641. *Reaction of Nitric Oxide with Gaseous Hydrocarbon Free Radicals. Part I.* iso*Propyl Radical.*

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The reaction products of the pyrolysis of di*iso*propylmercury in a flow system with nitrogen and nitric oxide as carrier gas have been studied. Absorption spectra and chemical tests show that acetoxime and a nitroso-compound are formed. Various physical properties of the mixture have been studied and are discussed in relation to the monomeric and dimeric states of nitroso-compounds and isomerization of the nitroso-compound to the acetoxime.

The inhibiting effect of nitric oxide on radical chain reactions in the decomposition of certain organic compounds has been summarised by Hinshelwood ("Kinetics of Chemical Change," Oxford Univ. Press, 1940, p. 92). It is suggested that the reaction R + NO ⟶ R·NO takes place, where R is a free radical. Nitroso-compounds have never been isolated in nitric oxide-inhibited reactions involving gaseous hydrocarbon free radicals, although they are formed in the reaction of nitric oxide in solution with triphenylmethyl (Schlenk and Mair, *Ber.*, 1911, **44**, 1170), diphenylnitrogen (Wieland, *Annalen*, 1911, **381**, 200), triphenylhydrazyl (Goldschmidt, *Ber.*, 1920, **53**, 44), and diphenylnitric oxide (Wieland and Offenbächer, *ibid.*, 1914, **47**, 2111). It is to be noted that the radical αα-diphenyl-β-trinitrophenylhydrazyl and that from 9-chloro-10-hydroxyphenanthrene do not react with nitric oxide in solution (Goldschmidt and co-workers, *Ber.*, 1922, **55**, 628; *Annalen*, 1924, **438**, 202; 1925, **445**, 123). It has been assumed that nitroso-compounds formed in gaseous reactions are decomposed according to such mechanisms as

$$CH_3{\cdot}NO \longrightarrow H_2C{:}N{\cdot}OH \longrightarrow HCN + H_2O$$

The evidence concerning the decomposition products of nitroso-compounds is summarised in Table 1. It will be seen that the mechanism cited is not unambiguously supported. It is, however, established that formaldoxime decomposes to give hydrogen cyanide and water (H. A. Taylor and Bender, *J. Chem. Phys.*, 1941, **9**, 761), the products interacting to give principally carbon monoxide and ammonia, together with some nitrogen, hydrogen, ethane, and traces of an unsaturated hydrocarbon. The rate of reaction of methyl radicals with nitric oxide has been measured by Durham and Steacie (*ibid.*, 1952, **20**, 582), who give no details about any products of the reaction.

Nitroso-paraffins are difficult to prepare by normal chemical methods, only *tert.*-nitroso-aliphatic compounds having been so prepared. Nitroso-paraffins are colourless crystalline dimeric compounds in the solid state, dissociated by heat or dissolution to the intensely blue monomeric compound. Halogenonitroso-paraffins such as 2-chloro- and 2-bromo-2-nitrosopropane exist as the blue monomers, whereas those that have secondary hydrogen atoms, *e.g.*, 1-chloro-1-nitrosoethane, rapidly dimerise and isomerise to the corresponding oxime. Nitrosomethane has been prepared by the photolysis of *tert.*-butyl nitrite (Coe and Doumani, *J. Amer. Chem. Soc.*, 1948, **70**, 1516), its properties being similar to those of other nitroso-paraffins apart from the fact that isomerization to formaldoxime is slow.

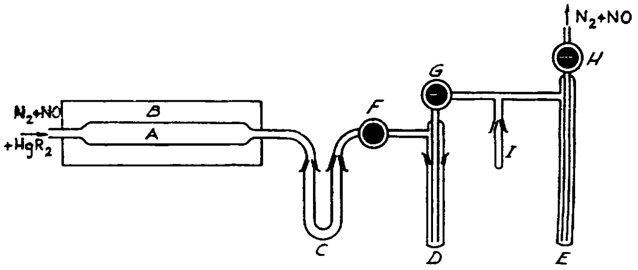
TABLE 1. *Products from nitric oxide-inhibited decompositions.*

Organic compound	Product	Ref.	Remarks
C_2H_6	Trace of cyanide	*a*	Thermal decomposition
Bu^nOMe	Trace of cyanide	*b*	
Me_2O	NH_3. Blue product at −180°	*c*	
Et_2O	$Me{\cdot}NH_2$	*c*	
Me_2Hg	Unidentified white solid	*d*	Photochemical decomposition
CF_3I	Deep blue solid at −180°	*e*	

(*a*) Küchler and Theile, *Z. physikal. Chem.*, 1939, **42**, *B*, 359. (*b*) Magram and H. A. Taylor, *J. Chem. Phys.*, 1941, **9**, 760. (*c*) Meissner and Thompson, *Nature*, 1937, **139**, 1018. (*d*) Thompson and Linnett, *Trans. Faraday Soc.*, 1937, **33**, 874. (*e*) Dacey, *Discuss. Faraday Soc.*, 1953, **14**, 84.

