865. *Perfluoroalkyl Compounds of Nitrogen. Part VI.*[1] *The Photolysis of Trifluoronitrosomethane.*

By (Mrs.) J. Mason (née Banus).

The photolysis of trifluoronitrosomethane with red light to give the dimer [a *N*-nitritoamine, $(CF_3)_2N{\cdot}O{\cdot}NO$] and other products has been followed spectrophotometrically. Quantum yields are about 0·2 mole (of nitroso-compound decomposed) per quantum in a fresh silica cell, rising to about 2 moles after seasoning, for small conversions, when the dimer is formed quantitatively; longer irradiation leads to secondary reactions and decomposition products.

The rate-determining step is the photo-formation of the monomeric intermediate, only one of which is used to form the dimer, since initial rates are proportional to the light absorbed. It is roughly independent of the pressure in the range 30—500 mm. of nitroso-compound, with or without sulphur hexafluoride to raise the pressure to 730 mm. However, an excited-molecule mechanism is no less likely on present information than one involving free radicals, because of the low energy of the 5400—10,000 Å light compared with the expected CF_3–NO bond dissociation energy.

The decomposition of trifluoronitrosomethane and of heptafluoronitroso-n-propane on longer irradiation and in the dark is discussed.

Trifluoronitrosomethane[2] gas at 30—500 mm. pressure (with or without sulphur hexafluoride to raise the pressure to 730 mm.) has been irradiated with tungsten light restricted by filters to the region of the nitroso n_N–π^* absorption,[3] 5400—10,000 Å (see Figure), and the photolysis followed spectrophotometrically. The dark reaction, the spontaneous decomposition of trifluoronitrosomethane, which will be discussed below, is much slower than the photolysis at room temperature.

For small conversions, the dimer, namely, the *N*-nitritoamine[1] $(CF_3)_2N{\cdot}O{\cdot}NO$, was formed quantitatively, for its dark decomposition is relatively slow at room temperature, and the light which decomposes it was excluded (the dimer has $\varepsilon_{max.}$ 19·7 at 3720 Å, tailing to $\varepsilon \sim 0$ at 5200 Å). Longer irradiation leads to a variety of secondary reactions and products, the rate coefficient decreasing during the run in an irregular manner. Thus only initial rates could be interpreted quantitatively (for the first hour or two of irradiation), with about 5% conversion, although the photolysis was followed for longer periods.

The initial rate of disappearance of the nitroso-compound and formation of the dimer rose

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[1] Part V, Mason (née Banus), preceding paper.

[2] Part I, Banus, *J.*, 1953, 3755; *Nature*, 1953, **171**, 173.

[3] Part IV, Mason (née Banus), *J.*, 1957, 3904.

in successive experiments in a fresh silica cell, which was kept evacuated between experiments; it fell again if air was admitted between experiments. Quantum yields of about 0·2 were observed in fresh cells, rising to ~1·8 after about 6 experiments. The dimer is formed quantitatively for short irradiations, irrespective of the yield, and when it decomposes no nitroso-compound is regenerated. Low yields may then imply recombination of radical intermediates, or deactivation of an energised molecule.

The initial rate of disappearance of trifluoronitrosomethane was about 8×10^{-8} moles $l.^{-1}$ $sec.^{-1}$ for a quantum yield of 2 at the average rate of light absorption at an initial pressure of 30 mm. In experiments where the light intensity was reduced by wire-mesh screens the initial rates were proportional to the light absorbed, so that formation of the dimer by the active intermediate involves only one of these at a time. The initial rate was independent of the pressure of nitroso-compound (for a given light absorption), or of the inert gas sulphur hexafluoride, in the range studied. The rate-determining step is then the formation of the active intermediate by absorption of light.

