THERMAL DECOMPOSITION OF ISO-BUTANE. I
RATE-PRESSURE RELATIONS AND THE PRODUCTS OF THE REACTION

L. SERES, F. MÁRTA, Á. KISS
Institute of General and Physical Chemistry, the Attila József University, Szeged

(Received May 22, 1969)

The pyrolysis of iso-butane has been investigated at temperatures between 480 and 560 °C and at initial pressures of 30—300 torr. Particular attention was paid to the nature of the secondary reactions. On the basis of our analytical results it has been concluded that a) at the later stages of the reaction the generation of iso-propyl radicals must occur in some other step beside the primary one, *b)* the only possible source of ethane is the formation from ethylene.

Introduction

A considerable amount of work has been done recently on the pyrolysis of iso-butane, but certain features of the reaction are still not quite clear and there is some contradiction among the experimental data given by various authors. The main features of the results reported so far concerning this reaction may be summarized as follows.

The reaction was found to be homogeneous and the main directions of the overall decomposition were described by the equations:

$$i\text{-}C_4H_{10} \rightarrow i\text{-}C_4H_8 + H_2 \qquad \text{(a)}$$

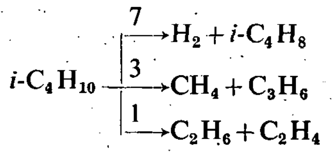
$$i\text{-}C_4H_{10} \rightarrow C_3H_6 + CH_4 \qquad \text{(b)}$$

Step (a) is considered to be more important in the early stages of the reaction, however, an increase in either the temperature, the pressure or the conversion favours step (b) [1].

It has been established that the decomposition proceeds only through radical chains; hydrogen atoms and methyl radicals are postulated to be the chain carriers [2].

The kinetics of the reaction was found to be of first order [3], however, the rate constants decreased with increasing conversion [4], which was attributed to the inhibiting effect of the olefins formed in the reaction.

According to STEPUKHOVICH *et al.* [5], there are three main directions of the reaction



$$i\text{-}C_4H_{10} \begin{cases} \xrightarrow{7} H_2 + i\text{-}C_4H_8 \\ \xrightarrow{3} CH_4 + C_3H_6 \\ \xrightarrow{1} C_2H_6 + C_2H_4 \end{cases}$$

(the figures over the arrows indicate the relative importance of the steps). The distribution of the products of the thermal decomposition of iso-butane changes with changing temperature at a given conversion. The decrease observed in the yield of hydrogen with increasing temperature is somewhat unexpected on the basis of the RICE mechanism; it can be interpreted, however, by the isomerisation of the tertiary-butyl radicals into iso-butyl ones [5].

$$(CH_3)_3C + i\text{-}C_4H_{10} \rightarrow (CH_3)_2CHCH_2 + i\text{-}C_4H_{10}$$

A detailed analysis of the products at higher temperatures and at later stages of the decomposition shows a sharp increase and decrease in the yield of products with lower and higher molecular weight, respectively [6].

FUSY, MARTIN, DZIERZYNSKY and NICLAUSE [7] investigated the effect of change in the S/V ratio and the effect of modification of the surface with KCl or PbO. The increase in the S/V ratio and the coating of the Pyrex surface of the reaction vessel were both found to inhibit the reaction. The inhibiting effect was considered to be the consequence of a heterogeneous termination step of the chain carrier hydrogen atoms.

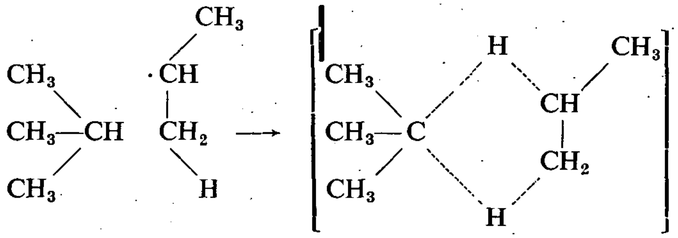
Studying the reaction, KONAR, PURNELL, and QUINN found that the changes in the distribution of the major products — also observed by STEPUKOVICH at the later stages of the reaction — occur also at the very early stages. As an interpretetion of this phenomenon, they concluded that steps

$$H + (CH_3)_2C{=}CH_2 \rightarrow (CH_3)_3C$$

$$(CH_3)_3C + i\text{-}C_4H_{10} \rightarrow (CH_3)_2CHCH_2 + i\text{-}C_4H_{10}$$

also play an important role in the reaction.

