

The modes of decomposition of *n*-pentane

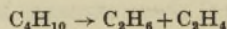
III. Fate of ethane at low pressures

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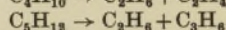
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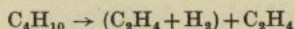
In the nitric-oxide-inhibited decompositions of *n*-butane and *n*-pentane respectively, the reactions



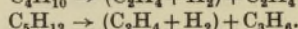
and



give place as the initial pressure drops to the reactions



and



It is now shown that ethane added to the pentane system does not suffer any induced decomposition. Thus a change with pressure in the predominant mode of activation of the normal paraffin molecules is indicated.

In the thermal decomposition of *n*-butane (Stubbs, Ingold, Spall, Danby & Hinshelwood 1952) the ethane, which is an important product of the nitric-oxide-inhibited reaction at the higher pressures, gives place increasingly as the pressure falls to equivalent amounts of ethylene and hydrogen. Ethane itself at similar temperatures and pressures would be stable during the reaction times in question.* It appears, therefore, either that some participating species in the main reaction can catalyze the decomposition of ethane, or else that in the lower pressure range the type of activated butane molecule coming into predominance is such as to decompose into ethylene and hydrogen rather than into ethane, which is the product from the type predominating in the higher pressure range. A variant of this idea is that activated ethane molecules formed from the first type of activated butane molecules themselves decompose before losing their energy.

A similar phenomenon was next found in the decomposition of normal pentane (Danby, Spall, Stubbs & Hinshelwood 1954), though the detailed investigation in

* Recently, Crawford & Steacie (1953) have studied the thermal decomposition of *n*-butane and state that the relative proportions of the products from the uninhibited reaction (involving chains) are different from those of the nitric-oxide-inhibited reaction, and quote the results of Stubbs *et al.* (1952) in support of this. In fact, the results which they say refer to products from the normal and fully inhibited reactions respectively are derived from the first column of table 8 (Stubbs *et al.*), where *both* sets of figures refer to the fully inhibited decomposition though at 1400 and 8 mm butane respectively. The marked differences over the range of pressure are an example of the phenomenon referred to in the present paper, namely the shift from ethane to ethylene plus hydrogen with falling pressure. Previous work in this laboratory (Ingold, Stubbs & Hinshelwood 1951) indicated that the products from the uninhibited and fully inhibited reactions were very similar. Recently, a few mass-spectrometric analyses have been made of the products from the uninhibited decomposition of *n*-pentane. The relative proportions of the major products—methane, hydrogen, ethylene and butene are almost the same as for the nitric-oxide-inhibited reaction.

this rather more complex system was rendered difficult by the coincidence of the main peak in the mass spectrum of ethane with that of nitric oxide. The present investigation has two objects: first to find whether the replacement of ethane by its decomposition products still occurs at the lower pressures when propylene is used instead of nitric oxide as the inhibitor, and secondly, to find whether in a system where pentane is decomposing added ethane suffers an induced decomposition. If it does not, this is evidence in favour of a difference between the types of activated pentane molecule tending to predominate in the reaction at higher and at lower pressures respectively.

EXPERIMENTAL METHODS

All experimental methods were as in the previous investigations.

USE OF PROPYLENE AS INHIBITOR

This has already been shown to give the same limiting reaction rate as nitric oxide, though the amount of propylene needed to produce a given degree of inhibition is about ten times that of nitric oxide. In all experiments the concentration of propylene inhibitor equalled the initial concentration of pentane. The value of the ratio $-\Delta[\text{pentane}]/\Delta p$ (Δp being the pressure increase measured in the reaction vessel) is nearly independent of temperature and of initial pressure, and rather close to that found in the reaction inhibited by nitric oxide (table 1).

TABLE 1. VALUES OF $-\Delta[\text{PENTANE}]/\Delta p$

mean over range 530 to 580° C		mean over range 20 to 200 mm (550° C)	
propylene	nitric oxide	propylene	nitric oxide
0.86	0.82	0.81	0.80

This circumstance is fortunate for the use of pressure measurements in the kinetic investigations, but is to some extent fortuitous, since a decomposition of the propylene inhibitor, both spontaneous and induced by the radicals which it removes, is balanced by reduction of pressure in some other side reactions (such as slight polymerization of the inhibitor). The methane formation is greater in the presence of the propylene than with nitric oxide, but the important fact here is that $\Delta[\text{methane}]/\Delta p$ still shows no systematic trend with temperature or pressure, as is shown in table 2.