EXPERIMENTAL

The apparatus was a modification of that used by Butler and Polanyi (*Trans. Faraday Soc.*, 1943, **39**, 19) and the relevant section of it is illustrated in the Figure. The carrier gas, a mixture of nitrogen and nitric oxide in approximately equal amounts and at a total pressure of about 3·7 mm., picked up di*iso*propylmercury at a pressure of about 0·1 mm. by means of the trap system devised by Warhurst (*ibid.*, 1939, **35**, 674) and passed through the reaction vessel *A* heated by the furnace *B*. The pyrolyses were performed in the temperature range 230—280°. The products were condensed out in the U-tube *C* and the traps *D* and *E*, which were cooled to −78°, −130°, and −183°, respectively. Nitric oxide was used up (presumably owing to reaction with *iso*propyl radicals), and therefore it was added throughout the experiment, the pressure in *A* being kept constant to within ±0·2 mm. Nitrogen was made by heating sodium azide in a high vacuum. Nitric oxide was prepared by Rees (M.Sc. Thesis, Wales, 1925) according to Winkler's method (*Ber.*, 1901, **34**, 1408), and intensively purified. It was still colourless, and some was passed through a solid carbon dioxide–acetone trap, frozen in liquid air, and the white solid allowed to evaporate slowly, the gas being collected in an evacuated bulb. Di*iso*propylmercury was prepared according to Marvel and Gould's method (*J. Amer. Chem. Soc.*, 1922, **44**, 153) as modified by Gilman and Brown (*ibid.*, 1930, **52**, 3314) : it was fractionally distilled in high vacuum and further distilled to constant vapour pressure within the Warhurst trap system. Except during runs, it was kept at −78° under high vacuum; under such conditions it survives for considerable periods without decomposition. On the completion of a run, the traps were examined : the U-tube *C* contained a thin film of mercury and some di*iso*propylmercury, the trap *D* contained a yellow solid and a liquid (mainly C_6 hydrocarbons with a little di*iso*propylmercury), and the trap *E* contained a small amount of a yellow solid together with C_3 hydrocarbons. Air was admitted into the section containing *A* and *C*, up to trap *F*, and *C* was detached, allowed to warm to room temperature, and washed



out with ether. The washings were pale blue, the colour rapidly fading. The section between traps *F* and *H* was evacuated with the low-temperature baths in position, and then the taps *G* and *H* were closed. It was observed on removing the liquid-oxygen bath from *E* that the small amount of yellow solid condensed on the walls of the trap melted and then formed a white solid. The m. p. of the yellow solid on the walls of trap *D* was therefore estimated approximately. The trap was cooled by a pentane bath in an evacuable unsilvered Dewar vessel that was cooled by liquid oxygen. The liquid oxygen was removed, and the pentane bath allowed to warm slowly. A chromel–alumel thermocouple in a thin glass tube was inserted into the pentane so that the junction of the thermocouple was approximately at the central point of the yellow deposit. As the bath warmed, the deposit was observed, the temperature readings being made simultaneously. The deposit melts within the range $-78°$ to $-85°$ to a yellow-brown liquid which speedily changes into a white solid. The pentane bath was then removed, the tap *G* opened, and liquid oxygen placed around the tube *I*, whereupon all remaining products other than the white solid distilled over into *I*.

Experiments with the White Solid.—A detailed investigation of the white solid was made. It was a white waxy substance, the lower part of the deposit in trap *D* having a leaf-like structure. It had a camphor-like smell and a sharp bitter odour, and was fairly volatile. When kept for a few hours, the white solid changed to colourless crystals, some needle-shaped and others minute square plates. The m. p. varied between 40° and 59° according to the run. In one case the solid melted between 44° and 47°, softening taking place about 37°. Close examination during the m. p. determination by the capillary tube method showed that there were two types of crystal present, one melting to a colourless liquid, and the other to a blue liquid the colour of which rapidly faded at the m. p. Further heating to about 90° caused bubbling to take place, and at about 95° the liquid became green. On cooling, the liquid decolorized, and when it was reheated to 95° the green colour reappeared. This process was continually repeated. In another case the m. p. was 52°, and the green colour appeared at about 85° whereat boiling also took place.

The behaviour of the solid in various solvents was investigated, and the appearance of colours on dissolving, on gentle warming, and on boiling was noted. The colour that appeared on dissolution faded completely, the rate of disappearance varying considerably with the solvent. Chloroform and bromoform were the only solvents in which the colour that appeared on gentle warming could not be regenerated by cooling and further gentle heating. The colour that appeared on boiling disappeared on cooling and could be regenerated by boiling except for the dioxan solution where a yellow-green colour remained on cooling. The results are given in Table 2.

