780. *1-Phenylethoxyl Radicals in the Thermal Decomposition of 1-Phenylethyl Nitrite.*

By Peter Gray, M. J. Pearson, and P. Rathbone.

The thermal decomposition of 1-phenylethyl nitrite has been studied in solution and as the pure liquid in the temperature range 80—140° c. Decomposition is initiated by O–N bond fission; in cumene, essentially complete conversion into 1-phenylethanol occurs: $\mathrm{Ph{\cdot}CHMe{\cdot}O{\cdot}NO} \longrightarrow \mathrm{Ph{\cdot}CHMe{\cdot}O{\cdot}} + \mathrm{NO}$; $\mathrm{Ph{\cdot}CHMe{\cdot}O{\cdot}} \xrightarrow{\mathrm{XH}} \mathrm{Ph{\cdot}CHMe{\cdot}OH}$. Decomposition of the pure liquid follows approximately first-order kinetics and leads mainly to acetophenone and 1-phenylethanol; benzoic acid is a minor product. A significant portion of the nitric oxide is reduced to nitrous oxide and nitrogen. At 132°, decomposition may be represented by the overall equation: $1{\cdot}00\mathrm{Ph{\cdot}CHMe{\cdot}O{\cdot}NO} \longrightarrow 0{\cdot}55\mathrm{Ph{\cdot}COMe} + 0{\cdot}20\mathrm{Ph{\cdot}CHMe{\cdot}OH} + 0{\cdot}05\mathrm{Ph{\cdot}CO_2H} + 0{\cdot}55\mathrm{NO} + 0{\cdot}15\mathrm{N_2} + 0{\cdot}028\mathrm{N_2O} + 0{\cdot}030\mathrm{CO_2} + \mathrm{C_{1{\cdot}62}H_{2{\cdot}30}O_{0{\cdot}51}N_{0{\cdot}09}}$.

The 1-phenylethoxyl skeleton is largely retained in the products, indicating that the free 1-phenylethoxyl radical is fairly stable. Interrelations between 1-phenylethyl nitrite and benzyl nitrite and between 1-phenylethoxyl and other alkoxyl radicals are examined.

Early work[1,2] on the thermal decomposition of nitrite esters led to the adoption of equations (1) and (2) respectively for the initial step and for the overall stoicheiometry:

$$(1)\quad \mathrm{RR'CH{\cdot}O{\cdot}NO} \longrightarrow \mathrm{RR'CH{\cdot}O{\cdot}} + \mathrm{NO}$$

$$(2)\quad \mathrm{2RR'CH{\cdot}O{\cdot}NO} \longrightarrow \mathrm{RR'CH{\cdot}OH} + \mathrm{RR'CO} + \mathrm{NO}$$

Nitrite decompositions do not, however, end with the products of reactions (2) even

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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.

though they are initiated[3-7] according to reaction (1): some nitric oxide is always reduced[5-8] and some of the alkoxyl radicals decompose.[2,9]

Comparatively little has been done on the decomposition of aryl-substituted nitrites. In recent work[5] on benzyl nitrite it was found that nitric oxide and benzyloxyl radicals were formed initially according to reaction (1) (R = Ph, R′ = H). The major organic products are benzaldehyde, benzyl alcohol, and benzoic acid (in that order of importance). The nitric oxide is extensively reduced to nitrous oxide and nitrogen. Reaction is autocatalytic and the benzoyl radical Ph·CO·, formed from benzaldehyde, plays an important part in stoicheiometry and kinetics.

4-Nitrobenzyl nitrite[10] has also been studied. It is very labile and decomposes even at room temperature. The final products (per mole of initial nitrite) are 0·25 mole of *p*-nitrobenzaldehyde and 0·25 mole of its acetal with 4-nitrobenzyl alcohol. These results are explicable[5] on a " normal " free-radical mechanism, though this explanation has not been subjected to an experimental test.

Benzyl nitrite and 4-nitrobenzyl nitrite are primary nitrites; whether a secondary homologue will show the same behaviour is unknown.