Recent investigations by KONAR, PURNELL and QUINN [8], and by KONAR, MARSHALL and PURNELL [9] gave an excellent interpretation for the reaction at low conversion. The concentrations of the products formed only in non-chain steps were measured, and the rate determined on this basis proved to be identical with that of initiation. They concluded that the iso-propyl radical produced in the initial step forms an activated complex with an iso-butane molecule.



The decomposition of this complex leads to the following species

a) $n\text{-}C_3H_7 + i\text{-}C_4H_{10}$

b) $C_3H_8 + (CH_3)_3C$

c) $i\text{-}C_3H_7 + i\text{-}C_4H_{10}$.

The rate constants of the above steps were also determined.

The mechanism of the decomposition at the early stages of the reaction can be well interpreted on the basis of the results of PURNELL *et al.* However, in order to clear up the mechanism at the later stages it seemed worth while to carry out experiments to obtain additional data concerning the nature of the secondary reactions, the route of the formation of some minor products, the effect of surface and different additives on the distribution of products.

Experimental

The experiments were carried out in a conventional static system. Two supremax reaction vessels were used, both of 250 ml capacity; an unfilled one and one packed with an S/V ratio of 1,3 cm^{-1} and 12 cm^{-1}, respectively. The reaction vessel was inserted in a metal block, the temperature of which was electrically controlled to within ±0,2°C. The reproducibility of the absolute value of the temperature was within ±1°C. Routine runs were carried out in a reaction vessel, conditioned by heating 200 torr of iso-butane at 600°C for 24 hours. After this pre-treatment there was no more decrease to be observed in the initial rate. Prior to conditioning, the vessels were washed with concentrated nitric acid followed by rinsing with distilled water. A Pyrex pressure gauge was used to follow pressure changes.

The iso-butane used was 99,5 per cent pure. It was further purified by bulb-to bulb distillations until traces of other components were no longer detectable gas-chomatographically.

The analyses were carried out on a Carlo Erba Fractovap Model C gas-chromatograph supplied with thermistor sensing elements. Two columns were used; one for the analysis of ethane, ethylene, propane, propylene, iso-butane, iso-butene, and one for the separation of hydrogen and methane. Helium (2,6 l/hr) was used as carrier gas for the analysis of hydrocarbons on a 2,5 m long column filled with activated alumina (60—80 mesh), and argon (1,8 l/hr) for the analysis of hydrogen and methane on a 1,60 m column filled with molecular sieve 5A (40—80 mesh). Both columns were of 5 mm internal diameter.

In order to avoid the disturbing effect of the dead volume of the short tube connecting the reaction vessel to the sampling valve, a preliminary expansion of the reaction products into the evacuated sampling valve was performed 20 seconds before taking samples for analysis. Thus, the composition of the gas in the connecting tubing was almost the same as in the reaction vessel. Two samples of the same volume were taken in each case and were analyzed.

Results and Discussion

The pyrolysis of iso-butane was studied in the temperature range between 480 and 560°C and at pressures between 30 and 300 torr. In agreement with the data found in the literature, the increase in pressure proved to be suitable for following the decrease in the pressure of iso-butane at low conversions. However, at higher conversions this was no longer applicable. Therefore the pressure of iso-butane had to be measured by a gas-chromatograph.

The values obtained from pressure-change measurements were used only for determining initial rates, which were utilized only for calculating the rate constants and the order of the reaction.

Owing to the self-inhibiting effect of the products, the first order rate constants diminish with time. For the calculation of the rate constants the introduction of other formulae has not proved to be successful either.

The value of the overall order with respect to the initial pressure of iso-butane varies between 0,8—1,5 as the temperature increase.