TABLE 2.*

			Colour of solution on:						Colour of solution on:		
Solvent	B. p.	ε	dissolving	gentle heating	boiling	Solvent	B. p.	ε	dissolving	gentle heating	boiling
n-C_5H_{12} ...	36°	1·85		(Insoluble)		$CH_3\cdot CO_2H$	118°	6·13	—	B	B
n-C_6H_{14} ...	69	1·91		(Insoluble)		$CH_3\cdot CO_2Me$	51	8·02	—	B	—
CCl_4	77	2·22	—	—	—	$H\cdot CO_2Me$...	32	8·37	—	—	—
Dioxan ...	101	2·24	B	G	G	CH_2Cl_2......	40	9·14	—	B	—
C_6H_6	80	2·30	B	—	pale B	$COMe_2$ ...	56	21·45	—	—	—
PhMe	111	2·38	B	—	B	EtOH	78	25·80	—	—	—
Et_2O	35	4·36	B	—	—	Pr^nNO_2 ...	131	~30	—	B	B
$CHCl_3$	61	4·64	B	B	—	$CH_3\cdot CN$ ...	82	37·5	—	B	—
$CHBr_3$ ...	150	4·73	B	B	—	H_2O	100	80	—	—	—
$CH_3\cdot CO_2Et$	77	6·11	B	—	—						

* B. p. of solvent given to nearest degree, dielectric constant (ε) to two decimal places. Values taken from Weissberger and Proskauer ("Organic Solvents," Oxford Univ. Press, 1935); B = blue, G = green. Solid is soluble in all but the first two solvents listed.

Chemical tests were made for the presence of nitroso- and oxime groups according to Feigl's method ("Spot Tests," Elsevier, Amsterdam, 1939). The Liebermann nitroso-test (*idem, ibid.*, p. 267) gave a green colour, the product becoming green-yellow in sodium hydroxide solution. The oxime test (*idem, ibid.*, p. 291) gave a pink colour and when the solid was fused with diphenylamine, and concentrated sulphuric acid added, a faint pale blue colour resulted (Coe and Doumani, *loc. cit.*).

Investigations of the ultra-violet absorption spectra of solutions of the solid were made with a Unicam S.P. 500 photoelectric quartz spectrophotometer. As the composition of the substance was unknown, only the data for $\lambda_{max.}$ in dilute solutions are presented, no determination of ε values being made. The values obtained are given in Tables 3 (aqueous solutions) and 4 (ethereal solutions), literature data being taken from Braude (*Ann. Reports*, 1945, **42**, 112). It is to be noted that the $\lambda_{max.}$ values are the same for Pyrex, silica, and silicon-coated traps (trap *D* in Fig. 1) and also for the product when a packed reaction vessel (increase in surface/volume ratio by factor of 11) is used.

TABLE 3.

Substance	$\lambda_{max.}$ (mμ)	Substance	$\lambda_{max.}$ (mμ)
Solid (Pyrex trap)	<200, 266	Acetoxime	<200
Solid + HCl (Pyrex trap)	<200, 266	Acetoxime (Braude)	190

A specimen of the solid was sealed off under vacuum in a small Pyrex tube and kept in the dark. The solid changed from its usual white, waxy appearance to colourless moist square crystals, which sublimed within the tube. Examination with a high-powered lens showed no differences in appearance between these crystals and acetoxime. After some time some of the crystals disappeared and a pale yellow oil was formed. The yellow oil sometimes became a yellow-white wax that melted to a yellow oil when the tube was warmed with the hand. The tube was opened after 10 weeks, the cutting being made so as to separate the portion containing the crystals from that containing the oil. The crystals had no detectable odour, gave no colour in ether, melted at 57—60° (m. p. of acetoxime 59°), and gave no colour change on further heating. They were readily soluble in cold water, and in ethereal solution absorption maxima were found at 209—210 and 289—291 mμ (small peak). The oil dissolved in ether with no coloration and gave absorption maxima at 289—291 and 209 mμ (small peak). On warming, the oil became green at about 94° and boiled at about 145°, leaving a water-soluble white solid on cooling. Reference to Table 4 shows that a partial separation of acetoxime and a nitroso-compound has been made by sealing off *in vacuo*.

Solutions of the solid in ether and ethyl alcohol were kept in corked tubes for about 6 weeks. Spectroscopic examination then showed absorption maxima at 208 mμ (ether) and 206 and 285—290 mμ (alcohol), the second peak for the alcoholic solution being very small. Reference to Table 4 shows that the nitroso-compound has disappeared in ethereal solution and almost disappeared in alcoholic solution.

TABLE 4.

