Trichloronitrosomethane. Part II. Thermal Decomposition, and an Improved Synthesis, of Trichloronitrosomethane

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Trichloronitrosomethane decomposes within 3 hours at 100 °C to give nitrogen, nitric oxide, nitrosyl chloride, carbon tetrachloride, *N*-(dichloromethylene)trichloromethylamine *N*-oxide, and phosgene. The dichloronitroso-methyl radical is postulated as a reaction intermediate and a simple MO picture of bonding in that radical is outlined.

EARLY syntheses of trichloronitrosomethane, carried out at relatively high temperatures, gave a wet, impure product.[1,2] More recently, a low-temperature synthesis has been developed which gives a dry purer product.[3] This latter method has now been modified so as to avoid the use of a sealed reaction vessel and at the same time to remove sulphur dioxide, an inhibitor to the formation of trichloronitrosomethane, from the reaction zone.

When gaseous nitrosyl chloride is passed through a cooled bed of sodium trichloromethanesulphinate, a reaction occurs as witnessed by the appearance of a blue colour. The progress of the reaction is easily observed by the movement of the coloured reaction zone through the bed of reactant. Purification of the product is simplified since the sulphur dioxide and excess of nitrosyl chloride are vented and the trichloro-nitrosomethane is collected in a cooled trap.

Recently a synthesis from chloroform has been reported but as yet no satisfactory method of separating trichloronitrosomethane from unchanged chloroform has been devised.[4]

Prandtl and Sennewald [1] reported the formation of the compounds $CCl_3N{:}CCl_2$, $CCl_3{\cdot}NO_2$, NOCl, together with smaller amounts of nitric oxide and hexachloro-ethane during the thermolysis of trichloronitrosometh-ane. This reaction was carried out under reflux in an atmosphere of carbon dioxide using an oil-bath at 120 °C. The main thermal decomposition was repre-sented by equation (1). During the course of the

$$3CCl_3{\cdot}NO \longrightarrow CCl_3{\cdot}N{:}CCl_2 + CCl_3{\cdot}NO_2 + NOCl \quad (1)$$
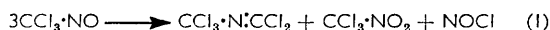
present work Tattershall reported confirmation of

this mode of decomposition but no experimental details were quoted.[5]

In the present work a careful examination of the thermal decomposition at 100 °C has been made. The main products are nitric oxide, carbon tetrachloride, and *N*-(dichloromethylene)trichloromethylamine *N*-oxide,[6] † together with smaller amounts of nitrosyl chloride, nitrogen, phosgene, and chloropicrin (trichloro-nitromethane). An unidentified compound (A) having a pink colour has also been noted. The yields of these compounds are given in the Table. Compound (A) is found in the carbon tetrachloride fraction; its pink colour fades on exposure to light and nitrogen gas is evolved. The carbon tetrachloride solution of (A) shows weak absorption in its visible spectrum at 265—290 nm and absorption bands at 5·7 and 9·5 μm in the i.r. region which are not attributable to either carbon tetrachloride or chloropicrin. The ease of breakdown to elemental nitrogen suggests two possibilities for (A), namely CCl_2N_2 or $CCl_3{\cdot}N{:}N{\cdot}CCl_3$, but no positive con-firmation has yet been obtained.

The high yield of carbon tetrachloride and nitric oxide is attributed to initial cleavage of the C–N bond in trichloronitrosomethane followed by chlorine ab-straction by $CCl_3{\cdot}$ from a molecule of $CCl_3{\cdot}NO$ [equations (2) and (3)].

$$CCl_3{\cdot}NO \xrightarrow{\text{Heat}} CCl_3{\cdot} + NO \quad (2)$$

$$CCl_3{\cdot} + CCl_3{\cdot}NO \longrightarrow CCl_4 + {\cdot}CCl_2{\cdot}NO \quad (3)$$

It is interesting at this stage to consider the bonding

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† In previous work, this compound has been named αα-dichloro-*N*-trichloromethyl nitrone.

