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# GAS PHASE REACTION OF NITROGEN DIOXIDE WITH TRIMETHYL- AND TRIETHYLSILANE

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## SUMMARY

The reactions between nitrogen dioxide and trimethyl- and triethylsilane have been studied. Under certain conditions ignition can occur. The main features of the reacting system are discussed and a reaction mechanism is proposed.

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## INTRODUCTION

The features of the gas phase reactions of nitrogen dioxide with hydrocarbons have been summarised by Gray and Yoffe[1]. The initial step in such reacting systems is the hydrogen abstraction reaction (A):

$$R_1R_2R_3CH + NO_2 \rightarrow R_1R_2R_3C\cdot + HONO \qquad (A)$$

The corresponding reactions of nitrogen dioxide with organosilanes have not received any attention, with the exception of a preliminary study by Spialter and Austin[2] who report the results of passing gaseous nitrogen dioxide through liquid organosilanes for several hours at room temperature. Comparison of $D$(Si–H) values with the analogous $D$(C–H) values[3] implies that reaction (B) should be at least as facile

$$R_1R_2R_3SiH + NO_2 \rightarrow R_1R_2R_3Si\cdot + HONO \qquad (B)$$

as reaction (A). It is known that in the hydrocarbon/nitrogen dioxide systems variation of reaction conditions can change the slow reactions into explosive reactions accompanied by blue luminescence[4]. In view of the growing interest in gas phase reactions of organosilanes it was felt that an investigation of some suitable organosilane/nitrogen dioxide systems would provide a useful extension to the knowledge of reactions of gaseous organosilyl radicals.

## EXPERIMENTAL

### *Materials*

Commercially available trimethylsilane, triethylsilane, trichlorosilane, and tetramethylsilane were subjected to repeated bulb to bulb distillation *in vacuo*, with rejection of appropriate first and last fractions until gas chromatographically pure. Dimethylsilane was prepared by reduction of dichlorodimethylsilane using lithium aluminium hydride[5], the product being purified as for the other silanes.

Nitrogen dioxide was prepared both by reaction of cylinder nitric oxide with oxygen and by the heating of lead nitrate[6]. It was purified by repeated trap to trap distillation on the vacuum line.

### *Apparatus*

A conventional high vacuum apparatus was employed. The main features of importance were the reaction vessel, the measurement of pressure, and the gas chromatographic analysis of the products. A cylindrical Pyrex reaction vessel with plane polished windows was mounted within an electrically heated aluminium cylinder made up of two halves which were bolted together. A small recess in one half permitted the insertion of a chromel–alumel thermocouple for temperature measurement. The reaction vessel had two outlet tubes, one of which was connected to a pressure transducer (Langham–Thompson UP4) and the other of which led to the storage bulbs for reactants, the trapping system equipped with gas chromatographic take off tubes[7], and the connection to the high vacuum system. Gas analyses were carried out using an F and M model 720 gas chromatograph.

### *Experimental procedure*

The reaction vessel temperature was regulated to the required value. A sample of trimethylsilane was admitted to the reaction vessel and the pressure recorded from the off-balance output signal of the bridge circuit using a recording potentiometer. Nitrogen dioxide was added in small quantities to the reaction vessel, which was observed throughout the addition. After addition of a critical quantity of nitrogen dioxide, a visible red flash occurred. This was accompanied by a sharp cracking sound. The total minimum pressure required to initiate ignition was obtained from the chart record of the transducer response. Samples of the ignition products were collected in sample tubes for GC analysis. Under any given set of conditions the ignition results were reproducible. The procedure was repeated at the same temperature using different initial pressures of trimethylsilane. Extension of the procedure was studied by adding the trimethylsilane to the nitrogen dioxide. A range of temperatures was employed and the above procedure repeated wherever ignition occurred. At temperatures that were too low for ignition to occur, the reactions were monitored by pressure change and by GC analysis.

## RESULTS

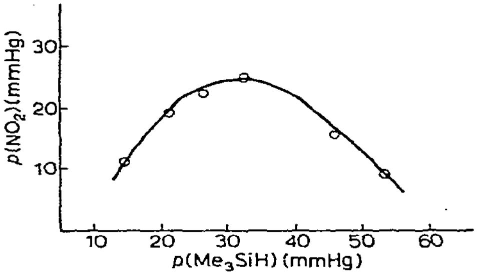
The detailed results obtained are confined to trimethyl- and triethylsilane. A very fast reaction (indicated by pressure drop) without ignition occurred for dimethylsilane (temperature range 25–350°). Study of the reaction of trichlorosilane with nitrogen dioxide was abandoned following the accidental occurrence of an explosive decomposition of small quantities of nitrogen dioxide with trichlorosilane in the introduction system, which extensively damaged the vacuum line. A preliminary investigation showed that no reaction takes place between tetramethylsilane and nitrogen dioxide over the temperature range 100–320°.

