1096. *Aryl-substituted Tertiary Alkoxyl Radicals. Part I. Thermal Decomposition of αα-Dimethylbenzyl Nitrite.*

By PETER GRAY and M. J. PEARSON.

The thermal decomposition of αα-dimethylbenzyl nitrite has been studied to extend knowledge of the role of aryl-substituted alkoxyl radicals in nitrite pyrolyses, hitherto confined to primary and secondary derivatives. Decompositions were carried out under an inert atmosphere between 130° and 180°. The principal products were αα-dimethylbenzyl alcohol, acetophenone, α-methylstyrene, water, nitrogen, and nitric oxide. No ethane, benzaldehyde, or diphenyl was found. Independent experiments showed that αα-dimethylbenzyl alcohol was very readily dehydrated to α-methylstyrene and this had to be taken into account when assessing the significance of alcohol and olefin yields.

At 151°, decomposition may be represented by the equation:

$$\begin{aligned} 1{\cdot}00\mathrm{PhCMe_2ONO} \longrightarrow\ & 0{\cdot}40\mathrm{PhCMe_2OH} + 0{\cdot}22\mathrm{PhCOMe} + 0{\cdot}14\mathrm{PhCMe{:}CH_2} + \\ & 0{\cdot}04\mathrm{PhCO_2H} + 0{\cdot}02\mathrm{MeNO_2} + 0{\cdot}02\mathrm{MeONO} + 0{\cdot}21\mathrm{N_2} + \\ & 0{\cdot}08\mathrm{NO} + 0{\cdot}025\mathrm{N_2O} + 0{\cdot}063\mathrm{CO_2} + 0{\cdot}003\mathrm{CO} + \\ & \mathrm{C_{1\cdot89}H_{2\cdot68}N_{0\cdot41}O_{0\cdot99}} \end{aligned}$$

Evidence for the initial step was afforded by the enhanced yields of alcohol resulting from decomposition in the hydrogen-donor solvent, cumene: decomposition is initiated by O–N bond fission. The origin of the major products is discussed in terms of this initial step.

The αα-dimethylbenzyloxyl radical is markedly less stable in this nitrite decomposition than is either benzyloxyl or 1-methylbenzyloxyl under corresponding circumstances. Some comparisons are made between its role here and in other situations, but a more general comparison is delayed until the second part of this Paper presents results for another tertiary aryl-substituted alkoxyl radical.

THE basic mechanism for the thermal decomposition of simple alkyl nitrites is well known. The initial step is the fission of the oxygen–nitrogen bond to give an alkoxyl radical and nitric oxide:

$$\mathrm{RONO} \longrightarrow \mathrm{RO{\cdot}+NO} \qquad (1)$$

When R is a simple primary alkyl group, it has been observed experimentally[1] and interpreted thermodynamically[2] that the principal reaction of the alkoxyl radical is disproportionation to the corresponding alcohol and aldehyde:

$$\mathrm{R'CH_2O{\cdot}+R'CH_2O{\cdot}} \longrightarrow \mathrm{R'CH_2OH+R'CHO} \qquad (2)$$

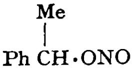
In many systems hydrogen abstraction by $RCH_2O{\cdot}$ is also favoured. However, a recent examination[3] of the pyrolysis of methyl nitrite has shown that, even for the simplest of the primary alkyl nitrites, there are considerable complications on top of the basic mechanism originally postulated[4] by Steacie.

If R is a secondary alkyl radical, unimolecular decomposition of the alkoxyl radical can compete with disproportionation. If R is a tertiary alkyl radical, it is to be expected that decomposition of the alkoxyl radical will be especially important, the probable competing reaction being the abstraction of hydrogen by alkoxyl to give the corresponding alcohol.

So far, very little attention has been given to the thermal decomposition of tertiary alkyl nitrites, only t-butyl nitrite having been investigated.[5–7] No tertiary aryl-substituted nitrites have been studied hitherto, though work has been done on benzyl[8] and 1-phenylethyl[9] nitrites. The decomposition of both these nitrites was found to be fairly complex, though in neither decomposition[8, 9] was any carbon–carbon bond rupture observed. However, if we replace both the hydrogen atoms of benzyl nitrite (I) by methyl groups to give αα-dimethylbenzyl nitrite (III), the basic skeleton contains only methyl and phenyl groups, and the likelihood of carbon–carbon bond rupture is increased. Particular interest is added because either a phenyl or methyl group could be eliminated, and although one of these modes may be favoured energetically, this may not necessarily prevent the other from competing with it. The nitrites are a suitable class of compounds for examining such competition, since the nitric oxide concurrently produced mops up other free radicals and prevents appreciable secondary reactions with the alkoxyl radicals.

