

Geometrical Isomerism of Dimeric Nitrosomethane.

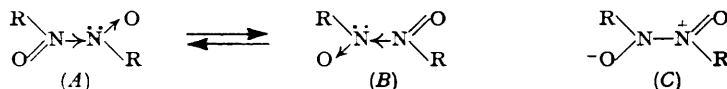
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Dimeric nitrosomethane is prepared by the photolysis of *tert.*-butyl nitrite vapour when nitrosomethane monomer dimerizes at an un-irradiated surface. A different dimer is prepared by dimerization at an irradiated surface or at low temperatures. The ultraviolet and infrared absorption spectra and other properties of the isomers are discussed, geometrical isomerism being invoked to explain them. The nitroso-hydroxyimino-system is briefly discussed. It is concluded that in the pyrolytic production of nitrosomethane from *tert.*-butyl nitrite some molecular elimination of nitrosomethane occurs.

BAMBERGER AND SELIGMAN (*Ber.*, 1903, **36**, 685) considered that it would be difficult to isolate nitrosomethane after oxidation of methylamine owing to its speedy isomerization to formaldoxime. Similarly, in the inhibition of free-radical chain reactions by nitric oxide, the reaction sequence $\text{CH}_3\cdot + \text{NO} \longrightarrow \text{CH}_3\cdot\text{NO} \longrightarrow \text{H}_2\text{C}:\text{N}\cdot\text{OH}$ has been assumed to be rapid. Although nitrosomethane has not been isolated on reaction of methyl radicals with nitric oxide, formaldoxime was isolated on decomposition of di-*tert.*-butyl peroxide in the presence of nitric oxide (Raley, Rust, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 88) and on pyrolysis of *tert.*-butyl nitrite (Yoffe, *Research*, 1954, **7**, S 44). Nitrosoalkanes, together with the isomeric oximes, have been obtained by Chilton and Gowenlock (*J.*, 1953,

3232; 1954, 3174) on reaction of *isopropyl* and ethyl radicals with nitric oxide. This method utilizes mercury dialkyls as the source of the free radicals and weight yields are small owing to the small weight proportion of the alkyl groups in mercury alkyls. Nitrosomethane has been isolated as the dimer on photolysis of *tert.*-butyl nitrite (Coe and Doumani, *J. Amer. Chem. Soc.*, 1948, **70**, 1516; Tarte, *Bull. Soc. roy. Liège*, 1953, **22**, 26) and some of its simple properties have been briefly discussed.



Dimeric nitroso-compounds have been formulated as resonance hybrids (A) \rightleftharpoons (B) (Hammick, New, and Williams, *J.*, 1934, 29) or resonance forms of the type (C) (Fenimore, *J. Amer. Chem. Soc.*, 1950, **72**, 3226; Darwin and Hodgkin, *Nature*, 1950, **166**, 827). However, it is well established that *cis-trans*-isomerism is possible for azo- (Campbell, Henderson, and Taylor, *J.*, 1953, 1281) and azoxy-compounds (Brough, Lythgoe, and Waterhouse, *J.*, 1954, 4096), so it seems reasonable to invoke *cis-trans*-isomerism (D, E) for



dimeric nitroso-compounds. Chilton and Gowenlock (*loc. cit.*) reported that dimeric nitrosomethane had λ_{max} . 266—267 $\text{m}\mu$ (in H_2O) and 287 $\text{m}\mu$ (in Et_2O). Later, a specimen prepared by irradiation under different conditions (Coe and Doumani, *loc. cit.*) had λ_{max} . 276 $\text{m}\mu$ (in H_2O) and 287 $\text{m}\mu$ (in Et_2O), indicating a possibility that two different dimers of nitrosomethane might exist.