The lack of pressure-dependence suggests at first sight that the active intermediate is not an excited molecule that would be deactivated by collision (but see below). For a free-radical mechanism, processes consistent with quantitative dimer formation and the zero-order rate law are:

$$CF_3{\cdot}NO + h\nu = CF_3{\cdot} + NO \tag{1}$$

$$CF_3{\cdot} + NO(+ M) = CF_3{\cdot}NO(+ M) \tag{2}$$

$$CF_3{\cdot} + CF_3{\cdot}NO \rightleftharpoons (CF_3)_2N{\cdot}O{\cdot} \tag{3}$$

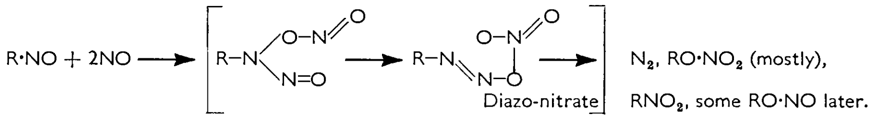
$$NO + CF_3{\cdot}NO = CF_3{\cdot}N_2O_2 \longrightarrow \text{Products} \tag{4}$$

$$(CF_3)_2N{\cdot}O{\cdot} + NO(+ M) = (CF_3)_2N{\cdot}O{\cdot}NO(+ M) \tag{5}$$

$$(CF_3)_2N{\cdot}O{\cdot} + CF_3{\cdot}NO = (CF_3)_2N{\cdot}O{\cdot}NO + CF_3{\cdot} \tag{6}$$

$$(CF_3)_2N{\cdot}O{\cdot} + CF_3{\cdot} = (CF_3)_2N{\cdot}O{\cdot}CF_3 \tag{7}$$

Reaction (2) is the mode of preparation of the nitroso compound.[2] It should be fast: the apparent second-order rate coefficient when methyl radicals combine with nitric oxide [4] is $\sim 7 \times 10^{11}$ ml. $mole.^{-1}$ $sec.^{-1}$ at 25°. The nitroxide radical formed in reaction (3) has a stable analogue in the di-t-butylnitroxide radical.[5] Reaction (4) has been included since nitric oxide hastens the dark decomposition of trifluoronitrosomethane, and adds to arylnitroso-compounds to form the diazonium nitrate.[6] Brown [7] and Donaruma and Carmody [8] have suggested that its reaction with alkylnitroso-compounds follows a similar route:



where R is $CMe_2{\cdot}CH_2{\cdot}NO_2$ [7] or cyclohexyl.[8]

In Donaruma and Carmody's experiments the absorption of an unstable intermediate at 1820, 1730, and 1665 $cm.^{-1}$, by comparison [1] with that of the bistrifluoromethyl-*N*-nitritoamine and -nitrosoamine, is consistent with the *N*-nitroso-nitrite structure. Their reaction in cyclohexane solution was of zero order in nitric oxide, the first-order coefficient being $\sim 10^{-3}$ at 25°. Christie [9] has found a third-order reaction in the gas phase: $Me{\cdot}NO + 2NO \longrightarrow$ Unidentified product(s), with a rate coefficient $\sim 10^{6}$ $ml.^{2}$ $sec.^{-1}$ at

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[4] Christie, *Proc. Roy. Soc.*, 1958, *A*, **249**, 248; Sleppy and Calvert, *J. Amer. Chem. Soc.*, 1959, **81**, 769; and refs. therein.

[5] Hoffmann and Henderson, *J. Amer. Chem. Soc.*, 1961, **83**, 4671.

[6] Bamberger, *Ber.*, 1897, **30**, 508; 1918, **51**, 634; Nesmeyanov and Ioffe, *J. Gen. Chem. U.S.S.R.*, 1944, **11**, 392.

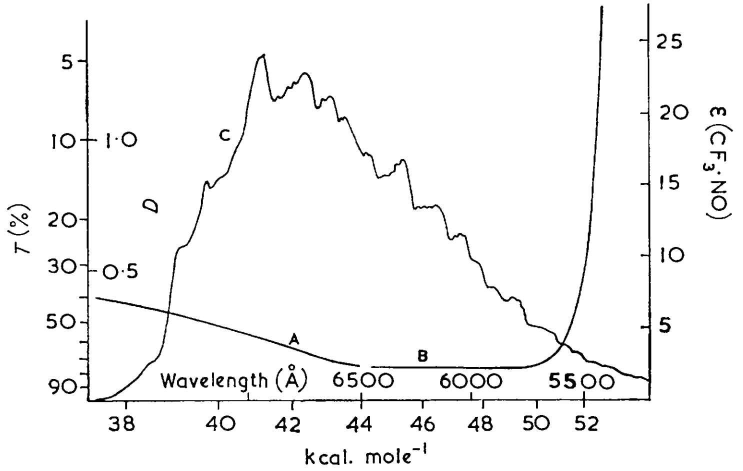
[7] Brown, *J. Amer. Chem. Soc.*, 1957, **79**, 2480.