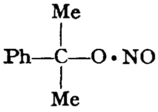
$\mathrm{Ph\,CH_2{\cdot}ONO}$

(I)



$$\mathrm{Ph\,\overset{\overset{\large Me}{|}}{C}H{\cdot}ONO}$$

(II)



$$\mathrm{Ph{-}\underset{\underset{\large Me}{|}}{\overset{\overset{\large Me}{|}}{C}}{-}O{\cdot}NO}$$

(III)

Hence the thermal decomposition of αα-dimethylbenzyl nitrite has been undertaken as a part of the programme under which benzyl and 1-phenylethyl nitrites were decomposed with

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[1] F. O. Rice and E. L. Rodowskas, *J. Amer. Chem. Soc.*, 1935, **57**, 350.
[2] P. Gray and A. Williams, *Chem. Rev.*, 1959, **50**, 239.
[3] L. Phillips, *J.*, 1961, 3082.
[4] E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold, New York, 1946.
[5] A. D. Yoffe, *Research*, 1954, **7**, 44.
[6] J. B. Levy, *Ind. Eng. Chem.*, 1956, **48**, 762.
[7] B. G. Gowenlock and J. Trotman, *J.*, 1955, 4190.
[8] P. Gray, P. Rathbone, and A. Williams, *J.*, 1960, 3932.
[9] P. Gray, M. J. Pearson, and P. Rathbone, *J.*, 1961, 4006.

a view to illuminating some of the similarities and differences in the series of nitrites. Our aims are to establish (i) the nature of the initial step, (ii) the stoicheiometry of decomposition, and (iii) the broad outlines of kinetics and mechanism, especially in the light of thermochemical requirements.

EXPERIMENTAL

Materials.—αα-Dimethylbenzyl nitrite could not be prepared in satisfactory yield by the conventional method (acidified sodium nitrite and the corresponding alcohol). Good yields were obtained by an alternative route[10] due to Kornblum and Oliveto. Liquid nitrosyl chloride was allowed to evaporate slowly from a cooled trap into a stirred solution of αα-dimethylbenzyl alcohol in dry pyridine maintained at 0—5° in a water-free atmosphere. The nitrite was extracted with ether, washed, dried, and purified by repeated bulb-to-bulb distillations *in vacuo*. It was stored in the dark *in vacuo* at $-196°$.

The nitrosyl chloride was prepared[11] by passing a stream of nitrogen dioxide up a long column of moist potassium chloride. αα-Dimethylbenzyl alcohol was prepared by the Grignard reaction from acetone and phenylmagnesium bromide; ice-cold ammonium chloride solution was used to bring about decomposition of the addition complex because dilute sulphuric acid caused considerable dehydration of the alcohol. αα-dimethylbenzyl alcohol was purified by fractionation under reduced pressure (b. p. 91—93°/12 mm.).

Cumene (B.D.H. Ltd.) was purified by vacuum distillation to remove any traces of αα-dimethylbenzyl peroxide. Chromatographic standards were purchased from both B.D.H. Ltd. and Hopkins and Williams. Oxygen-free nitrogen was obtained from British Oxygen Gases, Ltd.

Spectra.—There are no published data on either the infrared or ultraviolet spectra of αα-dimethylbenzyl nitrite. These are therefore recorded below.

The infrared spectrum was measured for a thin film by a Grubb–Parsons double-beam recording spectrometer. Wavelengths in microns and strengths (w, s, etc.) of absorption maxima are: 3·44w, 6·10vs, 6·68vw, 6·90w, 7·20w, 7·30m, 7·87m, 8·28vw, 8·70w, 9·04vw, 9·30vw, 9·71vw, 10·50vw, 10·82vw, 11·0vw, 12·80vs, 13·12vs, 13·77s, 14·30s.

Ultraviolet spectra of solutions of the nitrite in light petroleum were recorded on an Optica double-beam absorption spectrometer. The wavelengths in mμ and extinction coefficients (ε) are: 330 (8), 342 (30), 355 (63), 368·5 (76), 385 (78), 401 (68).

It is noteworthy that the infrared spectrum shows only a single absorption in the 6·0 μ region; this corresponds to the N=O stretching frequency for the *trans*-isomer and is indicative[12] that this nitrite exists almost exclusively in the *trans*-form. The ultraviolet spectrum is sharper, and contains fewer maxima than that of a primary or secondary nitrite: this again confirms that the *trans–cis*-equilibrium is right over at the *trans*-side for this tertiary nitrite.

Procedure.—The nitrite was pyrolysed under nitrogen in an apparatus similar to that described[8] earlier. The progress of the decomposition was followed by measurement of the increase in the volume of the evolved gases. Gaseous and liquid products of the decomposition were analyzed separately and estimated quantitatively.

Analysis of Gaseous Products.—The gaseous products of the decomposition included nitric oxide, nitrous oxide, nitrogen, carbon dioxide, and carbon monoxide. These had all been encountered in earlier work and were estimated in the manner described[8, 9] previously. In addition, hydrogen cyanide was identified by its infrared absorption at 3·02 μ and 14·05 μ; quantitative estimation was impossible because of its high b. p. (25°). The presence of methyl nitrite was suspected from the infrared spectrum and was confirmed by mass spectrometry; a semi-quantitative determination was made from the infrared absorptions at 6·0 μ and 12·0 μ. To determine whether ethane was a reaction product, the gaseous products were fractionated and examined by gas chromatography on a silica gel column; no ethane was detected.

