

1048. *The Abstraction of Nitric Oxide from Alkyl Nitrites in the Vapour Phase by Methyl Radicals.*

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Methyl radicals, produced by pyrolysis of di-*t*-butyl peroxide, readily abstract nitric oxide from methyl, ethyl, *n*-propyl, isopropyl, and *t*-butyl nitrite in the vapour phase at 160–180°, forming, initially, nitrosomethane and alkoxy radicals. The latter abstract hydrogen from the nitrosomethane to form the corresponding alcohols. Trimethylhydroxylamine is formed by addition of methyl radicals to nitrosomethane; this is of relevance in the understanding of the inhibition of free-radical reactions by nitric oxide.

THE normal reaction of methyl radicals with a hydrogen-containing substrate in vapour-phase photolysis or pyrolysis is hydrogen abstraction to form methane, and reactions of this type have been studied extensively.¹ Until recently very few of the so-called inversion reactions, in which alkyl radicals abstract another atom or group in preference to hydrogen, were known.² Abstraction of nitric oxide from *s*-butyl and 1-ethylpropyl nitrite in the liquid phase by methyl radicals has been reported by Kharasch *et al.*³ and has been postulated on theoretical grounds by Gray⁴ to explain some anomalies in the vapour-phase pyrolysis of *t*-butyl nitrite. The first experimental evidence for the occurrence of this reaction between methyl radicals and alkyl nitrites in the vapour phase was reported by Jest and Phillips⁵ in a preliminary note on the methyl radical–methyl nitrite reaction. Subsequently Gray and Rathbone⁶ have demonstrated its occurrence in the liquid phase with *t*-butyl nitrite. Other recently reported inversion reactions of methyl radicals are abstraction of chlorine atoms from *t*-butyl hypochlorite in the liquid⁷ and the gas phase,⁸ and of halogen atoms from alkyl halides.⁹

This paper reports detailed results of studies on the reaction of methyl radicals, from the pyrolysis of di-*t*-butyl peroxide, with methyl, ethyl, *n*-propyl, isopropyl, and *t*-butyl nitrite in the vapour phase at 160–180°.

EXPERIMENTAL

Materials.—Methyl and ethyl nitrite were prepared by simple exchange between the corresponding alcohols and pentyl nitrite. *n*- and iso-Propyl and *t*-butyl nitrite were prepared by reaction of nitrous acid with the alcohols in the normal way.¹⁰ After low-temperature fractionation, purity, established by infrared spectroscopy and vapour-phase chromatography, was at least 99.5% except for *n*-propyl nitrite, which contained about 3% of propionaldehyde. In the last case, mild esterification *via* aluminium nitrite by the method of Chrétien and Longi¹¹ failed to effect any improvement. Methyl nitrite was stored as the vapour in blackened flasks; the other nitrites were stored as liquids at –30°.

Di-*t*-butyl peroxide, supplied by Laporte, was fractionated several times at low temperature; the middle fraction contained no detectable impurities.

The Reaction.—Requisite pressures of peroxide and nitrite were measured out individually into a 561 ml. flask, with a mercury–oil manometer (magnification 10).¹² The vapours were

¹ Trotman-Dickenson, "Gas Kinetics," Butterworths Scientific Publ., London, 1955, p. 196.

² Ref. 1, p. 237.

³ Kharasch, Meltzer, and Nudenberg, *J. Org. Chem.*, 1957, **22**, 37.

⁴ Gray, *Chem. and Ind.*, 1960, 120.

⁵ Jest and Phillips, *Proc. Chem. Soc.*, 1960, 73.

⁶ Gray and Rathbone, *Proc. Chem. Soc.*, 1960, 316.

⁷ Walling and Jacknow, *J. Amer. Chem. Soc.*, 1960, **82**, 6104.

⁸ Phillips, *Proc. Chem. Soc.*, 1961, 338.

⁹ Evans, Fox, and Szwarc, *J. Amer. Chem. Soc.*, 1960, **82**, 6414.

¹⁰ *Org. Synth.*, Coll. Vol. II, p. 108.

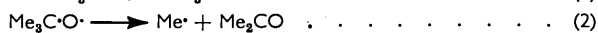
¹¹ Chrétien and Longi, *Compt. rend.*, 1945, **220**, 746.