[8] Donaruma and Carmody, *J. Org. Chem.*, 1957, **22**, 635.

[9] Christie, *Proc. Roy. Soc.*, 1958, *A*, **249**, 258.

16—20°. In the absence of added nitric oxide, then, the reaction of nitric oxide with nitrosomethane is negligible compared with the recombination with a methyl radical, and it is likely that the reaction of nitric oxide with trifluoronitrosomethane is much slower than with free radicals, *i.e.*, negligible here. Reaction (7) has an analogue in the addition of methyl radicals to nitrosomethane,[10] but is unlikely to be significant here in the absence of an excess of trifluoromethyl radicals.

If the most important processes were (1) with a quantum yield of unity, (3), and (5), the measured (*i.e.*, overall) quantum yield would be 2. This would be increased by reaction (6), if present, and reduced by (2). Reactions (3) and (6) allow for reaction chains, but these would have to be very short for the low quantum yields observed. Such radical reactions are usually sensitive to traces of inhibitors, the state of the wall, and the pressure; the seasoning of vessels is often due to the removal of oxygen which ends reaction chains. A heterogeneous process should be disfavoured, *e.g.*, by flash photolysis, and favoured at low pressures, below those which could be used with the technique adopted here, as explained in the Experimental section. It is hoped that the reaction will be studied under other conditions, to settle some of these questions.



Filters. *T* is % transmission, *D* is optical density, of filters and CF_3·NO gas. ε is extinction coefficient of CF_3·NO gas.

(A) 0·5% aqueous solution of cupric chloride, 1 cm. thick. The transmission is very low at 10,000 Å. (B) Wratten no. 21 filter, monobromofluorescein. (C) 100 mm. of CF_3·NO gas in 10-cm. cell.

Rupture of the CF_3–NO bond is a possible (though not a necessary [3]) explanation of the blurring of the rotational structure of the n_N–π^* absorption band. This was examined in the first order of a 20-foot Ebert grating spectrograph,[11] which resolves lines separated by 0·025 Å in this region, but no measurable fine structure could be found.

An objection to the trifluoromethyl radical as reactive intermediate under the conditions studied is the low energy of the red light, 38—52 kcal. mole^{-1} (see Figure). Photolysis of a bond usually requires about 150% of the bond dissociation energy,[12] and one would not in the present instance expect to recoup more than about 10 kcal. mole^{-1} from the reorganisation of the NO fragment.[13] $D(CF_3–NO)$ can be estimated from $D(CH_3–NO_2)$,[14] which

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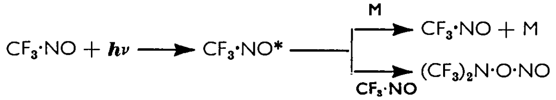
[10] Bromberger (Jest) and Phillips, *J.*, 1961, 5302.
[11] King, *J. Sci. Instr.*, 1958, **35**, 11.
[12] Steacie, " Atomic and Free Radical Reactions," Reinhold, New York, 1954, Vol. II, p. 242.
[13] Johnston and Bertin, *J. Amer. Chem. Soc.*, 1959, **81**, 6402.
[14] Gray, *Trans. Faraday Soc.*, 1955, **51**, 1367; Cottrell, " The Strengths of Chemical Bonds," Butterworth, London, 1958.

is 54—57 kcal. mole^{-1}. The CF_3–NO_2 bond is slightly longer (by about 0·08 Å)[15] than the CH_3–NO_2 bond, and so should be slightly weaker, and the CF_3–NO bond is probably somewhat longer and weaker (because of the n_N electrons) than the CF_3–NO_2 bond. The X–NO bond is longer and weaker (by a few kcal. mole^{-1}) than the X–NO_2 bond where X is F, Cl, Br, NO, NO_2, or OH, though they are about the same when X is MeO. $CF_3{\cdot}NO$ will probably be included in the list of unusually long bonds to nitrogen (longer by 0·05—0·27 Å than the radius sum), which now comprises N–N in dinitrogen trioxide and tetroxide, C–N in the halogenopicrins, and N–halogen in the nitrosyl and nitryl halides (except nitryl fluoride); but the lengthening increases with weight of the halogen and is not very large for fluorine compounds.

