

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Kinetics of the Decomposition of *n*-Butane. II. Inhibition by Nitric Oxide and Propylene

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In the first paper of this series,¹ evidence was presented which indicates that the thermal decomposition of *n*-butane is by no means the simple unimolecular process originally postulated on the basis of flow experiments. There is an initial period during which the rate decreases rather rapidly, this decrease being associated with a "product effect" which seems to approach a limiting value. The data correspond to a rate equation of the form

$$-\frac{dP_B}{dt} = k_1 P_B^{1.5} + \frac{k_2 P_B^2}{P_{0B} - P_B}$$

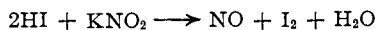
where P_B is the pressure of butane and P_{0B} is the initial pressure of this gas. It thus appears that the reaction eventually attains an order of 1.5 rather than 1.0.

Further it was remarked that the decomposition is inhibited by nitric oxide² as are a number of other organic vapor phase reactions.³ This effect is now generally considered as indicative of chain reaction.

With these evidences of intermediate order of reaction, limited inhibition by products (as shown by the second term of the equation), and a chain mechanism, a more detailed study of the effects of nitric oxide and of products has been undertaken, the results being here presented.

Apparatus and Method.—Experiments were conducted as in the previous work by making pressure measurements at constant volume. The increase in pressure during the reaction was correlated with the percentage reaction by analysis. It is considered that up to 30% decomposition the pressure increase is a satisfactory measure of reaction.

Nitric oxide was prepared, following Giauque and Johnston,⁴ by the reaction



The product was purified by scrubbing with potassium hydroxide followed by low temperature fractionation. Butane, ethylene and propylene were prepared from commercial products by fractionation.

Reaction products were analyzed volumetrically. Nitric oxide was determined by adding excess oxygen, absorbing the NO_2 in potassium hydroxide solution, then removing the remainder of the oxygen by Oxsorbent. Net decrease in volume was nitric oxide. Olefins were

determined by absorption in bromine water under conditions which rendered attack on saturated hydrocarbons negligible. In one case residual butane was determined by low temperature fractionation.

Two points of importance follow from the analytical results. In the first place the amounts of olefin formed and butane reacted checked the pressure increase as a measure of extent of reaction. Secondly, relatively little nitric oxide was consumed in the reaction. Thus in a run with 80 mm. of nitric oxide and 200 mm. of *n*-butane in which 45 mm. of olefins was formed ($\Delta P = 44.5$ mm.) not more than 4.5 mm. of nitric oxide was consumed. Analogous results were obtained consistently.

The reaction bulb was of Pyrex (3.7×22 cm.) and was coated internally by flowing fused potassium chloride over the surface.

Inhibition by Nitric Oxide.—Data on the effect of nitric oxide are presented in Table I and Fig. 1, the latter referring to experiments with 200 mm. of *n*-butane and various amounts of nitric oxide at 520°. It will be seen at once that the nitric oxide sharply depresses the initial rate but that as the reaction proceeds the rates increase and seem to become entirely normal at some point beyond 15% reaction. The inhibition is thus only transient in nature. It is also clear from Table I that the effect of increasing amounts of

TABLE I
INHIBITION BY NITRIC OXIDE

Init. press., mm. <i>n</i> -C ₄ H ₁₀	NO	Time to indicated % reaction, min.					
		<i>t</i> ₁	<i>t</i> ₅	<i>t</i> ₁₀	<i>t</i> ₁₅	<i>t</i> ₂₀	(<i>t</i> ₂₀ - <i>t</i> ₁₅)
Temp. 500°							
200	0	..	9.0	25.8	47.2
	10	..	83	129	166	197	..
	20	..	109	158	200
Temp. 510°							
200	0	..	5.2	14.4	26.4
	10	..	43.0	70.0	92
	20	..	51	82	101
Temp. 520°							
200	0	0.5	3.3	9.3	16.8	26.0	9.2
	0.5	1.0	5.5	13.2	22.7	33.3	10.6
	3.3	3.6	16.9	31.0
	5.0	5.5	20.0	34.5	45.0
	7.5	7.0	26.0	43.5	58.5	71.5	13.0
	10	7.5	28.0	46.0	61.0
	15	12.5	36.0	54.5	69.0	80.0	11.0
	20	9	31.5	47.5	60.5	70.2	9.2
	44	9.9	39.5	57.5	74.5	88.0	13.5
	80	10.8	32.2	48.5	60.7	71.3	10.6
400	0	0.5	2.7	7.7	14.0	21.7	7.7
	10	3.2	14.2	24.3	33.3	41.5	8.2
600	0	0.3	2.1	6.4	11.8	17.8	6.0
	10	3.0	10.5	18.0	25.5	32.0	6.5