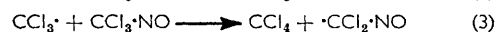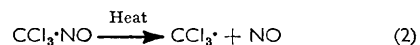[1] W. Prandtl and K. Sennewald, *Ber.*, 1929, **62**, 1754.
[2] W. Prandtl and W. Dollfus, *Ber.*, 1932, **65**, 754.

[3] Part I, H. Sutcliffe, *J. Org. Chem.*, 1965, **30**, 3221.
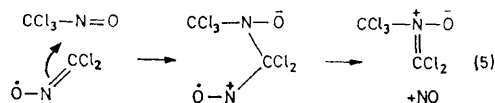[4] B. W. Tattershall, *J. Chem. Soc.* (*A*), 1970, 3261.
[5] B. W. Tattershall, *J. Chem. Soc.* (*A*), 1970, 3263.
[6] V. Astley and H. Sutcliffe, *Tetrahedron Letters*, 1971, **29**, 2707.

of the $\cdot CCl_2 \cdot NO$ radical since this will influence its stability and reactivity.

The carbon atom will form three σ-bonds to chlorine and nitrogen leaving an orbital which is essentially p in character. The nitrogen atom in addition to having a lone pair of electrons will form σ-bonds to oxygen and carbon and will have a p-orbital available for further bonding. Similarly, the oxygen atom will have a σ-bond

equation (5). The latter mechanism is similar to that

$$CCl_3-N=O \underset{\dot{O}-N}{\overset{\cdot}{\diagup}} CCl_2 \longrightarrow CCl_3-N-\bar{O} \underset{\dot{O}-N}{\diagup} CCl_2 \longrightarrow \underset{+NO}{\overset{CCl_3-\overset{+}{N}-\bar{O}}{\underset{\parallel}{CCl_2}}} \quad (5)$$

proposed by Baldwin *et al.* for the reaction of diazomethane with nitroso-compounds.[9] The alternative

Product distribution

Experiment	Products	NO	CCl₄ *	CCl₃N(O)CCl₂	CCl₃NO₂	COCl₂	NOCl	SO₂	(A)	CCl₄ †	N₂
1	23·3 g	1·16	10·03	5·3	0·66	1·45	3·69	2·73	N.E.		0·0
	157 mmol	38·8	66	23·2	4·0	14·9	56·3	42·6			
	Yield (%)	24·7	42	14·8	2·6		35·9				
2	9·65 g	1·53	4·67	3·0	0·3	0·49	0·15	0·0	N.E.		0·0
	65 mmol	35·0	30·7	13·0	1·85	5·0	30·7	0·0			
	Yield (%)	54	47·2	20	2·8	7·7	3·5	0·0			
3	15·8 g	1·745	7·1	5·5	0·5	0·86	0·207	0·0	1·7 ‡	5·4 †	0·02
	106·4 mmol	58·3	46	23·8	3·2	8·8	3·2	0·0	6·5 ‡	35·1 †	0·725
	Yield (%)	54·8	43·3	22·4	3·0	8·3	3·0	0·0	6·1	33 †	0·68

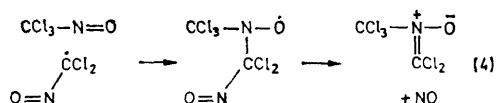* Not corrected for (A). † Corrected for (A). ‡ Estimated assuming (A) is $CCl_3N_2CCl_3$. N.E. = Not estimated.

to nitrogen, two lone pairs of electrons and a p-orbital. The structure C–N–O is expected to be bent at nitrogen since the molecule from which it is derived is also bent at this point. Taking a linear combination of the three p-orbitals will give three molecular orbitals. One of these resulting orbitals, the bonding orbital, will extend over all three atoms and contain two electrons. The other two molecular orbitals may be of a non-bonding or antibonding character and one of these will contain the unpaired electron. The situation is thus not unlike that of a π-allyl ligand, and the orbital shapes may be expected to be similar.[7] Some additional delocalisation of the unpaired electron onto the two chlorine atoms may also be expected, analogous to that observed in the case of bis(trichloromethyl)nitroxide.[8] The overall effect will be a stabilisation of the $\cdot CCl_2 \cdot NO$ radical relative to one in which no delocalisation can occur. This concept may also be expressed in resonance terms, thus

$$Cl_2\dot{C}-N=O \longleftrightarrow Cl_2C=N-\dot{O}$$

The possibility that this radical is of the iminoxyl type cannot be excluded, but in the absence of e.s.r. data no firm conclusion can be reached.