Accordingly, this paper describes experiments on the thermal decomposition of 1-phenylethyl nitrite. Its aims are to establish the nature of the initial step, the stoicheiometry of decomposition, and the broad outlines of the kinetics and mechanism. The differences and similarities found between the primary benzyl nitrite and the secondary 1-phenylethyl nitrite are discussed in terms of the substitution of methyl for hydrogen and of the thermochemistry[11] of the two alkoxyl radicals involved.

EXPERIMENTAL

Materials.—Attempts to prepare 1-phenylethyl nitrite by the addition of 1-phenylethanol, dissolved in sulphuric acid, to a cold solution of sodium nitrite failed. The method of Chrétien and Longi[12] (in which aqueous aluminium sulphate is the " acid ") was found to be successful, and yields of at least 50% of 1-phenylethyl nitrite were obtained. The crude product was washed successively with saturated sodium chloride and sodium hydrogen carbonate solution, dried (MgO), and purified and distilled *in vacuo*, the middle portion only being retained. The purified nitrite was stored *in vacuo* in the dark in a trap cooled in liquid nitrogen.

The 1-phenylethanol, cumene, benzaldehyde, and acetophenone were purchased from B.D.H. The benzaldehyde and acetophenone were purified by successive fractional distillations *in vacuo*, in order to remove any traces of acids (especially benzoic acid). Oxygen-free nitrogen was obtained from British Oxygen Co. Ltd.

Spectra.—As infrared and ultraviolet spectra 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 the following wavelengths (μ): 3·30w, 3·35w, 3·40w, 6·05vs, 6·18m, 6·66w, 6·89m, 7·24s, 7·35s, 7·53w, 7·62w, 7·75vw, 8·25w, 9·30m, 9·69vw, 9·80vw, 10·87m, 12·30vs, 12·46vs, 13·15vs, 14·27vs.

Ultraviolet spectra of solutions in light petroleum were recorded on an Optica "A" double-beam absorption spectrometer. Absorption maxima (mμ) and extinction coefficients are: 325 infl. (ε 39), 340 (ε 49), 350 (ε 66), 365 (ε 82), 378 (ε 80), 394 infl. (ε 50). The absorption maxima of the ultraviolet spectrum were not as sharp as were those of benzyl nitrite.[5] Tarte has commented[13] on a similar decrease in definition in other secondary nitrites.

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[3] Gowenlock and Trotman, *J.*, 1956, 1670; Lossing, personal communication, 1959.
[4] Yoffe, *Research*, 1954, **7**, 44.
[5] Gray, Rathbone, and Williams, *J.*, 1960, 3932.
[6] Gingras and Waters, *J.*, 1954, 3508.
[7] Kornblum and Oliveto, *J. Amer. Chem. Soc.*, 1949, **71**, 226.
[8] Levy, *J. Amer. Chem. Soc.*, 1956, **78**, 1780.
[9] Adler, Pratt, and Gray, *Chem. and Ind.*, 1955, 1517.
[10] Kornblum and Weaver, *J. Org. Chem.*, 1958, **23**, 1213.
[11] Gray and Williams, *Chem. Rev.*, 1959, **59**, 239.
[12] Chrétien and Longi, *Compt. rend.*, 1945, **220**, 746.
[13] Tarte, *J. Chem. Phys.*, 1952, **20**, 1570.

Procedure.—The decompositions were carried out in a nitrogen atmosphere in the apparatus described previously.[5,14] The gaseous and liquid products were analysed quantitatively. The progress of the reaction was followed by measurement of the gas evolved.

Analysis of gaseous products. The gaseous product of decomposition contained nitrogen, nitric oxide, nitrous oxide, and carbon dioxide. The analytical scheme adopted for these gases has been previously described.[5] Total nitrogen was estimated by condensing the other gases at $-196°$; that part of it arising from reaction was obtained by subtracting the known amount initially present. Nitric oxide, nitrous oxide, and carbon dioxide were estimated by infrared spectroscopy.

