Mass-spectrometric Study of the System H + NO

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THE reaction of hydrogen atoms with nitric oxide has been studied in a microwave discharge-flow system using continuous mass-spectrometric sampling to follow the course of the reaction. The reactor was fitted with six inlets for the injection of NO at different distances downstream from the discharge tube. Experiments were carried out at 296°K and 2·30 mm. Hg pressure.

Upon starting the reaction, a small increase was observed in the peak at $m/e = 31$. This was identified with the parent peak of HNO formed by reaction (1).

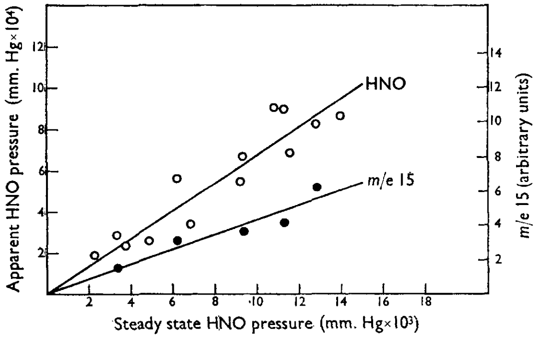
$$H + NO + M \rightarrow HNO + M \qquad (1)$$

In addition, larger increments in the peaks at $m/e = 14$, 15, 16, and a decrease in $m/e = 30$ were readily observable. It was not possible to detect any secondary products due to reactions of HNO with itself [*i.e.*, N_2O, H_2O, $(HNO)_2$, at $m/e = 44$, 18, 62, respectively] or with NO (*i.e.*, N_2, HNO_3, at $m/e = 28$, 63), all of which have been observed or postulated by Strausz and Gunning.[1] It was therefore concluded that HNO was removed almost exclusively by the rapid reaction

$$H + HNO \rightarrow H_2 + NO \qquad (2)$$

leading to an overall NO-catalysed recombination of H as originally suggested by Smallwood.[2]

Assuming that (1) and (2) do represent the main course of the reaction occurring in this system, then the steady-state HNO concentration is given by $(HNO) = (k_1/k_2)(NO)(M)$ so that the HNO concentration (or the amount of NO consumed) should be a linear function of the steady-state NO concentration. The actual behaviour is shown in the Figure (upper line) from which the ratio k_1/k_2 can be calculated as $k_1/k_2 \geqslant 5{\cdot}4 \pm 0{\cdot}6 \times 10^5$ mole^{-1} cm.^{3} This value represents a lower limit because any contribution to $m/e = 30$ due to HNO will tend to diminish the observed gradient below the true value. It is in good agreement with the photometric work of Clyne and Thrush[3] whose results lead to a value of $< 8{\cdot}0 \times 10^5$ mole^{-1}cm.^{3} for k_1/k_2, and in very close agreement with later work of the same authors.[4] Using their



FIGURE

more accurate value for k_1 with the result given here leads to $k_2 \leqslant 2{\cdot}7 \pm 0{\cdot}6 \times 10^{10}$ mole^{-1}cm.^{3}sec.$^{-1}$, compared with their estimate of $> 3{\cdot}0 \times 10^{10}$ mole^{-1}cm.^{3}sec.$^{-1}$ in the range 211—703°K.

The variation of $m/e = 15$ with steady-state NO concentration which is also shown in the Figure (lower line) and is paralleled by the behaviour of $m/e = 14$ and 16, strongly suggests that all three ions arise from HNO. The increment in $m/e = 31$ was too small to allow measurements of any accuracy to be made on its variation, but it seems reasonable to ascribe it to HNO^+. Further, it is possible to calculate an upper limit for the contribution of HNO to $m/e = 30$ from the discrepancy between the value for k_1/k_2 obtained here and that calculated from the data of Thrush. The resulting fragmentation pattern for HNO at 70 ev is given in the Table. The intensities at $m/e = 14$, 15, 16, have been corrected for mass interference due to NO. If it is true to assume that the total ionisation efficiency of HNO is of the same order of magnitude as that of NO at 70 ev, then the five-fold difference between the decreased ion current due to NO and the ion current due to the corresponding amount of HNO carried by the above ions, suggests that an appreciable proportion of HNO must ionise by yet another process. The most likely route is $HNO + e \rightarrow H^+ + NO + 2e$. No observations could be made on $m/e = 1$ as this was beyond the mass range of the instrument.

TABLE

Fragmentation of HNO *at* 70 *eV*

m/e	Relative intensity
14	17·1
15	55·4
16	100·0
30	<210·0
31	6·0

The variation of NO consumption with reaction time at constant NO flow rate corresponds at least roughly to a steady-state HNO concentration being established down the reactor. In fact, an increase in NO consumption of about 40% was observed when the reaction time was increased by a factor of ten. This gradual increase may have been due to the occurrence of other secondary reactions involving HNO of the type proposed by Strausz and Gunning. Failure to observe the products of such reactions directly may have been due to the low HNO concentration in the system, coupled with unfavourably large background signals at the appropriate mass numbers.

(*Received, October 25th,* 1966; *Com.* **823.**)

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[2] H. M. Smallwood, *J. Amer. Chem. Soc.*, 1929, **51**, 1985.
[3] M. A. A. Clyne and B. A. Thrush, *Trans. Faraday Soc.*, 1961, **57**, 1305.
[4] M. A. A. Clyne and B. A. Thrush, *Discuss. Faraday Soc.*, 1962, **33**, 139.