Analysis of Liquid Products.—Examination of the liquid product by vapour-phase chromatography using a polyethylene glycol and a silicone oil column showed that the following compounds were present: αα-dimethylbenzyl alcohol, acetophenone, α-methylstyrene, benzoic acid, nitromethane, and water. The volatile fraction was separated by distillation into three fractions

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[10] N. Kornblum and E. P. Oliveto, *J. Amer. Chem. Soc.*, 1947, **69**, 465.
[11] C. W. Whittaker, F. O. Lundstrom, and A. R. Merz, *Ind. Eng. Chem.*, 1931, **23**, 410.
[12] P. Gray and M. J. Pearson, *Trans. Faraday Soc.*, 1963, **59**, 347.

and the infrared spectrum of each examined. The first fraction contained nitromethane (principal peaks at 6·42, 7·13, 7·27 μ) and α-methylstyrene (6·13, 11·24 μ). The remaining two fractions appeared to be principally acetophenone (5·93 μ) and αα-dimethylbenzyl alcohol (2·91 μ).

Acetophenone was characterised as its 2,4-dinitrophenylhydrazone (m. p. and mixed m. p. 236°) and was quantitatively estimated (gravimetrically) as the same derivative.

αα-Dimethylbenzyl alcohol, α-methylstyrene, and nitromethane were estimated by vapour-phase chromatography on a polyethylene glycol column at 150°. These components were determined relative to the acetophenone on the chromatogram, standardisation being achieved with calibration mixtures containing the compounds in ratios approximately the same as in the products.

Benzoic acid was characterised and estimated gravimetrically[8] as in earlier work. The gravimetric determinations agreed with estimates made on the vapour-phase chromatograms by comparing peak areas relative to acetophenone.

Distillation of the products on the vacuum line at 50° removed the acetophenone, αα-dimethylbenzyl alcohol, and any more volatile components and left a viscous, dark-red residue. The temperature was raised to 140° and a yellow oil (Found: C, 66·05; H, 5·95; N, 7·0%) slowly distilled over. The residue (Found: C, 75·0; H, 5·85; N, 6·65%) was a solid black tar. Although vapour-phase chromatography indicated the presence of three distinct compounds in the oil, these could not be separated by vacuum distillation. The infrared spectrum of the oil (in chloroform) showed $\mu_{\text{max.}}$ 6·45s, 7·46s, 6·61m, and 7·27m and the ultraviolet spectrum (in ethanol) showed strong continuous absorption in the lower-wavelength region and a pronounced maximum at 290—292 mμ. This indicates the presence of nitroso-compound.[13,14] The chemical test[7] for nitroso-compounds (diphenylamine in concentrated sulphuric acid turns blue) was also positive and it was concluded that nitrosomethane was probably present. Under the conditions of the experiments α-methylstyrene is known[15] to form small proportions of a dimer. This is a high-boiling oil and a likely constituent of the involatile fraction.

RESULTS

Decomposition of Pure Liquid αα-Dimethylbenzyl Nitrite.—Even at room temperature, when αα-dimethylbenzyl nitrite was exposed to light and air, decomposition was fairly rapid. After several hours the initial pale yellow colour of the nitrite had changed to green, and this gradually became yellow-brown. Analysis of the liquid products after a week (when decomposition was complete) showed no measurable amount of acetophenone. Difficulties experienced in the preparation of the nitrite indicated that it was very easily hydrolysed; so that decomposition in air may well be partly by hydrolysis.

Stoicheiometry.—The pure nitrite was pyrolysed in an inert atmosphere (nitrogen) at temperatures from 135° to 175°. At 132°, decomposition was slow, taking about 30 hr. to go to completion. Hence, most runs were conducted at higher temperatures and at 175° complete decomposition took only 1 hr. During decomposition, the pale yellow nitrite gradually turned red-brown and separate globules of an immiscible liquid (identified as water) were formed. About 75% of the products could be distilled to a clear liquid at 100° under reduced pressure leaving about 25% as a dark, viscous residue.

The principal products of decomposition were αα-dimethylbenzyl alcohol, acetophenone, α-methylstyrene, water, nitrogen, and nitric oxide, together with smaller quantities of benzoic acid, nitromethane, nitrous oxide, carbon dioxide, carbon monoxide, and methyl nitrite. There was also an unknown quantity of hydrogen cyanide. No ethane, benzaldehyde, or biphenyl was found.

The product yields for the decomposition of the pure nitrite at the various temperatures are given in Table 1. The relative yields showed considerable temperature-dependence; αα-dimethylbenzyl alcohol yield at 132° was twice that of the acetophenone but at 175° it was considerably less. The nitric oxide yield was much lower than that expected from the ideal Steacie equation, and it was no longer the major gaseous product (in contrast to other nitrite decompositions). Molecular nitrogen was a major product, and accounted for three times as much of the total nitrogen as did nitric oxide.

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[13] B. G. Gowenlock and J. Trotman, *J.*, 1956, 1670.

[14] P. Kabasakalian, E. R. Townley, and H. D. Yudis, *J. Amer. Chem. Soc.*, 1962, **84**, 2716.

