrite in cumene has a half-life of about 70 min. at 150°; in the gas phase a temperature of 190° is required for this speed of decomposition.

The Origin of the Major Products.—With O–N bond fission established as the initial step, the nature and amounts of the decomposition products as well as the kinetic features of the decomposition must be explained in terms of the chemistry of the benzyloxyl radical and the nitric oxide molecule. The key features of the stoicheiometry and kinetics are (1) that nearly all the nitrogen is accounted for as nitrogen, nitrous oxide, and nitric oxide,

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[16] Kornblum and Weaver, *J. Org. Chem.*, 1958, **23**, 1213.

[17] Jest and Phillips, *Proc. Chem. Soc.*, 1960, 73; Gray and Rathbone, *Proc. Chem. Soc.*, 1960, Oct.

[18] Gray, *Chem. and Ind.*, 1960, 120.

(2) that nearly all the carbon ends as benzaldehyde, benzyl alcohol, benzoic acid, and benzyl benzoate (in order of diminishing abundance), and (3) that reaction is catalysed by benzaldehyde although benzaldehyde is not readily oxidised by nitric oxide alone. The almost complete retention of the benzyl skeleton in all the carbon products reflects the unusual stability towards decomposition of the benzyloxyl radical. When we consider in turn the origins of the major products it becomes apparent that as well as the benzyloxyl radical, free benzoyl Ph•CO• has an important part to play.

Benzyl alcohol arises from hydrogen abstraction reactions of benzyloxyl radicals. The three substrates are the parent nitrite, another benzyloxyl radical (disproportionation), and benzaldehyde:

$$\text{(8)}\quad \mathrm{Ph{\cdot}CH_2{\cdot}O{\cdot} + Ph{\cdot}CH_2{\cdot}O{\cdot}NO \longrightarrow Ph{\cdot}CH_2{\cdot}OH + Ph{\cdot}CHO + NO}$$
$$\text{(9)}\quad \mathrm{Ph{\cdot}CH_2{\cdot}O{\cdot} + Ph{\cdot}CH_2{\cdot}O{\cdot} \longrightarrow Ph{\cdot}CH_2{\cdot}OH + Ph{\cdot}CHO}$$
$$\text{(10)}\quad \mathrm{Ph{\cdot}CH_2{\cdot}O{\cdot} + Ph{\cdot}CHO \longrightarrow Ph{\cdot}CH_2{\cdot}OH + Ph{\cdot}CO{\cdot}}$$

The increased yield of alcohol in the presence of added benzaldehyde is obtained at the expense of producing benzoyl radicals Ph•CO•. These are also present, therefore, in the normal decomposition. Their association with benzyloxyl radicals contributes to the formation of benzyl benzoate, present in small amounts:

$$\text{(11)}\quad \mathrm{Ph{\cdot}CO{\cdot} + Ph{\cdot}CH_2{\cdot}O{\cdot} \longrightarrow Ph{\cdot}CO{\cdot}O{\cdot}CH_2Ph}$$

Benzaldehyde is formed in reactions (8) and (9) but these alone cannot explain the fact that there is an excess of benzaldehyde over benzyl alcohol. Any excess of aldehyde over alcohol requires nitric oxide reduction and the problems of benzaldehyde formation and of nitric oxide reduction are linked. Moreover since benzaldehyde is so much more readily oxidised than is benzyl alcohol, its preponderance implies that nitric oxide is oxidising the precursor of both aldehyde and alcohol, *viz.*, the benzyloxyl radical. The excess of benzaldehyde reflects the successful competition of reaction (12) with (8), (9), and (10).

$$\text{(12)}\quad \mathrm{Ph{\cdot}CH_2{\cdot}O{\cdot} + NO \longrightarrow Ph{\cdot}CHO + HNO}$$
$$\text{(13)}\quad \mathrm{2HNO \longrightarrow N_2O + H_2O}$$

The HNO species is well authenticated; even its structure is precisely known.[19] Reactions (12) and (13) were first invoked by Levy [11] in the analogous decomposition of ethyl nitrite.

Benzoic acid is, of course, the oxidation product of benzaldehyde. This oxidation is a radical-chain process when accomplished by oxygen and our results show that free radicals ~~are essential to bring about rapid oxidation by nitric oxide. The first intermediate is the~~ benzoyl (Ph•CO•) radical. The last intermediate before benzoic acid is also known: it is the benzoate radical. The step from benzoyl to benzoate is accomplished by nitrous oxide or nitric oxide: the former is the readier oxidising agent though the latter cannot be completely ruled out on the present evidence:

$$\text{(14)}\quad \mathrm{Ph{\cdot}CO{\cdot} + N_2O \longrightarrow Ph{\cdot}CO_2{\cdot} + N_2} \qquad \Delta H,\ -45\ \text{kcal. mole}^{-1}$$

The benzoate radical then abstracts [20] hydrogen to yield the acid. The simultaneous, competing decomposition of the benzoate radical is the source of the small amounts of carbon dioxide formed. Conditions in which the benzoate radical yields a large $\mathrm{Ph{\cdot}CO_2H : CO_2}$ ratio (as found here) have also been reported by Barson and Bevington.[21]

The production of nitric oxide is explained, of course, by the initial step (1). The reverse reaction is also expected,[22,23] but it cannot have any effect on the stoicheiometry and appears not to influence the kinetics under our experimental conditions. The reduction

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[19] Dalby, *Canad. J. Phys.*, 1958, **29**, 883.