TABLE 2. VALUES OF $\Delta[\text{METHANE}]/\Delta p$ FOR PROPYLENE-INHIBITED REACTION

temperature (°C) (100mm)	530	540	550	560	570	580
$\Delta[\text{methane}]/\Delta p$	0.52	0.48	0.49	0.54	0.50	0.53
pressure (at 550°)	20	50	100	200	—	—
$\Delta[\text{methane}]/\Delta p$	0.45	0.52	0.49	0.53	—	—

The previously observed increase, at the lower pressures, of ethylene and hydrogen relative to ethane can be inferred from the values in table 3 to occur also

with propylene as inhibitor. So much ethylene is produced from other sources, including the decomposition of propylene itself, that the trend is best inferred from the amounts of hydrogen and ethane, this latter now being easily determined (which could not be conveniently done with nitric oxide as the inhibitor).

The results are expressed as ratios of products formed to pressure change (which measure the overall course of the decomposition of pentane) since otherwise they are obscured by small variable intercepts on the axis caused by slight losses of pentane in sampling and other causes.

TABLE 3. TREND OF ETHANE AND HYDROGEN PROPORTIONS WITH FALLING PRESSURE

<i>Propylene inhibited reaction</i>				
	initial pressure of pentane	$\frac{\Delta[\text{ethane}]}{\Delta p}$	$\frac{\Delta[\text{hydrogen}]}{\Delta p}$	$\frac{\Delta[\text{methane}]}{\Delta p}$
at 550° C	200	0.42	0.096	0.53
	100	0.31	0.11	0.49
	50	0.27	0.11	0.50
	20	0.24	0.14	0.45

Uninhibited reaction

(The figures in brackets are for the nitric-oxide-inhibited reaction)

	initial pressure of pentane	relative percentages in products	
		ethane	hydrogen
at 550° C	100	14.8	8.3 (7.6)
	50	13.2	10.0 (8.6)
	20	10.8	12.4 (10.2)
	10	9.5	13.2 (11.3)
	5	9.0	14.0 (12.2)

EXPERIMENTS WITH ETHANE ADDITIONS

In these experiments, 20 mm of ethane were added initially to 20 mm *n*-pentane + 20 mm propylene at 550° C. Samples of reaction products were analyzed in the usual way by the mass spectrometer.

In figure 1 $-\Delta[\text{pentane}]$ is plotted against Δp for the two experiments with and without added ethane. The two lines have their origins arbitrarily chosen and displaced by one unit so that the slopes may be conveniently compared. The slopes are nearly equal, so that $-\Delta[\text{pentane}]/\Delta p$ is the same whether or not ethane is added. In other words, the addition of the ethane does not affect the rate of disappearance of pentane.

Figure 2 shows that $\Delta[\text{CH}_4]/\Delta p$ is also little changed by the presence of ethane. This confirms the conclusion to be drawn from figure 1, since previous work has shown that $\Delta[\text{CH}_4]/\Delta p$ is a reliable measure of the reaction rate of the pentane.

Ethane added initially has also no effect on $\Delta[\text{H}_2]/\Delta p$ or $\Delta[\text{C}_2\text{H}_4]/\Delta p$ as shown in figures 3 and 4 respectively, or on the actual rate of fresh ethane formation. The values of $\Delta[\text{C}_2\text{H}_6]$ found with initially added ethane show a slight scatter in

figure 5, but this is not surprising, since in the analysis there is an increment of only 1 mm of ethane over the 20 mm originally present. For ease of comparison, in all cases, as in figure 1, there has been arbitrary relative displacement of the zero for all the plots referring to experiments with added ethane.