¹² Drucker, Jimeno, and Kangro, *Z. phys. Chem.*, 1915, **A**, **90**, 513.

frozen individually into a ~150 ml. reaction vessel (previously cleaned with nitric acid and water) fitted with a seal-off construction and breaker tip, and the vessel was sealed whilst the reactants remained frozen. This procedure was necessary in order to achieve partial pressures of peroxide of the order 100 mm. in the reaction vessel at 160—180°, which preliminary work had shown necessary for extensive reaction of methyl radicals with the nitrites. The mixture in the reaction vessel was then preheated to 80° for 10 min. to ensure good mixing and immersed in an "Arochlor" bath which was thermostatically controlled to $\pm 0.1^\circ$ at 160—180°. At the end of the reaction period, the vessel was rapidly removed from the bath and quenched in cold water. It was then opened *via* the breaker tip under a vacuum, and the products were fractionated through a Leroy still. The first and the second fraction were removed at -193° and -150° and analysed on a Metrovick M.S.3 mass spectrometer. The first fraction contained methane, carbon monoxide, and most of the nitric oxide; the second was mainly ethane with sometimes a little nitric and nitrous oxides and higher hydrocarbons. The liquid products left in the still were removed, measured as vapour, and analysed by infrared spectroscopy and on a Perkin-Elmer model 116 Fraktometer. Doubtful products shown up in the vapour-phase chromatography were frozen out of the hydrogen stream and identified mass-spectrometrically. The stationary phases used in the analysis varied according to the nitrite used and the products obtained. They were usually tetraethylene glycol monomethyl ether for methyl and n-propyl nitrite, tritoyl orthophosphate-polyethylene glycol for ethyl and t-butyl nitrite, and dinonyl phthalate for isopropyl nitrite. The yellowish-brown involatile oils usually left in the reaction vessel were subjected to spot tests for nitroso-compounds, etc., and aqueous extracts examined in a Unicam ultraviolet spectrophotometer.

RESULTS

On the basis of the results of Raley, Rust, and Vaughan,¹³ di-t-butyl peroxide should undergo about 70% decomposition in 30 min. at 160°, and complete decomposition in 30 min. at 180°, according to the equations:



Check experiments confirmed this and also showed the presence of small amounts of methane and carbon monoxide, as previously reported. Phillips's data¹⁴ for methyl nitrite show that negligible pyrolysis should occur in 30 min. at 180°; check experiments confirmed this. Similarly Levy's results¹⁵ on ethyl nitrite indicate negligible decomposition in 30 min. at 160° and this was confirmed. The results of Ferguson and Phillips¹⁶ on s-propyl nitrite and of Steacie and Shaw¹⁷ on n-propyl nitrite suggested that about 5% decomposition of each should occur in 30 min. at 160°; this was confirmed.

The analytical results for the reaction of methyl radicals with each of the nitrites are presented separately below. At least four runs were done on each nitrite.

Methyl Nitrite.—Results are assembled in Table 1. In addition to the products shown several very small amounts of unidentified products were revealed on chromatography; infrared spectra showed the presence of small amounts of hydrogen cyanide.

Yellowish-brown involatile oily residues having a fishy odour were left in the reaction vessel; these gave the Liebermann nitroso-reaction, and aqueous solutions gave continuous absorption in the 210—250 μ range, characteristic of formaldoxime. Infrared spectra of the oil at 100—180° suggested the presence of C-N bonds. The chromotropic acid test for formaldehyde gave a positive result, but this is also given by formaldoxime. In order to check whether appreciable amounts of formaldehyde were formed, a run was carried out at 180° in which the products were expanded into an infrared cell maintained at 120° and the infrared spectrum was obtained; at the most a trace (not more than 0.5 mm.) of formaldehyde was detected from the 3.68 μ absorption.

¹³ Raley, Rust, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 88.

¹⁴ Phillips, *J.*, 1961, 3082.

¹⁵ Levy, *J. Amer. Chem. Soc.*, 1956, **78**, 1780.

¹⁶ Ferguson and Phillips, unpublished work.