EXPERIMENTAL

tert.-Butyl nitrite, prepared by Coe and Doumani's method (*loc. cit.*), was purified by repeated bulb-to-bulb distillation *in vacuo*, only the middle fractions being retained. Nitrogen was made by heating sodium azide in a high vacuum, being released into an evacuated bulb. The *tert.*-butyl nitrite was pyrolyzed in Chilton and Gowenlock's apparatus (*loc. cit.*), with a nitrogen pressure of ~ 4 mm., a butyl nitrite pressure of ~ 0.1 mm., and a reaction time of ~ 0.5 sec., the temperature of the reaction vessel being 330—390°. The pyrolysis products, together with undecomposed nitrite, were condensed in a trap cooled with liquid oxygen, and consisted of a yellow-brown solid and a white solid. On warming, the latter soon melted to a faintly yellow liquid, and the yellow-brown solid gave a yellow-brown liquid which rapidly changed to a white solid (X), the melting and resolidifying taking place between -45° and -40° (measured as by Chilton and Gowenlock, *loc. cit.*). The faintly yellow liquid was distilled off *in vacuo*. It boiled at $60\text{--}61^\circ/760$ mm., contained small amounts of *tert.*-butyl nitrite, and gave acetone semicarbazone, m. p. and mixed m. p. 187° . During the pyrolysis an increase in pressure was regularly observed; admission of air to the apparatus gave brown vapours, indicating that this increase was due, in part or in whole, to nitric oxide which is not completely condensed in liquid oxygen. The white solid (X) had the composition C, 26.9; H, 6.8; N, 30.2% (Calc. for CH_3ON : C, 26.7; H, 6.7; N, 31.1%), and was dissolved in aqueous ethanol at about 30° and then cooled in solid carbon dioxide-acetone; colourless crystals of *dimeric nitrosomethane*, m. p. 97.5° , were deposited [Found: C, 27.0; H, 6.5; N, 29.4%; *M* (cryoscopic in benzophenone), 92.0. CH_3ON requires C, 26.7; H, 6.7; N, 31.1%; *M*, 90].

Photolysis was effected in a 250-ml. transparent silica bulb or in a transparent silica trap of length 14 cm. and diameter 3 cm. In both cases about 1 ml. of *tert.*-butyl nitrite was in the vessel and was shielded from ultraviolet light; its pressure was about 110 mm. When the bulb was used, the vapour was irradiated for *ca.* 150 mm. by a Hanovia S500 lamp focused by means of a silica bulb containing water, or by a Thermal Syndicate Mercury Vapour Discharge lamp T/M5/369 placed within 2 cm. of the bulb: the former led to long needles of dimeric nitrosomethane, m. p. 122° , obviously identical with Coe and Doumani's and Tarte's specimens (*loc. cit.*); the latter led to small crystals with ultraviolet absorption maxima identical with those of the white solid (X). When the trap was used, irradiation was performed (a) with the Hanovia lamp placed 2 cm. from the trap, for 90 min., (b) with the Thermal Syndicate lamp

placed 2 cm. from the trap, for 90 min., or (c) with the Hanovia lamp placed 12 cm. from the trap, for ca. 300 min., most of the trap being shielded by a Pyrex beaker. Under conditions (a) and (b) the above-mentioned small crystals were obtained, and under conditions (c) the long needles, m. p. 122°.

Ultraviolet Absorption Spectra.—All measurements were made with a Unicam SP 500 photoelectric quartz spectrophotometer with corrected scale and 1-cm. or 0.5-cm. quartz cells. Solvents were water, ethanol (Bladon, Henbest, and Wood, *J.*, 1952, 2738), carbon tetrachloride (Spectrosol), chloroform (Spectrosol), cyclohexane (Spectrosol), *n*-hexane (B.D.H.), or ether (McFarlane). The ultraviolet absorption spectra are summarised in Table 1.

TABLE 1. *Ultraviolet absorption.*

Solvent	Dimer A (m. p. 122°)		Dimer B (m. p. 97.5°)	
	λ_{\max} (m μ)	log ϵ	λ_{\max} (m μ)	log ϵ
H ₂ O	276	4.03	265	4.00
EtOH	282.5	4.01	269 *	4.00
CHCl ₃	286	4.05	275 †	4.00
Et ₂ O	286	4.01	286 ‡	—
	213	3.48	213 ‡	—
<i>cyclo</i> Hexane	288	3.99	288 ‡	—
	218	3.14	218 ‡	—
<i>n</i> -C ₆ H ₁₄	288	3.97	288 ‡	—
	218	3.12	218 ‡	—
CCl ₄	291	4.06	291 ‡	—

* Increases slowly with time (282.5 m μ after 36 hr.). † Increases with time (286 m μ after 20 hr.). Warming to 60° for 30 sec. gives λ_{\max} 286 m μ . Product after storage and crystallisation has m. p. 122°, λ_{\max} 276 m μ (in H₂O). ‡ Dimer B was only slightly soluble (log ϵ not determined). Solvent was removed under reduced pressure and water added, or the product was directly extracted with water; λ_{\max} was 276 m μ in H₂O. These figures indicate conversion of dimer B into dimer A in these solvents.

