

NITRIC OXIDE INFLUENCED THERMAL DECOMPOSITION OF ISOBUTANE

By

M. GÖRGÉNYI, L. SERES and F. MÁRTA

Gas Kinetics Research Group of the Hungarian Academy of Sciences, Szeged, and
Institute of General and Physical Chemistry, Attila József University, Szeged

(Received January 25, 1974)

Pyrolysis of isobutane has been studied in the presence of different amounts of nitric oxide in the temperature range of 773 to 823 K. Beside hydrogen and hydrocarbons, compounds containing oxygen and nitrogen were identified. The initial rate of formation of hydrogen and hydrocarbons decreased in the presence of small amounts (0–15%) of nitric oxide. The initial rate of formation of all products increased in the presence of greater amounts of nitric oxide.

The mechanism suggested includes the formation of "polymeric" radicals followed by isomerization and decomposition.

Introduction

The effect of nitric oxide on hydrocarbon pyrolytic processes has been extensively studied. The interpretations given in early studies were based on the principle of a molecular mechanism excluding the possibility of the contribution of chain processes in the "maximally inhibited region". This idea was accepted in the only paper published on nitric oxide influenced thermal decomposition of isobutane [1].

Nowadays the radical chain character of the pyrolysis of hydrocarbons in the presence of nitric oxide is generally recognized and the formation of compounds containing the oxygen and nitrogen atoms of the nitric oxide has been observed [2, 3].

Experimental

The reaction was studied in a conventional static system. Different quantities of nitric oxide (up to 200 torr) and 200 torr isobutane were mixed and admitted in a Supremax reaction vessel.

The isobutane used was of 99.5% purity, major impurities being propane, propene, isobutene and ethylene. Nitric oxide was prepared from potassium nitrite and potassium iodide. Both gases were further purified by trap to trap distillation in vacuum. The composition of the reaction mixture was determined by gas chromatography. Two columns were used: activated alumina (60–80 mesh) for the separation of ethane, nitrous oxide, ethylene, propane, propene, isobutane, isobutene; molecular sieve 5A for that of hydrogen, nitrogen and methane. Water and acetonitril were identified by mass spectrometry.

Results

The initial rates of formation of hydrogen and hydrocarbons decreased in the presence of small amounts (1—15%) of nitric oxide. Higher amounts of nitric oxide gave rise to an increase in the rate formation of most of the products.

The relative rate of hydrogen and methane production decreased considerably with increasing nitric oxide partial pressure (Fig. 1).

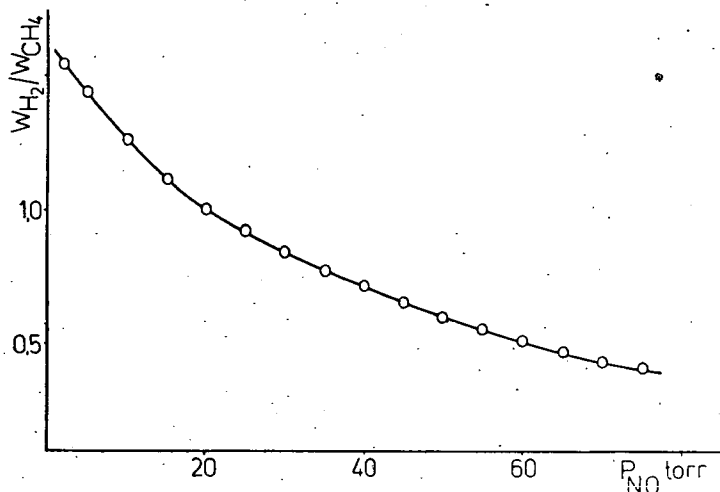


Fig. 1. Influence of nitric oxide on the ratio of initial rates of formation of hydrogen and methane ($T=793$ K).