[15] M. S. Kharasch, A. Fono, and W. Nudenberg, *J. Org. Chem.*, 1951, **16**, 113.

Decomposition at 151° may be represented by the following scheme:

$$1{\cdot}00\mathrm{Ph{\cdot}C(Me)_2{\cdot}O{\cdot}NO} \longrightarrow 0{\cdot}22\mathrm{Ph{\cdot}COMe} + 0{\cdot}40\mathrm{Ph{\cdot}C(Me)_2{\cdot}OH} + 0{\cdot}14\mathrm{Ph{\cdot}C(Me){=}CH_2} + 0{\cdot}04\mathrm{Ph{\cdot}CO_2H} + 0{\cdot}02\mathrm{MeNO_2} + 0{\cdot}21\mathrm{N_2} + 0{\cdot}08\mathrm{NO} + 0{\cdot}025\mathrm{N_2O} + 0{\cdot}063\mathrm{CO_2} + 0{\cdot}003\mathrm{CO} + 0{\cdot}02\mathrm{Me{\cdot}O{\cdot}NO} + \mathrm{C_{1{\cdot}89}H_{2{\cdot}68}O_{0{\cdot}99}N_{0{\cdot}41}}$$

Approximately 55% of the initial nitrogen was present in the gaseous products. Microanalysis showed that the nitrogen content of the liquid phase was 3·7% which is equivalent to a further 0·39 atom of nitrogen, therefore 94% of the initial nitrogen was accounted for. (Some or all of the remainder is accounted for by the hydrogen cyanide present in the gaseous phase.)

TABLE 1.

Product analysis for the decomposition of liquid αα-dimethylbenzyl nitrite (yields are expressed in moles/100 moles nitrite).

Run no.	Decomp. temp.	Decomp. time (min.)	Acetophenone	αα-Dimethylbenzyl alcohol	α-Methylstyrene	Benzoic acid	Nitromethane	N_2	NO	N_2O	CO_2	CO	$CH_3{\cdot}O{\cdot}NO$	Gas (total)
4	132°	30 (hr.)	17	34	18	4·7	3	19·3	14·8	2·6	4·0	0·7	2	42
5	132	31·5 (hr.)	17	26	26	5·8	3	19·0	14·0	3·1	5·4	0·7	2	43
8	151	330	22	39	14	4·2	2	20·4	8·2	2·2	6·4	0·4	2	39
9	151	304	22	39	14	4·3	2	21·3	8·0	2·9	6·3	0·4		41
10	151	317	22	41	14	4·6	2	21·8	8·4	2·3	6·0	0·3		40
16	151	182						10·0	5·8	0·4	1·0	0·1		18
13	151	284							7·8	1·1	4·0			36
18	168	85	31	28	19									
19	170·5	72	33	24	19									
20	175	59	35	22	21			19·0	21·0	1·8	7·3			49

During decomposition, the percentage of nitric oxide appeared to decrease and that of nitrous oxide and carbon dioxide to increase, suggesting secondary reactions and a complex mode of decomposition. The percentage of nitrogen in the gaseous phase did not vary significantly.

At 151°, about 80% of the phenyl groups were accounted for as αα-dimethylbenzyl alcohol, α-methylstyrene, acetophenone, and benzoic acid; the remainder were in the dark residue. There was just over 50% retention of the αα-dimethylbenzyl skeleton in the identified products.

Kinetics.—The rate of decomposition of αα-dimethylbenzyl nitrite was followed by measurements of the volume of evolved gas as a function of time. In Fig. 1, curves depicting gas evolution are given for decompositions at 132°, 151°, and 175° (these correspond to runs 4, 8, and 20, respectively). The curves show clearly that decomposition is autocatalytic. The plots for 132° and 151° show this markedly, whilst at 175°, when the initial decomposition is fast, autocatalysis is only apparent to a minor extent.

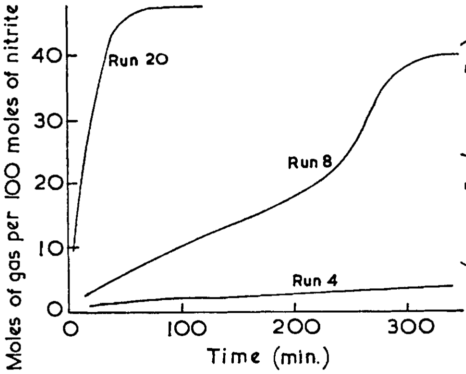

FIG. 1. Gas evolution during decomposition of liquid αα-dimethylbenzyl nitrite (results for 3 selected runs). Run 4, pure nitrite at 132°; run 8 at 151°; run 20 at 175°.

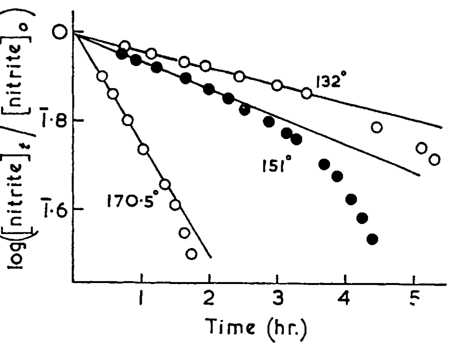

FIG. 2. First-order plots (1 + log [nitrite]$_t$/[nitrite]$_0$ against time) for thermal decomposition of pure liquid αα-dimethylbenzyl nitrite at 132°, 151°, and 170·5°, showing onset of departure from first-order kinetics.

