The Thermal Decomposition of Octyl Nitrite in Hydrocarbon Solvents.

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The thermal decomposition of octyl nitrite in solution gives rise to nitric oxide and octyloxy-radicals. The latter abstract hydrogen from the solvents, giving octyl alcohol and hydrocarbon radicals which are easily oxidised to the corresponding aldehydes or ketones. Both the nitric oxide and products derived from these hydrocarbon radicals have been characterised by combination with 2-cyano-2-propyl (1-cyano-1-methylethyl) radicals: thus the decomposition in toluene has given, amongst other products, *N*-benzyl-*ON*-di-(2-cyano-2-propyl)hydroxylamine, the obvious precursor of which is α-nitrosotoluene.

The vapour-phase pyrolysis of alkyl nitrites at 170—240°, which can be represented as

$$\mathrm{2R{\cdot}CH_2{\cdot}O{\cdot}NO \longrightarrow R{\cdot}CHO + R{\cdot}CH_2{\cdot}OH + 2NO}$$

(Steacie, "Atomic and Free Radical Reactions," pp. 141—143, Reinhold Publ. Corp., New York, 1946) can be explained (Rice and Rodowskas, *J. Amer. Chem. Soc.*, 1935, **57**, 350) by the mechanism

$$\mathrm{R{\cdot}CH_2{\cdot}O{\cdot}NO \longrightarrow R{\cdot}CH_2{\cdot}O{\cdot} + NO}\ (E = 37 \pm 1\ \text{kcal.}) \quad . \quad . \quad . \quad (1)$$

$$\mathrm{R{\cdot}CH_2{\cdot}O{\cdot} + R{\cdot}CH_2{\cdot}O{\cdot}NO \longrightarrow R{\cdot}CH_2{\cdot}OH + R{\cdot}\dot{C}H{\cdot}O{\cdot}NO} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\mathrm{R{\cdot}\dot{C}H{\cdot}O{\cdot}NO \longrightarrow R{\cdot}CHO + NO} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

though (1) is reversible and (4) is a possible alternative to (2) and (3) (Levy, *ibid.*, 1953, **75**, 1801).

$$\mathrm{2R{\cdot}CH_2{\cdot}O{\cdot} \longrightarrow R{\cdot}CHO + R{\cdot}CH_2{\cdot}OH} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Vapour-phase photolysis, which appears not to give alcohols (Thomson and Purkis, *Trans. Faraday Soc.*, 1936, **32**, 1466; Thomson and Dainton, *ibid.*, 1937, **33**, 1546), has been represented as giving molecular decomposition products and not free radicals,

e.g.,

$$\mathrm{R{\cdot}CH_2{\cdot}O{\cdot}NO \longrightarrow R{\cdot}CHO + HNO} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

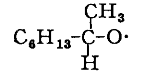
and

$$\mathrm{Me_3C{\cdot}O{\cdot}NO \longrightarrow Me_2CO + Me{\cdot}NO} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

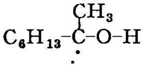
(Coe and Doumani, *J. Amer. Chem. Soc.*, 1948, **70**, 1516).

Rice and Rodowskas's mechanism (*loc. cit.*) has received strong support from Kornblum and Oliveto (*ibid.*, 1949, **71**, 226) who examined the pyrolysis of optically active liquid (+)-2-octyl nitrite at 100° and isolated nitric oxide, octan-2-one, and active (+)-octan-2-ol, thus demonstrating that the asymmetric free radical (I) picks up hydrogen without any rearrangement to (II).

(I)



$$C_6H_{13}\text{–}\underset{H}{\overset{CH_3}{C}}\text{–}O\cdot$$



$$C_6H_{13}\text{–}\underset{\bullet}{\overset{CH_3}{C}}\text{–}O\text{–}H$$

(II)

Since the evidence for the presence of transient alkyloxy-radicals in pyrolyses of alkyl nitrites depends wholly on the validity of the reaction mechanism, we have attempted to demonstrate the formation of *n*-octyloxy-radicals, $C_7H_{15}\cdot CH_2\cdot O\cdot$, from octyl nitrite by carrying out its decomposition in hydrocarbon solvents in the presence of decomposing αα'-azo*iso*butyronitrile, hoping that the reaction (7) might occur sufficiently to allow us to isolate the diagnostic radical combination product. This aim has not been achieved, for the octyloxy-radicals abstract hydrogen from the solvents used, giving hydrocarbon radicals from which typical derivatives have been isolated.

$$C_8H_{17}\cdot O\cdot + \cdot CMe_2\cdot CN \longrightarrow C_8H_{17}\cdot O\cdot CMe_2\cdot CN \quad \text{. . . . .} \quad (7)$$

