

## THERMAL DECOMPOSITION OF *n*-PENTANE. III Effect of Nitric Oxide

L. SZIROVICZA and F. MÁRTA

Institute of General and Physical Chemistry, Attila József University, Szeged

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The kinetics of *n*-pentane pyrolysis have been studied at temperatures from 520 to 560 °C, with 0 to 100% of added nitric oxide. The rates of production of hydrogen and hydrocarbon products have been studied by gas-chromatography. Nitrogen-containing products have been analysed by mass-spectrometry.

The rates of formation of some products and the rate of decomposition of *n*-pentane are strongly altered by effect of nitric oxide.

A mechanism is proposed in agreement with the observed results. Its main features are: 1. Nitric oxide reacts with alkyl radicals; 2. Initiation takes place by unimolecular dissociation of *n*-pentane and by hydrogen abstraction from *n*-pentane by nitric oxide.

### Introduction

The effect of nitric oxide on organic pyrolyses has been extensively studied. Most of the results were based on pressure measurements. Product analyses have recently been made for hydrocarbon pyrolyses [1—4]. Papers dealing with the thermal decomposition of *n*-pentane were published more than a decade ago and were mainly based upon pressure measurements.

From this point of view it seemed worth while to investigate the thermal decomposition of *n*-pentane in the presence of nitric oxide. Experiments were carried out in the temperature range 520—560 °C and at initial pressure of 50—200 torr of *n*-pentane and of nitric oxide.

### Experimental

The apparatus and the method have been described earlier [5]. Different quantities of *n*-pentane and of nitric oxide were mixed and admitted into the reaction vessel between 520—560 °C. The initial rates of formation of some products and the initial decomposition rate of *n*-pentane were determined by gas-chromatography at 520 °C and at initial pressures of 200 torr of *n*-pentane and 0—200 torr of nitric oxide. The initial rates were determined by extrapolating concentration/time *versus* time plots to zero time.

Samples were taken from the reaction vessel by means of a sampling valve and analysed on a gas-chromatograph equipped with a thermal conductivity detector. Three columns were used in the gas-chromatographic analyses. One of them was packed with molecular sieve 5A, a second with activated alumina and the third

with didecyl phthalate. The method and the sizes of the columns have been described previously [5]. The products of the reaction were identified on a Finnigan 1015 mass spectrometer combined with a gas-chromatograph. In this apparatus two columns were used. One of them was 0.4 cm in diameter and 220 cm in length and was packed with 40—80 mesh (A.S.T.M) alumina; this column was used for the analysis of hydrocarbons. The other column was 0.4 cm in diameter and 220 cm in length and packed with 80—100 mesh Chromosorb 101, and was used for the analysis of the products containing nitrogen.

Nitric oxide was prepared from potassium nitrite by reduction with hydrogen iodide.

### Results

1. The dependence of the manometric rate of decomposition on nitric oxide concentration shows a minimum for all experimental conditions investigated. The

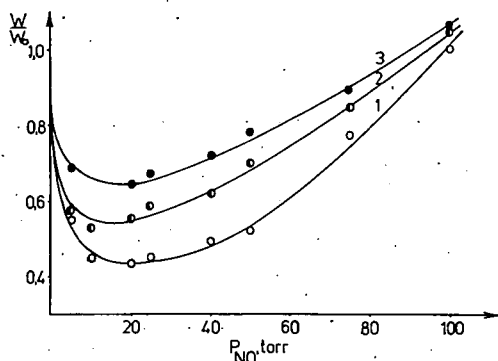


Fig. 1. Effect of nitric oxide on the initial rate measured manometrically. Initial pressure of *n*-pentane 50 torr at 520 °C (1); 540 °C (2); and 560 °C (3).

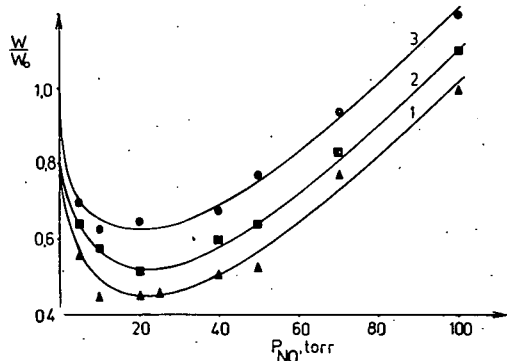


Fig. 2. Effect of nitric oxide on the initial rate measured manometrically at 520 °C. Initial pressure of *n*-pentane: 50 torr (1); 100 torr (2); 200 torr (3).

effect of nitric oxide was characterised by the quotient  $w/w_0$  where  $w_0$  is the initial rate of decomposition without nitric oxide and  $w$  is the initial rate of decomposition in the presence of a given quantity of nitric oxide. At elevated temperature the value of the minimum of the  $w/w_0$  vs. partial pressure of nitric oxide curve was greater than at lower temperature (Fig. 1). The value of the minimum of the  $w/w_0$  curve depends on the initial pressure of *n*-pentane (Fig. 2).

2. Added nitric oxide slightly increased the initial rate of decomposition of *n*-pentane measured by gas-chromatography (Fig. 3).

3. The rate of formation of some products strongly changed; that of ethylene gradually increased with increasing nitric oxide concentration; the rate of formation of hydrogen, ethane and methane decreased; that of propylene decreased first with increasing nitric oxide concentration but increased at high concentration; the rate of formation of butane-1 was unchanged (Fig. 4). In Table I the rates of reaction measured manometrically and by gas-chromatography are compared at two nitric oxide pressures.