If we assume that the volume of gas evolved at a particular time is directly proportional to the nitrite consumed (this will at least be reasonably true for the initial stages of the decomposition), then velocity constants can be determined from graphs of log[nitrite]$_t$/[nitrite]$_0$ versus time at the different temperatures studied. These plots for 132°, 151°, and 175° are shown in Fig. 2. Only the first portion, corresponding to 30—35% decomposition at the lower temperatures was linear. This indicates that decomposition was of the first order initially, but thereafter showed considerable deviations in the direction of accelerated decomposition. Values of velocity constants (k) at different temperatures (calculated from the linear portions of the first-order plots) were:

Temp. (°c)	132	151	168	170·5	175
10^5k (sec.$^{-1}$)	0·54	4·28	28·8	51·1	108

The activation energy, deduced from the variation of log$k$ with $1/T$(°K), was $E = 40$ kcal. mole^{-1}.

Decomposition of αα-Dimethylbenzyl Nitrite in Cumene.—In order to determine whether the αα-dimethylbenzyloxyl radical is formed in the initial step of the decomposition, solutions of αα-dimethylbenzyl nitrite in cumene were pyrolysed at 132° and 151°. Amounts of products (which are expressed in Table 2 as αα-dimethylbenzyl alcohol:acetophenone ratios) were determined by vapour-phase chromatography. The relative αα-dimethylbenzyl alcohol yield (which is a minimum value since some alcohol undergoes dehydration to α-methylstyrene) showed a considerable increase over that obtained from the pure nitrite.

TABLE 2.

Decomposition of αα-dimethylbenzyl nitrite in cumene at 132° and 151°.

Run no.	Temp. (°c)	Decomposition time (hr.)	Initial αα-dimethylbenzyl nitrite (mole l.$^{-1}$)	Quotient $\left(\frac{\text{αα-dimethylbenzyl alcohol}}{\text{acetophenone}}\right)$
15	132	40	0·178	11·5
17	151	6	0·042	5·5
11	151	7	0·099	2·80
14	151	6	0·118	2·14

Decomposition of Pure Liquid αα-Dimethylbenzyl Alcohol.—It is important to establish whether αα-dimethylbenzyl alcohol is dehydrated under the conditions of these experiments. Therefore, αα-dimethylbenzyl alcohol was maintained at the temperature of the nitrite decompositions. It was found that αα-dimethylbenzyl alcohol which had simply been redistilled under reduced pressure underwent considerable dehydration. Consequently, a second sample of the alcohol was carefully shaken up with sodium hydrogen carbonate and redistilled *in vacuo* several times before heating in the nitrogen atmosphere. This second sample was still olefin-free after 5 hr. at 151°. Dehydration of αα-dimethylbenzyl alcohol can thus be induced very readily by trace impurities (probably acids), although pure αα-dimethylbenzyl alcohol is stable at these temperatures.

DISCUSSION

The Initial Step.—It was at one time suggested[7] that the structurally related t-butyl nitrite decomposed by intramolecular elimination of nitrosomethane. Though the suggestion was not generally accepted,[16] it is necessary to consider the possibility in the present system. First, the fact that αα-dimethylbenzyl alcohol yields are increased considerably when decomposition is carried out in cumene solution indicates the participation of the αα-dimethylbenzyloxyl radical. Secondly, all the "αα-dimethylbenzyl-skeleton" products can be accounted for in terms of the αα-dimethylbenzyloxyl radical. Thirdly, over 50% of the nitrogen in the products is found in the gaseous phase, so that the decomposition cannot be initiated simply by intramolecular elimination of nitrosomethane. The evidence is thus in favour of the initial step (3) being the fission of the O–N bond to give the αα-dimethylbenzyloxyl radical and nitric oxide:

$$\text{Ph·CMe}_2\text{·O·NO} \longrightarrow \text{Ph·CMe}_2\text{·O·} + \text{NO} \qquad (3)$$

In this respect, αα-dimethylbenzyl nitrite falls into line with other nitrites.

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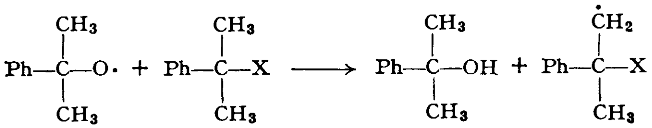
[16] P. Gray, *Chem. and Ind.*, 1960, 120.