### *Trimethylsilane/nitrogen dioxide*

It was found that reaction, as evidenced by pressure change, commences at about 50° and that ignition occurs at temperatures greater than 240°. The time for disappearance of the brown colour of nitrogen dioxide from the reaction mixture varied from about 15 min at 50° to about 15 sec at 200°, using pressures of each reactant of the order of 30 mmHg. The possibility of monitoring the reaction by change in optical density was considered, but abandoned because of the deposition of small amounts of product(s) (hexamethyldisiloxane and polymeric siloxanes) in the reaction vessel.

The main reaction products are hexamethyldisiloxane, nitric oxide, and water, together with small quantities of ethane. There was evidence for the production of small quantities of nitrogen, nitrous oxide and methane in some but not all of the analyses. Carbon dioxide was invariably absent.

Examples of ignition boundaries are given in Fig. 1–4. Attempts were made to initiate ignition of trimethylsilane/nitrogen dioxide mixtures at 23° and 50°



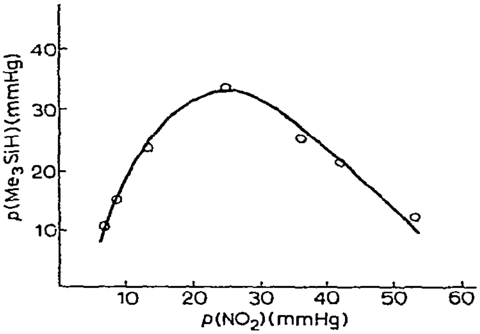
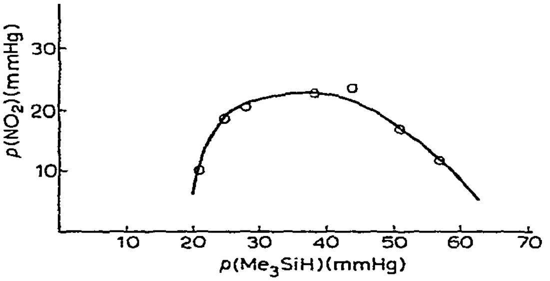


Fig. 1. Ignition profile of trimethylsilane/nitrogen dioxide at 280°. (Addition of nitrogen dioxide to constant quantity of trimethylsilane.) [In all the figures the area below the curve represents the absence of ignition.]

Fig. 2. Ignition profile of trimethylsilane/nitrogen dioxide at 280°. (Addition of trimethylsilane to constant quantity of nitrogen dioxide.)



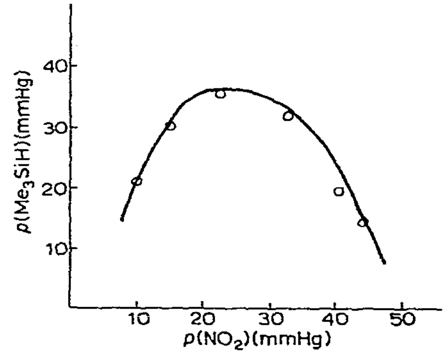


Fig. 3. Ignition profile of trimethylsilane/nitrogen dioxide at 320°. (Addition of nitrogen dioxide to constant quantity of trimethylsilane.)

Fig. 4. Ignition profile of trimethylsilane/nitrogen dioxide at 320°. (Addition of trimethylsilane to constant quantity of nitrogen dioxide.)

using both tungsten filament and mercury vapour lamps (wavelengths above 320 nm only). Although reaction occurred as evidenced both by analysis and transducer response, ignition was not observed. When either nitrogen or helium was added as a diluent to the trimethylsilane (temperature 320°) at a pressure equal to that for ignition by nitrogen dioxide, and then nitrogen dioxide was added, it was found that ignition did not take place.

### *Triethylsilane/nitrogen dioxide*

It was found that reaction commences at about 50° and that ignition occurs at temperatures greater than 320°. The reaction vessel and exit tubing rapidly became coated with a deposit of hexaethyldisiloxane, which was identified by IR spectroscopy. The other main reaction products were nitric oxide and water, together with small quantities of ethylene. There was evidence for the production of small quantities of nitrogen and nitrous oxide in some of the samples. Carbon dioxide was invariably absent.