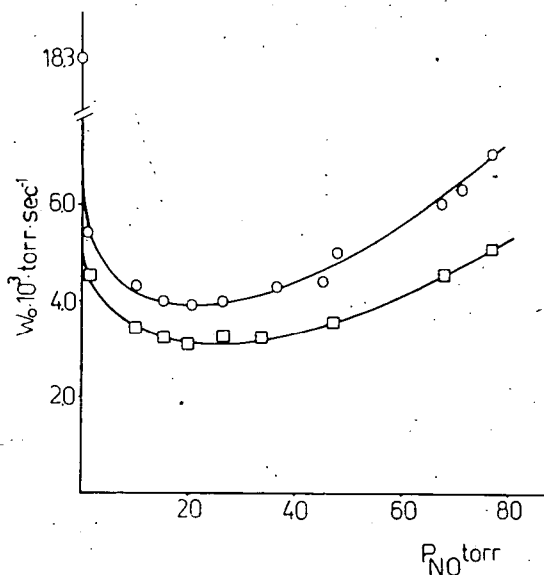


Fig. 2. Effect of nitric oxide on the initial rate of formation of methane and propylene (\circ methane; \square propylene; $T=793$ K).

The increase in the rate of production of methane and propylene was remarkable at higher nitric oxide partial pressures (Fig. 2).

This effect is less pronounced in the case of hydrogen and isobutene (Fig. 3).

It is surprising that the rate of formation of propylene increases to a higher extent than that of isobutene.

An induction period can be observed in the ethane formation (Fig. 4). Its length shows a minimum at moderate nitric oxide pressures. The position of the minimum shifts to higher nitric oxide pressures with increasing temperature.

The same type of behaviour can be observed in propane and ethylene formation. A considerable increase can be observed in ethylene formation with increasing nitric oxide partial pressures (Fig. 5).

The plot of nitrogen partial pressures against time gives a good straight line (Fig. 6). An induction period can be observed at lower temperatures.

The order of nitrogen formation with respect to nitric oxide was found to be 1.05 ± 0.05 and did not exhibit any systematic change in the temperature range of 773–823 K. Similarly, an order of 1.10 ± 0.06 with respect to isobutane was obtained.

The production of nitrous oxide shows no induction period. Its rate of formation is considerably lower than that of nitrogen and decreases at relatively moderate conversions (Fig. 7).

Discussion

The mechanism of the reaction influenced by olefins was described earlier [4]. On the basis of the above

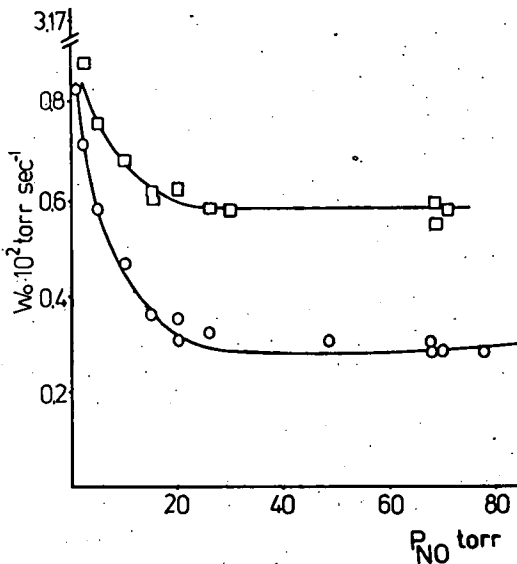


Fig. 3. Effect of nitric oxide on the initial rate of formation of hydrogen and isobutene (\circ hydrogen; \square isobutene; $T = 793$ K)

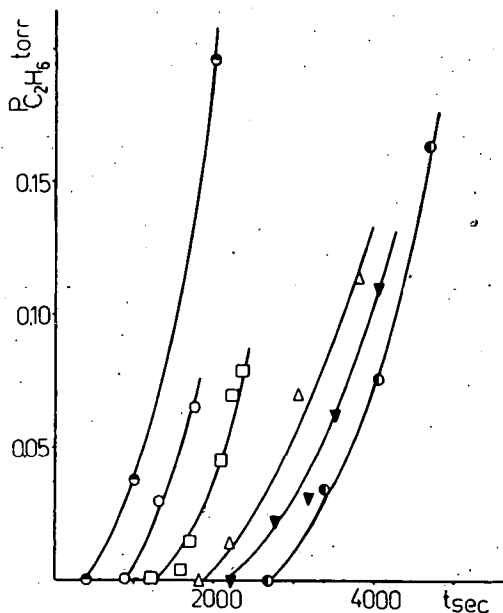
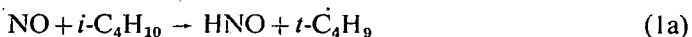


Fig. 4. Effect of nitric oxide on ethane formation (P_{NO} : \circ 0; \bullet 10; \blacktriangledown 25; \triangle 50; \square 100; \circ 200 torr; $T = 773$ K)

experimental data, some features of the nitric oxide influenced reaction can be elucidated. The importance of the possible bimolecular initiation steps



increases with the amount of nitric oxide present. There is no experimental evidence for the bimolecular initiation (1a, 1b); but this assumption can be supported by other experimental data [5].