It seems obvious that the determination of the initial rates on the basis of pressure measurements at temperatures of about 550°C and above is somewhat in error owing to the inhibiting effect of olefins formed during the period of admission of the iso-butane into the reaction vessel. Accordingly, at $\Delta P=0$, the gas in the reaction vessel contains different quantities of inhibiting products and the rates of the reactions measured are those of differently influenced reactions even if the time period of admission is strictly the same. This effect is only partly compensated by the diminishing efficiency of the inhibitors with increasing temperature. Hence, the data obtained at lower temperatures are more reliable. These observations may even be genaralized for all reactions in which inhibiting products are formed. In these cases the initial rate determined on the basis of pressure measurements is always in error.

In order to eliminate the error caused by the above phenomenon the concentrations of hydrogen and methane were measured at different times in the conversion range of 0—3 per cent. From the data so obtained, the initial rates of the formation of these products were determined and the sum of W_{O,H_2} and W_{O,CH_4} were taken as the initial rate of the disappearance of iso-butane.. The rate determined this way is much less influenced by the mentioned effect.

The dependence of the rate on temperature has been determined in the range 520°C—560°C, and, on the basis of the results, the overall activation energy was found to be 65,2 ± 2,6 kcal/mole at an initial pressure of 200 torr of iso-butane.

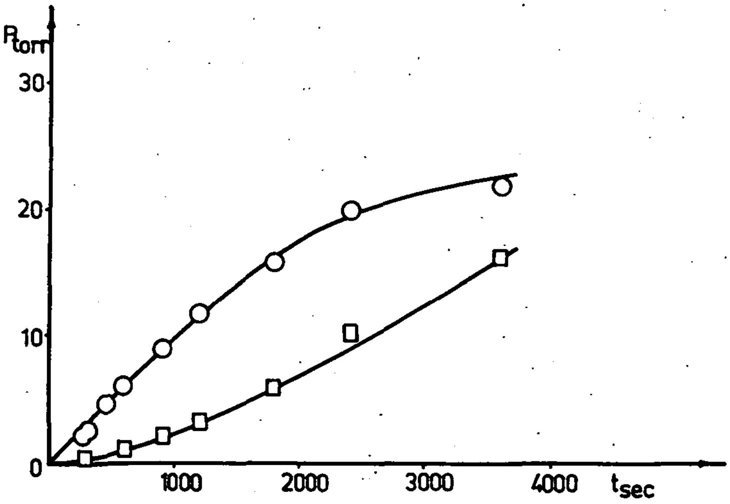


Fig. 1. Partial pressure of ethane (□) and ethylene (○) against time

The products of the reaction found by gas-chromatographic analysis carried out on samples taken at the later stages of the reaction are: hydrogen, methane, ethane, ethylene, propane, propylene, and iso-butene, in agreement with the data to be found in the literature. The partial pressures of all products were measured. In Fig. 1 and Fig. 2 the partial pressures of some products are plotted against time ($T = 560°C$, $P_0 = 200$ torr).

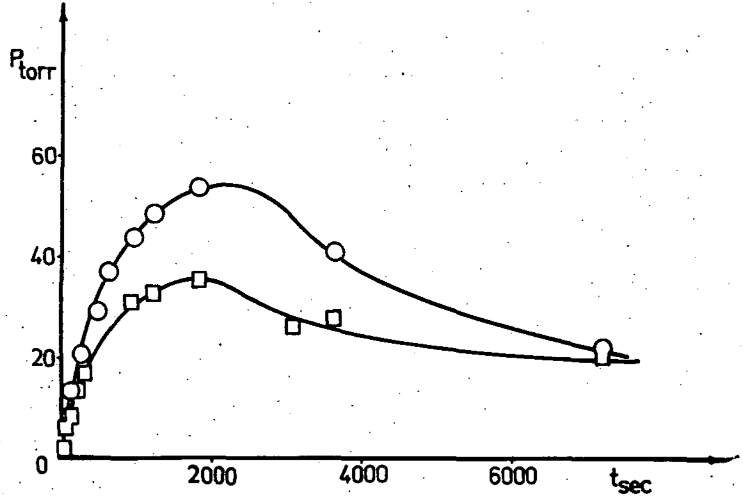


Fig. 2. Partial pressure of propylene (□) and iso-butene (○) against time

As can be seen from Fig. 1, an induction period is to be observed in the formation of ethane but not in the case of ethylene. The pressures of propylene and isobutane change according to maximum curves (Fig. 2), in agreement with EGLOFF and THOMAS' measurements.