$D(CF_3$–$NO)$ should then be in the range 35—50 kcal. mole^{-1} [cf. also 36—39 for D(MeO–NO), 48 for D(H–NO), and 55 kcal. mole^{-1} for D(F–NO). A trifluoromethyl radical formed by red light at room temperature must then be a remarkably cool one (and the lighter NO fragment will take a large share of what little kinetic energy there is, to conserve momentum). A cool trifluoromethyl radical may be essential for the addition to trifluoronitrosomethane to form the labile dimer, since fragmentation occurs even with near-ultraviolet light, and any trifluoromethyl groups left intact are in the form of the nitro-compound. (Much less dimer is formed by heptafluoronitrosopropane with red light, as described below.) But this does not dispose of the thermochemical objection.

Thus the primary process (1) probably has a quantum efficiency less than one for 5400—10,000 Å light. If it is between 0 and 1, reaction chains might account for the overall yields; but, if it is zero, and the reactive intermediate is an excited molecule, then yields less than 2 imply deactivation:



$$CF_3{\cdot}NO + h\nu \longrightarrow CF_3{\cdot}NO^* \longrightarrow \begin{cases} \xrightarrow{M} CF_3{\cdot}NO + M \\ \xrightarrow[CF_3{\cdot}NO]{} (CF_3)_2N{\cdot}O{\cdot}NO \end{cases}$$

Such a mechanism is not necessarily precluded by the lack of pressure-dependence in the range studied here. The fluorescence of trifluoronitrosomethane will be investigated. Fluorine compounds are often poor quenching agents, and although nitroso-compounds are often good ones,[16] di-isopropyl bromonitrosomethane has been observed to fluoresce weakly with $\lambda_{max.}$ 7350 Å and " short " lifetime.[17]

Decomposition products identified after longer irradiations on a larger scale with visible light include fluoropicrin, nitric and nitrous oxide, nitrogen dioxide, carbon dioxide, and some silicon fluoride from attack on the glass (by carbonyl fluoride, and possibly nitrosyl or nitryl fluoride); pentafluoro-2-azapropene was also detected (as below) in small amount.

Decomposition products observed spectroscopically after longer irradiations in the quartz cell included some that do not survive condensation and warm-up on transfer to a vacuum system. Thus after six hours' irradiation of trifluoronitrosomethane there was some absorption at 2600 Å, added to the n_O–π^* absorption of the nitroso- and nitro-compounds,[3] and in parallel experiments with added sulphur hexafluoride there appeared faint structure on the short-wavelength side of the 2600 Å band, and 28 strongly marked bands between 2650 and 3150 cm.$^{-1}$ with a spacing of 230 cm.$^{-1}$. The band and the vibrational structure could not be explained by any possible product of known spectrum (including the NF_2 radical,[18] with $\varepsilon_{max.}$ 565 at 2602 Å, since too much of it would be required). Nitrosyl fluoride was suspected (see below), but its n_N–π^* band has[19] $\varepsilon_{max.}$ 300 at 3110 Å and upper-state frequencies of 1450, 343, and 1086 cm.$^{-1}$. Possible contributors

[15] Karle and Karle, *J. Chem. Phys.*, 1962, **36**, 1969.

[16] Zelinskiĭ, *Doklady Akad. Nauk S.S.S.R.*, 1947, **56**, 383.

[17] Lewis and Kasha, *J. Amer. Chem. Soc.*, 1945, **67**, 994.

[18] Johnson and Colburn, *J. Amer. Chem. Soc.*, 1961, **83**, 3043.

[19] Johnston and Bertin, *J. Mol. Spectroscopy*, 1959, **3**, 683.

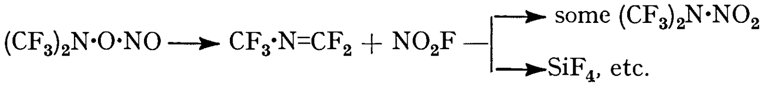
to the absorption include nitryl fluoride, carbonyl fluoride, and pentafluoro-2-azapropene. These are all formed at some stage in the decomposition of the monomer or the dimer; all are expected to have n–π^* (*i.e.*, relatively low intensity) absorption in the 2500—3000 Å region, and all have low out-of-plane bending frequencies that might well be active in the transition.