Stoicheiometry and Origin of the Major Products.—With reaction (3) established, it is necessary to account for all the products in terms of the reactions of the αα-dimethylbenzyloxyl radical and the nitric oxide molecule. The key features of the stoicheiometry and kinetics are (i) that nearly all the nitrogen in the gas phase is accounted for as nitrogen, nitric oxide, and nitrous oxide, (ii) that nearly all the carbon ends as αα-dimethylbenzyl alcohol, acetophenone, α-methylstyrene, benzoic acid, and carbon dioxide, and (iii) that decomposition is markedly autocatalytic. The degree of retention of the αα-dimethylbenzyloxyl skeleton in the carbon products indicates that the αα-dimethylbenzyloxyl radical has a marked stability at these temperatures.

αα-Dimethylbenzyl alcohol arises from the αα-dimethylbenzyloxyl radical by the abstraction of a hydrogen atom from some substrate present in the system. Possible substrates are other compounds with the αα-dimethylbenzyl skeleton, [though these are not very ready sources of hydrogen, since the removal of primary hydrogen as in reaction (4) is not energetically favoured]:



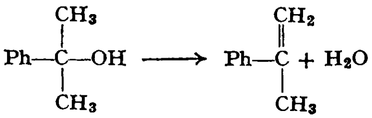
$$\text{Ph—}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\text{—O}\cdot + \text{Ph—}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\text{—X} \longrightarrow \text{Ph—}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\text{—OH} + \text{Ph—}\overset{\displaystyle \dot{C}H_2}{\underset{\displaystyle CH_3}{C}}\text{—X}$$

The fate of the free radical formed in the above reaction has not been determined but it would probably combine with nitric oxide to form a nitroso-compound. An alternative source of hydrogen atoms is nitroxyl:

$$\text{Ph}\cdot\text{CMe}_2\cdot\text{O}\cdot + \text{HNO} \longrightarrow \text{Ph}\cdot\text{CMe}_2\cdot\text{OH} + \text{NO} \qquad (5)$$

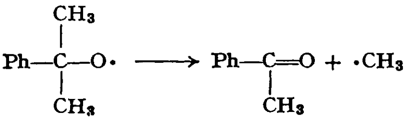
This has previously been proposed as a substrate in the decompositions of benzyl,[8] cyclohexyl,[17] and 1-phenylethyl[9] nitrites. There are other plausible substrates, *e.g.*, α-methylstyrene, acetophenone, and water. However, as there is water present among the products, and as αα-dimethylbenzyl nitrite is very readily hydrolysed, it is likely that some of the αα-dimethylbenzyl alcohol is formed from the nitrite by hydrolysis.

α-Methylstyrene cannot very feasibly arise by any direct termination reactions of the αα-dimethylbenzyloxyl radical. It is most likely to be formed by dehydration of αα-dimethylbenzyl alcohol [reaction (6)]; this is borne out by the large quantities of water found in the products. Experiments showed (see also Kharasch[15]) that only slight traces of acids are necessary to catalyse the dehydration. There are such acids present in this system, *viz.*, benzoic acid and hydrogen cyanide. Therefore it is presumed that α-methylstyrene is formed by the acid-catalysed dehydration of αα-dimethylbenzyl alcohol in a reaction secondary to the principal decomposition. Theoretically, α-methylstyrene could also be formed directly from αα-dimethylbenzyl nitrite by intramolecular elimination of nitrous acid. Although this is believed to occur in the decomposition at higher temperatures of the isomeric nitroparaffins, there is as yet no positive evidence of it occurring in nitrite decompositions.



$$\text{Ph—}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\text{—OH} \longrightarrow \text{Ph—}\overset{\displaystyle CH_2}{\underset{\displaystyle CH_3}{\overset{\|}{C}}} + H_2O \qquad (6)$$

Acetophenone is formed directly from the αα-dimethylbenzyloxyl radical by cleavage [reaction (7)] of one of the carbon–methyl bonds. Since no evidence has been found of any free



$$\text{Ph—}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\text{—O}\cdot \longrightarrow \text{Ph—}\underset{\displaystyle CH_3}{C}\text{=O} + \cdot CH_3 \qquad (7)$$

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[17] P. Gray, P. Rathbone, and A. Williams, *J.*, 1961, 2620.

phenyl radicals and since there is no acetone in the reaction products, breakdown must occur by the rupture of the carbon–methyl bond and carbon–phenyl bond-fission is insignificant.

For every molecule of acetophenone formed, one methyl radical is generated. There are several possible fates for the methyl radical (combination in pairs to give ethane, abstractions of hydrogen to give methane, addition to α-methylstyrene, and reaction with nitric oxide to give nitrosomethane). Since ethane was absent, reaction (8) was not occurring in the present system. Methane certainly was not a major product. Methyl radicals probably add to α-methylstyrene in small but unknown proportions. Nitrosomethane is known to be present and is probably the principal fate for methyl radicals.

$$\cdot CH_3 + \cdot CH_3 \longrightarrow C_2H_6 \tag{8}$$

$$\cdot CH_3 + RH \longrightarrow CH_4 + R\cdot \tag{9}$$

$$\cdot CH_3 + NO(\text{or } RNO) \longrightarrow CH_3NO(\text{or } + R\cdot) \tag{10}$$

In the investigation of the thermal decomposition of 1-phenylethyl nitrite,[9] it was shown that the origin of benzoic acid was oxidation of the acetophenone formed, brought about by oxides of nitrogen. As acetophenone is a product of this decomposition also, it is likely that benzoic acid is formed here by a similar mechanism.