The mechanism postulated by STEPUKHOVICH *et al.* requires that the yield of ethane and ethylene should be the same and independent of the conversion. In our experiments, however, it was found that the yield of ethane in the early stages of the reaction is far below that of ethylene as can be seen in the subsequent Fig. 3. This is in good agreement with the results of FUSY *et. al* [7] and those of KONAR, PURNELL and QUINN [10]. From Fig. 3 it can also be seen that the yield of ethane sharply increases with increasing conversion. This fact clearly shows that the two products cannot be formed in the same step, and suggests that ethane is produced, in some way, from ethylene. Another source of ethane and ethylene may be the decomposition of propylene, which is known to produce them in considerable amounts.

A sharp increase in the production of propane with increasing conversion (Fig. 4) shows that, except at the very early stages of the reaction, another source of the iso-propyl radicals must be taken into consideration besides the initiation step.

If the production of propane takes place via another path than the initial step, the calculation of the chain-length on the basis of propane concentration at greater conversions is erroneous.

The yield of hydrogen decreases with increasing conversion. The hydrogen/methane ratio shows a sharp decrease as can be seen from the diagram in Fig. 5. This clearly shows that RICE's mechanism is not satisfactory for the interpretation of the reaction. To account for this experimental fact, STEPUKHOVICH [11], KONAR, PURNELL and QUINN [10] postulated the addition of hydrogen atoms to

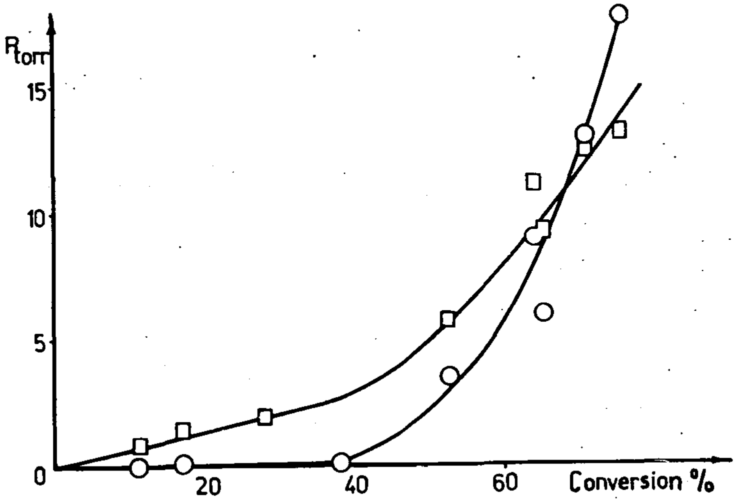


Fig. 3. Plot of the partial pressure of ethylene and ethane against conversion (T = 520 °C, P_0 = 200 torr)

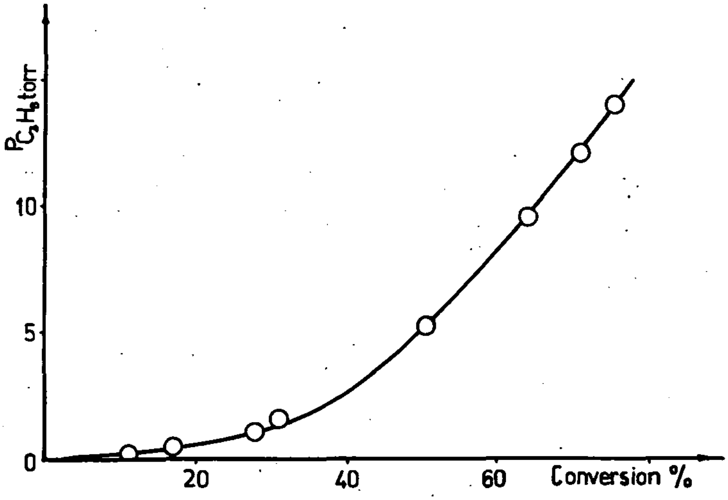


Fig. 4. Plot of the partial pressure of propane against conversion (T = 520 °C, P_0 = 200 torr)