The slow thermal decomposition of octyl nitrite in boiling toluene containing αα'-azo*iso*butyronitrile gave octyl alcohol, benzaldehyde, *ONN*-tri-(2-cyano-2-propyl)hydroxylamine (the addition product of nitric oxide and 2-cyano-2-propyl radicals; Gingras and Waters, *J.*, 1954, 1920), and *N*-benzyl-*ON*-di-(2-cyano-2-propyl)hydroxylamine (IV). Consequently the following reactions must have occurred :

$$C_8H_{17}\cdot O\cdot NO \longrightarrow C_8H_{17}\cdot O\cdot + NO \quad \text{. . . . .} \quad [\textit{i.e.}\ (1)]$$

$$NO + 3\dot{C}Me_2\cdot CN \longrightarrow (Me_2C\cdot CN)_2N\cdot O\cdot CMe_2\cdot CN \quad \text{. . . . . . .} \quad (8)$$

$$C_8H_{17}\cdot O\cdot + Ph\cdot CH_3 \longrightarrow C_8H_{17}\cdot OH + Ph\cdot CH_2\cdot \quad \text{. . . . .} \quad (9)$$

$$Ph\cdot CH_2\cdot + NO \longrightarrow Ph\cdot CH_2\cdot NO\ (III) \quad \text{. . . . .} \quad (10)$$

$$Ph\cdot CH_2\cdot NO + 2\dot{C}Me_2\cdot CN \longrightarrow Ph\cdot CH_2\cdot N(CMe_2\cdot CN)\cdot O\cdot CMe_2\cdot CN\ (IV) \quad \text{. . .} \quad (11)$$

α-Nitrosotoluene (III) has never yet been prepared, but it evidently exists in boiling toluene solution, without rearranging to benzaldoxime, for a sufficient time to combine with two cyanopropyl radicals to give the tertiary hydroxylamine (IV) which has a very similar infra-red spectrum to those of the related tertiary hydroxylamines previously prepared by us from aromatic nitroso-compounds (Gingras and Waters, *loc. cit.*). Reduction of (IV) with zinc dust and acetic acid gave an amide, probably $Ph\cdot CH_2\cdot N(OH)\cdot CMe_2\cdot CO\cdot NH_2$, having an infra-red spectrum indicative of a secondary hydroxylamine.

Benzaldehyde, but not octaldehyde, was also identified as a product of the decomposition of octyl nitrite in boiling toluene under carbon dioxide in the absence of αα'-azo*iso*butyronitrile. Neither dibenzyl nor 2-cyano-2-methyl-1-phenylpropane, $Ph\cdot CH_2\cdot CMe_2\cdot CN$, could be isolated, so that the combination of benzyl radicals with nitric oxide to give (III) must be a very fast reaction.

In the above reaction only a small percentage of the free 2-cyano-2-propyl radicals combine with the nitric oxide or α-nitrosotoluene, for the usual radical dimer, tetramethylsuccinonitrile, was a major reaction product. The trimer, 2 : 3 : 5-tricyano-2 : 3 : 5-trimethylhexane (Bickel and Waters, *Rec. Trav. chim.*, 1950, **69**, 1490), was also formed, and in addition a trace of a new isomeric dimer, 2 : 4-dicyano-2-methylpentane $NC\cdot CMe_2\cdot CH_2\cdot CHMe\cdot CN$ (V), was isolated. Bickel and Waters (*ibid.*, p. 312) had isolated the corresponding dimethyl ester in 15% yield from the decomposition of dimethyl αα'-azo*iso*butyrate and had suggested that the expected yield of the dimer (V) from αα'-azo*iso*butyronitrile would be less than 0·5% : slightly less than this has been isolated.

The reaction in boiling ethylbenzene proceeded somewhat differently, for resulting products, apart from dimers and trimer of 2-cyano-2-propyl radicals, were octyl alcohol, acetophenone, and 2 : 5-dicyano-2 : 5-dimethyl-3-phenylhexane (VI), which had previously been prepared in this laboratory by Dr. A. F. Bickel from the direct reaction of αα′-azo*iso*butyronitrile with styrene. The following reaction sequence may be postulated :

$$\mathrm{Ph{\cdot}CH_2{\cdot}CH_3 + C_8H_{17}{\cdot}O{\cdot} \longrightarrow Ph{\cdot}\dot{C}H{\cdot}CH_3 + C_8H_{17}{\cdot}OH} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$\mathrm{Ph{\cdot}\dot{C}H{\cdot}CH_3 + C_8H_{17}{\cdot}O{\cdot} \longrightarrow Ph{\cdot}CH{:}CH_2 + C_8H_{17}{\cdot}OH} \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

or

$$\mathrm{2Ph{\cdot}\dot{C}H{\cdot}CH_3 \longrightarrow Ph{\cdot}CH{:}CH_2 + Ph{\cdot}CH_2{\cdot}CH_3} \quad . \quad . \quad . \quad . \quad . \quad (14)$$

$$\mathrm{Ph{\cdot}CH{:}CH_2 + 2{\cdot}CMe_2{\cdot}CN \longrightarrow NC{\cdot}CMe_2{\cdot}CHPh{\cdot}CH_2{\cdot}CMe_2{\cdot}CN\ (VI)} \quad . \quad . \quad . \quad (15)$$