The nitrogenous products in the liquid phase have not been conclusively identified, but it is possible to consider some of the reactions involving nitrogen which are taking place.

Nitrosomethane may arise through two possible reactions. The first is the combination of a methyl radical with nitric oxide [reaction (11)], and the second, the abstraction of nitric oxide from the parent nitrate by a methyl radical [reaction (12)]:

$$\cdot CH_3 + NO \longrightarrow CH_3NO \tag{11}$$

$$\cdot CH_3 + Ph\cdot CMe_2\cdot O\cdot NO \longrightarrow CH_3NO + Ph\cdot CMe_2\cdot O\cdot \tag{12}$$

The abstraction reaction is well authenticated[18] as it has recently been shown to occur in the decomposition of methyl, 1-methylbutyl, and t-butyl nitrites in the liquid phase.

The presence of hydrogen cyanide in the gaseous products is further indication that nitrosomethane may be formed at an intermediate stage of the decomposition. The following series of reactions is well established:

$$CH_3\cdot NO[\rightleftharpoons (CH_3\cdot NO)_2] \longrightarrow CH_2{:}N\cdot OH \longrightarrow HCN + H_2O$$

Levy[19] has shown that the decomposition of formaldoxime in the above sequence of reactions is rapid at 150°. In addition, polymers of formaldoxime have been isolated from systems containing nitrosomethane. The other relevant fates that have been observed for nitrosomethane are addition reactions with (i) methyl radicals[20] and (ii) substituted ethylenes[21] to give four-membered rings. Both methyl radicals and α-methylstyrene are formed in appreciable amounts, and are likely to react with nitrosomethane.

Nitromethane could arise in two ways. The first is the oxidation by NO of the nitrosomethane, the precursor postulated[19] by Levy who found nitromethane among the products of decomposition of t-butyl nitrite. The second way is the combination[22] of methyl radical and nitrogen dioxide (indications are that NO_2 is present in small quantities).

Nitric oxide is formed in the initial step. The yields are very low compared with those expected on the basis of equation (1). The yields also show fluctuations with temperature, somewhat similar to those shown by α-methylstyrene. The reduced nitrogen content in the gaseous products compared with other nitrite decompositions[8,9] is entirely due to reduced nitric oxide yields. Nitric oxide must be removed in secondary reactions, *e.g.*, with methyl radicals.

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[18] P. Gray and P. Rathbone, *Proc. Chem. Soc.*, 1960, 316; J. E. Curran, M.Sc. Thesis, Leeds, 1963.
[19] J. B. Levy, *Ind. Eng. Chem.*, 1956, **48**, 762.
[20] L. Phillips, *Proc. Chem. Soc.*, 1961, 204.
[21] B. G. Gowenlock and W. Luttke, *Quart. Rev.*, 1958, **12**, 321.
[22] E. A. Arden and L. Phillips, *Proc. Chem. Soc.*, 1962, 354.

Nitrous oxide is produced by the reduction of nitric oxide. Its yield is only 3%. It is now commonly proposed that nitroxyl is the precursor of nitrous oxide in nitrite decomposition systems, though this rests more on plausibility than proof. HNO originates by reaction (13), where RH is any of the substrates discussed in the formation of αα-dimethylbenzyl alcohol:

$$RH + NO \longrightarrow R\cdot + HNO \tag{13}$$

$$2HNO \longrightarrow N_2O + H_2O \tag{14}$$

Nitrogen must arise by the reduction, directly or indirectly, of nitric oxide, probably by a mechanism similar to that recently suggested[22] by Arden and Phillips.

Autocatalysis.—The precise nature of the catalytic effect is not known. There are three reactions which probably contribute to the observed autocatalysis. The first is the induced decomposition of the nitrite brought about by a methyl radical abstracting a molecule of nitric oxide from the parent nitrite. (This is potentially a methyl-radical chain-reaction.) The second is hydrolysis of αα-dimethylbenzyl nitrite, which occurs in the later stages of the decomposition: evidence for this induced decomposition has already been put foward. The third possibility arises from a comparison with the thermal decomposition[9] of 1-phenylethyl nitrite. In that case, there was only a slight autocatalytic affect which was attributed to the oxidation of acetophenone to benzoic acid by oxides of nitrogen. As all the necessary chemical components are present in this decomposition it is likely that this same oxidation contributes to accelerated decomposition here. The overall decomposition is too complex for any precise conclusions to be drawn about the relative contributions.

Stability of the αα-Dimethylbenzyloxyl Radical.—If the stability of the αα-dimethylbenzyloxyl radical is assessed by the ratio of αα-dimethylbenzyl alcohol to acetophenone found in the final products, then there is decreasing stability with increasing temperature. At 132°, the stability ratio is 2, whilst at 175° it has fallen to 0·6. Thus, the αα-dimethylbenzyloxyl radical in the nitrite system is comparatively unstable at higher temperatures. This is apparently a complete contrast to benzyloxyl and 1-phenylethoxyl radicals which show[9] complete stability in the irnitrite systems, but it must be emphasised that, for the αα-dimethylbenzyloxyl radical, opportunities for disproportionation are fewer.