With ultraviolet light (2537 Å) fragmentation is much faster. Nitrosyl silicofluoride is formed, probably by the interaction with silica of nitrosyl fluoride.[20] This is probably formed by way of trifluoromethyl nitrite, a compound which has not yet been characterised but is likely to be responsible for the ultraviolet absorption of the product residue after removal of the acid gases: there is end-absorption and, as well as the fluoropicrin n_O–π^* band at 2775 Å, a series of fairly weak bands with maxima at 3650, 3520, 3400, 3290, 3190, and 3100 Å. This upper-state frequency of about 1000 cm.$^{-1}$ resembles that of the N:O stretching modes in the alkyl nitrites; thus, methyl nitrite has N:O stretching frequencies in the ground state of 1624 cm.$^{-1}$ (*cis*) and 1681 (*trans*), and ultraviolet maxima in the n_N–π^* band at 3920, 3655, 3510, 3390, 3282, 3190, and 3030—3010 Å, the complexity of the spectrum being increased by rotational isomerism which is expected to be absent from the trifluoro-compound. (With fluorination of an attached alkyl group, the n–π^* absorption of a chromophore such as O·N:O is usually little changed in energy and somewhat reduced in intensity.) Dialkylnitrosoamines absorb similarly, but with fewer vibrational bands and smaller N:O stretching frequencies than alkyl nitrites. Thus all the components of the following reaction sequence are present:

$$CF_3\cdot + NO_2 \longrightarrow CF_3{\cdot}NO_2 + \text{some } CF_3{\cdot}O{\cdot}NO \xrightarrow{(h\nu)}$$
$$COF_2 + NOF \xrightarrow{SiO_2} CO_2 + SiF_4 + (NO)_2SiF_6 + NO + NO_2$$

Fluoropicrin also is decomposed by 2537 Å radiation, with rupture of the C–N bond.

The Dark Decomposition.—Although liquid trifluoronitrosomethane can be stored pure for years at liquid-oxygen temperature, or under pressure at room temperature, the gas slowly becomes green and inhomogeneous in the dark at room temperature. Some dimer is formed and slowly decomposes, as described in Part V,[1] to form the azapropene $CF_3{\cdot}N{=}CF_2$, as well as fragmentation products, and a little of the nitroamine:



$$(CF_3)_2N{\cdot}O{\cdot}NO \longrightarrow CF_3{\cdot}N{=}CF_2 + NO_2F \longrightarrow \begin{cases} \longrightarrow \text{some } (CF_3)_2N{\cdot}NO_2 \\ \longrightarrow SiF_4, \text{ etc.} \end{cases}$$

There is much autoxidation to the nitro-compound, with, as side products, nitrogen and its oxides (nitric oxide, nitrogen dioxide, and nitrous oxide) and some carbon dioxide and silicon fluoride. Addition of nitric oxide accelerates the decomposition, to give many of the same products.

The mechanism of the dark decomposition of trifluoronitrosomethane is obscure. Radical schemes involving nitric oxide and nitrogen dioxide (which is usually found to be active in reactions of nitric oxide, *e.g.*, with olefins [7]) are readily written, as for the photolysis; but thermal energy is insufficient at room temperature and below for unimolecular rupture of the CF_3–NO bond in the gas phase. The reaction may perhaps be initiated on the wall. A study by electron paramagnetic resonance has shown that trifluoronitrosomethane gives a signal " only in the presence of certain co-joiners [unspecified in the abstract] while other nitroso-compounds give identifiable spectra in the pure state, liquid phase, at room temperature."[21]

However the reaction begins, it seems unlikely that a diazonium nitrate [7,8] is involved, as this requires a 3 : 1 ratio of NO to CF_3 groups. Nitric oxide is consumed to form the

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[20] Andreades, *J. Org. Chem.*, in the press.

[21] Crawford, Rice, and Piette, Abs. 2nd Internat. Symposium on Fluorine Chemistry, 1962, p. 76.

dimer, NO_2, etc., and the proportion of trifluoromethyl groups decomposing on the wall is not very large. It seems likely that much of the decomposition goes through the dimer.