The effect of heat on both solids was investigated, a Kofler block being used. Dimer A melted at 122° to a colourless liquid giving a momentary blue-green colour at about 125°. Dimer B melted at 97.5° to a colourless liquid giving a pale-green colour between 108° and 135°. Each solid was then heated rapidly to the m. p., and cooled, and dissolved in water and the ultraviolet absorptions were determined: both products had λ_{\max} 276 m μ and increased absorption at 210 m μ , presumably owing to formation of formaldoxime (λ_{\max} < 210 m μ).

The effect of heat on solutions of the two solids, investigated by means of the ultraviolet absorptions, is shown in Table 2, increased absorption at 210 m μ in H₂O or EtOH being considered as evidence for oxime formation.

TABLE 2. *Products formed by heating of solutions.*

Solvent	Dimer A	Dimer B
H ₂ O	Oxime	Oxime + A (λ_{\max} 276 m μ)
EtOH	Oxime	Oxime + A (λ_{\max} 282.5 m μ)
Et ₂ O	Oxime (λ_{\max} 207 m μ)	—

The effect of ultraviolet irradiation (Hanovia lamp) is summarised in Table 3.

TABLE 3. *Products of ultraviolet irradiation of solutions.*

Solvent	Dimer A	Dimer B
H ₂ O	Oxime + B (λ_{\max} 265 m μ)	Oxime
EtOH	Oxime + B (λ_{\max} 269 m μ)	Oxime

Dimer A, which was more volatile than dimer B, was pyrolyzed at 350° under flow conditions similar to those used for *tert.*-butyl nitrite. A blue solid, condensed by liquid oxygen, gave a white solid on warming. The latter in aqueous solution had λ_{\max} 265 m μ and gave only slight increase in intensity of absorption at 210 m μ compared with a pure specimen of B, indicating only slight formation of formaldoxime.

Solubilities.—Both dimers were easily soluble in water. In other solvents, dimer B was less soluble than dimer A (see Table 1 for evidence of interconversion). In general, it appeared that solubility decreased with decreasing dielectric constant of the solvent, dimer B being almost insoluble in solvents of low dielectric constant and converted into A on dissolution. Neither

form gave a blue colour on dissolution or gentle warming. In boiling chloroform, ethanol, and methanol dimer B gave blue colours and both dimers gave blue colours in boiling toluene or 1- or 2-nitropropane.

Spot Tests.—Both dimers gave the diphenylamine-concentrated sulphuric acid test (Coe and Doumani, *loc. cit.*); they did not give the Liebermann nitroso-test (Feigl, "Spot Tests," Elsevier, Amsterdam, 1939, p. 267), yellow-green colours in sulphuric acid and yellow-brown colours in sodium hydroxide solution being produced.

Effect of Solvents on Monomeric Nitrosomethane.—Monomeric nitrosomethane (produced pyrolytically) with nitrogen as carrier gas and other pyrolysis products was passed over solvents maintained at $+5^\circ$ or at -78° . Also the effect of condensing together the monomer and solvent at liquid-oxygen temperature was investigated. Solvents investigated at -78° gave blue-green colours; no colour was observed at $+5^\circ$; at -183° the usual yellow-brown solid was formed. In each case, after warming to room temperature, the solvent was pumped off and the

TABLE 4. *Effect of solvent on CH₃·NO.*

Solvent	$+5^\circ$	-78°	-183°
H ₂ O	No dimer, oxime formed	—	No dimer, oxime formed
MeOH	—	Dimer B	Dimer B
EtOH	No dimer, oxime formed	—	Dimer B
CCl ₄	Trace of dimer B, oxime formed	—	{ CCl ₄ -insol., dimer B CCl ₄ -sol., λ_{\max} , 271 μ (?A + B)
Et ₂ O	—	Dimer B	Dimer B

ultraviolet absorption of the residue in water was determined. With carbon tetrachloride at -183° , the product dissolved only partly on warming to room temperature; separation into two portions was thus achieved and the absorption of each in water was determined; insoluble material was always white. Table 4 summarizes the results, strong absorption below 220 μ (in H₂O) with a peak below 200 μ again being taken as evidence for oxime formation. Except where specified, " λ_{\max} , 265 μ " indicates formation of dimer B, and " λ_{\max} , 276 μ " indicates formation of dimer A.