Analysis of liquid products. The liquid product of decomposition contained acetophenone, 1-phenylethanol, and a little benzoic acid. Its constituents were separated on a gas-chromatography column. The peaks due to acetophenone and 1-phenylethanol were readily identified; these were the predominant products. Two higher-boiling constituents were present, one of which was identified as being benzoic acid. Other constituents present in minute proportions were not identified.

The acetophenone and the 1-phenylethanol were further identified by infrared analysis; no conclusive evidence of other products was obtained by this method, though the spectrum of the more involatile fraction of the products showed a strong absorption at 9·2 μ which could be due to a benzoate ester.

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

The 1-phenylethanol was estimated quantitatively by infrared spectroscopy. Solutions were made up in cumene or chlorobenzene and the intensity of the 2·70 μ peak (hydroxyl stretching frequency) was determined and compared against that of standard solutions. 1-Phenylethanol was also estimated by gas chromatography on a polyethylene glycol (M ~1500) column, which separated it from the acetophenone very satisfactorily.

Benzoic acid was extracted from the liquid products with sodium hydroxide. It was characterised by its m. p. and mixed m. p. (122°) and estimated quantitatively by titration against standard sodium hydroxide (a little pyridine being added before titration to increase the solubility of the liquid products).

To determine whether acetic acid was a product of decomposition the liquid product was fractionated *in vacuo* at 100°. It gave a colourless distillate (mainly 1-phenylethanol and acetophenone) and an involatile, viscous, dark-red residue. The distillate was not acidic, and it is therefore most unlikely that acetic acid (b. p. 119°) is a product of the decomposition. No acetic acid was detected from the vapour-phase chromatogram.

RESULTS

Decomposition of Pure Liquid 1-Phenylethyl Nitrite.—1-Phenylethyl nitrite, like benzyl nitrite, is comparatively unstable; when kept in the light in an open vessel, the pale yellow nitrite gradually darkens and after about a week is deep yellow. Decomposition is negligible *in vacuo* in the dark in a trap cooled in liquid nitrogen.

Stoicheiometry.—Decomposition of the pure liquid was carried out in nitrogen at 80—140°. The pale yellow nitrite gradually became red-brown. The products of decomposition consist of acetophenone, 1-phenylethanol, nitric oxide, nitrogen, and small quantities of benzoic acid, nitrous oxide, and carbon dioxide. Neither benzaldehyde nor acetaldehyde or acetic acid was found.

The yields of the major products of decomposition of the pure liquid at 100°, 110°, and 132° are given in Table 1. The yield of acetophenone (55%) is considerably greater than twice the yield of 1-phenylethanol; the yield of benzoic acid is only 5%. The yield of nitric oxide is only 55% of that expected from the Steacie equation,[1] though it is the major gaseous product. About 90·6% of the nitrogen is present in the gaseous products. The liquid product had a nitrogen content of 0·95%, corresponding to a further 8·7% of the original nitrogen: thus within experimental error more than 99% of the total nitrogen is accounted for. About 80%

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[14] Gray, Rathbone, and Williams, *J.*, 1961, 2620.

TABLE 1. *Product analysis of decomposition of liquid* 1-*phenylethyl nitrite* (*in an inert atmosphere*) *and the influence on the stoicheiometry of added acetophenone and benzaldehyde.* (*The products are expressed in moles per* 100 *moles of initial nitrite.*)

Run no.	Decomp. temp.	Decomp. time (min.)	Product yields							
			Ph·CO·Me	Ph·CHMe·OH	$Ph\cdot CO_2H$	NO	N_2O	CO_2	N_2	Gas (total)
			Pure 1-*phenylethyl nitrite*							
42	100°	428	58	26					18	70
43		900			4·6				15	68
44		1140			5·7				19	68
40	110	367	56	25	4·3					67
41	,,	515							15	70
36	132	9·5				21	0·35	0	6·2	28
37	,,	84	53		5·5	58	1·4	0·6	15	75
38	,,	172	55	20	5·2	55	2·7	3·3	13	76
39	,,	202	56		4·8	54	2·8	2·7	16	74
			1-*Phenylethyl nitrite in the presence of initially added acetophenone*							
47	132	14 hr.	41 *		14	23	4·0	6·4	23	57
			1-*Phenylethyl nitrite in the presence of initially added benzaldehyde*							
45	132	65			18	38	1·8	1·2	22	63