[20] Dannley and Zaremsky, *J. Amer. Chem. Soc.*, 1955, **77**, 1588.

[21] Barson and Bevington, *J. Polymer Sci.*, 1956, **20**, 13.

[22] Levy, *J. Amer. Chem. Soc.*, 1953, **75**, 180; *Ind. Eng. Chem.*, 1956, **48**, 762.

[23] Birss, Danby, and Hinshelwood, *Proc. Roy. Soc.*, 1957, *A*, **239**, 1541.

of nitric oxide is almost certainly a stepwise process, though the possibility of some direct reduction to nitrogen cannot be ruled out. The reduction occurs in all nitrite pyrolyses and, though in the lower nitrites it does not go beyond nitrous oxide, nitrogen is formed in the decomposition of 1-methylheptyl nitrite.[8] We have indicated the links between nitric oxide reduction and the aldehyde yield and invoked the HNO radical as the precursor of nitrous oxide. It is possible that an additional source of nitrous oxide is the reaction of nitric oxide with the benzoyl radical. This step is sufficient (but not essential) in interpreting the reduction by benzaldehyde of nitric oxide from t-butyl nitrite found here.

In turn, nitrogen arises from nitrous oxide and the yields of nitrogen and nitrous oxide (24 and 2·1 moles % respectively) are more than sufficient to explain all the production of benzoic acid and carbon dioxide (12 and 2·5 moles % respectively). The 5 mole % excess of nitrogen must have arisen in reactions other than (14).

The Rôle of Benzaldehyde in Pyrolysis of Benzyl Nitrite.—Attention has been drawn to the focal point which benzaldehyde occupies in the stoicheiometry. Implicit in this and in the other results concerning benzaldehyde is the importance of the benzoyl radical. Thus, benzaldehyde alone is not attacked by nitrous or nitric oxide (*i.e.*, not under the conditions of our experiments), though its oxidation is rapid in the presence of free radicals. These remove the weakly bound aldehydic hydrogen to form free benzoyl which in turn gives rise to benzoic acid, benzyl benzoate, and carbon dioxide.

Benzaldehyde is also a catalyst, causing autocatalysis in normal decomposition and greatly increasing the initial rate when added artificially. A qualitatively similar influence of added acetaldehyde on ethyl nitrite was discovered by Levy.[11] He attributed the two-fold increase in rate to the suppression of recombination of the nitric oxide and ethoxyl radicals produced in the initial step:

$$C_2H_5{\cdot}O{\cdot}NO \longrightarrow C_2H_5{\cdot}O{\cdot} + NO$$

$$C_2H_5{\cdot}O{\cdot} + CH_3{\cdot}CHO \longrightarrow C_2H_5{\cdot}OH + CH_3{\cdot}CO{\cdot}$$

Anderson and Rollefson [24] found nitrogen and nitrous oxide when acetone was photolysed in the presence of nitric oxide, so it is possible that the acetyl radicals produced can augment the effect of acetaldehyde by removing nitric oxide, though Levy did not invoke this possibility. However, even if the parallels to both these reactions occur in the benzyl nitrite system they are unlikely to lead to the acceleration observed. Nor are the other reactions invoked hitherto able to furnish an explanation. There are alternative possibilities. Either benzaldehyde may be able to form an unstable intermediate (*e.g.*, by an addition or condensation with benzyl nitrite) which then rapidly yields the final products by a new, molecular, reaction; or the benzoyl radical may abstract nitric oxide from the parent nitrite and induce decomposition by a chain reaction; such nitric oxide abstractions from nitrites by added radicals have now been recognised and seem quite possible here: [9,17]

$$\left.\begin{array}{r} Ph{\cdot}CH_2{\cdot}O{\cdot}NO + Ph{\cdot}CO{\cdot} \longrightarrow Ph{\cdot}CO{\cdot}NO + Ph{\cdot}CH_2{\cdot}O{\cdot} \\ Ph{\cdot}CO{\cdot}NO \longrightarrow Ph{\cdot}CO{\cdot} + NO \qquad\qquad\quad \end{array}\right\} \longrightarrow \text{Products}$$

Comparison of the Reactions of the Benzyloxyl Radical with Other Primary and Aryl-substituted Alkoxyl Radicals.—The benzyloxyl radical is the parent of the aryl-substituted alkoxyl radicals and its thermochemistry and reactivity are standards of comparison for the series. It is also typical of primary alkoxyl radicals and might be expected to share much of their chemistry. From them, however, it differs in one important respect. All the simple primary alkoxyl radicals,[3] other than methoxyl, readily undergo carbon–carbon bond fission at elevated temperatures: $R{\cdot}CH_2{\cdot}O{\cdot} \longrightarrow R{\cdot} + CH_2O$. The almost complete retention of the Ph·C (benzyl) skeleton in the decomposition products demonstrates its unusual stability. This is also reflected in the way that hydrogen-abstraction is independent of temperature: there is no fall in efficiency as the temperature rises from 130° to 150°, such as would arise from the onset of decomposition. By contrast, the

[24] Anderson and Rollefson, *J. Amer. Chem. Soc.*, 1941, **63**, 817.