Infrared Absorption Spectra [carried out by M. St. C. FLETT].—The following infrared absorption bands (cm.⁻¹) were measured on a Grubb-Parson S4 double beam spectrophotometer (w = weak, m = medium intensity, s = strong, vs = very strong):

Trimeric formaldoxime (2 mg. in 0.350 g. of KBr): 3448 s, 3279 s, 2942 m, 2415 w, 2364 w, 2083 w, 1631 m, 1464 m, 1385 vs, 1198 w, 1147 m, 1124 m, 1036 m, 958 m, 842 s.

Dimer A (2 mg. in 0.170 g. of KBr): 3049 s, 1543 w, 1427 m, 1397 s, 1282 vs, 1130 vs, 936 vs, 824 w, 766 w.

Dimer A (2.5% in CHCl₃; 0.1-mm. cell): 3004 m, 1520 w, 1477 w, 1422 m, 1395 m, 1294 vs, 1208 vs, 1144 m, 1131 s, 1044 w, 934 s, 877 w, 848 w.

Dimer B (2 mg. in 0.170 g. of KBr): 3049 s, 2967 s, 1667 m, 1471 s, 1399 vs, 1342 vs, 1103 m, 1058 m, 1022 vs, 875 w, 740 s.

Dimer B (2.5% in CHCl₃; 0.1-mm. cell): 3003 m, 1513 w, 1481 w, 1405 m, 1341 w, 1297 s, 1231 m, 1143 w, 1132 w, 1042 w, 1025 w, 933 w, 875 w, 847 w.

DISCUSSION

It is shown that dimeric nitrosomethane exists in two interconvertible forms which, by analogy with azo- and azoxy-compounds, are probably *cis-trans*-isomers. It was suggested in a preliminary communication (Chilton, Gowenlock, and Trotman, *Chem. and Ind.*, 1955, 538) that dimer A is probably the *trans*- and dimer B the *cis*-isomer; the evidence for this may be summarized as follows. Dimer A can be obtained from dimer B by heat, the reverse change being effected by irradiation with ultraviolet light. It is well-known that maleic and fumaric acid and azo- and azoxy-compounds behave similarly. In addition it is known that some aromatic nitroso-dimers are *trans*-forms (Fenimore, *loc. cit.*; Darwin and Hodgkin, *loc. cit.*), as are the thermally stable azo-compounds. On molecular models it is impossible to form the *cis*-dimer of 2-methyl-2-nitrosopropane owing to the shape of the *tert.*-butyl groups. Similar considerations apply for other *tert.*-alkyl groups and for chlorinated *tert.*-alkyl groups. Tarte (*Bull. Soc. chim. belges*, 1954, 63, 525) has determined the N-O frequency in the following solid dimeric nitroso-compounds: nitrosomethane 1294, 2-methyl-2-nitrosopropane 1268, 1-chloro-2-methyl-2-nitrosopropane 1236 cm.⁻¹.

These values may be compared with our values for dimer A (1282 cm.^{-1}). Dimer B shows no absorption maxima in this region, the N=O frequency being tentatively identified with the 1399 cm.^{-1} absorption which is the strongest band in the spectrum. Comparison with the N-O frequency data for dimeric nitrosocyclohexane (1198 cm.^{-1}), dimeric 4-nitrosoheptane (1183 cm.^{-1}), and dimeric α -nitrosotoluene (1166 cm.^{-1}) (Müller and Metzger, *Chem. Ber.*, 1955, **88**, 165) substantiates this argument, it being assumed that the N=O frequency decreases in dimers of type A with increasing size of the hydrocarbon group.

An approximate determination of the dipole moment of dimer A in benzene by Dr. J. W. Smith indicates that the dipole moment is less than 0.7 D and possibly zero. Owing to the rapid isomerization of dimer B into dimer A in solvents of low dielectric constant suitable for dipole-moment determination, it is impossible to measure the dipole moment of dimer B. On the basis of this evidence, we therefore assign the configurations *trans* and *cis* to dimers A and B respectively. It may be noted that Hammick, New, and Williams (*loc. cit.*) obtained a value of $0.99 \pm 0.10\text{ D}$ for the dipole moment of dimeric 2:5-dimethyl-2-nitrosohexane which on steric grounds can only be the *trans*-isomer. This value is too high, as atom polarization has been neglected in calculating the dipole moment, and it is possible that the error limit suggested is too small in view of the assumptions made in calculating μ .