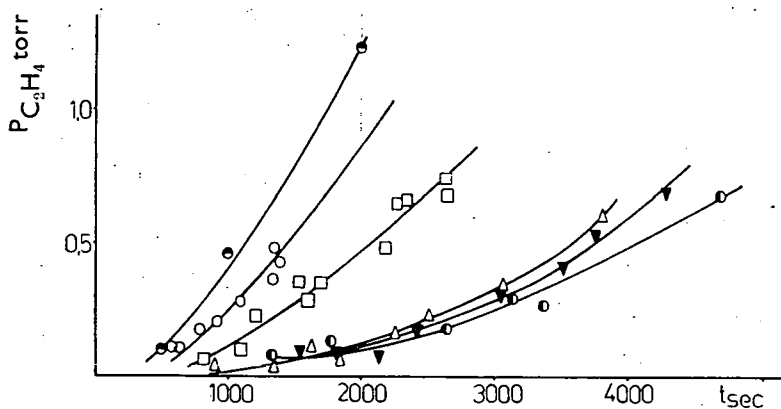


Fig. 5. Effect of nitric oxide on ethylene formation (p_{NO} : \circ 0; \bullet 10; \blacktriangledown 25; \triangle 50; \square 100; \circ 200 torr; $T=773$ K)

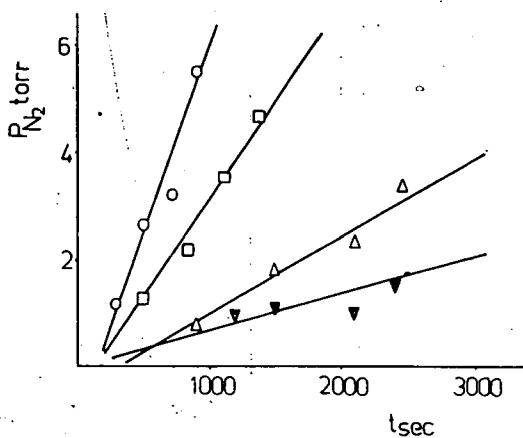


Fig. 6. Nitrogen formation in the nitric oxide influenced thermal decomposition of isobutane (p_{NO} : \circ 200; \square 100; \triangle 50; \blacktriangledown 25 torr; $T=773$ K)

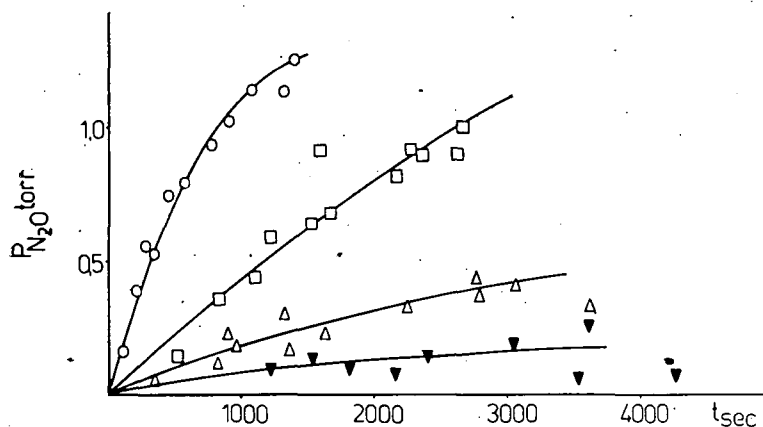


Fig. 7. Nitrous oxide formation in the nitric oxide influenced thermal decomposition of isobutane (p_{NO} : \circ 200; \square 100; \triangle 50; ∇ 25 torr; $T = 773 \text{ K}$)