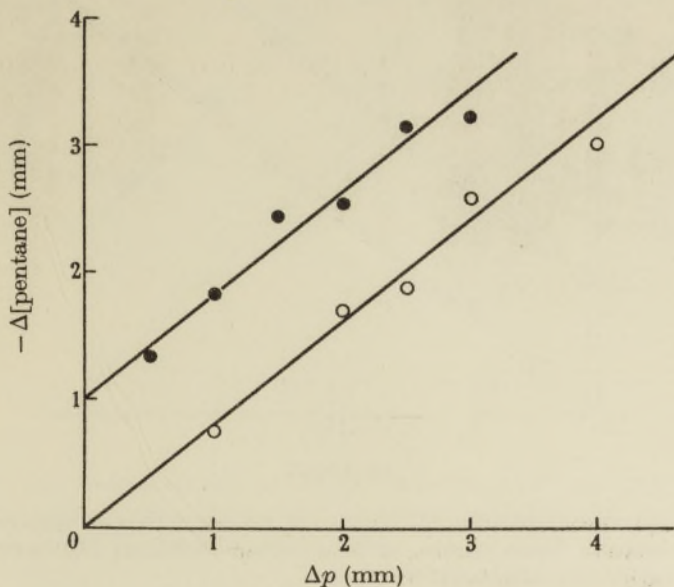


FIGURE 1. Thermal decomposition of 20 mm *n*-pentane + 20 mm propylene at 550° C; pentane reacted. Open circles, without ethane addition; full circles, with 20 mm ethane (zero arbitrarily displaced by 1.0 mm).

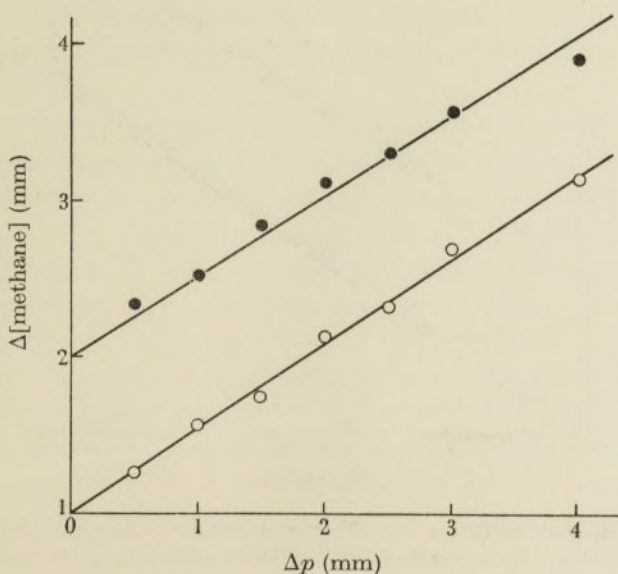


FIGURE 2. Thermal decomposition of 20 mm *n*-pentane + 20 mm propylene at 550° C; methane formation. Open circles, without ethane addition; full circles, with 20 mm ethane (zero arbitrarily displaced by 1.0 mm).

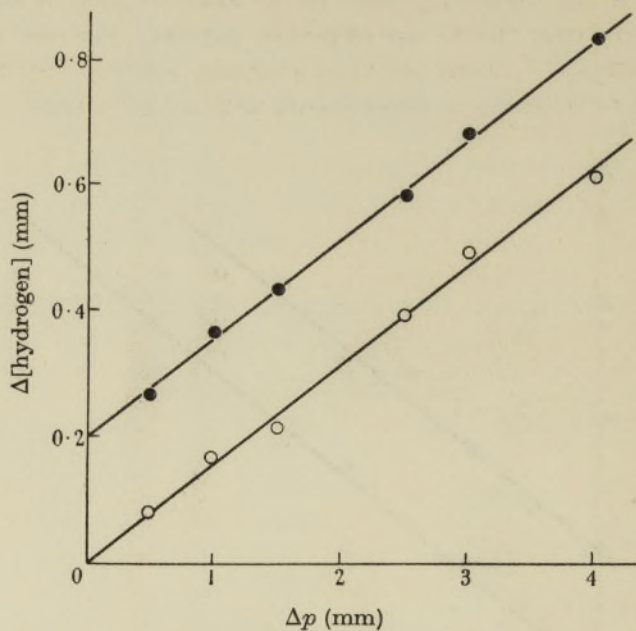


FIGURE 3. Thermal decomposition of 20 mm *n*-pentane + 20 mm propylene at 550°C; hydrogen formation. Open circles, without ethane addition; full circles, with 20 mm ethane (zero arbitrarily displaced by 0.2 mm).