* Net gain; total acetophenone 150 moles, of which 109 were added initially.

of the phenyl groups are accounted for as Ph·COMe, Ph·CHMe·OH, and $Ph\cdot CO_2H$. Decomposition at 132° may be represented by the overall scheme:

$$1{\cdot}00Ph\cdot CHMe\cdot O\cdot NO \longrightarrow 0{\cdot}55Ph\cdot COMe + 0{\cdot}20Ph\cdot CHMe\cdot OH + 0{\cdot}05Ph\cdot CO_2H + 0{\cdot}55NO + 0{\cdot}15N_2 + 0{\cdot}028N_2O + 0{\cdot}030CO_2 + C_{1\cdot 62}H_{2\cdot 30}O_{0\cdot 51}N_{0\cdot 09}.$$

The percentage of the major gaseous products (nitric oxide and nitrogen) does not seem to vary appreciably with percentage decomposition in the range of conditions studied. However, the percentages of the minor products (nitrous oxide and carbon dioxide) appear to increase considerably with percentage decomposition. At 35% decomposition, the gaseous products contain 1·3% of nitrous oxide; this value has increased to 3·8% by complete decomposition.

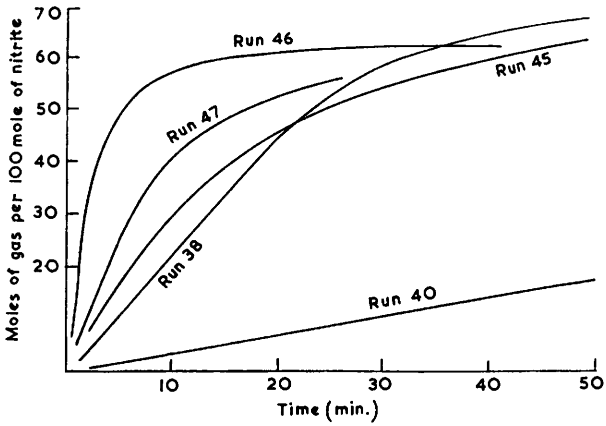

FIG. 1. *Gas evolution during decomposition of liquid* 1-*phenylethyl nitrite* (*results for* 5 *selected runs*). *Run* 38, *pure nitrite at* 132°; *run* 40, *pure nitrite at* 110°; *runs* 45 *and* 46, *nitrite plus initially added benzaldehyde at* 132° (*molar ratios* Ph·CHMe·O·NO : Ph·CHO *were* 2 : 1 *and* 1 : 1 *respectively*); *run* 47, *nitrite plus initially added acetophenone at* 132° (*molar ratio* Ph·CHMe·O·NO : Ph·COMe *was* 1 : 1·09.)

Variation in temperature in the range 80—140° does not appreciably affect the nature and yields of the products. There appears to be a slight increase in the total yield of gaseous products with increase in decomposition temperature, although, in the light of the slight variations in gaseous yields experienced in these decompositions, this may not be significant.

Kinetics.—The kinetics of the decomposition of the pure liquid were followed by measuring gas evolution as a function of time. In Fig. 1, curves of gas evolution with time are given; the results are expressed in terms of moles of gas produced from 100 moles of initial nitrite. Curves 38 and 40 are the curves for decomposition of the pure liquid (in the absence of any additive) at temperatures of 132° and 110°, respectively. The half life at 80° is about 14 hr., and at 132° is 16 min.

If it is assumed that throughout the decomposition the composition of the gaseous products remains virtually unchanged, and that the ratio of nitrogen in the liquid decomposition products to nitrogen in the gaseous products remains sensibly constant, then the concentration of unchanged nitrite may be obtained as a function of time. In Fig. 2, log{[nitrite]/[nitrite]$_0$} is plotted as a function of time for decompositions carried out at 80°, 110°, and 132°. The first portion of the plot, corresponding to about the first 50% of decomposition, is linear, indicating that the decomposition is initially of the first order. After about 50% decomposition, the rate becomes a little faster than that expected from the initial first-order rate-constant.