	$\lg A$	E	$\lg k_{800}$	
$\dot{\text{C}}\text{H}_3 + \text{C}_2\text{H}_6 \rightarrow \text{CH}_4 + \dot{\text{C}}_2\text{H}_5$	11.3	10.4	8.46	(a)
$\dot{\text{C}}\text{H}_3 + (\text{CH}_3)_2\text{O} \rightarrow \text{CH}_4 + \dot{\text{C}}\text{H}_2\text{OCH}_3$	11.5	9.5	8.91	(b)
$\text{NO} + (\text{CH}_3)_2\text{O} \rightarrow \text{HNO} + \dot{\text{C}}\text{H}_2\text{OCH}_3$	14.0	43.4	2.15	(c)

Using the above kinetic parameters, the rate coefficient of the initiation step:



can be estimated by making the following assumptions:

- (a) $k_b/k_c = k_a/k_d$
- (b) the rate coefficients of primary H-atom abstractions from $i\text{-C}_4\text{H}_{10}$ and C_2H_6 corresponds to the ratio of primary H atoms present in the molecules (9:6)
- (c) the rate of tertiary H-atom abstraction exceeds that of primary atoms by a factor of two [6].

By using these assumptions the ratio of the rates of the unimolecular: $i\text{-C}_4\text{H}_{10} \rightarrow \dot{\text{C}}\text{H}_3 + 2\dot{\text{C}}_3\text{H}_7$ (1) and the bimolecular reactions (1a) and (1b) can be calculated:

$$\frac{w_1}{w_2} = \frac{k_1[i\text{-C}_4\text{H}_{10}]}{k_2[i\text{-C}_4\text{H}_{10}][\text{NO}]} = \frac{10^{-4.7}}{10^{2.2}10^{-5.7}} = 10^{-1.2}$$

The error involved in the above calculation is probably large. All the same, it can be regarded as an evidence that H-atom abstraction by nitric oxide contributes to the initiation.

The concentration of methyl radicals drops less drastically than that of hydrogen

atoms in the presence of nitric oxide (Fig. 1). The decrease in hydrogen formation (Fig. 3) can be accounted for by the reactions



as the hydrogen atoms are produced mainly from the $t\text{-}\text{C}_4\text{H}_9$ radicals. As a consequence, the rate of all reactions involving H-atoms decreases.

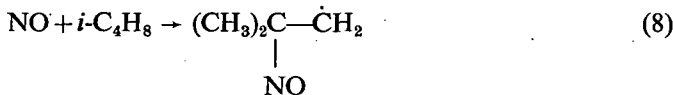
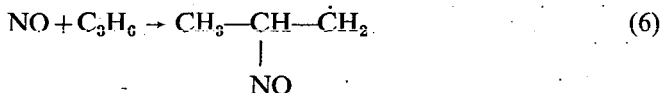
The decreases in the radical concentration in reactions (2), (3), (4) and (5)



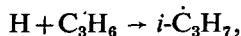
results in the inhibition of the formation of secondary products (ethane and propane) (Fig. 4).

To account for the increase in the rate of the overall process and the pattern of rate increase in the formation of various products, other reactions involving nitric oxide must also be included in the mechanism.