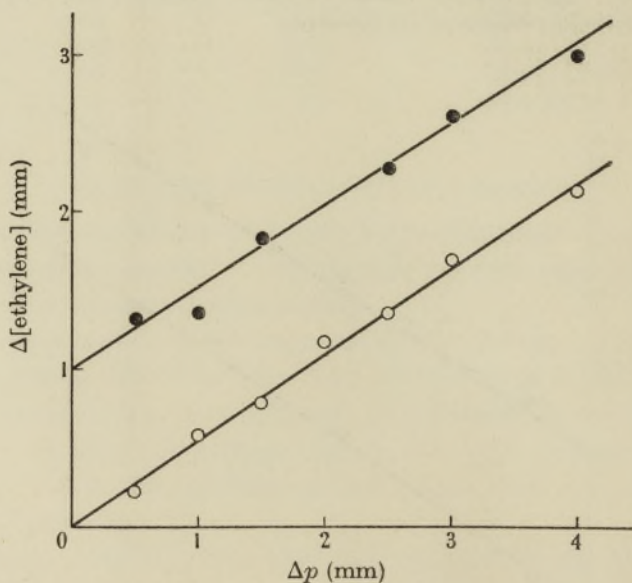


FIGURE 4. Thermal decomposition of 20 mm *n*-pentane + 20 mm propylene at 550°C; ethylene formation. Open circles, with ethane addition; full circles, with 20 mm ethane (zero arbitrarily displaced by 1.0 mm).

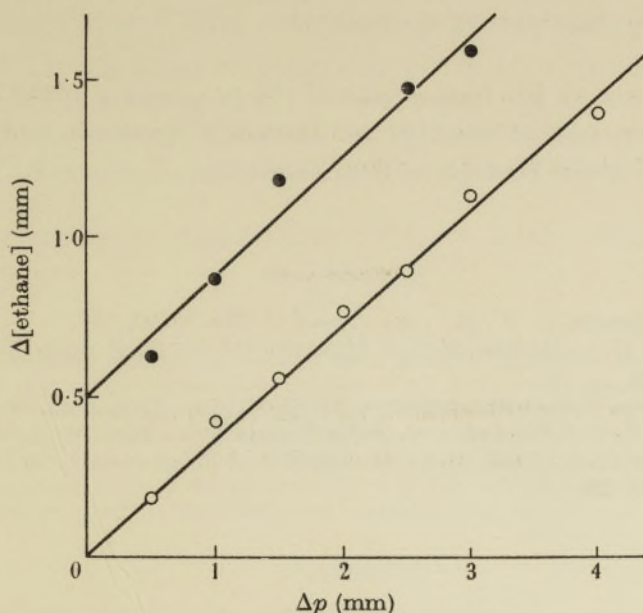


FIGURE 5. Thermal decomposition of 20 mm *n*-pentane + 20 mm propylene at 550°C; ethane formation. Open circles, without ethane addition; full circles, with 20 mm ethane (zero arbitrarily displaced by 0.5 mm).

DISCUSSION

The value of $-\Delta[\text{pentane}]/\Delta p$ for the propylene-inhibited decomposition of *n*-pentane being almost independent of temperature, and close to that found when nitric oxide is the inhibitor, the conclusion is strengthened that the rather remarkable kinetic characteristics of the inhibited reaction indicated by pressure measurements are, in fact, real.

In particular, for the propylene-inhibited decomposition of *n*-pentane, the amount of ethane formed from a given amount of pentane becomes less as the pressure falls and there is a correspondingly increased proportion of hydrogen and ethylene. Ethane added at low pressures having now been shown not to suffer induced decomposition, it seems possible that in the lower pressure range some different type of behaviour of activated molecules leads to the appearance of the decomposition products of ethane rather than ethane itself. It has been suggested (Spall, Stubbs & Hinshelwood 1954) that the low-pressure mode of reaction may be associated with a special kind of activation process characterized by a critical energy in the whole system of hydrogen atoms regarded as a unit. Although detailed predictions about the chemical behaviour of such a system are difficult, it might yield molecular hydrogen rather readily. Thus the replacement of ethane by ethylene and hydrogen may possibly be correlated with the relative dominance of what has been called hydrogen activation over the alternative activation of the carbon framework. The fact that there are indications of this apparent secondary decomposition of ethane in the uninhibited reaction (table 3) suggests, however,

that the seat of the effect lies in the ethane itself, or in the ethyl radical from which it is formed in the chain part of the reaction.

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