Heptafluoronitrosopropane, made[2] by photolysis of heptafluoropropyl iodide in the presence of nitric oxide, was shown to be the n-propyl derivative by its nuclear magnetic resonance spectrum (by courtesy of Dr. R. E. Richards and his co-workers). One of the fluorine resonances was a very well-defined triplet, another a quartet superimposed on a triplet, as for the iodide spectrum, so that no detectable isomerisation had occurred while the C_3F_7 radical was free in the reaction sequence:

$$C_3H_7{\cdot}CO_2H \xrightarrow[\text{fluorination}]{\text{Electrochem.}} C_3F_7{\cdot}CO_2H \xrightarrow{Ag^+} C_3F_7{\cdot}CO_2Ag \xrightarrow{I_2} C_3F_7I \xrightarrow[h\nu]{NO} C_3F_7{\cdot}NO$$

When heptafluoronitrosopropane was stored in the dark it slowly decomposed, by about 20% in two years. No dimer could be isolated, although from spectroscopic evidence traces may have been present. Among the products were (totalling nearly 20% of them by weight) carbon dioxide, silicon fluoride, nitric oxide, nitrous oxide, and nitrogen dioxide; also present were the nitro-compound $C_3F_7{\cdot}NO_2$, the acid fluoride $C_2F_5{\cdot}COF$ (the analogue of the carbonyl fluoride formed in the decomposition of trifluoronitrosomethane, perhaps by loss of nitrosyl fluoride from the nitrite), some hexafluoropropene, and smaller amounts of material of higher molecular weight (which may have contained some aza-olefin $C_3F_7{\cdot}N{=}C_2F_5$).

With diffuse daylight, or light from a tungsten lamp, the glass was attacked and decomposition was much faster, but there was a smaller proportion of fragmentation products than in the dark reaction. The fluorocarbon derivatives seemed to be similar, but were not studied in detail.

EXPERIMENTAL

Infrared spectra were measured with Perkin-Elmer spectrophotometers, models 12C and 21, some by courtesy of Professor A. Albert of the Australian National University, in London 1954—1955.

Photochemistry.—Quantitative irradiations were carried out in a light-box on an optical bench, with three compartments to protect the reaction cell and thermocouple from heat and stray light. The image of the tungsten strip filament of a projector lamp (Siemens 6 v, 108 w, type f/50) was used as source, and the absorption of the filters is shown in the Figure. A parallel beam was passed through trifluoronitrosomethane in a 10 cm. (30·8 ml.) fused-silica Cary cell, and then focused on the junctions of an 18-element thermopile of sensitivity (N.P.L.) 67·8 mv. watt^{-1} cm.^{-2}, shielded when not in use. Thermopile readings were about 160—200 mv (depending on lamp fluctuations) with the reaction cell removed, less about 27 mv with the empty cell in the beam, less a further 10—60 mv for the cell with various pressures of reactant, where 1 mv corresponds to $2{\cdot}66 \times 10^{-7}$ mole quanta per hr. The lamp was switched on 20 or more minutes before irradiation was begun, and the temperature in the light-box was usually about 25—30°.

The overall quantum yield was corrected for reflections at the cell windows. The cell surface was very little attacked in the longer irradiations; some silicon tetrafluoride was formed, but no etching was visible after 15 runs, the loss of light on transmission through the empty cell rising slightly from 13—14 to 16—17%.

Vacuum-system methods were used for all manipulations, but there was no contact with mercury during the irradiations. The nitroso-compound was prepared and purified as before.[22] The sulphur hexafluoride was found in a sealed flask labelled " K. G. Denbigh, Leeds University, June 1934. About 99·5% pure," and this purity was confirmed by the saturation vapour pressures and infrared and (blank) ultraviolet spectra.

The cell was filled to the required pressure and then removed to the light-box, or to a Cary spectrophotometer for qualitative examination of the reagents and products. More accurate measurements were made with a Unicam S.P. 500 spectrophotometer. Optical densities of

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[22] Part II, Mason (née Banus) and Dunderdale, *J.*, 1956, 754.