¹⁷ Steacie and Shaw, *J. Chem. Phys.*, 1935, **3**, 344.

Trimethylhydroxylamine was identified by freezing out an unknown component, which appeared from its retention volume to have a boiling point of about 30°, from the effluent hydrogen stream from the Fraktometer and determining the mass-spectrometer cracking pattern. Separation of this unknown from the other products was complete except for another unknown which was present in very small amount relative to the amine and could not be separated because of the closeness of the two peaks. The main features of the cracking pattern are shown in Table 2, with that of an authentic sample of trimethylhydroxylamine, prepared

TABLE 1.
Reaction of methyl nitrite with methyl radicals.

Volatile products (mm. at reaction temp.)	DTBP * 96.8 mm. } 30 min. at 180°		DTBP * 101.3 mm. } 30 min. at 160°	
	MeO·NO 128.9 mm.		MeO·NO 107.9 mm.	
CH ₄	15.7		10.6	
C ₂ H ₆	22.4		10.0	
CO	8.8		3.8	
NO	2.6		1.2	
N ₂ O	1.7		0	
MeO·NO	61.9		63.5	
Me ₂ CO	196		128.6	
MeOH	53.8		32.0	
DTBP	0		35	
CH ₂ N·OH	14		NE	
Me ₂ N·OMe	NE		9	
Bu ^t OH	NE		5	
MeO·NO decompd.	67.0		44.4	

NE = not estimated. * Di-*t*-butyl peroxide.

TABLE 2.
Some cracking patterns.

<i>m/e</i>	Unknown	Me ₂ N·OMe	<i>m/e</i>	Unknown	Me ₂ N·OMe	<i>m/e</i>	Unknown	Me ₂ N·OMe
14	6.1	3.7	40	4.7	5.6	59	8.0	0.3
15	38.3	32.0	41	6.4	6.9	60	100.0	100.0
28	36.5	33.9	42	55.9	56.1	61	2.7	2.2
29	28.0	15.6	43	25.0	25.5	74	3.6	3.7
30	18.5	11.4	44	33.3	16.7	75	34.2	34.5
31	11.4	9.8	45	12.5	15.2	76	1.3	1.3
39	2.4	1.7						

by the method of Jones and Major.¹⁸ Agreement between the major peaks is very good; the differences observed at *m/e* 14, 15, 28, 29, 30, 44, and 59 are due to the presence of the small amount of the other unknown, referred to above, which could not be separated. The spectrum differs considerably from those of other products of the reaction; there is no doubt of the identification as trimethylhydroxylamine. The chromatographic retention volume of synthetic sample was also identical with that found in the reaction products.

Control experiments showed that acetone, formed from the peroxide, had no effect on the straight pyrolysis of methyl nitrite at 180°; neither did small amounts of water vapour which might have been formed in the reaction.

Ethyl Nitrite.—Results are reported in Table 3. Several unidentified products were again detected in very small amount. Yellowish-brown involatile oils were left in the reaction vessel; these gave no characteristic Liebermann colours but formaldoxime was indicated by the chromotropic acid test and by ultraviolet spectra of an aqueous extract.

n-Propyl Nitrite.—Results are reported in Table 4.

The usual yellowish-brown involatile oil was left in the reaction vessel. No characteristic Liebermann colours were obtained, but traces of formaldoxime were detected as before. After the liquid fraction, condensed at -140° to -150°, had been vaporized and refrozen and revaporized before chromatography, a small amount of a viscous colourless liquid was left; this was probably a product of polymerisation involving *n*-propyl alcohol and other products.

Isopropyl Nitrite.—Results are reported in Table 5.

¹⁸ Jones and Major, *J. Amer. Chem. Soc.*, 1928, **50**, 2742.

TABLE 3.
Reaction of ethyl nitrite with methyl radicals.