Acetophenone was also produced in the absence of αα′-azo*iso*butyronitrile.

The reaction in boiling *iso*propylbenzene gave a very small yield of a white compound which appears to be 2-cyano-2-methyl-4-nitro-4-phenylpentane: this could possibly be formed by successive additions of nitric oxide and 2-cyano-2-propyl radicals to α-methylstyrene. Decompositions in diphenylmethane and in 1-methylnaphthalene gave octyl alcohol and respectively benzophenone and 1-naphthaldehyde but no significant amounts of other products.

EXPERIMENTAL

Freshly prepared *n*-octyl nitrite was used throughout: material which had been kept for 2 weeks had to be rejected since it contained aldehyde.

Reaction in Toluene.—(*a*) A solution of octyl nitrite (45 g., 0·28 mole) in toluene (50 ml.) containing a little αα′-azo*iso*butyronitrile (0·5 g.) was heated slowly to boiling and as soon as nitrous fumes were evolved a solution of αα′-azo*iso*butyronitrile (45 g., 0·28 mole) in toluene (1 l.) was added dropwise during 24 hr. A few drops of the reaction mixture when treated with 2 : 4-dinitrophenylhydrazine gave benzaldehyde 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 233°. After distillation of the toluene the remaining liquid was distilled in steam. The aqueous layer of the distillate, on cooling, gave tetramethylsuccinonitrile (20 g.); light petroleum (b. p. 40—60°) precipitated a further 5 g. of this from the other layer (total recovery 67%). The petroleum solution on distillation gave octyl nitrite (b. p. 64°/20 mm.; 9 g., 20%) and octyl alcohol (b. p. 89°/20 mm.; 16 g., 54%): benzaldehyde and more tetramethylsuccinonitrile remained in higher-boiling residues. The organic material which had not distilled in steam was collected (7·7 g.) and chromatographed through an alumina column, giving first an oil, then the radical trimer (2 : 3 : 5-tricyano-2 : 3 : 5-trimethylhexane) (1·4 g.; m. p. and mixed m. p. 81°) and a few mg. of the new dimer (V), 2 : *4-dicyano-2-methylpentane*, which, crystallised from aqueous alcohol, had m. p. 152—153° (Found: C, 70·8; H, 8·3; N, 21·2. $C_8H_{12}N_2$ requires C, 70·5; H, 8·8; N, 20·6%). Its infra-red spectrum was almost identical with that of tetramethylsuccinonitrile, with typical absorption bands at 4·49 μ (CN) and 7·23 and 7·30 μ (Me_2C group). When the oil was carefully fractionated through two more columns in succession there were obtained N-*benzyl*-ON-*ai*-(2-*cyano*-2-*propyl*)*hydroxylamine* (IV) (2 g.), which after crystallisation from light petroleum (b. p. 40—60°) had m. p. 58·5° (Found: C, 70·0; H, 7·5; N, 16·4. $C_{15}H_{19}ON_3$ requires C, 70·0; H, 7·4; N, 16·4%), and *ONN*-tri-(2-cyano-2-propyl)hydroxylamine (1·1 g.), m. p. and mixed m. p. 78°. Both compounds gave infra-red spectra showing the presence of CN and Me_2C groups and had similar absorptions in the 8—9μ region; the former also showed the strong band at 14·37 μ characteristic of a phenyl group. The nitrile (IV) (0·3 g.) in boiling acetic acid (10 ml.) was reduced by adding zinc dust (0·3 g.) in portions during 1 hr. After refluxing for a further 5 hr. the hot mixture was filtered, cooled, made alkaline, and extracted with ether. Chromatography of the extract gave a few mg. of N-*benzyl*-N-iso*butyramidohydroxylamine* which when crystallised from ether–light petroleum had m. p. 102°, and infra-red absorption bands at 2·95 μ (*s*, OH), 3·05 and 3·16 μ (*m*, NH), 6·00 and 6·18 μ (*m*, amide CO), 7·28 (*w*) and 7·34 μ(*m*) (Me_2C) and 14·29 μ (C_6H_5) (Found: C, 63·4; H, 7·7; N, 13·5. $C_{11}H_{16}O_2N_2$ requires C, 63·5; H, 7·7; N, 13·45%).