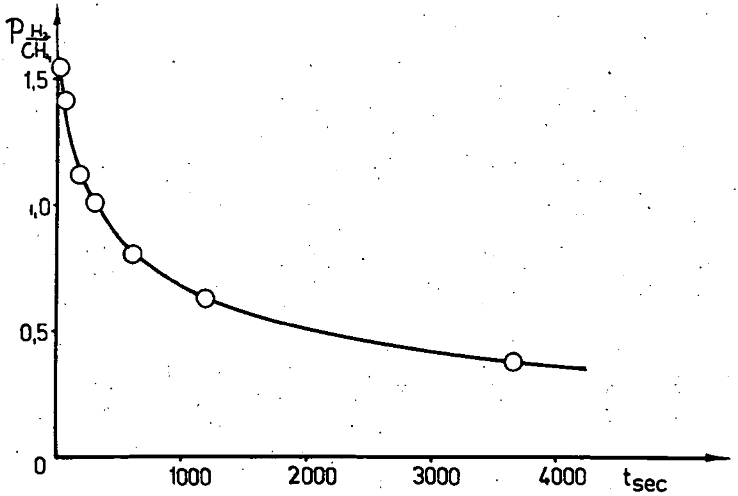


Fig. 5. P_{H_2}/P_{CH_4} ratio against conversion

isobutylene formed in the decomposition and the isomerization of the tertiary butyl radicals into iso-butyl ones.

In order to obtain a more precise picture of the route of the production of ethane and excess propane, it seems worth while and, in fact, necessary to carry out further investigations on the reaction in the presence of added unsaturated products of the reaction.

References

[1] *Hurd, D., L. U. Spence:* J. Amer. Chem. Soc. **51**, 3353 (1929).
[2] *Rice, F. O.:* Amer. Chem. Soc. **53**, 1959 (1931).
]3] *Hepp, H. J., F. E. Frey:* Ind. Eng. Chem. **45**, 410 (1953).
[4] *Dinces, A. J., A. V. Frost:* Zh. Obs. Khim., **3**, 747 (1953).
[5] *Stepukhovich, A. D., R. V. Kosyreva, V. I. Petrosyan:* Zh. Fiz. Khim. **35**, 1331 (1961).
[6] *Illés, V.:* unpublished work.
[7] *Fusy, J., R. Martin, M. Dzierzynski, M. Niclause:* Bull. Soc. chim. France, 3783 (1966).
[8] *Konar, R. S., J. H. Purnell, C. P. Quinn:* J. Chem. Soc. (A), 1543 (1967).
[9] *Konar, R. S., R. M. Marshall, J. H. Purnell:* Trans. Faraday Soc. **64**, 405 (1968).
10] *Konar, R. S., J. H. Purnell, C. P. Quinn:* Trans. Faraday Soc. **64**, 1319 (1968).
[11] *Stepukhovich, A. D.:* Kinetika i Mekhanizm termicheskogo krekinga alkanov. Izd. Saratovskogo Universiteta (1965).

ТЕРМИЧЕСКОЕ РАЗЛОЖЕНИЕ ИЗО-БУТАНА. I

Л. Шереш, Ф. Марта, А. Кишш

Изучалось термическое разложение изобутана в интервале температуры 480—560 °C и давления 30—300 мм. рт. ст. Особенное внимание уделено к изучению характера второчных реакций. На основе наших аналитических данных было заключено; *а)* при глубоком разложении зарождение изо-пропильных радыкалов должно происходить кроме инициирования по какому-то другому пути, *б)* единственным возможным источником этана является его возникновение из этилена.