

SYNTHESIS OF NITROGEN OXIDES  
IN A MICROWAVE DISCHARGE

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ABSTRACT

In this experimental work we have determined the influence of different parameters on the chemical and energetical yields for synthesis of nitrogen oxides by a microwave discharge. A very simple kinetic law fits the results observed.

1. INTRODUCTION

It is well known that a microwave discharge in a nitrogen-oxygen mixture produces nitrogen oxides. However, the mechanism and the kinetic law of the reaction are not yet elucidated and for any industrial purpose it is necessary to determine the optimal conditions for the synthesis. A spectroscopic study of the discharge has been done and is reported in another communication (1). The main species detected  $O_1$ ,  $NO(\gamma)$ ,  $N_2(C)$  and  $N_2^+$ .

2. EXPERIMENTAL

The experimental device has been conceived to be as versatile as possible and to allow large modifications of parameters. Yet the role of two important factors has not been explored: the frequency and the mode of transmission to the gases of the electrical power. A microwave discharge (2450 MHz) is produced in nitrogen-oxygen mixtures flowing through a silica tube (the reactor) that crosses a resonant cavity described in (7). The gases are allowed to react in a post-reactor before analysis (fig. 1). Different parameters can be varied independently: total pressure of  $N_2$  or  $O_2$ , composition, flow rate D, microwave power W, tubes diameters, cooling of the walls. Analysis has been performed first by a chemical method: the nitrogen oxides  $NO$  and  $NO_2$  were oxidised by a solution of hydrogen peroxide and titrated as  $HNO_3$  by acidimetry. This

method is precise and gives absolute measurements. However it needs the trapping of the gases for 15 minutes and the results cannot be obtained rapidly. So a second method has been used: it works with a Photometer n°411 of Dupont de Nemours and allows separate determinations of the partial pressures of NO<sub>2</sub> and of the mixture of NO + NO<sub>2</sub> with a 4% accuracy.

### 3. RESULTS

Results are expressed in terms of chemical yields:

$$R_1 = \frac{\text{moles of NO (produced)}}{\text{moles of N}_2 + \text{moles of O}_2(\text{initial})}$$

$$R_2 = \frac{\text{moles of NO}_2(\text{produced})}{\text{moles of N}_2 + \text{moles of O}_2(\text{initial})}$$

$$R = R_1 + R_2$$

energetical yield:

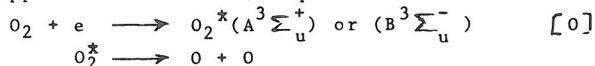
$$P = \frac{\text{moles of NO}_x}{\text{Joules (of microwave power)}}$$

- 3.1 Influence of the flow rate D. The flow rates in the reactor are in the range 0.05 to 1 l.mn<sup>-1</sup> S T P (Standard Temperature and Pressure). They correspond to a linear speed of gases of 5 to 100 cm.s<sup>-1</sup>. Under these conditions the flow is laminar (Reynolds Numbers: 42-220); the residence time in the post reactor is 0.2 to 4 s and in the discharge it may be supposed to be of the order of 0.2-0.01 s. Results are shown on fig. 2.
- 3.2 Influence of ratio N<sub>2</sub>/O<sub>2</sub>: cf fig. 3.
- 3.3 Influence of total pressure P<sub>t</sub> : cf. fig. 4
- 3.4 Influence of microwave power W : No significant relation is found, as we cannot estimate the energy losses.
- 3.5 Influence of reactor and post-reactor diameters and temperature of the walls: No significant effect.

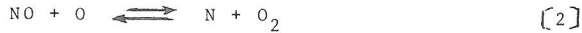
### 4. CHEMICAL MECHANISM.

We distinguish two different reaction zones.

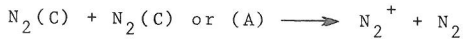
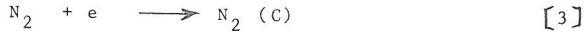
- 4.1 In the discharge. An initiation reaction is caused by electron impact on the reactants. As a result of (1), we may suppose two different sequences:



As shown by (2), this process needs 5.1 or 7.1 eV to give oxygen atoms in the states  $^3P$  or  $^1D$ . Nitrogen monoxide is then produced by the classical mechanism proposed by Zeldovich:

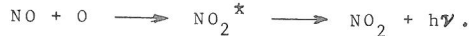


(the reverse reactions of 1 and 2 are written -1 and -2). The alternative sequence for initiation reaction would be:



According to (3) reaction [3] needs 11 eV. As the plasma is at relatively high pressure, the energy distribution of electrons is maxwellian: so the first process is, by far, more probable than the second. However this one may explain the presence of  $NO(\gamma)$ , formation of  $N_2^+$  (at  $\lambda = 3914 \text{ \AA}$ ) and its quenching by  $O_2$  (1).

4.2 In the post discharge zone. Nitrogen dioxide is formed by the reaction:



so, the mechanism formed by reactions [0], [1], [2] and [4], may be supposed to correspond to the main reactions that determine the chemical yield. Evidently, many other reactions occur but are negligible from the chemical point of view. We must notice that all  $NO$  is formed in the discharge and a part is converted into  $NO_2$  in the post reactor.