The formation of N-(dichloromethylene)trichloromethylamine N-oxide is considered to arise by attack of the dichloronitrosomethyl radical on trichloronitrosomethane followed by elimination of nitric oxide. Two alternative mechanisms may be envisaged; either equation (4) since the nitrogen atom of the nitroso-
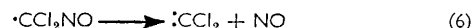
$$CCl_3-N=O \underset{O=N}{\overset{\dot{C}Cl_2}{\diagup}} \longrightarrow CCl_3-N-\dot{O} \underset{O=N}{\diagup} CCl_2 \longrightarrow \underset{+NO}{\overset{CCl_3-\overset{+}{N}-\bar{O}}{\underset{\parallel}{CCl_2}}} \quad (4)$$

function is known to be susceptible to radical attack, or

dichlorocarbene route [equations (6) and (7)] is not pre-

$$\cdot CCl_2NO \longrightarrow :CCl_2 + NO \qquad (6)$$

$$CCl_2: + CCl_3 \cdot NO \longrightarrow CCl_3 \cdot \overset{+}{N}(\bar{O})CCl_2 + NO \qquad (7)$$
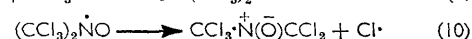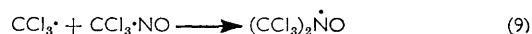
ferred in view of the expected stabilisation of the dichloronitrosomethyl radical.

The overall reaction giving rise to the main reaction products may be represented by equation (8).

$$3CCl_3 \cdot NO \longrightarrow CCl_4 + CCl_3 \cdot \overset{+}{N}(\bar{O})CCl_2 + 2NO \qquad (8)$$

Another possible mode of formation of N-(dichloromethylene)trichloromethylamine N-oxide is *via* the intermediate formation of bis(trichloromethyl) nitroxide followed by the expulsion of a chlorine atom [equations (9) and (10)]. This is not favoured since the chlorine

$$CCl_3 \cdot + CCl_3 \cdot NO \longrightarrow (CCl_3)_2\dot{N}O \qquad (9)$$

$$(CCl_3)_2\dot{N}O \longrightarrow CCl_3 \cdot \overset{+}{N}(\bar{O})CCl_2 + Cl \cdot \qquad (10)$$

atom would react with nitric oxide to give nitrosyl chloride in a yield compatible with that of the nitrone Only a low yield of nitrosyl chloride is observed, therefore at best this reaction makes only a minor contribution to the overall reaction scheme.

The reaction sequence summarised by equation (8) is not the complete picture since the molar ratio of the three main products is not exactly 1 : 1 : 2. Taking a corrected value for the yield of carbon tetrachloride and assuming the NOCl is derived from the NO, then

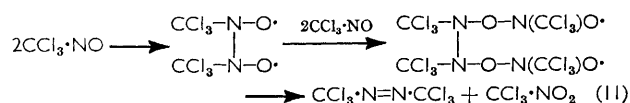$$CCl_4 : CCl_3 \cdot N(O)CCl_2 : NO = 1\cdot1 : 0\cdot8 : 2\cdot0.$$

Thus there is a greater yield of carbon tetrachloride than predicted but a reduced yield of the N-oxide. This could be due to other reactions of the radical $\cdot CCl_2 \cdot NO$ especially in the later stages of the reaction when the concentration of $CCl_3 \cdot NO$ is considerably reduced, and the chance of reaction (4) or (5) taking place is also

[7] G. E. Coates, M. L. H. Green, and K. Wade, 'Organometallic Compounds,' vol. 2, Methuen, 1948, p. 45.
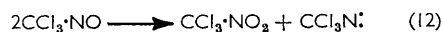[8] H. Sutcliffe and H. Wardale, *J. Amer. Chem. Soc.*, 1967, **89**, 5487.