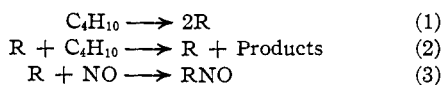
(1) Echols and Pease, *THIS JOURNAL*, **61**, 208 (1939).(2) Echols and Pease, *ibid.*, **59**, 786 (1937); **60**, 170 (1938).(3) Staveley and Hinshelwood, *J. Chem. Soc.*, 1568 (1937).(4) Giauque and Johnston, *THIS JOURNAL*, **51**, 3201 (1929).

nitric oxide approaches a maximum. Thus the highest value of t_{10} is attained at about 40 mm. of nitric oxide.

The existence of a maximum of this type has been found for a wide variety of organic decompositions⁵ but the transient effect has not been reported except in this one case.²

It was at first thought that the slow restoration of the normal rate was due to a destruction of the nitric oxide, but analysis of the reacted gases showed that substantially all of the nitric oxide was still present even after the rates had risen to the normal uninhibited values. There thus seems to be no alternative to the assumption that at least a portion of the small amount of nitric oxide which has disappeared is in a form which can regenerate radicals.

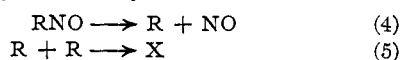
Assuming for illustrative purposes a simple type chain mechanism for the decomposition of *n*-butane with nitric oxide as inhibitor we have for the initial stages of the reaction



whence

$$-\frac{d[\text{C}_4\text{H}_{10}]}{dt} = k_1[\text{C}_4\text{H}_{10}] + \frac{k_1 k_2}{k_3} \frac{[\text{C}_4\text{H}_{10}]^2}{[\text{NO}]} \quad (I)$$

As the reaction proceeds to build up the concentration of the unstable complex⁶ NOR the reverse of reaction (3) comes into importance eventually completely negating the effect of nitric oxide. A new chain ending process must then come into play. We may write



whence

$$-\frac{d[\text{C}_4\text{H}_{10}]}{dt} = k_1[\text{C}_4\text{H}_{10}] + k_1 \sqrt{\frac{k_2}{k_3}} [\text{C}_4\text{H}_{10}]^{1.5} \quad (II)$$

representing the complete restoration of the normal rate.

We thus account for the effects observed in a formal and qualitative way.

With regard to the initial rate in the presence of nitric oxide it may be said that so far as can be determined maximum inhibition gives a rate of change of pressure less than ($1/20$) that of the normal reaction. Presumably this rate corresponds to the portion of the reaction (5%) which is not involved in the chain reaction. This may either

(5) *E. g.*, Ethyl ether, Staveley and Hinshelwood, *Proc. Roy. Soc. (London)*, **154A**, 335 (1936).

(6) It is to be remarked that when R is an alkyl radical the compound NOR is isomeric with the oxime. Thus CH_3NO is $\text{CH}_2=\text{N}-\text{OH}$.

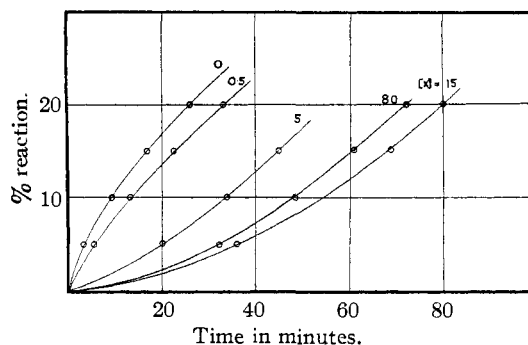


Fig. 1.—Inhibition by nitric oxide: runs with 200 mm. C_4H_{10} + [x] mm. NO at 520° .

be "molecular" reaction or may in some way represent the chain starting processes. It is to be noted, however, that on the seemingly necessary assumption that the nitric oxide is picking up the initial radicals there should be no pressure increase. It is for this reason that we do not attempt to evaluate the chain length from these results. We shall assume that the initial pressure increase is either the result of "molecular" reaction or that it represents the decomposition of (NOR) formed before observations can be commenced in the experiment. Further discussion is deferred to later publications.

Inhibition by Propylene.—The kinetics of the normal reaction indicate the occurrence of an inhibition by products. It being highly unlikely that the saturated lower hydrocarbons, which make up half the product gases, are active as inhibitors we chose to investigate the effects of ethylene and propylene when added to the reactant gas.

Ethylene in amounts up to 50% of a starting mixture showed if anything a slight accelerating effect. On the other hand, propylene was definitely an inhibitor. Results with the latter are presented in Table II and Fig. 2.