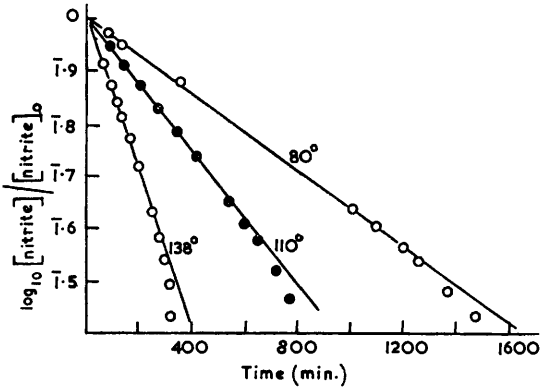

FIG. 2. *First-order plots* (log [nitrite]/[nitrite]$_0$ *against time*) *for thermal decomposition of pure liquid* 1-*phenylethyl nitrite at* 80°, 110°, *and* 138°, *shewing eventual departure from first-order kinetics.*

(*Graphs are displayed together for convenience. Abscissæ* (*elapsed times*) *are correct for* 80° *results*; *divide by* 16 *for* 110° *and by* 35 *for* 138°).

Values of velocity constants *k* at different temperatures (calculated from the linear portions of the plots on the first-order law) are:

Temp.	80°	100°	110·5°	118°	132°	138°
10^5k (sec.$^{-1}$)	1·38	5·24 *	9·36 *	26·6	75·7 *	117

* Mean of two determinations; errors *ca.* 5%.

Approximate Arrhenius parameters corresponding to the variation of log *k* with $1/T$(° K) implied by these values have been derived (see Fig. 3). Though, in the absence of a detailed investigation, they are subject to considerable uncertainty, they may be set at E = *ca.* 25 kcal. mole^{-1} and A = *ca.* 10^{10} sec.$^{-1}$.

Decomposition of 1-*Phenylethyl Nitrite in Cumene Solution.*—To establish whether 1-phenylethyl nitrite decomposes initially to an alkoxyl radical and nitric oxide, it was decomposed in the hydrogen-donor solvent, cumene. ~0·1M-Solutions of the nitrite in cumene were decomposed to completion (12—14 hr. at 132°). Complete conversion into 1-phenylethanol was achieved. Typical results were: initial concn. 0·090 mole l.$^{-1}$, alcohol yield 109%; initial concn. 0·147 mole l.$^{-1}$, alcohol yield 110%.

Decomposition of 1-*Phenylethyl Nitrite in the Presence of Added Acetophenone.*—Acetophenone is a major product of the decomposition and may influence its course just as benzaldehyde influences the course of decomposition of benzyl nitrite. To see if this is so, decomposition in the presence of initially added acetophenone was examined in outline. A mixture consisting of about equimolar quantities of acetophenone and 1-phenylethyl nitrite was decomposed for several hours at 132°. The amounts of benzoic acid formed and of acetophenone remaining at the end of the reaction and the yields of gaseous products were determined; the results are shown in Table 1. It is seen that there is a net increase in the acetophenone content of 40 moles (per 100 moles initial nitrite); in the normally decomposed nitrite, the yield is 55 moles per cent. The yield of benzoic acid is considerably greater than in the decomposition of the pure nitrite, as is also the yield of nitrogen; however, the yield of nitric oxide is less.

Initially added acetophenone also accelerates the rate of decomposition to some extent, as indicated in curve 47 of Fig. 2 which shows the decomposition curve for added acetophenone. The slight acceleration in rate of decomposition due to acetophenone probably accounts for the deviation from first-order kinetics in the later stages of the decomposition of the undiluted nitrite.

Decomposition of 1-*Phenylethyl Nitrite in the Presence of Added Benzaldehyde.*—Though benzaldehyde has not been detected in the decomposition products of pure 1-phenylethyl nitrite, there is a possibility that a small amount may have been produced and then destroyed in subsequent reactions. The effect of initially added benzaldehyde upon the decomposition of 1-phenylethyl nitrite was therefore investigated.