[9] J. E. Baldwin, A. K. Qureshi, and B. Sklarz, *J. Chem. Soc.* (C), 1969, 1073.

reduced. Furthermore, chlorine abstraction by $CCl_3\cdot$ may take place from species other than $CCl_3\cdot NO$, notably $CCl_3\cdot\overset{+}{N}(\bar{O})CCl_2$, thus increasing the yield of carbon tetrachloride at the expense of that of the nitrone. It is noteworthy that the total molar yield of CCl_4 and $CCl_3\cdot\overset{+}{N}(\dot{:}\bar{O})CCl_2$ approximately equals that of nitric oxide.

The formation of chloropicrin may be attributed to a reaction analogous to that postulated for the thermal decomposition of trifluoronitrosomethane [10] [equation (11)] or to a disproportionation reaction [equations (12) and (13)]. Neither of these products has as yet

$$2CCl_3\cdot NO \longrightarrow \begin{matrix} CCl_3{-}N{-}O\cdot \\ | \\ CCl_3{-}N{-}O\cdot \end{matrix} \xrightarrow{2CCl_3\cdot NO} \begin{matrix} CCl_3{-}N{-}O{-}N(CCl_3)O\cdot \\ | \\ CCl_3{-}N{-}O{-}N(CCl_3)O\cdot \end{matrix}$$

$$\longrightarrow CCl_3\cdot N{=}N\cdot CCl_3 + CCl_3\cdot NO_2 \quad (11)$$

been identified but the unknown compound (A) may be one of them.

$$2CCl_3\cdot NO \longrightarrow CCl_3\cdot NO_2 + CCl_3N\dot{:} \quad (12)$$

$$CCl_3N\dot{:} + CCl_3\cdot NO \longrightarrow CCl_3\cdot N(O)N\cdot CCl_3 \quad (13)$$

Further decomposition of chloropicrin satisfactorily accounts for the formation of phosgene and nitrosyl chloride.[12]

In one thermal decomposition experiment sulphur dioxide was observed among the reaction products. This is attributed to the presence of the unstable compound $CCl_3\cdot SO_2\cdot NO$ present in the trichloronitrosomethane. This compound has been suggested previously as a possible intermediate during the synthesis of trichloronitrosomethane.[3] The compound $CCl_3\cdot SO_2\cdot NO$ breaks down into $CCl_3\cdot NO$ and SO_2 when stored at 0 °C for 12 h which enables purification of trichloronitrosomethane to be carried out.

EXPERIMENTAL

Trichloronitrosomethane was prepared by the method previously described [3] and also by the method described below. The product was purified by trap-to-trap fractionation in vacuo.

I.r. spectra were measured on a Perkin-Elmer model 221 spectrophotometer, mass spectra on an A.E.I. model MS12, and u.v. spectra on a Perkin-Elmer model 137 spectrophotometer. G.l.c. analysis was carried out with a 5-m $\times$ 3-mm i.d. column packed with 20% dinonyl-phthalate on Celite using helium as the carrier gas.

Nitrosyl chloride was prepared by the method of Morton and Wilcox.[12]

Preparation of Trichloronitrosomethane.—Sodium trichloromethanesulphinate ($36\cdot7$ g, $0\cdot178$ mol) prepared from trichloromethanesulphonyl chloride by the procedure of Prandtl and Sennewald,[1] was loosely packed into the centre tube of a conventional water condenser. This was mounted in a sloping position with the lower end attached to a trap cooled to 0 °C and the upper end attached to the nitrosyl chloride generator. Cooling water was passed through the jacket of the condenser and nitrosyl chloride passed slowly through the sodium trichloro-

methanesulphinate. Reaction began as soon as the gaseous nitrosyl chloride contacted the sodium salt and the blue-green reaction zone passed slowly through the bed of sodium trichloromethanesulphinate. At the end of the reaction the tube was flushed with nitrogen to ensure complete transfer of the product into the cooled trap. The impure product ($18\cdot0$ g.) was transferred to a vacuum line and purified by trap-to-trap fractionation in vacuo to give pure trichloronitrosomethane ($15\cdot5$ g, $0\cdot105$ mol) in 60% yield.