TABLE II
INHIBITION BY PROPYLENE AT 520°

Init. press. mm. <i>n</i> - C_4H_{10}	C_3H_6	Time to indicated % reaction, min.				
		t_5	t_{10}	t_{15}	t_{20}	$(t_{20} - t_{15})$
200	0	3.3	9.3	16.8	26.0	9.2
195	16.5	5.7	12.7	21.0	29.0	8.0
197	45	8.7	17.2	25.9	..	9
196	105	9.8	17.3	24.9	32.9	8.0
200	176	9.4	16.0	22.2	28.5	6.3

Our data are not as extensive as for nitric oxide, but they suffice to show that the character of the inhibition is the same. As before there is the initial inhibition approaching a limit as the

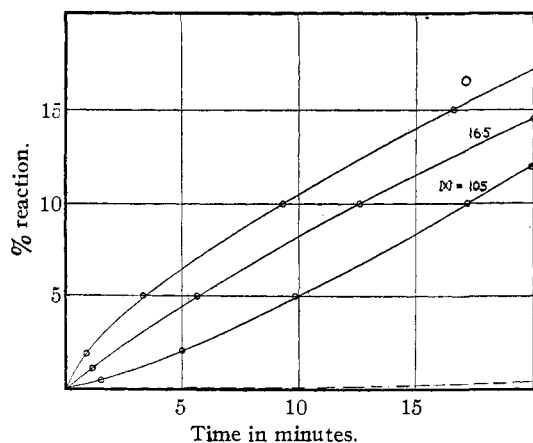
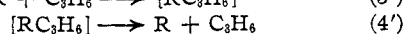


Fig. 2.—Inhibition by propylene: runs with 200 mm. of C_4H_{10} + [x] mm. C_3H_6 at 520° .

concentration of propylene is increased. Subsequently the rate approximates that of the normal reaction, except with the highest concentration of propylene where the rate is actually greater than that of the normal reaction. This is certainly in part due to the noticeable reaction of propylene itself; the dotted curve represents the pressure change for 200 mm. of propylene alone. Cross activation with the decomposing butane might substantially raise the rate of this secondary reaction.

We note that propylene is somewhat less effective than nitric oxide in a ratio of about 1 to 20 or 30.

Assuming again the reversible formation of an intermediate we substitute for reactions 3 and 4



This leads to an expression for the initial rate

$$-\frac{dC_4H_{10}}{dt} = k_1(C_4H_{10}) + \frac{k_1k_2}{k_3} \frac{(C_4H_{10})^2}{(C_3H_6)} \quad (I')$$

and for the steady-state rate

$$-\frac{d(C_4H_{10})}{dt} = k_1[C_4H_{10}] + k_1 \sqrt{\frac{k_2}{k_3}} [C_4H_{10}]^{1.5} \quad (II')$$

It is illuminating to recall at this point the semi-empirical equation which was obtained for the normal reaction.¹ This had the form

$$-\frac{d[C_4H_{10}]}{dt} = k_A[C_4H_{10}]^{1.5} + k_B \frac{[C_4H_{10}]^2}{[C_4H_{10}]_0 - [C_4H_{10}]} \quad (III)$$

In general features the equations I' and II' are consistent with III, it being remembered that with reasonably long chains (>20) the $k_1[C_4H_{10}]$ term is negligible compared to the total rate. We note that the first term on the right of III and

the second term of II' refer to the steady-state rate with

$$k_A = k_1 \sqrt{\frac{k_2}{k_3}}$$

Similarly the second terms of equations I' and III each represent the inhibition by products (propylene) which is the governing factor in the initial stages of reaction. There is this difficulty, however. The second term of equation III was put in to take care of the high initial rates—several times the steady-state rate. It does this by representing the denominator (product effect) as starting from zero. But this simply implies that chains are not then ended by product (*e. g.*, propylene). This would seem to leave radical recombination (reaction 5) as the chain ending mechanism in the initial stages. This, however, has already been used to account for chain ending in the steady state, when the reaction is much slower.

More simply we are confronted with the problem of explaining why one can produce a permanent inhibition only of the portion of the reaction represented by the second term in the semi-empirical equation whether the inhibitor be propylene, nitric oxide, or normal products.

It would seem that either there are two different chain mechanisms or that there are two types of chain carriers one of which can only be transiently inhibited (reversible complex formation) while the other is permanently inhibited (irreversible complex formation). Roughly the first term of equation III represents the first type of reaction while the second term expresses the other type.

Pending the publication of results with nitrous oxide as an initiator of chains, the inhibition of these chains by nitric oxide, the effect of surface nature and extent on the normal and inhibited reactions as well as certain features of the analysis of products it is deemed best to postpone further discussion.