In the lower temperature region (50–80°), the pressure drop measurements showed that the reaction is approximately second order overall, with an activation energy of about 6.6 ± 1.5 kcal · mole$^{-1}$. Examples of ignition boundaries are given in

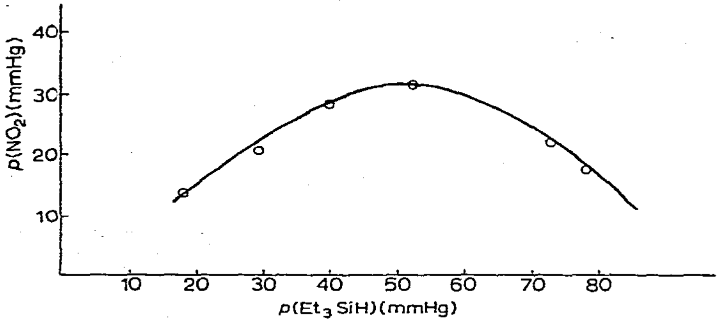


Fig. 5. Ignition profile of triethylsilane/nitrogen dioxide at 380°. (Addition of nitrogen dioxide to constant quantity of triethylsilane.)

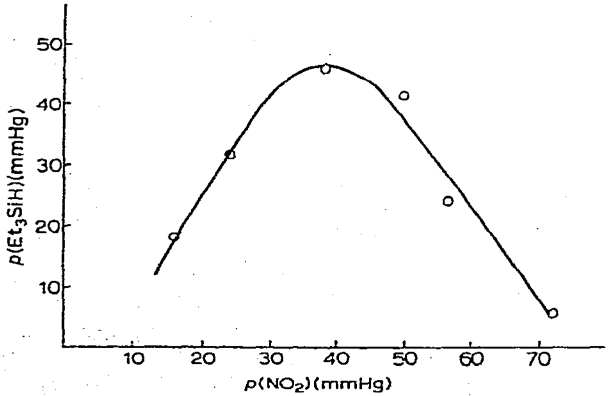
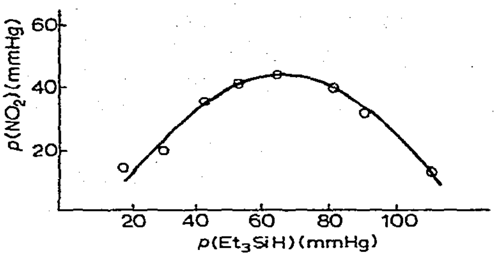


Fig. 6. Ignition profile of triethylsilane/nitrogen dioxide at 380°. (Addition of triethylsilane to constant quantity of nitrogen dioxide.)



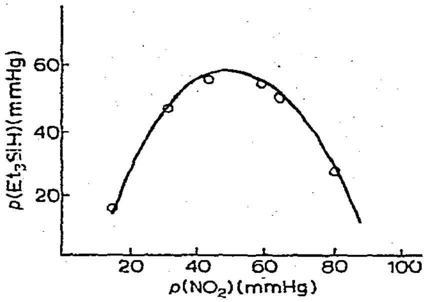


Fig. 7. Ignition profile of triethylsilane/nitrogen dioxide at 425°. (Addition of nitrogen dioxide to constant quantity of triethylsilane.)

Fig. 8. Ignition profile of triethylsilane/nitrogen dioxide at 425°. (Addition of triethylsilane to constant quantity of nitrogen dioxide.)

Fig. 5–8. Attempts to initiate ignition photochemically revealed the same characteristics as for trimethylsilane. Inert diluents had the same effect upon ignition as for trimethylsilane.

## DISCUSSION

It is apparent that any discussion of the possible reaction mechanisms must be able to account for the products formed and the explosion boundary characteristics. It is also obviously desirable that the main features of any scheme proposed be in accord with the established picture of the gas phase reactivity of both organosilanes and nitrogen dioxide. We suggest that the following scheme is a basis for interpreting our observations

$$Me_3SiH + NO_2 \rightarrow Me_3Si\cdot + HONO \tag{1}$$
$$HONO \rightarrow HO\cdot + NO \tag{2}$$
$$Me_3SiH + \cdot OH \rightarrow Me_3Si\cdot + H_2O \tag{3}$$
$$Me_3Si\cdot + \cdot OH \rightarrow Me_3SiOH \tag{4}$$
$$2\,Me_3SiOH \rightarrow (Me_3Si)_2O + H_2O \tag{5}$$
$$Me_3Si\cdot + NO_2 \rightarrow Me_3SiO\cdot + NO \tag{6}$$
$$Me_3SiO\cdot + Me_3Si\cdot \rightarrow (Me_3Si)_2O \tag{7}$$
$$Me_3Si\cdot + NO \rightarrow Me_3SiON \tag{8}$$
$$2\,Me_3SiON \rightarrow 2\,Me_3SiO\cdot + N_2 \text{ or } (Me_3Si)_2O + N_2O \tag{9}$$