Volatile products (mm. at reaction temp.)	DTBP 113.6 mm. } 30 min. at 160° EtO·NO 108.8 mm. }		DTBP 101.4 mm. } 30 min. at 170° EtO·NO 108.6 mm. }	
	CH ₄	12.2		18.0
C ₂ H ₆	10.5		16.5	
CO	6.5		8.6	
NO	0.8		0.6	
N ₂ O	1.0		0.8	
EtO·NO	68		52	
Me ₂ CO	139		194	
EtOH	30		44	
Me·CHO	~2		~3	
DTBP	41		0	
Me ₂ N·OMe	8		N.E.	
Bu ^t OH	4		N.E.	
EtO·NO decompd.	40.8		56.6	

TABLE 4.
Reaction of n-propyl nitrite with methyl radicals.

Volatile products (mm. at reaction temp.)	DTBP 90.9 mm. } 30 min. Pr ⁿ O·NO 104.7 mm. } at 160°		Volatile products (mm. at reaction temp.)	DTBP 90.9 mm. } 30 min. Pr ⁿ O·NO 104.7 mm. } at 160°	
	CH ₄	15.8			Me ₂ CO
C ₂ H ₆	10.2		Pr ⁿ OH	17	
CO	7.7		DTBP	20	
NO	1.3		Me ₂ N·OMe	9	
N ₂ O	1.2		Bu ^t OH	7	
C ₂ H ₄	1.4				
Pr ⁿ O·NO	62		PrO·NO decompd.	42.7	

TABLE 5.
Reaction of isopropyl nitrite with methyl radicals.

Volatile products (mm. at reaction temp.)	DTBP 98.1 mm. } 30 min. Pr ⁱ O·NO 109.8 mm. } at 160°		Volatile products (mm. at reaction temp.)	DTBP 98.1 mm. } 30 min. Pr ⁱ O·NO 109.8 mm. } at 160°	
	CH ₄	16.5			Pr ⁱ OH
C ₂ H ₆	13.0		DTBP	25	
CO	5.8		Me ₂ N·OMe	8	
NO	0.2		Me·CHO	11	
N ₂ O	0.9		Bu ^t OH	6	
Pr ⁱ O·NO	65*				
Me ₂ CO	145		Pr ⁱ O·NO decompd.	34.8	

* This figure may be slightly high, owing to overlap of a small amount of an unidentified product with the nitrite in the record.

The usual yellowish-brown involatile oil was left in the reaction vessel; traces of formaldoxime were detected in the aqueous washings.

t-Butyl Nitrite.—Only a few experiments were done on *t*-butyl nitrite. The liquid products from a mixture of 84 mm. of di-*t*-butyl peroxide and 116 mm. of *t*-butyl nitrite after 30 min. at 160° contained *t*-butyl nitrite 76 mm., acetone 164 mm., DTBP 17 mm., *t*-butyl alcohol 29 mm., and trimethylhydroxylamine 10 mm.

DISCUSSION

The results show that about 40% decomposition of the nitrites studied occurs on reaction with di-*t*-butyl peroxide at 160° for 30 min.; slightly more reaction occurs as the temperature is raised to 170–180°. Under these conditions simple pyrolysis accounts for losses of only 1–2% with methyl and ethyl nitrite, about 5% with *n*- and iso-propyl nitrite, and about 8% with *t*-butyl nitrite.

5306 Bromberger and Phillips: Abstraction of Nitric Oxide from

The gross deficiencies in methyl balances ($\text{CH}_3 + 2\text{C}_2\text{H}_6$), compared with peroxide decomposed suggest a direct reaction between methyl radicals and the nitrites. The normal hydrogen-abstraction reactions

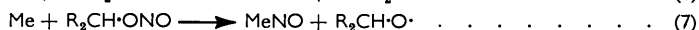
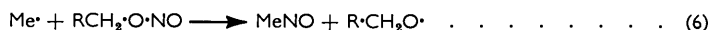


cannot account for more than a small fraction of the nitrite decomposed because yields of methane are low. Thus, after allowance for the small amounts of methane produced in the pyrolysis of di-*t*-butyl peroxide itself, the methane produced in 30 min. at 160° in relation to the nitrite decomposed is:

Nitrite	Me	Et	Pr ⁿ	Pr ^t
Nitrite decompd. (mm.)	44.4	40.8	42.7	34.8
CH ₄ produced (mm.)	0.8	1.2	7.0	7.0

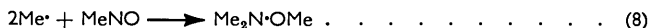
Also no large yields of aldehydes are obtained from the primary nitrites; admittedly they would be expected to react rapidly with methyl radicals but then yields of methane and carbon monoxide would be high.^{14, 23}

The large yields of the corresponding alcohols are consistent with the intermediate formation of alkoxy radicals, and the only logical reaction is abstraction of nitric oxide from the nitrites by methyl radicals to form nitrosomethane, as proposed in an earlier note:⁵



Energetically this reaction is feasible; *e.g.*, for methyl nitrite the enthalpy is -19 kcal./mole.