Substance	$\lambda_{max.}$ (mμ)	Substance	$\lambda_{max.}$ (mμ)
Solid (Pyrex trap)	211, 292, 665 *	Di*iso*propylmercury	218
,, (silica trap)	211, 289—291	Washings of U-tube	218—220, 290
,, (silicone-coated trap)	207, 290—291	Acetoxime	210—212
,, (packed reaction vessel)	209, 289	Nitroso-compound (Braude)	300, 665

* Only taken for Pyrex trap; weak absorption, colour fades during determination.

DISCUSSION

The product is evidently a mixture of acetoxime and a nitroso-compound, probably 2-nitrosopropane. We suggest the following mechanism to account for these results, the *iso*propyl radicals being produced by dissociation of the Hg–C bonds.

$$\mathrm{Me_2CH + NO \longrightarrow Me_2CH{\cdot}NO} \quad (1)$$

$$\mathrm{Me_2CH{\cdot}NO \longrightarrow Me_2C{:}NOH} \quad (2)$$

$$\mathrm{2Me_2CH{\cdot}NO \longrightarrow Dimer} \quad (3)$$

$$\mathrm{2Me_2CH \longrightarrow Me_2CH{\cdot}CHMe_2} \quad (4)$$

$$\mathrm{2Me_2CH \longrightarrow C_3H_8 + C_3H_6} \quad (5)$$

Reaction (2) may occur in the gaseous phase, at the wall of the reaction vessel, or at the trap surface. As neither alteration of the trap surface nor packing of the reaction vessel produces any significant change in the nature of the white solid, it is probable that reaction (2) is a gas-phase isomerization reaction. From the reaction conditions, it is probable that reaction (2) has an activation energy in the range of 30—40 kcal./mole. This isomerization reaction can also take place slowly in non-aqueous solution at room temperature, but is not accelerated in aqueous solution by hydrochloric acid, again suggesting a non-ionic mechanism of isomerization. The variation of the m. p. of the white solid is due to the varying proportions of the two constituents present. It is probable from comparison with previous work (see p. 3233) that the blue liquid obtained in m. p. experiments is the 2-nitrosopropane monomer whereas the yellow-white solid melting to a pale oil in the sealed tube experiment is the dimer (contaminated with a small amount of acetoxime). We can tentatively assign a m. p. of about 15—25° to the dimer and a b. p. of about 145° to the monomer, the monomer–dimer transition taking place in the region 85—95°. The melting and transition of the yellow solid at −78° to −85° to a yellow-brown liquid and then a white solid may be associated either with the change 2-nitrosopropane monomer (solid) ⟶ 2-nitrosopropane monomer (liquid) ⟶ 2-nitrosopropane (dimer, solid) as suggested by us in a preliminary communication (*Nature*, 1953, **172**, 73), or may be due to acetoxime monomer (solid) ⟶ acetoxime monomer (liquid) ⟶ acetoxime trimer (solid). The colour of the solid as a thin film on the inside of a glass tube was seen by reflected light, and the difference between this colour and the blue or green colour in transmitted light usually associated with monomeric nitroso-compounds may be due to these conditions.

The behaviour of the solid when dissolved in various solvents requires correlation. The simplest feature is that of colour change on boiling. We suggest that it is almost solely a temperature effect, the blue coloration only occurring for solvents whose b. p. is above 80°. However, bromoform, acetonitrile, and water do not give this blue colour. The colour change on solution is given only for those solvents with dielectric constants in the range 2·24—6·11. Although such a correlation may be fortuitous, we suggest that it is too well marked to be disregarded, as the solvents concerned have singularly few other features in common. It must also be noted that from ether to dioxan the blue colour fades with increasing rapidity. The production of the blue colour on gentle warming is difficult of explanation. It seems that the scheme proposed by Coe and Doumani (*loc. cit.*) for nitrosomethane, generalised as

$$\underset{\text{colourless}}{(\mathrm{RNO})_2} \rightleftharpoons \underset{\text{blue}}{2\mathrm{RNO}}$$

is unable to account for all these variations or even for all their observations, for they record a blue colour above the m. p. of the dimer (122°) and a blue colour on heating in toluene (b. p. 110°). It is necessary that solvation states must be considered in any explanation of these data. We reserve further comments until parallel observations are available for other nitroso-compounds.

The general failure to isolate nitroso-paraffins in nitric oxide-inhibited reactions is probably due to the decomposition of these compounds under the usual conditions associated with pyrolysis by the static method. The short time of reaction associated with the flow method, together with the lower temperatures necessary to break the relatively weak Hg–C bonds (Gowenlock J. C. Polanyi, and Warhurst, *Proc. Roy. Soc.*, 1953, *A*, **218**, 269; Chilton and Gowenlock, to be published) compared with C–C and C–O bonds, favour the isolation of the nitroso-compound.

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