0·25—0·7 were measured at 20 wavelengths in the visible spectrum (no products absorb in this region) and the average, reproducible to 2%, used to follow the pressure of nitroso-compound. This fell linearly with time in the initial reaction but, as the change was limited to 10% or less, the uncertainty in a measured yield of 1—2 may be as high as ±0·2—0·4 when lamp fluctuations are taken into account. Direct measurement of the dimer produced was less accurate because of the low concentration; the quantitative formation in the initial reaction was known from larger-scale irradiations (without measurement of the light intensity), and from the absence of decomposition products such as nitrogen dioxide, which is readily detected in very small amounts by the visible absorption.

A limiting factor was the intensity of light available: the " effective " optical density (averaged over the range of wavelengths in the incident light), as measured by thermopile in comparison with an empty cell, was 0·038 at 30 mm. of trifluoronitrosomethane, corresponding to 8% of the incident light absorbed (rising to about 17% at 100 mm. and levelling off at about 30% for pressures above 400 mm.). The percentage was proportionately less at pressures below 30 mm., which were therefore not studied by this technique.

The brass-wire gauzes used to vary the light intensity (gauge nos. 41 and 44, 100-mesh) transmitted 31·0% or 42·3% of the incident light. With either or both in place the quantum yield was unaffected, *i.e.*, the amount of nitroso-compound destroyed is directly proportional to the light absorbed.

Successive quantum yields in one series of (separate) experiments with 31·5 mm. pressures of trifluoronitrosomethane irradiated for 2 hr. in the same new cell were 0·20, 0·23, 0·35, 0·53, 1·8, and then about 1·9 molecules per quantum. Substantially similar results were obtained with pressures of 50, 100, 240, 360, and 500 mm. of nitroso-compound, with or without added sulphur hexafluoride to raise the pressure to 730 mm., *i.e.*, the quantum yield depended on the history of the cell rather than on the pressure. At the higher pressures, whether of nitroso-compound or of sulphur hexafluoride, there was some reduction in the quantum yield which was probably outside experimental error, but the effect was not marked.

There were some indications of induction periods, *e.g.*, small rate changes if the irradiation was stopped and re-started. Sometimes a low yield was observed in a seasoned cell, and if the cell was left in the dark for several hours during a run there was often a subsequent increase in rate, so this procedure was avoided.

Qualitative irradiations of trifluoronitrosomethane for product analysis were carried out in Pyrex soda glass, or silica bulbs (removed from the vacuum-system and from contact with mercury), with sunlight, diffuse daylight, unfiltered tungsten light, or mercury light (4047 and 4358 Å, or 2537 Å). Since filters greatly reduce the incident light and the amount of product, some of the light was of wavelength less than 5200 Å which can slowly decompose the dimer.[1] The blue gas became green, and eventually straw-coloured or orange-brown depending on the amount of nitrogen dioxide present.

Only in short irradiations, *e.g.*, an hour with a 500 w lamp for a small reaction vessel, or a day in sunlight for a large bulb of the gas, was the dimer formed nearly quantitatively, and readily separable by distillation (see Part V [1]). In longer irradiations the vessel is attacked and the crude reaction mixture contains labile products; nitrogen dioxide is visible, or readily recognised by its visible spectrum, and, if the mixture is shaken with mercury and oxygen to remove nitrogen dioxide, a grey-black deposit is formed which contains mercurous oxide and fluoride as well as nitrite and nitrate. When these are removed, more nitrogen dioxide is formed in the gaseous mixture on storage. Treatment of the product mixture with aqueous alkali or ground potassium hydroxide removes fluoro-derivatives of higher molecular weight as well as low-boiling acid gases (carbon dioxide, carbonyl fluoride, nitrogen dioxide, silicon fluoride, and possibly nitryl fluoride), and these were separated when no trifluoronitrosomethane was present by distillation in a Fenske-packed still with −80° reflux. In the presence of nitroso-compound they were separated by low-temperature filtration,[22] followed by distillation.