This scheme implies attack at the weakest bond (Si–H), and this is in agreement with the absence of reaction for tetramethylsilane. There will be two differences from the analogous hydrocarbon systems discussed by Gray and Yoffe[1], namely (a) the much lower stability of $>Si=O$ compounds compared with $>C=O$ compounds and (b) the production of $\geq Si-N=O$ compounds is much less likely than $\geq C-N=O$ compounds, and hence the participation of reactions (8) and (9) can be expected (*cf.* Gunning *et al.*[8]). The low yields of nitrous oxide relative to water (always $< 1/50$) suggest that the intermediacy of nitroxyl (HNO) and reaction (10) is unlikely.

$$2\,HNO \rightarrow H_2O + N_2O \qquad (10)$$

The reactions [(1)–(9)] above could lead to explosions provided that these are thermal and not chain branching. The requirement for exothermic reactions which lead to thermal explosions is met by reactions (3), (4), (5), (7) and probably (6). This is based upon the weakness of the Si–H bond compared with the O–H and H–OH bonds and the strength of the Si–O bond. If branching chain explosions participate in our reaction system, it is necessary to invoke the chain branching step (12) based upon (11).

$$NO_2 \rightarrow NO + O\cdot \qquad (11)$$

$$Me_3SiH + O\cdot \rightarrow Me_3Si\cdot + \cdot OH \qquad (12)$$

Attempts to discriminate between the two explosion mechanisms, using the formulae given by Kondratiev[9] and Pratt[10] for pressure-temperature relationships at the ignition limit, were unsuccessful. The alteration of the ignition characteristics on addition of inert gases suggests that thermal explosions participate. It is also necessary to note that branching chain reactions are not completely isothermal.

The hexamethyldisiloxane, which is a major reaction product, contains some less volatile component not detected by GC analysis, but shown to be present by IR analysis of the deposited material. The strong absorption in the 1000–1150 $cm^{-1}$ region is characteristic of $\geq Si-O-Si \leq$ groups, and it seems likely that linear polymeric or cyclic structures are possible. Reaction (13) would produce the required inter-

$$Me_3SiO\cdot \rightarrow Me_2SiO\cdot + Me\cdot \qquad (13)$$

mediate and the precursor of the methane and ethane produced. So little is known of the reactions of silyloxy radicals that this can only be regarded as a tentative hypothesis. It is, however, analogous to the reaction (14), for which there is some experimental evidence[11].

$$Me_3SiCH_2\cdot \rightarrow Me_2Si{=}CH_2 + Me\cdot \qquad (14)$$

The proposed reaction scheme for triethylsilane is similar to the above. The apparently greater reactivity of trichlorosilane is presumably related to the greater rapidity of the initial reaction (1). This is paralleled by the results of Kerr *et al.*[12] for the corresponding abstraction of hydrogen by methyl radicals from trialkyl- and trichlorosilanes.

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## REFERENCES

1 P. Gray and A. D. Yoffe, *Chem. Rev.*, 55 (1955) 1069.
2 L. Spialter and J. D. Austin, *J. Amer. Chem. Soc.*, 88 (1966) 1828.
3 B. G. Gowenlock and J. Stephenson, *J. Organometal. Chem.*, 13 (1968) 13.
4 A. D. Yoffe, *Research (London)*, 6 (1953) 75.
5 A. E. Finholt, A. C. Bond and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 69 (1947) 1199.
6 H. W. Melville and B. G. Gowenlock, *Experimental Methods in Gas Reactions*, Macmillan, London 1964, p. 202.

7 J. R. Dickson and B. G. Gowenlock, *Justus Liebigs Ann. Chem.*, 745 (1971) 152.
8 M. A. Nay, G. N. C. Woodall, O. P. Strausz and H. E. Gunning, *J. Amer. Chem. Soc.*, 87 (1965) 179.
9 V. N. Kondratiev, *Chemical Kinetics of Gas Reactions*, Pergamon, London, 1964, Chapter 9.
10 G. L. Pratt, *Gas Kinetics*, Wiley, London, 1969, Chapter 4.
11 R. P. Clifford, B. G. Gowenlock and C. A. F. Johnson, *J. Organometal. Chem.*, 34 (1972) 53.
12 J. A. Kerr, D. H. Slater and J. C. Young, *J. Chem. Soc. A.*, (1966) 104; (1967) 134.