Thermal Decomposition of Trichloronitrosomethane.—Trichloronitrosomethane ($26\cdot1$ g, $0\cdot176$ mol) was sealed in vacuo in a heavy walled glass Carius' tube and heated to 100 °C for $3\frac{1}{2}$ h; at the end of this time the blue colour of the nitroso-compound had completely faded. The tube was cooled and the volatile products were removed to leave a colourless involatile oil together with traces of a white solid.

The volatile products were fractionated in vacuo through traps cooled to -46, -63, -96, -131, and -196 °C. Each fraction was analysed by molecular-weight measurement, i.r. spectroscopy, g.l.c., and, in some cases, mass spectrometry. The products and yields are given in the Table.

The mass spectrum of the involatile oil indicates the presence of the following fragments: Cl, CCl, CCl_2, CCl_3, CNCl, COCl, C_2NCl, $CNCl_2$, C_2NCl_3, C_2NOCl_2, C_2NOCl_3, C_2NCl_2, C_2NCl_4, C_2NOCl_4, and is consistent with the formulation of the nitrone $CCl_3\cdot\overset{+}{N}(O)\overset{-}{C}Cl_2$. The i.r. spectrum was measured in the liquid phase, in the region 2000—700 cm^{-1} and shows the following main absorption bands: 1639, 1613, 1016, 931, 801, and 777 cm^{-1}. The u.v. spectrum shows an absorption maximum at 210 nm with $\varepsilon_{max.}$ $6,400$ (Found: C, $10\cdot8$; H, $0\cdot2$; N, $6\cdot3$. C_2Cl_5NO requires C, $10\cdot4$; H, $0\cdot0$; N, $6\cdot1\%$.)

The variation of vapour pressure with temperature was measured in the range 20—150 °C using an isoteniscope, the results were treated by a computerised least-squares plot to give equation (14). The correlation is $-0\cdot996$

$$\log_{10}(p/\text{mmHg}) = 6\cdot473 - 1566/T \quad (14)$$

indicating a very good fit of the data to a straight line. The calculated latent heat of vaporisation is 7140 cal mol^{-1}, the calculated boiling point of the liquid is 163 °C and the Trouton constant $16\cdot4$ cal deg^{-1} mol^{-1}.

The thermal decomposition was repeated using trichloronitrosomethane which had been stored at 0 °C for 12 h prior to final purification to allow the postulated intermediate, $CCl_3\cdot SO_2\cdot NO$, time to break down into $CCl_3\cdot NO$ and SO_2. The results are given in the Table, and show that this technique is effective in removing sulphur dioxide.

During the course of these two experiments a pink colour was noticed in those fractions containing carbon tetrachloride. This colour faded on exposure to light with the formation of a small amount of non-condensable gas. A third experiment was carried out with the object of identifying the cause of this pink colour.

Trichloronitrosomethane ($15\cdot8$ g) was heated in a sealed Carius' tube at 100—110 °C for 3 h. On freezing the contents of the tube and opening in vacuo a small amount of nitrogen ($0\cdot02$ g) was found. The volatile products

[10] R. E. Banks, M. G. Barlow, R. N. Haszeldine, M. K. McCreath, and H. Sutcliffe, J. Chem. Soc., 1965, 7209.

[11] P. G. Ashmore and R. G. W. Norrish, Proc. Roy. Soc., 1950, A204, 34.

[12] J. R. Morton and H. Wilcox, Inorg. Synth., 1953, 4, 48.

were fractionated and analysed as described above, with some additional treatment as described below.

Fraction condensing at −96 °C. This was of a pink colour although i.r. and g.l.c., and measurements indicated carbon tetrachloride and chloropicrin, both of which are colourless. Measurement of the u.v. and visible spectra showed maxima at 520 and 265—290 nm. The i.r. spectrum also showed two absorption bands at 5·7 and 9·5 µm which could not be attributed to either carbon tetrachloride or chloropicrin. The pink colour of the sample faded on exposure to light. A sample (0·1 g) of the fraction was sealed *in vacuo* and exposed to daylight until the pink colour had faded. On freezing the sample 2·2 ml of nitrogen was removed by Toepler pump.