α-cumyloxyl ($\mathrm{Ph{\cdot}CMe_2{\cdot}O{\cdot}}$) radical [25] gives a yield of alcohol (αα-dimethylbenzyl alcohol) which rapidly diminishes with rising temperature as decomposition to acetophenone and free methyl sets in. The consequences of the stability of benzyloxyl have been observed by Gowenlock [5] who failed to obtain nitrosobenzene on pyrolysis of benzyl nitrite, and by Lossing [13] who obtained no free phenyl radicals from the same source.

TABLE 4. *Thermochemical aspects * of decomposition of phenyl-substituted alkoxyl radicals.*

Parent *O*-radical	Atom or *C*-radical eliminated	Residual carbonyl compound	Enthalpy increase (kcal. mole^{-1})	Stability 1 = most stable 6 = least stable
$\mathrm{Ph{\cdot}CH_2{\cdot}O{\cdot}}$	Ph	$\mathrm{CH_2O}$	16·3	1
	H	Ph·CHO	19·9	
$\mathrm{Ph_2CH{\cdot}O{\cdot}}$	Ph	Ph·CHO	15·8	2
	H	$\mathrm{Ph_2{\cdot}CO}$	19·4	
$\mathrm{Ph_3C{\cdot}O{\cdot}}$	Ph	$\mathrm{Ph_2{\cdot}CO}$	11·5	3
Ph·CHMe·O·	Me	Ph·CHO	6·8	4
	Ph	Me·CHO	10·7	
	H	Ph·CO·Me	9·6	
$\mathrm{Ph_2CMe{\cdot}O{\cdot}}$	Me	$\mathrm{Ph_2{\cdot}CO}$	2·4	5
	Ph	Ph·CO·Me	5·6	
$\mathrm{Ph{\cdot}CMe_2{\cdot}O{\cdot}}$	Me	Ph·CO·Me	0·3	6
	Ph	$\mathrm{Me_2{\cdot}CO}$	8·0	

* Enthalpies of unimolecular decomposition have been calculated from group-energy terms by using values listed by Gray and Williams.[3]

The relative stabilities of benzyloxyl and its homologues may be examined in the light of their thermochemistry. In Table 4 the energy (ΔH) requirements for bond fission are tabulated for one primary, two secondary, and three tertiary aryl-substituted radicals.

Benzyloxyl is known to be more stable than the two secondary radicals, and α-methyl benzyloxyl (CHPhMe·O·) is the least stable. The latter is said [26] not to abstract hydrogen from cumene although it will remove hydrogen from thiophenol at 125°. When it decomposes, it is by loss of the methyl and not the phenyl radical. Diphenylmethoxyl radicals [27] (from bisdiphenylmethyl peroxide) do abstract hydrogen from cumene at 115—152°, though only 15—24% of the theoretical alcohol yield is produced.

Two of the three tertiary radicals in Table 4 are known. The α-cumyloxyl ($\mathrm{Ph{\cdot}CMe_2{\cdot}O{\cdot}}$) is the least stable, readily losing a methyl radical to form acetophenone; [25] elimination of its phenyl radical is not known. Triphenylmethoxyl is encountered in the thermal decompositions of its nitrite,[28] peroxide,[29] and hydroperoxide; [29] in addition to undergoing rearrangement,[29] it decomposes and yields the phenyl radical (which ends as biphenyl, phenol, or a phenolic derivative) and benzophenone.

The thermochemical basis for the kinetic relations is displayed in Table 4. For a given O-radical with a choice of decomposition mechanisms, the ease of unimolecular elimination diminishes in the order Me > Ph > H. This is the order of increasing energy requirements. When different radicals are compared the order of stability indicated by the thermochemistry, *viz.*, $\mathrm{Ph{\cdot}CH_2{\cdot}O{\cdot} > Ph_2CH{\cdot}O{\cdot} > Ph_3C{\cdot}O{\cdot} > PhMeCH{\cdot}O{\cdot} > PhMe_2C{\cdot}O{\cdot}}$ is wholly consistent with the observed behaviour of the radicals.

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[28] Cristol and Leffler, *J. Amer. Chem. Soc.*, 1954, **76**, 4468.
[29] Wieland and Maier, *Ber.*, 1911, **44**, 2533; 1931, **64**, 1205.