Solutions containing 1-phenylethyl nitrite and benzaldehyde in molar ratios 2 : 1 and 6 : 1 were decomposed (at 132°) for about 1—2 hr. The results for these two runs are shown in Fig. 1, curves 45 and 46. It is seen (Fig. 1) that benzaldehyde appreciably accelerates the rate of decomposition of the nitrite; its effect is about 6 times greater than that produced by acetophenone. The catalytic effect of the benzaldehyde is approximately proportional to the first power of the benzaldehyde concentration.

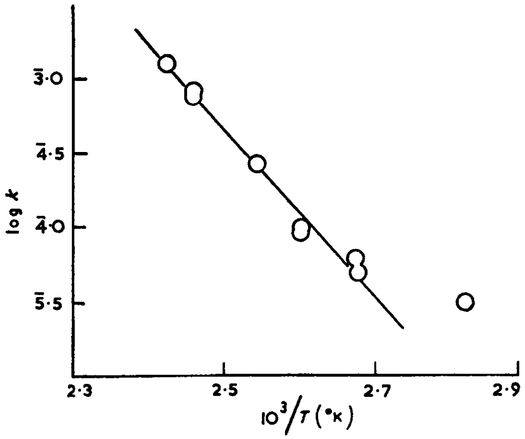

Fig. 3. *Arrhenius plot for first-order portion of thermal decomposition of pure liquid* 1-*phenylethyl nitrite.*

In Run 45, the benzoic acid and gaseous products were analysed quantitatively.

Discussion

The Initial Step.—The products of decomposition in the liquid phase and the enhanced yields of 1-phenylethanol obtained in the presence of the hydrogen-donor cumene, provide evidence that the decomposition in both systems begins by fission of the oxygen–nitrogen bond:

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

In this respect, 1-phenylethyl nitrite resembles other nitrites [1-9] and, in particular, benzyl nitrite. The decomposition of 4-nitrobenzyl nitrite [10] may be similarly interpreted.[5]

A personal communication from Professor N. Kornblum [15] provides some further evidence that the 1-phenylethoxyl radical is formed and that it does not undergo rearrangement. When L-1-phenylethyl nitrite was decomposed at 100° for 24 hr. in the liquid phase L-1-phenylethanol was produced and it had at least 67% retention of optical purity.

Kornblum and De La Mare [16] reported that 1-phenylethoxyl radicals formed during the thermal decomposition of 1-phenylethyl t-butyl peroxide would not abstract hydrogen from cumene at 130° and that, although at about the same temperature (125°) they would abstract hydrogen from thiophenol, only 55—57% yields of the alcohol were obtained.

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[15] Kornblum, personal communication; see also Kornblum, Fishbein, and Smiley, *J. Amer. Chem. Soc.*, 1955, **77**, 6261.

[16] Kornblum and De La Mare, *J. Amer. Chem. Soc.*, 1952, **74**, 3079.

In contrast with this we find that at 130° in dilute cumene (XH) solution, hydrogen abstraction occurs extensively and high (100%) yields of alcohol are obtained:

$$(3)\ \mathrm{Ph{\cdot}CH{\cdot}MeO{\cdot} + XH \longrightarrow Ph{\cdot}CHMe{\cdot}OH + X.}$$

Once again, dimerization to bi-α-cumyl is not observed and the possible fates of the cumyl radicals are discussed elsewhere.[5,14]

Stoicheiometry and the Origin of the Major Products.—Having established the initial step as the formation of nitric oxide and free 1-phenylethoxyl radicals, we must be able to account for the observed stoicheiometry and kinetics in terms of the reactions of these species. The key features are (1) that nearly all the nitrogen is accounted for by nitric oxide, nitrous oxide, and nitrogen, and (2) that nearly all the carbon ends as acetophenone, 1-phenylethanol, benzoic acid, and carbon dioxide. The fact that there is very considerable survival of the Ph•C•Me skeleton indicates that the 1-phenylethoxyl radical does not undergo much decomposition. In this it resembles benzyloxyl[5] and comparison with benzyl nitrite is generally valuable in considering the behaviour of 1-phenylethyl nitrite.