The *cis*-dimer appears to be the more stable at low temperatures, for in every experiment in absence of water the condensed monomeric nitrosomethane gave the *cis*-dimer on warming. Chilton and Gowenlock (*loc. cit.*) in their study of the reaction products of *isopropyl* and ethyl radicals with nitric oxide obtained λ_{max} values of $266\text{--}227\text{ m}\mu$ (in H_2O) and $289\text{--}291\text{ m}\mu$ (in Et_2O) which suggest that *cis*-dimers were obtained in these cases. The observation that such solids produced blue colours in solvents of low dielectric constant, this colour then fading, suggests a dissociation into the monomer and subsequent formation of the *trans*-dimer.

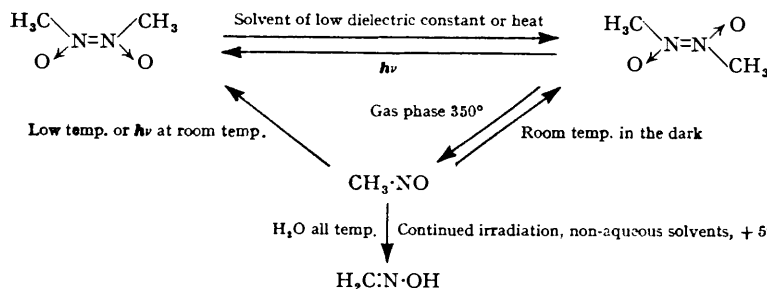
The early measurements by Baly and Desch (*J.*, 1908, **93**, 1747) of the absorption spectra of 2-methyl-2-nitrosopropane in ether, λ_{max} 300 (ϵ 100) and $655\text{ m}\mu$ (ϵ 20), have been quoted as standard in Braude's review (*Ann. Reports*, 1945, **42**, 105), together with the incorrect name nitrosobutane. Jander and Haszeldine's more recent measurements (*J.*, 1954, 912) (λ_{max} 296 and $675\text{ m}\mu$) give no values for the extinction coefficients. The extinction coefficient datum for the lower-wavelength maximum is probably in error owing to dissociation into the monomer in ether, whereas the intensity of absorption associated with monomeric nitroso-compounds is of the right order, *i.e.*, ϵ 15—30 (Hammick *et al.*, *J.*, 1935, 1679; 1937, 489). Both *cis*- and *trans*-dimers show high intensity ($\epsilon \sim 10,000$) in the ultraviolet spectrum and Müller and Metzger (*loc. cit.*) give ϵ values in the region $6800\text{--}12,200$ for the dimeric nitroso-compounds which they have recently prepared. Thus, in relation to the intensity of absorption, dimeric nitroso-compounds show a much greater resemblance to azoxy-compounds (Langley, Lythgoe, and Rayner, *J.*, 1952, 4191), nitramines, and nitrosamines (Haszeldine and Jander, *J.*, 1954, 691) than to monomeric nitroso-compounds and nitroalkanes (Kortüm, *Z. phys. Chem.*, 1939, **43**, B, 271; *Z. Elektrochem.*, 1941, **47**, 55). The effect of solvent on the ultraviolet absorption is similar to that for other polar non-conjugated chromophoric groups, λ_{max} being displaced to lower wavelengths with increasing dielectric constant of the solvent [cf. acetone (Gillam and Stern, "Electronic Absorption Spectroscopy," Arnold, 1954, p. 264), the *R*-band of mesityl oxide (*op. cit.*, p. 265) and the long-wavelength band of ethyl diazoacetate (*op. cit.*, p. 57)]. There has been little, if any, consideration of this effect from a theoretical angle; it can be shown that a plot of λ_{max} against either $\log \epsilon$ or $(\epsilon - 1)/(2\epsilon + 1)$ (where ϵ is the dielectric constant of the solvent) gives a smooth curve. The significance of such an empirical relation is unknown. The lower values for λ_{max} in ether ($213\text{ m}\mu$), or cyclohexane and *n*-hexane ($218\text{ m}\mu$), are not due to oxime formation, formaldoxime giving peaks at $207\text{ m}\mu$ in these solvents, but presumably are due to the dimeric nitroso-group's exhibiting a second characteristic peak. It is to be noted that both the aqueous and the ethanolic solution exhibit increasing absorption below $210\text{ m}\mu$, possibly owing to a maximum below $200\text{ m}\mu$.