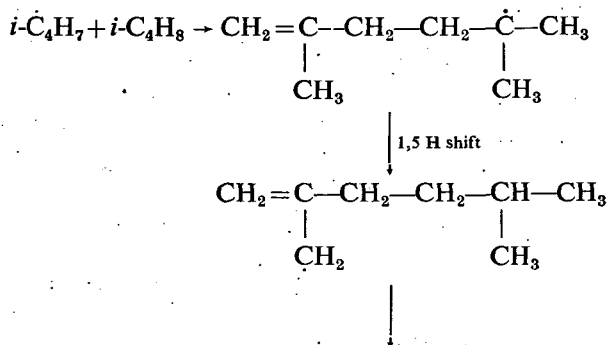
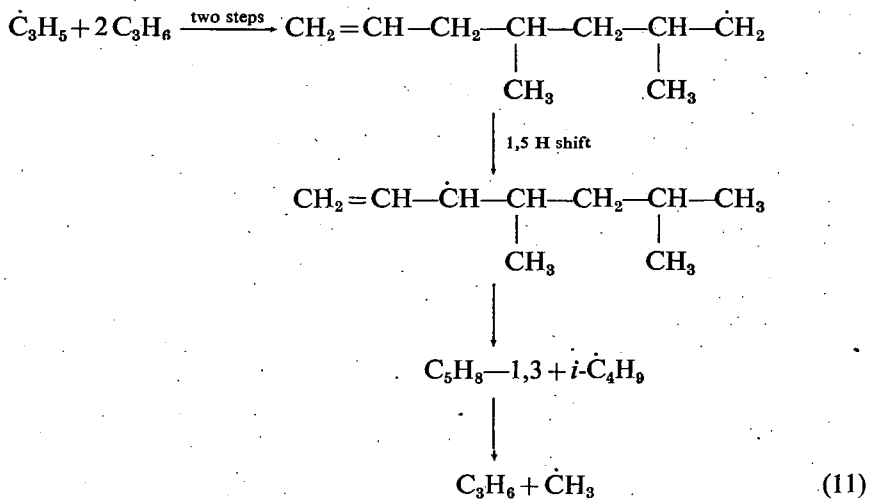
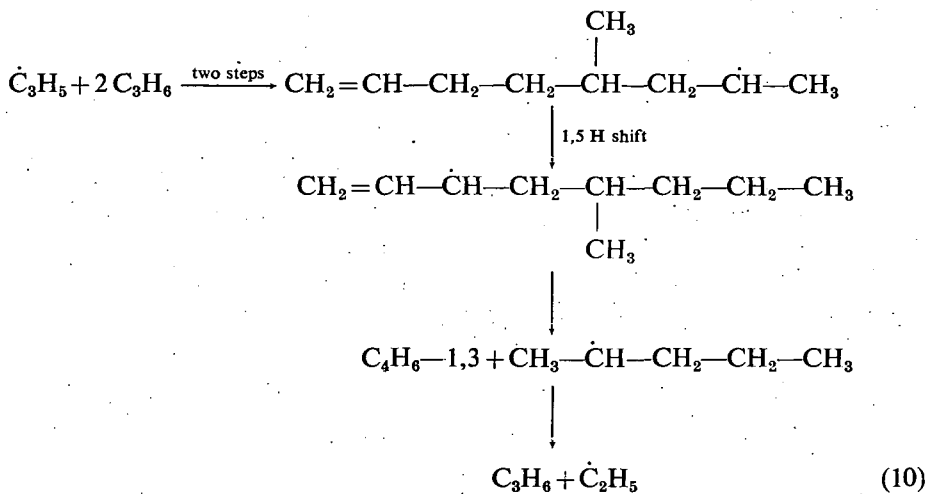
The addition of nitric oxide to the double bond and H-atom abstraction from olefins by nitric oxide can yield radicals, too.

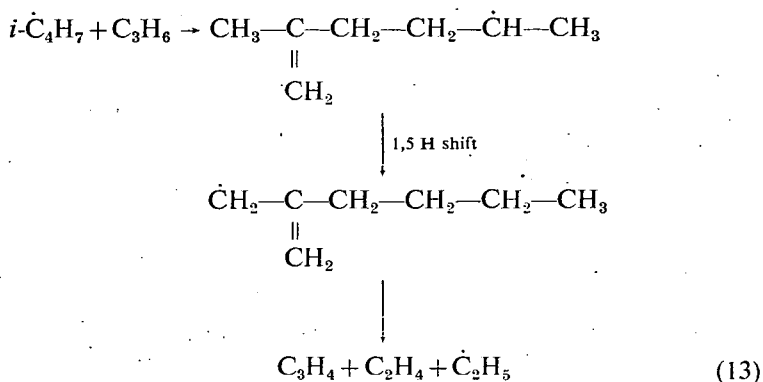
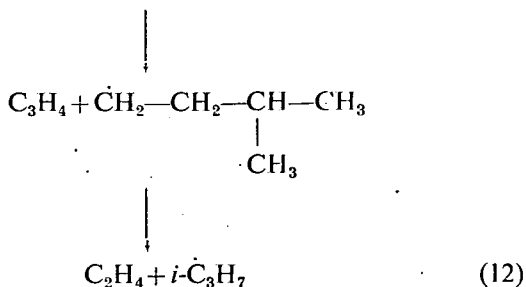


The observed increase in the rate of formation of ethane and propane in the presence of higher amounts of NO reflects a similar change in the concentration of ethyl and secondary propyl radicals. They are not formed in the addition steps.



since the formation of hydrogen does not show any major increase. Ethane and propane are shown to be the products of propylene and isobutene pyrolysis and the above radicals are suggested to be formed from "polymeric" radicals undergoing internal H-atom transfer processes and dissociation [7, 8].