(*a*) Nitric oxide, the major gaseous product (55% yield), is accounted for by the initial step. The possible reversibility of this reaction cannot influence the stoicheiometry.

(*b*) Nitrous oxide is produced by the reduction of nitric oxide. Its yield is only 2·8%. In work on ethyl nitrite, Levy postulated the intervention of nitroxyl HNO; and this species (which is not a free radical) or its isomer HON (which is a " diradical ") has been invoked generally in nitrite pyrolyses as the precursor of nitrous oxide. It is formed when nitric oxide abstracts hydrogen from the 1-phenylethoxyl radical:

$$(4)\ \mathrm{Ph{\cdot}CHMe{\cdot}O{\cdot} + NO \longrightarrow Ph{\cdot}COMe + HNO}$$

$$(5)\ \mathrm{2HNO \longrightarrow N_2O + H_2O}$$

Although HNO is well authenticated,[17] its chemistry still rests more on plausible inferences than on definitely demonstrated facts.

(*c*) Nitrogen also must come from the reduction of nitric oxide. Its yield (15%) is here considerably greater than that (2·8%) of nitrous oxide. Whether it is produced *via* nitrous oxide is not established. Independent work on the reduction of nitric and nitrous oxide and HNO is needed to solve this problem.

(*d*) 1-Phenylethanol arises from hydrogen-abstraction by 1-phenylethoxyl radicals. The most likely substrates are the parent nitrite or another 1-phenylethoxyl radical (disproportionation). Acetophenone and nitroxyl are also possible substrates, but since acetophenone does not play a very active secondary rôle in the decomposition (in contrast to benzaldehyde in benzyl nitrite decomposition) it seems not to be a ready source of hydrogen atoms:

$$(6)\ \mathrm{Ph{\cdot}CHMe{\cdot}O{\cdot} + Ph{\cdot}CHMe{\cdot}O{\cdot}NO \longrightarrow Ph{\cdot}CHMe{\cdot}OH + Ph{\cdot}COMe + NO}$$

$$(7)\ \mathrm{Ph{\cdot}CHMe{\cdot}O{\cdot} + Ph{\cdot}CHMe{\cdot}O{\cdot} \longrightarrow Ph{\cdot}CHMe{\cdot}OH + Ph{\cdot}COMe}$$

$$(8)\ \mathrm{Ph{\cdot}CHMe{\cdot}O{\cdot} + HNO \longrightarrow Ph{\cdot}CHMe{\cdot}OH + NO}$$

These are all stoicheiometrically equivalent if the radical formed from the nitrite by loss of hydrogen is unstable and if the origin of nitroxyl is attack by nitric oxide on the free 1-phenylethoxyl radical.

(*e*) Acetophenone is formed in reactions (6) and (7), but these alone cannot explain the 2·75-fold excess of acetophenone (yield 55%) over 1-phenylethanol (yield 20%). Reduction of nitric oxide, as in reactions (4) and (5), must be invoked for this, and the problems of reduction of nitric oxide and the acetophenone : alcohol ratio are linked. If all the molecular nitrogen formed came originally *via* HNO (or *via* HNO and N_2O) then its yield would be more than sufficient to explain the yield of acetophenone in terms of (4).

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[17] Dalby, *Canad. J. Phys.*, 1958, **10**, 1336; Brown and Pimentel, *J. Chem. Phys.*, 1958, **29**, 883.

Acetophenone is more stable than benzaldehyde, and their relative yields in the appropriate nitrite decompositions (55 and 44% respectively) are in accord with this.

(*f*) The small amount of benzoic acid produced is probably formed by oxidation of acetophenone. Support for this comes from the enhanced yield of benzoic acid obtained when decomposition of the nitrite is carried out in the presence of initially added acetophenone. The absence of acetic acid shows that it is the carbon–methyl bond which breaks, in agreement with bond energy data[18] and with the fact that other oxidizing agents yield benzoic, but not acetic, acid. Ketone oxidation in the pyrolysis of wholly aliphatic nitrites is not so specific: octan-2-one yields[19] both acetic and heptanoic acid.