Pentafluoro-2-azapropene, $CF_3{\cdot}N{=}CF_2$, and fluoropicrin, which both boil at −34°, were collected together during the distillation, but were readily recognised by their infrared spectra: the azapropene has strong C=N absorption at 1810, 1825 cm.$^{-1}$ compared with the NO_2 asymmetric stretching frequency at 1626, 1614 cm.$^{-1}$ of fluoropicrin, and the C–N stretching frequency in the azapropene is raised to 997, 1004, 1010 compared with 855, 863, 871 cm.$^{-1}$ of fluoropicrin.[23] The dimer was not readily separable from other fluoro-derivatives of lower

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[23] Part III, Mason (née Banus) and Dunderdale, *J.*, 1956, 759.

molecular weight when this amount of decomposition had occurred, and the presence of a smaller molecule with similar volatility (and absorbing near the minimum of the dimer absorption in the ultraviolet region) was suspected.

At the other extreme of actinic dosage, even quite short irradiation of trifluoronitrosomethane in a silica Carius tube of 25 mm. outside diameter inside a spiral 2537 Å mercury lamp led to fragmentation. After an hour the gas was pale orange-brown, its average molecular weight (gas density) was 69, and the internal surface of the silica was clouded. Flaming the evacuated tube caused a white solid to sublime within it and to release nitric oxide. With air-free water the solid gave silicate, fluoride, and nitrite ions, and no fluorocarbon material; it was probably nitrosyl silicofluoride, which is formed together with nitric oxide and nitrogen dioxide by the action of nitrosyl fluoride on silica or glass.[20]

Removal of the acid gases (carbon dioxide, silicon fluoride, nitrogen dioxide, carbonyl fluoride, etc.) by passage through ground potassium hydroxide left some nitrous oxide, nitrogen, and rather little fluorocarbon material, containing some fluoropicrin, and some material with ultraviolet end-absorption and weak maxima at 3650, 3520, 3400, 3290, 3190, and 3100 Å, which may have been $CF_3{\cdot}O{\cdot}NO$.

Dark Decomposition.—In a typical experiment, about 3 l. (at S.T.P.) of pure trifluoronitrosomethane gas were kept for three months at room temperature in a black-painted 5 l. Pyrex bulb and shielded from light in the subsequent examination. The gas was then found to be hard to transfer in the vacuum-system owing to the presence of small amounts of nitrogen and nitric oxide (and perhaps carbon monoxide) which were pumped off. The nitroso-compound was too volatile to reflux in the Fenske-packed still at −80°, and was distilled through traps cooled in standard pentane baths (at about −140°). These traps held about 0·2 g. of an orange low-boiling liquid of average molecular weight 147. On further fractionation, this was found to contain about 40% by weight of the nitritoamine, another ~40% (*i.e.*, half the yield of dimer, measured on the nitroso-compound) of fluoropicrin containing some pentafluoro-2-azapropene, about 1 mole% of nitrogen dioxide, and some less volatile fluorocarbon-containing material. The infrared spectrum of this contained all the bands of the nitroamine[24] $(CF_3)_2N{\cdot}NO_2$ (*e.g.*, the NO_2 asymmetric stretching frequency, 1675 cm.$^{-1}$), and there was strong absorption below 2500 Å in the ultraviolet region, as for dialkyl-*N*-nitroamines,[25] although the molecular weight was low (180—190).

The main fraction, trifluoronitrosomethane containing the more volatile impurities, was then filtered at liquid-air temperatures in an apparatus described earlier,[22] and about 30 mg. of white material subliming at low temperatures were separated. This contained silicon fluoride, carbon dioxide, probably some carbonyl fluoride (which decomposes on glass to give silicon fluoride and carbon dioxide), and, after treatment with alkali, some nitrous oxide. Longer storage of trifluoronitrosomethane in the gas phase led to further degradation. If the decomposition products are shaken with mercury to remove nitrogen dioxide, more of this is generated in a day or so.

The author thanks Dr. Allan Maccoll and Dr. H. G. Poole for help with the optical equipment, Dr. G. W. King for examining the visible spectrum of trifluoronitrosomethane with his grating spectrograph, and Dr. (now Professor) D. R. Llewellyn for the wire gauzes. She thanks also Dr. T. J. Brice for the infrared spectrum of pentafluoro-2-azapropene, and Dr. S. Andreades for copies of his papers in the press,[20] and Dr. R. E. Richards and his co-workers for the nuclear magnetic resonance spectra.

William Ramsay and Ralph Forster Laboratories,
University College, Gower Street,
London, W.C.1.

[*Received, August* 13*th*, 1962.]

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