Decomposition of the αα-dimethylbenzyloxyl radical has here been found to occur exclusively by fission of the C–Me bond. This is in agreement with thermochemical predictions,[2] as elimination of a methyl group requires an enthalpy increase of 0·3 kcal. mole^{-1}, whilst a phenyl group would require 8·0 kcal. mole^{-1}. However, this does not mean that the methyl group is split off easily; it has been found[23] that decomposition of the 1-methyl-1-phenylpropoxy-radical is almost exclusively by loss of ethyl radical (where methyl and ethyl groups compete for elimination at 25° it has been shown[23] that loss of methyl is more than 100 times slower than ethyl). Kabasakalian *et al.*[24] found that the difficulty of elimination of a methyl group from the t-butoxyl radical leads to a 3-fold reduction in the quantum yield for the photolysis of t-butyl nitrite compared with that for a primary nitrite. Thus, the αα-dimethylbenzyloxyl radical has a comparatively long lifetime, certainly long enough for some hydrogen-atom transfer to take place to give αα-dimethylbenzyl alcohol.

Although αα-dimethylbenzyl nitrite has not been previously studied, the αα-dimethylbenzyloxyl radical has been produced by the thermal and photochemical decomposition of both peroxide and hydroperoxide. In all the systems examined, both αα-dimethylbenzyl alcohol and acetophenone were formed; though acetone was found in the photochemical decomposition[25] of αα-dimethylbenzyl peroxide and hydroperoxide in carbon tetrachloride at 2537 Å, this is a situation involving surplus energy. In the thermal decompositions, the αα-dimethylbenzyl alcohol : acetophenone ratios depend considerably upon the temperature and solvent used; Kharasch *et al.*[26] found dodecane was twice as efficient as cumene for donating

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[23] J. Kochi, *J. Amer. Chem. Soc.*, 1962, **84**, 1193.

[24] P. Kabasakalian, E. R. Townley, and H. D. Yudis, *J. Amer. Chem. Soc.*, 1962, **84**, 2718.

[25] R. G. W. Norrish and M. H. Searby, *Proc. Roy. Soc.*, 1956, *A*, **237**, 464.

[26] M. S. Kharasch, F. S. Aromoto, and W. Nudenberg, *J. Org. Chem.*, 1951, **16**, 105.

hydrogen atoms to the αα-dimethylbenzyloxyl radical. Decomposition of αα-dimethylbenzyl peroxide in different solvents has led[26, 27] to stability ratios of 0·3—2·0 in the same temperature range as that studied here. Workers on αα-dimethylbenzyl hydroperoxide found[15, 28, 29] somewhat larger values of the stability ratio than were obtained from the peroxide (generally in the range 2—3); α-methylstyrene was also found in some cases. Bailey *et al.*[27] measured a series of stability ratios at different temperatures in cumene as solvent and found the difference in activation energy between the processes producing acetophenone and αα-dimethylbenzyl alcohol, *i.e.*, $E_{\text{fission}} - E_{\text{abstraction}}$, was 7·3 kcal. mole^{-1}.

The similarities between the products obtained from αα-dimethylbenzyl nitrite and those obtained from αα-dimethylbenzyl peroxide and hydroperoxide leave no doubt that the αα-dimethylbenzyloxyl radical is a common intermediate. The relative yields of αα-dimethylbenzyl alcohol and acetophenone are not very easily compared owing to the different availability of hydrogen atoms. However, the yields of αα-dimethylbenzyl alcohol from the decomposition of αα-dimethylbenzyl nitrite indicate that there must be a fairly ready source of hydrogen, and one can only conclude that this probably involves nitric oxide in some form, for example as nitroxyl. In turn, this may well be related to the fairly extensive reduction of nitric oxide which is found to occur in the system.

In conclusion it is interesting to consider an analogy between nitrite and hydroperoxide. In the thermal decomposition[29] of αα-dimethybenzyl hydroperoxide, some of the methyl radicals formed in the breakdown of the αα-dimethylbenzyloxyl radical to acetophenone, abstract a hydroxyl group from the parent hydroperoxide, giving methanol. In the decomposition of αα-dimethylbenzyl nitrite, some of the methyl radicals abstract nitric oxide to give nitrosomethane.

$$\mathrm{CH_3\cdot + ROOH \longrightarrow CH_3OH + RO\cdot}$$

$$\mathrm{CH_3\cdot + R{\cdot}O{\cdot}NO \longrightarrow CH_3NO + RO\cdot}$$

These two reactions, involving the abstraction by a methyl radical of diatomic groups from the parent molecules, are unusual, very similar in nature, and afford a novel parallel between the hydroperoxide and nitrite decompositions.

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[29] G. H. Twigg, *Discuss. Faraday Soc.*, 1953, **14**, 240; G. H. Twigg, G. W. Godin, H. C. Bailey, and J. Holden, *Erdöl u. Kohle*, 1962, **17**, 74.