“Polymeric” radicals can be produced in the isobutane pyrolysis, too. Some of the possible reactions are shown above. They are intended only to demonstrate the possibility of interpreting the experimental facts using the basic idea outlined in [8].

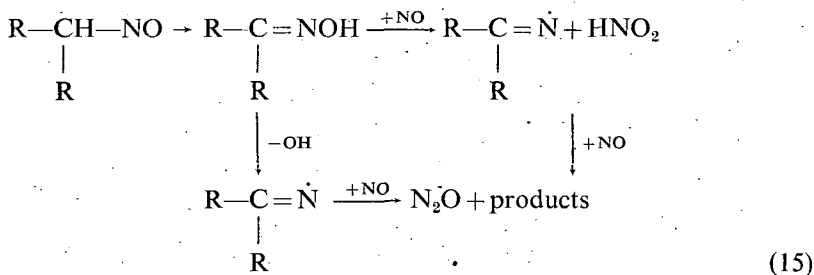
The steps suggested above and other addition—isomerization—decomposition steps result in the formation of products with increased rates of formation in the presence of nitric oxide. Allene is an exception. Under the condition of the reaction, this compound is converted into various products in fast reactions demonstrated in separate experiments.

The nitroso compounds formed from various R radicals present in the system are probably the source of nitrogen [3]:



In agreement with this assumption, increased nitrogen formation was observed in a system of 200 torr $i\text{-C}_4\text{H}_{10}$ + 100 torr NO + 25 torr C_3H_6 , compared to that in the absence of the olefin.

The formation of N_2O is proposed to occur in reactions similar to those suggested by ESSER and LAJDLER [2] in the nitric oxide influenced ethane decomposition.



With $\text{R}=\text{CH}_3$ and $\text{R}=\text{H}$, reaction (15) results in the formation of CH_3CN .
The OH radicals formed in reactions (15) and (16)



give rise to water formation



HNO formed in various reactions is a source of N_2O



Termination is expected to occur between NO and the various radicals present.



However, no reliable information specifying these processes is available.

References

- [1] Peard, M. G., F. S. Stubbs, C. N. Hinshelwood: *Proc. Roy. Soc.* **A214**, 330 (1952).
- [2] Esser, J., K. J. Laidler: *Int. J. Chem. Kinetics* **2**, 37 (1970).
- [3] Eastmond, G. B. M., G. L. Pratt: *J. Chem. Soc.* **A1970**, 2329.
- [4] Seres, L., F. Márta, Á. Kiss: *Ber. Bunsenges. Phys. Chem.* **73**, 571 (1969).
- [5] Trotman-Dickenson, A. F., G. S. Milne: *Tables of Bimolecular Gas Reactions*, U.S. Government Printing Office, Washington, 1967, p. 122.
- [6] Konar, R. S., R. M. Marshall, J. H. Purnell: *Trans. Faraday Soc.* **64**, 403 (1968).
- [7] Görgényi, M., et al.: to be published.
- [8] Seres, L., P. Ausloos: *Symposium on the Mechanism of Hydrocarbon Reactions*, Siófok (Hungary), 5—7 June, 1973.

ВЛИЯНИЕ ОКИСИ АЗОТА НА ТЕРМИЧЕСКОЕ РАЗЛОЖЕНИЕ ИЗОБУТАНА

М. Гергени, Л. Шереш, Ф. Марта

Изучен пиролиз изобутана в присутствии различных концентраций окиси азота в интервале температур от 773 до 823 К. Наряду с водородом и углеводородами были определены также соединения содержащие кислород и азот. Скорости образования водорода и углеводородов уменьшались в присутствии (0—15%) окиси азота. Начальная скорость образования всех продуктов возрастала с повышением концентрации окиси азота. Предложенный механизм реакции включает в себе образование „полимерных“ радикалов, сопровождающееся изомеризацией и разложением.