The occurrence of this type of reaction between methyl radicals (from diacetyl peroxide) and *liquid s*-butyl and 1-ethylpropyl nitrite was first demonstrated by Kharasch *et al.*,³ and has recently been confirmed by Gray and Rathbone for liquid *t*-butyl nitrite.⁶ These investigators, working at *ca.* 80°, recovered dimeric nitrosomethane in large yields, but it has not been detected in the present work. However, the intermediate formation of nitrosomethane is shown by the detection of small amounts of formaldoxime, which is rapidly formed by isomerisation at 160°,¹⁹ and particularly by the identification of trimethylhydroxylamine which, as reported earlier in a preliminary note,²⁰ can only arise from addition of methyl radicals to nitrosomethane:



This reaction is analogous to that proposed by Gingras and Waters²¹ to explain the formation of trisubstituted hydroxylamines by reaction of 2-cyano-2-propyl radicals with aromatic nitroso-compounds and with nitric oxide. Hoare²² has also shown that, in the photolysis of acetone in the presence of small proportions of nitric oxide, up to three methyl radicals can add to one molecule of the latter, but no products were identified.

The large yields of alcohols formed must come from the initially formed alkoxy radicals by hydrogen abstraction. If this occurred mainly with the parent nitrites, *e.g.*,



large yields of aldehydes (or of methane plus carbon monoxide as a result of radical attack on the latter^{14, 23}) would be expected from the primary nitrites. Further, there is evidence¹⁴ that reaction (9) is slow at 180°. Hydrogen abstraction by the alkoxy radicals from the peroxide or acetone must be slight because yields of acetone are roughly theoretical, and no ethyl methyl ketone was detected. Disproportionation of alkoxy radicals cannot be

¹⁹ Lüttke, *Z. Elektrochem.*, 1957, **61**, 302.

²⁰ Phillips, *Proc. Chem. Soc.*, 1961, 204.

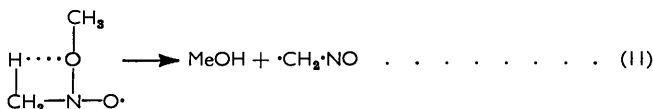
²¹ Gingras and Waters, *J.*, 1954, 1920.

²² Hoare, quoted by Batt and Gowenlock, *ref. 26* and personal communication.

²³ Toby and Kutschke, *Canad. J. Chem.*, 1959, **37**, 672.

a main source of the alcohols because (a) yields of alcohol are too high relative to the amount of nitrite decomposed and (b) aldehydes (or their decomposition products) are not detected in large amount, except in the case of isopropyl nitrite where the initially formed isopropoxyl radical breaks down partially into acetaldehyde and a methyl radical.¹⁶

The alkoxy radicals must, therefore, abstract hydrogen from nitrosomethane. The absence of mixed ethers (which would arise from addition of methyl and alkoxy radicals) in the products suggests that free alkoxy radicals do not exist for long; the probable course of this reaction is rapid addition of alkoxy radicals to nitrosomethane followed by elimination of the corresponding alcohol, *e.g.*:



Addition of free radicals to nitrosomethane is known to occur easily,²⁴ and it is confirmed by the formation of trimethylhydroxylamine. The absence of large yields of alcohols and the formation of dimeric nitrosomethane in the liquid-phase work of Kharasch *et al.*³ and Gray and Rathbone⁶ suggest that under their conditions reactions (10) and (11) do not compete with dimerisation of nitrosomethane.