### 5. INTERPRETATION

de SOETE (4) has shown that, under the condition  $[O_2] \gg [NO]$ , the Zeldovich's mechanism leads to the kinetic equation:

$$\frac{d[NO]}{dt} = 2 k_1 [N_2] \cdot [O] - 2 \frac{k_2 k_{-1}}{k_{-2}} \frac{[NO]^2 \cdot [O]}{[O_2]} \quad [5]$$

The rate constants  $k_i$  are obtained from (5). The temperature in the discharge, measured by rotation spectrometry (1), is evaluated to be 3500 K. Under these assumptions, the values are estimated:

$$k_1 \cong 1.5 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$k_{-1} \cong 1.8 \times 10^{13} \quad "$$

$$k_2 \cong 2.2 \times 10^{10} \quad "$$

$$k_{-2} \approx 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The oxygen atoms concentration in a microwave discharge has been studied by (6) and analysed by (2). The authors report contradictory results for different devices. Our experimental configuration is similar to what they call "reactor A"; under this assumption it is possible to suppose that  $[O]$  does not depend on  $W$  and  $[O] / [O_2] \approx \text{Cst} \approx 3\%$ . The kinetic equation is then

$$\frac{d [NO]}{dt} = a [N_2] [O_2] - b [NO]^2 \quad [6]$$

with

$$a \approx 9 \times 10^7 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$b \approx 2.4 \times 10^9 \text{ " " "}$$

This equation is coherent with the experimental results. We have to remark that all NO formed in the discharge is analysed as NO, O<sub>2</sub>, NO<sub>2</sub>; so, the term  $[NO]$ , in the previous equation corresponds to R.

5.1 Influence of the flow rate. For small values of  $[NO]$ , consumption of reactants must be neglected and eq [6] becomes:

$$\frac{d [NO]}{dt} = a [N_2]_0 [O_2]_0$$

If we convert  $[NO]$  into R for a 50% N<sub>2</sub>-O<sub>2</sub> mixture under 300 torrs, we obtain the numerical relation

$$R \approx 300 t$$

where  $t$  represents the residence time in the discharge. For  $D = 0,8 \text{ l.mn}^{-1}$ ,  $t \approx 0.02 \text{ s}$ , we calculate  $R \approx 6\%$ . The order of magnitude is correct. The maximum value  $[NO]_{\text{Max}}$  is reached when

$$a [N_2] [O_2] = b [NO]^2 \quad [7]$$

In a 50% mixture this condition leads to the value

$$R_{\text{Max}} = 8,6\%$$

which corresponds to approximate extrapolation of the curve of fig. 2

5.2 Influence of concentration. It is obvious on eq [6] that both reactants play a similar role, and that the maximum rate of formation of NO in the discharge is reached for the 50% mixture as in fig. 3.

5.3 Influence of total pressure. Eq [7] shows that R is independent of total pressure. This remark seems in opposition

with fig. 4. However it must be noticed that as  $P_t$  increases, the volume of the discharge zone decreases. So the effect may be attributed to the modification of the residence time. In fact, for different pressures  $R_{Max}$  reaches always the same value.

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**FIG. 1**

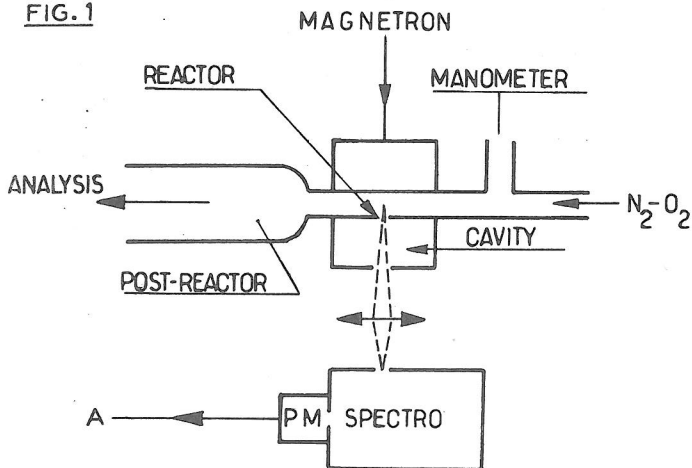


FIG. 2

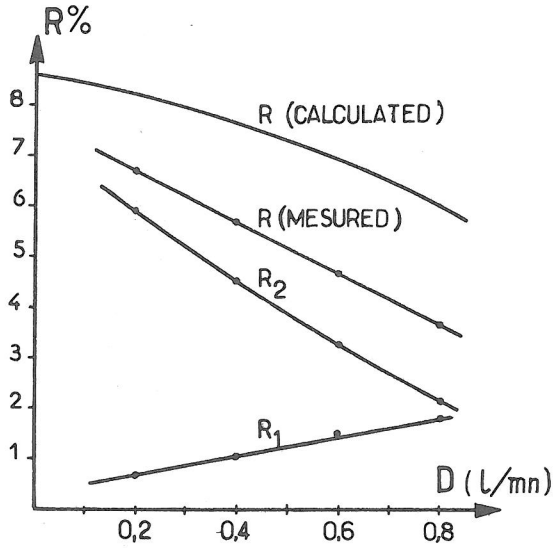


FIG. 3

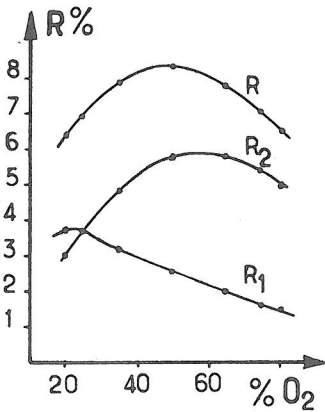


FIG. 4

