

Kinetic Mass Spectrometric Study of the Flash Photolysis of NO₂

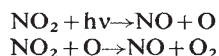
WE have re-examined the flash photolysis of NO₂ using a flash photolysis system coupled to an EAI 'Quad 200' series mass spectrometer. Initial experiments indicated that efficient electrical and optical screening must be provided between the flash lamp and the mass spectrometer chamber. A reactor with an aluminium outer case and base-plates was used to eliminate interference by the flash with the operation of the spectrometer and with the size of the background peaks *m/e* 17, 18, 28 and 44 resulting from desorption from the chamber walls. The nipple which protruded into the ion source was fitted with a molybdenum disk with a 50 μm aperture supplied by Aeon Laboratories. We calculated that in this way more than 80% of the reactants passed through the aperture directly into the ionization chamber and the spectra obtained were representative at all times of the composition of the gases inside the reactor. The outside wall of the reactor consisted of a glass tube 2.5 cm in diameter, 10 cm long, carrying a B24 conical socket joint and fastened with 'Araldite' into the base plate. A quartz flash lamp filled with 15 Torr of argon fitted coaxially inside the reactor. A 0.001 μF capacitor was connected across the leads to the flash lamp to eliminate interference from silent discharge during the charging of the main capacitor. The half-width duration of the flash was about 40 μs. The mass spectrometer signal was either displayed on an oscilloscope and photographed or recorded by an ultraviolet oscillograph.

The technique was checked by flash photolysing a 3 : 1 mixture of hydrogen and nitrogen dioxide. When profiles of peaks at *m/e* 17 and 18 were compared, it was found that there was an initial excess intensity of the *m/e* 17 peak which corresponded to that attributed by Meyer, in a similar experiment¹, to hydroxyl radicals.

The technique was found to be suitable for monitoring single ion peaks with 10 μs resolution or for providing complete mass spectra every 10 ms. Linear response of the system to reactant concentrations was achieved by working with reactor pressures which gave molecular flow through the 50 μm aperture. This made the addition of inert gas at high pressures impossible so experiments could not be conducted under strictly isothermal conditions.

Preliminary experiments have been performed on the flash photolysis of NO₂ at pressures of 0.33 to 1.48 Torr in the presence of 0.13 Torr of argon and in one case of 0.31 Torr of SF₆. A typical set of profiles, normalized against that of the argon *m/e* 40 peak, shown as a broken line, is illustrated in Fig. 1. Changing the pressure of nitrogen dioxide and adding SF₆ had little effect on the shapes of these profiles.

The peak *m/e* 32 can be attributed entirely to oxygen, because none of the oxides of nitrogen gave this peak and there was no ozone peak at *m/e* 48. The overall increase in oxygen and changes at *m/e* 30 and 46 cannot be explained by any of the mechanisms postulated by previous workers². The sharp initial changes in these peaks arise chiefly from



but these reactions are too fast to account for the slower changes which occur up to 300 ms later. These changes cannot be explained by the thermal decomposition of residual nitrogen dioxide, because a temperature of about 1,300 K would be necessary³ and this seems most likely 100 ms after flash. Also, the rate of oxygen formation and the decrease at *m/e* 46 were both linearly dependent on the pressure of NO₂, whereas the thermal decomposition follows a second order function⁴. Huffman and Davidson⁵ have shown that the unimolecular decomposition of NO₂ only becomes important at temperatures of about 3,000 K. The increase at *m/e* 46 after 40 ms cannot be due to the third order reaction of NO and O₂ which is 10 times too slow⁶. Comparison of the profiles reveals an initial mass

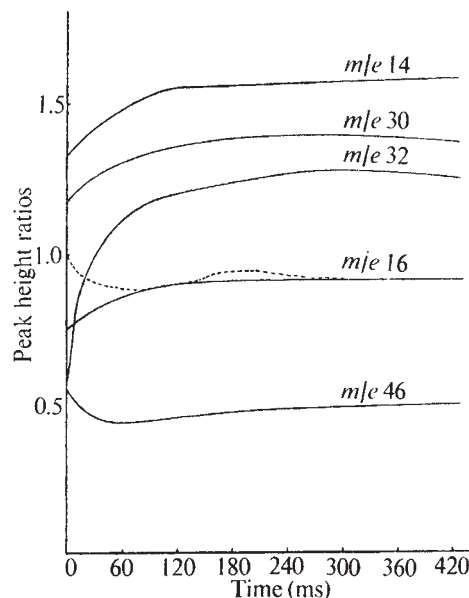


Fig. 1 Peak profiles for flashed NO₂. NO₂ 0.69 Torr, argon 0.13 Torr. Profiles *m/e* 14, 16, 30 and 46 plotted as a ratio of their pre-flash peak heights. Profile *m/e* 32 plotted as a ratio of the peak height produced by 0.138 Torr oxygen.

discrepancy which decays in parallel with the changes at *m/e* 30, 32 and 46, indicating a reaction involving some species other than NO₂, NO and O₂, either in the gas phase or on the walls. Similar profiles for these peaks were obtained in vessels constructed entirely of quartz so that the reactions cannot be attributed to the presence of aluminium, molybdenum or 'Araldite'.

A search for peaks at other mass numbers proved fruitless, but this does not rule out the presence of other oxides of nitrogen, for N₂O₅ gave the mass spectrum *m/e* 46 (72%), 30 (100%), 16 (10%) and 14 (4.5%). Similar spectra were obtained irrespective of whether the N₂O₅ was admitted through the reactor or through an all glass capillary inlet. Of the oxides of nitrogen only NO₃ and N₂O₅ are likely to produce oxygen in these conditions, and Husain and Norrish⁷ have shown that gaseous NO₃ has a life time of 40 μs and therefore cannot account for the observed reactions. The discrepancy in the mass balance cannot be explained by the presence of gaseous N₂O₅, which in any case only produces NO₂ in the presence of O (ref. 8). We therefore conclude that the flash photolysis of NO₂, an intermediate is rapidly formed, probably on the surface, which then reacts more slowly to produce O₂ and NO₂.

J. N. BRADLEY
W. D. CAPEY
J. R. GILBERT

Department of Chemistry,
University of Essex,
Wivenhoe Park,
Colchester,
Essex

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- Meyer, R. T., *J. Chem. Phys.*, **46**, 967 (1967).
- Ford, H., *Canad. J. Chem.*, **38**, 1780 (1960).
- Ashmore, P. G., and Burnett, M. G., *Trans. Faraday Soc.*, **58**, 253 (1962).
- Bodenstein, M., and Ramstetter, H., *Z. Phys. Chem.*, **100**, 106 (1922).
- Huffman, R. E., and Davidson, N., *J. Amer. Chem. Soc.*, **81**, 2311 (1959).
- Johnston, H. S., and Slentz, L. W., *J. Amer. Chem. Soc.*, **73**, 2948 (1951).
- Husain, D., and Norrish, R. G. W., *Proc. Roy. Soc., A* **273**, 165 (1963).
- Smith, J. H., and Daniels, F., *J. Amer. Chem. Soc.*, **69**, 1735 (1947).