In addition to dimerization, monomeric nitrosomethane can undergo isomerization to formaldoxime, and the mechanism of this nitroso-hydroxyimino-reaction is unknown. The facts that little formaldoxime is obtained in the pyrolysis of *tert.*-butyl nitrite or from

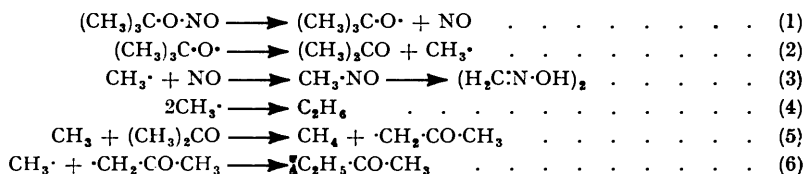
trans-dimeric nitrosomethane, and that in the direct reaction of gaseous alkyl radicals with nitric oxide (Chilton and Gowenlock, *loc. cit.*) little isomerization occurs, suggest an activation energy in the range 30—40 kcal./mole for the homogeneous gas-phase isomerization. Our results show that in water the reaction $\text{CH}_3\cdot\text{NO} \longrightarrow \text{H}_2\text{C}\cdot\text{N}\cdot\text{OH}$ is much faster than the dimerization. In non-aqueous solvents at -78° this isomerization is slow relatively to dimerization, whereas at room temperature the reverse holds good. If the rate of dimerization is assumed to be independent of the solvent, an ionic or a polar mechanism is probable for the isomerization. Alternatively if the rate of isomerization is independent of the solvent, then decrease in the dielectric constant of the solvent increases the rate of dimerization. An unambiguous answer cannot be given on the evidence available. The rapidity of the isomerization in water at room temperature affords a convincing explanation of the failure to isolate nitrosoalkanes containing α -hydrogen by controlled oxidation of the corresponding amine. Bamberger and Seligman's method (*loc. cit.*) for the oxidation, $\text{Bu}\cdot\text{NH}_2 \longrightarrow \text{Bu}\cdot\text{NO}$, was applied to *isopropylamine* under similar conditions. No blue colour was observed in the ether layer, and ultraviolet spectrophotometry indicated at most minute quantities of dimeric nitroso-compound in relation to oxime formation. The isolation of α -nitrosotoluene on oxidation of *N*-benzyl-hydroxylamine (Behrend and König, *Annalen*, 1891, 263, 212) is probably associated with the greater stability of the CH_2 group in benzyl compounds. Our evidence suggests that other preparative methods for nitrosoalkanes containing α -hydrogen might succeed in non-aqueous solvents where the tendency for the isomerization to the oxime could be suppressed by use of low temperatures. Alternatively, controlled oxidation of azo- and azoxy-alkanes should avoid the possibility of this speedy isomerization.

The conversion of the *cis*- into the *trans*-dimer in solvents of low dielectric constant may be ascribed to the increased energy of repulsion between the adjacent semi-polar $\text{N}\rightarrow\text{O}$ groups in such media. This would suffice to overcome the energy barrier for conversion into the *trans*-dimer in which the repulsion would be considerably reduced.

The reactions of nitrosomethane are summarised in the diagram.

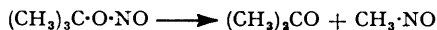


It remains to discuss the mechanism given by Yoffe (*loc. cit.*) for the decomposition of *tert*-butyl nitrite; he proposed



Our main products—nitrosomethane, acetone, and nitric oxide—could arise by this mechanism. [Reaction (3) implies formaldoxime dimer—this should be the trimer.] However, Yoffe's products do not account for his mechanism, the carbon balance being incorrect. Also, under these conditions, the concentrations of methyl radicals and nitric oxide being approximately equal, the relative yields of ethane and nitrosomethane should be proportional to the relative collision efficiencies of reaction 4 and 3 (Durham and Steacie,

J. Chem. Phys., 1952, 20, 582), *i.e.*, $\sim 100:1$. Yoffe's results however give a ratio of 0.05:1. It is therefore necessary to suggest that the predominating reaction is the molecular decomposition:



Support for such a mechanism is given by the predominance of the *trans*-rotational isomer of *tert.*-butyl nitrite (Tarte, *ibid.*, 1952, 20, 1570) and would thus afford a molecular decomposition mechanism for both photolysis and pyrolysis of *tert.*-butyl nitrite. Production of nitric oxide in the pyrolytic decomposition is due to Yoffe's reaction (1). Pyrolysis of the *trans*-dimer under similar conditions to those used for *tert.*-butyl nitrite yields the *cis*-dimer *via* monomeric nitrosomethane. This suggests that the reaction $\text{CH}_3\cdot\text{NO} \longrightarrow \text{CH}_3\cdot + \text{NO}$ could participate to a very small extent at most.

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