(*b*) Octyl nitrite (15 ml.) in toluene (100 ml.) was refluxed for 24 hr. in a rapid stream of carbon dioxide from a cylinder. After that time a few drops of the solution were sufficient to give an identifiable amount of benzaldehyde dinitrophenylhydrazone. The liquid on distillation yielded octyl alcohol (12·5 ml.) but no crystalline products could be isolated from the high-boiling residue.

Reaction in Ethylbenzene.—(*a*) αα′-Azo*iso*butyronitrile (16·4 g.) in ethylbenzene (1 l.) was added dropwise during 24 hr. to a gently refluxing solution of octyl nitrite (16 g.) in the same solvent (50 ml.) : all the nitrite had then decomposed. 1 ml. of the solution sufficed to give acetophenone 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 235°. Tetramethylsuccinonitrile (46%) and octyl alcohol (70%) were isolated by steam-distillation (as above) and the residue (9·3 g.) was chromatographically separated into the trimer (0·9 g.; m. p. and mixed m. p. 81°), and 2 : 5-dicyano-2 : 5-dimethyl-3-phenylhexane (1·04 g., m. p. 121—122°), which proved to be identical with a specimen previously prepared in this laboratory by Dr. A. F. Bickel from αα'-azo*iso*butyronitrile and styrene (Found: C, 79·3; H, 8·0; N, 12·3. $C_{15}H_{20}N_2$ requires C, 79·0; H, 8·7; N, 12·3%). The specimens had identical infra-red spectra showing bands at 4·5 μ (CN), 7·20 and 7·31 μ (Me_2C), and 14·29 μ (C_6H_5).

(*b*) Carbon dioxide from a cylinder was passed for 24 hr. through a gently boiling solution of octyl nitrite (15 ml.) in ethylbenzene (100 ml.). After this time acetophenone 2 : 4-dinitrophenylhydrazone was obtained from a few drops of the reaction mixture: no crystalline products could be obtained from the high-boiling residue after fractionation.

Reaction in iso*Propylbenzene.*—αα'-Azo*iso*butyronitrile (10 g.) and octyl nitrite (10·5 ml.), dissolved in *iso*propylbenzene (600 ml.), were added dropwise during 6·5 hr. to a gently refluxing mixture of octyl nitrite (10 ml.) and *iso*propylbenzene. After steam-distillation the residue (8 g.) was chromatographically separated into the 2-cyano-2-propyl radical trimer, m. p. and mixed m. p. 81°, and 2-*cyano*-2-*methyl*-4-*nitro*-4-*phenylpentane* (0·97 g.), which after crystallisation from light petroleum (b. p. 40—60°) had m. p. 67° (Found: C, 67·0; H, 6·9; N. 12·2. $C_{13}H_{16}O_2N_2$ requires C, 67·2; H, 6·9; N, 12·1%). Its infra-red spectrum showed absorption bands at 4·50 μ (CN), 7·22 and 7·33 μ (Me_2C), 14·28 μ (C_6H_5), and also strong bands at 6·53 and 7·38 μ indicative of a NO_2 group.

Reaction in Diphenylmethane.—Octyl nitrite (10 ml.) and diphenylmethane (50 g.) were heated for 6 hr. in an oil-bath at 155—160° during which time αα'-azo*iso*butyronitrile (7·25 g.) was added in small portions. Benzophenone 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 238°, was obtained from a few drops of the resulting liquid. After distillation under reduced pressure and then steam-distillation the residue (9·3 g.) was chromatographed, and there were obtained the radical trimer (m. p. 81°) and benzophenone (*ca.* 5 g., b. p. 140°/10 mm. Found: C, 85·4; H, 5·8. Calc. for $C_{13}H_{10}O$: C, 85·7; H, 5·5%). Benzophenone 2 : 4-dinitrophenylhydrazone was also obtained when αα'-azo*iso*butyronitrile was not used.

Reaction in α-*Methylnaphthalene.*—This was carried out at 160° by the procedure used for *iso*propylbenzene. A few drops of the resulting solution then gave α-naphthaldehyde 2 : 4-dinitrophenylhydrazone, m. p. 254—255° (Found: C, 61·2; H, 3·8; N, 16·6. Calc. for $C_{17}H_{12}O_4N_4$: C, 60·7; H, 3·6; N, 16·7%); Coles and Dodds (*J. Amer. Chem. Soc.*, 1938, **60**, 853) record m. p. 254°. The residue after steam-distillation gave the radical trimer, m. p. 81°, but no other crystalline product.

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