Mention should be made of the results obtained by Staveley⁷ and by Hinshelwood⁸ on the inhibition of the decomposition of methane, ethane, propane and hexane by nitric oxide, and of Rice's data on inhibition by propylene.⁹ In no case was the transient effect observed, presumably because only the initial stages of reaction were studied.

(7) Staveley, *Proc. Roy. Soc. (London)*, **162A**, 557 (1937).

(8) Hobbs and Hinshelwood, *ibid.*, **167A**, 440, 447 (1938).

(9) Rice and Polly, *J. Chem. Phys.*, **6**, 273 (1938).

Summary

Both nitric oxide and propylene inhibit the *n*-butane decomposition. The inhibition reaches a limit as the inhibitor concentration increases. It fades out as the reaction proceeds, the rate eventually becoming nearly equal to that of the normal decomposition. This phenomenon is attributed

to the reversible formation of an intermediate.

These results are compared with the normal reaction and the inference drawn that there are two chain processes involved with only one type of carriers or one mechanism concerned with the reversible inhibitor reaction.

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The Density of Aqueous Solutions of Sodium Hydroxide

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Introduction

As a preliminary to an extensive study of the thermodynamics of sodium hydroxide at very high concentrations, the density of its pure aqueous solutions was determined over a temperature range of 0 to 70° and the concentration range of 1 to 26 molal. The corresponding data given in Volume III of "International Critical Tables" are only in fair agreement with ours and differences frequently were found even in the third decimal place. A mathematical analysis of the former had shown, however, that they without much doubt do contain large errors. Although practically hidden by the manner of interpolating the original data, they show nevertheless distinct indications of a break occurring at relatively high concentrations in the isothermal curves for the apparent partial molal volume of the hydroxide. This break, which at 0° appears at a hydroxide concentration of about 10 molal and with rising temperature slowly shifts toward still higher concentrations, seems according to our measurements to be fairly sharp, and the curve on either side of the break follows at all temperatures nearly precisely a square root linear law. Similar breaks have been noticed previously by Scott in the case of the lithium halides, and earlier by Masson¹ for several other strong electrolytes.

Experimental Procedure.—Sodium hydroxide is extremely reactive, deliquescent in the solid phase and absorbs quantitatively any free carbon dioxide present. It is therefore difficult to prepare and preserve in a highly pure form. Since large quantities were needed, the preparation from pure sodium metal was excluded. The material used was an analytical reagent of unusually high purity and no attempts at further purification, except the

removal of carbonate present were considered necessary. A saturated solution of the hydroxide in air-free conductivity water was made up in an old soft glass bottle previously used for similar purposes over a number of years. The precipitate that appeared was allowed to settle during a period of about three weeks after which time the solution had become perfectly clear without the least trace of suspended matter visible. The careful study of Freeth² of the system sodium carbonate–sodium hydroxide–water at various temperatures does not allow an exact calculation of the concentration of the two electrolytes when they are both present as coexistent solid phases but apparently at ordinary temperatures the ratio between carbonate and hydroxide concentrations at this point is approximately 0.001 or lower. The change of the apparent partial molal volume of sodium carbonate in the presence of large amounts of the hydroxide cannot be obtained and thus any calculation of the error caused by the presence of the former electrolyte would only be approximate in nature. However, using the "I. C. T." density data for pure aqueous solutions of sodium carbonate which at 30° give as its apparent partial molal volume the equation

$$v_{30} = -4.163 + 10.849 \sqrt{m}$$

where *m* is the molality and assuming that no changes occur due to the presence of the hydroxide, it is found that for all practical purposes the error introduced is negligible or at least appreciably smaller than that caused by analytical errors in the determination of the hydroxide concentration.

All solutions used for the density measurements were made up to approximately the desired concentration in quantities of about 300 g. using boiled conductivity water and old, alkali-etched soft glass bottles provided with ground-in stoppers. The finished solutions were analyzed in triplicate by adding to weighed samples a slight excess of hydrochloric acid above the amount needed for neutralizing the hydroxide, evaporating to dryness and igniting lightly until constant weight had been obtained. As a rule the different analyses of a given solution agreed to better than one part in 5000. The analytical weights used were standardized with a high degree of precision and all the appropriate vacuum corrections were carefully observed. The calculation of the hydroxide concentra-

(1) Scott, *J. Phys. Chem.*, **39**, 1031 (1935); Masson, *Phil. Mag.*, [7] **8**, 218 (1929).

(2) Freeth, *Trans. Roy. Soc. London, Series A*, 223 (1922).