Table I

Initial rates of formation in  $\text{torr} \cdot \text{min}^{-1} \cdot P_0 = 200 \text{ torr} \cdot T = 520^\circ \text{C}$ 

Compounds	Initial pressure of NO in torr	0	20	50
CH <sub>4</sub>		0.70	0.68	0.63
C <sub>2</sub> H <sub>6</sub>		0.60	0.30	0.21
C <sub>3</sub> H <sub>8</sub>		0.05	0.05	0.05
C <sub>5</sub> H <sub>12</sub>		-1.0	-1.06	-1.10
C <sub>2</sub> H <sub>4</sub>		0.40	0.41	0.47
C <sub>3</sub> H <sub>6</sub>		0.60	0.36	0.52
C <sub>4</sub> H <sub>8</sub>		0.40	0.40	0.40
H <sub>2</sub>		0.10	0.09	0.08
Total		1.85	1.23	1.26
Manometrically found		1.87	1.15	1.39

4. In the presence of added nitric oxide the following new products were detected: nitrogen, nitrous oxide, water, hydrogen cyanide, pentene-1, *cis*- and *trans*-pentene-2.

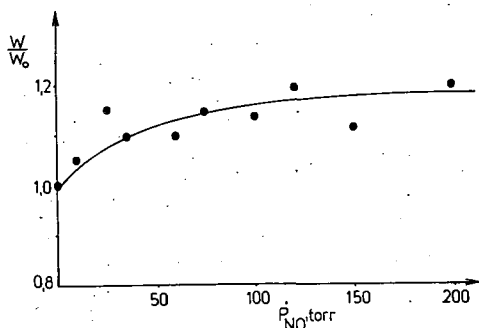


Fig. 3. Effect of nitric oxide on the initial rate measured by gas-chromatography. Initial pressure of *n*-pentane 200 torr;  $T = 520^\circ \text{C}$ .

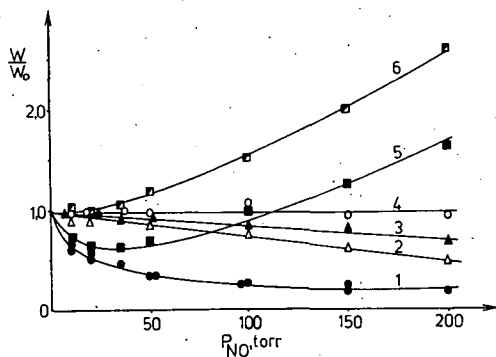


Fig. 4. Initial rates of formation of the products in the nitric oxide influenced reaction. Initial pressure of *n*-pentane 200 torr,  $T = 520^\circ \text{C}$ . (1) C<sub>2</sub>H<sub>6</sub>; (2) H<sub>2</sub>; (3) CH<sub>4</sub>; (4) 1-C<sub>4</sub>H<sub>8</sub>; (5) C<sub>3</sub>H<sub>6</sub>; (6) C<sub>2</sub>H<sub>4</sub>.

### Discussion

The effect of nitric oxide can be explained by the reaction of nitric oxide (a) with radicals present and (b) with *n*-pentane.

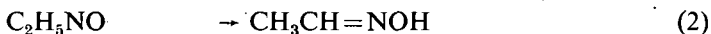
a) The concentration ratios of radicals in the pyrolysis of *n*-pentane are as follows [5]:

$$[\text{C}_2\text{H}_5]:[\text{CH}_3]:[\text{C}_3\text{H}_7]:[\text{H}] = 2802:340:233:1.$$

On the basis of this relationship, the reaction  $C_2H_5 + NO$  seems to be the most probable of the reactions between the free radicals and nitric oxide.

The ethyl radicals can react with nitric oxide in an addition reaction. The steps following this addition [2, 4] can explain the formation of nitrogen, nitrous oxide, hydrogen cyanide and water, as well as the increase in the initial rate of formation of ethylene at the expense of ethane.

The reaction between nitric oxide and ethyl radicals can be assumed as follows:



Step (4) is a complex reaction [3].

As there is a slight decrease in methane production with increasing NO concentration, the reaction between nitric oxide and methyl radical may be taken into consideration by the following steps:



Nitric oxide reacts with propyl radical gives propionaldoxime in reactions analogous with steps (1) and (2). The first step in pyrolysis of propionaldoxime [6] is:



which is followed by:

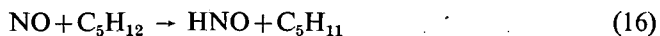


The increase in the rate of formation of propylene at higher NO concentration can be explained by step (13).

The decrease in hydrogen production with increasing nitric oxide concentration can be explained by the following reactions:



b) Because the rate of decomposition of *n*-pentane increased in the presence of nitric oxide, the following initiation step has to be assumed:



The concentration of pentyl radicals increases due to step (16). This increase explains the appearance of pentenes in the pyrolytic decomposition of *n*-pentane influenced by nitric oxide.

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### ТЕРМИЧЕСКОЕ РАЗЛОЖЕНИЕ *n*-ПЕНТАНА. III. ВЛИЯНИЕ ОКИСИ АЗОТА

*Л. Сировица и Ф. Марта*

Изучалась кинетика пиролиза *n*-пентана при температурах 520—560 °С в присутствии окиси азота; содержание окиси азота составляло от 0 до 100% исходного *n*-пентана. Водород и углеводородные продукты измерялись газо-хроматографически, азотосодержащие продукты анализировались с помощью масс-спектрометра.

Скорость образования некоторых продуктов и скорость разложения *n*-пентана сильно изменяются в присутствии окиси азота.

На основании измеренных данных предлагается механизм со следующими главными предположениями:

1. Окись азота реагирует с алкильными радикалами;
2. Инициирование происходит путем мономолекулярной диссоциации, *n*-пентана и с отрывом атома водорода от *n*-пентана окисью азота.