The $\cdot\text{CH}_2\text{NO}$ radical formed in reaction (11) probably undergoes further radical addition to give mainly the yellowish-brown involatile oils referred to. Another possibility is the formation of *N*-ethyl-*ON*-dimethylhydroxylamine: $3\text{Me}^\cdot + \cdot\text{CH}_2\text{NO} \longrightarrow \text{MeO}^\cdot\text{NMeEt}$. A further minor unidentified product in the chromatographic analysis of products from the methyl nitrite-di-*t*-butyl peroxide reaction, which appeared to have a boiling point (judged by its retention volume) of 50–60°, exhibited a mass-spectrometer cracking pattern similar to that which would be expected from *N*-ethyl-*ON*-dimethylhydroxylamine.

Since some of the nitrosomethane initially formed reacts with methyl radicals to form trimethylhydroxylamine, yields of the corresponding alcohols should always be less than the amount of nitrite consumed. Further, the formation of *t*-butyl alcohol from *t*-butyl nitrite and the peroxide shows that *t*-butoxyl radicals abstract hydrogen from nitrosomethane. Some of the *t*-butoxyl radicals initially formed in pyrolysis of the peroxide should therefore produce *t*-butyl alcohol on reaction with other alkyl nitrites. This is confirmed by the results although the small yields of *t*-butyl alcohol show that hydrogen abstraction by these radicals from nitrosomethane is not as easy as with the lower alkoxy radicals. The relation, $-\text{[RO}^\cdot\text{NO]} = \text{[ROH]} + \text{[Bu}^\text{t}\text{OH]} + \text{[Me}_2\text{N}^\cdot\text{OMe]}$, should give the nitrosomethane balance; reference to the results shows that this is roughly true.

Gray and Rathbone⁶ suggested that these nitric oxide abstraction reactions open a route for radical-chain decomposition in the pyrolysis of nitrites. Thus, at temperatures of at least 200° alkyl radicals are produced from the alkyl nitrites by C–C bond fission of the alkoxy radicals initially formed.²⁵ Any such chains could, however, be terminated by addition of the alkyl radicals produced to the nitrosomethane initially formed, affording trisubstituted hydroxylamines, as shown in this paper. This view is supported by the results given herein of the reaction of methyl radicals with *t*-butyl nitrite. Methyl radicals are regenerated by breakdown of the *t*-butoxy-radical formed in the nitric oxide abstraction reaction:



but the extent of decomposition of the nitrite is about the same as of methyl and ethyl

²⁴ Gowenlock and Lüttke, *Quart. Rev.*, 1958, 12, 321.

²⁵ Adler, Pratt, and Gray, *Chem. and Ind.*, 1955, 1517.

nitrite where no regeneration of methyl radicals occurs after the initial abstraction of nitric oxide.

The formation of trimethylhydroxylamine is of special interest in the inhibition of free-radical vapour-phase reactions by nitric oxide. The importance of further reactions of the nitrosomethane initially formed has recently been emphasised by several authors. Christie²⁶ suggested the formation of a substituted hydroxylamine by addition of nitric oxide to nitrosomethane, in the photolysis of methyl iodide with an excess of nitric oxide. Hoare²² has shown that, in the photolysis of acetone-nitric oxide mixtures, methyl radicals and nitric oxide can react in ratios of 3 : 1 and 1 : 3 depending on the relative amounts of each reactant. Batt and Gowenlock²⁷ isolated a product, which is probably *N*-nitrosohydroxylamine nitrite, from the reaction of nitrosomethane with nitric oxide at 400°. These observations, together with the identification of trimethylhydroxylamine in the present work, necessitate revision of earlier concepts of inhibition in which one nitric oxide molecule was assumed to remove only one free-radical.*

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* Wojciechowski and Laidler²⁸ recently suggested that the formation of nitrosoalkanes is of little or no importance in the nitric oxide inhibition of the decomposition of paraffins, and invoke mechanisms depending on formation of HNO. They concede, however, that for other organic molecules such as acetaldehyde and acetone, especially at lower temperatures, formation of nitrosoalkanes is an important termination step.

²⁶ Christie, *Proc. Roy. Soc.*, 1958, *A*, **249**, 259.

²⁷ Batt and Gowenlock, *Trans. Faraday Soc.*, 1959, **56**, 682.

²⁸ Wojciechowski and Laidler, *Canad. J. Chem.*, 1960, **38**, 1027.