It is not impossible that some of the benzoic acid formed might have come from benzaldehyde produced by unimolecular decomposition of the 1-phenylethoxyl radical:

$$\mathrm{Ph{\cdot}CHMe{\cdot}O{\cdot}} \longrightarrow \mathrm{Ph{\cdot}CHO} + \mathrm{Me{\cdot}}$$

Stability of the 1-*Phenylethoxyl Radical.*—Alkoxyl radicals may lose their essential structure[11] by rearrangement (*i.e.*, intramolecular radical migration) or decomposition (radical elimination).

The energy requirements[20] of decomposition favour loss of methyl radicals. Thermochemistry places 1-phenylethoxyl between α-cumyloxyl on the one hand and diphenylmethoxyl and benzyloxyl on the other. Cumyloxyl decomposes[21] readily at 130° while diphenylmethoxyl[22] requires a temperature of 210° for loss of the phenyl radical to reach a proportion of 1·5%. In our experiments, decomposition is very slight. This resembles the behaviour[5] of benzyloxyl and contrasts with the very ready decomposition[11] (by methyl-radical loss) of the secondary aliphatic radical, isopropoxyl.

Rearrangement, though thermochemically favoured[20] and observed for related radicals,[23] does not occur here.

Relations between the Decompositions of Benzyl Nitrite and 1-*Phenylethyl Nitrite: the Effects of Methyl-radical Substitution.*—There are marked qualitative resemblances between the two decompositions. Table 2 reveals that there are also significant contrasts. They reflect the influence of replacing a hydrogen atom by a methyl group.

TABLE 2. *Comparison of product yields from benzyl and* 1-*phenylethyl nitrite.*

Product yield (moles per 100 moles of initial nitrite.)

Nitrite	$\mathrm{Ph{\cdot}CH_2{\cdot}OH}$ or $\mathrm{Ph{\cdot}CHMe{\cdot}OH}$	$\mathrm{Ph{\cdot}CHO}$ or $\mathrm{Ph{\cdot}CO{\cdot}Me}$	$\mathrm{Ph{\cdot}CO_2{\cdot}H}$	NO	N_2O	N_2
Benzyl	22	44	11	36	2·1	24
1-Phenylethyl	20	55	5	55	2·8	15

The differences in the ratio, alcohol : carbonyl compound, and in production of benzoic acid are linked to the differences in reduction of nitric oxide. They arise from the relative ease with which the respective carbonyl derivatives are (i) formed, and (ii) attacked. The carbon–hydrogen bond dissociation energy in 1-phenylethoxyl (9·6 kcal. mole^{-1}) is only half that (20 kcal. mole^{-1}) in benzyloxyl. Hydrogen abstraction from the former is thus easier and acetophenone is more readily formed than is benzaldehyde. Moreover, acetophenone is more resistant than is benzaldehyde to oxidation and a greater fraction of acetophenone may be expected to survive. The yields of benzoic acid show the same influences; so, indirectly, do the yields of nitric oxide and nitrogen.

Kinetically, similar relationships exist, though 1-phenylethyl nitrite does not share the very marked autocatalytic behaviour (attributable to benzaldehyde) of benzyl nitrite.

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[18] Cottrell, " The Strengths of Chemical Bonds," Butterworths, London, 2nd edn., 1958.

[19] Kornblum and Oliveto, *J. Amer. Chem. Soc.*, 1955, **77**, 5173.

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

[21] Bailey and Godin, *Trans. Faraday Soc.*, 1956, **52**, 68.

[22] Cadogan, Hey, and Sanderson, *J.*, 1958, 4498.

[23] Wieland and Maier, *Ber.*, 1911, **44**, 2533; 1931, **64**, 1205; Kharasch, Fono, and Nudenberg, *J. Org. Chem.*, 1951, **16**, 1458.

The marked effect of initially added benzaldehyde on 1-phenylethyl nitrite is the more striking when viewed in this light. Decomposition is accelerated; reduction of nitric oxide is more extensive; the yield of benzoic acid goes up. In essence, the pattern shifts to that typical of benzyl nitrite itself.

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