806. *The Rôle of Surfaces in the Pyrolysis of* n-*Butane.*

By J. H. Purnell and C. P. Quinn.

The effects of a four-fold change of the surface : volume ratio (A/V) of the reaction vessel and of seven types of surface on the rate of pyrolysis of n-butane have been examined by gas-chromatographic product analysis. It has been found that, up to 9% conversion of n-butane, identical and reproducible rates are observed at all values of A/V and for clean, KCl-coated, and etched Pyrex vessels. A magnesium perchlorate coating leads to a large initial acceleration of rate, probably due to decomposition of the perchlorate to oxide; when this is complete the rate is less than with the other types of surface. Conditioning by carbon reduces the reaction rate considerably and the effect is cumulative.

It is concluded that in clean, KCl-coated, and etched vessels the reaction is homogeneous, but that in magnesium oxide or carbon-coated vessels heterogeneous termination processes may be important.

The mechanism of the pyrolysis of the lower paraffins has not yet been unequivocally established. In the first instance there is controversy as to the relative importance of molecular and free-radical processes,[1] although recent experimental evidence [2,3] favours

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[1] Stubbs and Hinshelwood, *Proc. Roy. Soc.*, 1950, *A*, **200**, 458; Jach, Stubbs, and Hinshelwood, *ibid.*, 1954, *A*, **224**, 283; McNesby and Gordon, *J. Amer. Chem. Soc.*, 1957, **79**, 4593; Bryce and Ruzicka, *Canad. J. Chem.*, 1960, **38**, 835; Wojciechowski and Laidler, *ibid.*, p. 1027.

[2] Wall and Moore, *J. Amer. Chem. Soc.*, 1951, **73**, 2840; Rice and Varnerin, *ibid.*, 1954, **76**, 324; Kuppermann and Larson, *J. Chem. Phys.*, 1960, **33**, 1264; Purnell and Quinn, *Nature*, 1961, **189**, 656.

[3] Voevodsky, *Trans. Faraday Soc.*, 1959, **55**, 65.

the view that the reactions are entirely free radical in character. Secondly, there is conflicting evidence concerning the effect on the rate of pyrolysis of the nature of the surface,[3-5] and of the surface : volume ratio [6] of the reaction vessel. It seems probable that some, at least, of the discrepancies discussed arise because the vessels used had been subjected to widely different surface treatments, while others may result from the almost exclusive use of the manometric technique supported only by occasional analysis, usually at high conversion. The conflict between the results of the various experimental studies of the rôle of the surface is sufficient to cast doubt on any mechanism proposed for the pyrolysis of the lower paraffins.

A detailed analytical study of the pyrolysis of n-butane has therefore been undertaken: the present work gives an account of an investigation of the effect of the nature and the extent of the surface of the reaction vessel on the rate of pyrolysis of n-butane at 527°.

EXPERIMENTAL

The reactant was prepared from a commercial sample of n-butane stated by the manufacturers to be of 99·5% purity. The gas was dried by passage over " Anhydrone " and " molecular sieve 5A; " traces of air, found by Engel *et al.*[7] to accelerate the pyrolysis of hydrocarbons, were carefully removed by prolonged and frequent degassing of the reactant at −107°. Gas chromatography of reactant purified in this manner indicated that the only impurity was isobutane, present to the extent of 0·05%.

Pyrex reaction vessels were used; they were heated in an electric furnace to a temperature which was constant in time to 0·2° and in space to 1·8°. The vacuum and gas-handling equipment was of conventional design and construction. During the experiments, the inner surface of each reaction vessels was subjected to one or more of the following treatments. (*a*) A " clean Pyrex " surface was prepared by washing the new vessel with three portions of concentrated nitric acid at 60° and three portions of distilled water. (*b*) A " potassium chloride " coating was deposited on the walls by rinsing with a 10% solution of " AnalaR " potassium chloride. The vessel was drained for 2 min. and dried at the pump on a water bath at about 60°. (*c*) A " magnesium perchlorate " coating was deposited on the surface of the vessel by rinsing it with a 10% solution of magnesium perchlorate [weighed as $Mg(ClO_4)_2,H_2O$]; the vessel was drained and dried as in (*b*). (*d*) An " etched " surface was produced by rinsing the vessel with 5% hydrofluoric acid, and then with 10% hydrofluoric acid, then washing it with distilled water, and drying it in the usual way. After this treatment etching lines were visible on the surface. (*e*) The reaction vessel was " conditioned once " by pyrolysing in the " etched " vessel at 527° one charge of 70 mm. Hg of n-butane for 40 hr. After the conditioning, the vessel was evacuated very thoroughly before use. (*f*) The reaction vessel was " conditioned twice " by the technique described in (*e*). (*g*) The reaction vessel was " conditioned three times " by the technique described in (*e*).

Before the start of each run the reaction vessel was evacuated to a pressure not greater than 10^{-5} mm. Hg. For most runs the initial rates of product formation were measured by analysing the products of the reaction halted after a residence time of exactly one minute. Under the experimental conditions used, this residence time corresponds to the consumption of between 1% and 1·5% of the reactant. Each run was halted by expanding the contents of the reaction vessel into an evacuated bulb from which samples were withdrawn by means of a rotary sampling valve, and injected into the gas-chromatographic analysis unit. The separation of the measured products of the reaction was achieved by the use of a chromatographic column (296 cm. long, 0·4 cm. internal diameter) packed with 120—140 mesh (A.S.T.M.) Sil-O-Cel firebrick impregnated with 17% by weight of squalane. Hydrogen was employed as carrier gas, and the composition of the effluent from the column was monitored by a hydrogen-flame ionisation detector. The column was maintained at 32° in a forced-circulation air thermostat. Each sample in the expansion bulb was analysed three times, the mean of the three analyses being reproducible within 2%.

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[4] Stepukhovich, *Zhur. fiz. Khim.*, 1958, **32**, 2571.

[5] Steacie and Puddington, *Canad. J. Res.*, 1938, **16**, *B*, 176.

[6] Pease and Durgan, *J. Amer. Chem. Soc.*, 1930, **52**, 1262; Ingold, Stubbs, and Hinshelwood, *Proc. Roy. Soc.*, 1950, *A*, **203**, 486; Laidler and Wojciechowski, *ibid.*, 1961, *A*, **260**, 91.

[7] Engel, Combe, Letort, and Niclause, *Rev. Inst. franç. Pétrole*, 1957, **12**, 627.

RESULTS

Preliminary Experiments.—A series of preliminary experiments indicated that, when not more than 7% of the reactant was allowed to decompose in any one run, the initial rates of reaction were reproducible to ±3% in all reaction vessels except those treated with magnesium perchlorate.

Methane, ethylene, ethane, and propene constituted not less than 97% of the hydrocarbon products during the initial stages of the reaction; these were therefore termed the major products. Hydrogen was produced in yields which were, in general, smaller than those of ethane, the least abundant of the major products. The distribution of the major products remained constant throughout the initial stages of any one reaction.

Effect of the Extent of the Surface.—Three reaction vessels of widely different shapes were constructed from Pyrex glass; the vessels were so designed as to have approximately the same volume (50—60 ml.) but different surface : volume ratios, and were treated before use as in (*a*).

The rates of formation of the major products in all three vessels at a single temperature (527° c) were determined for various initial pressures of n-butane in the range 10—30 mm. Hg. Because the vessels were of relatively small volume, it was not possible to determine accurately the initial rates of product formation; instead, average rates of product formation were determined for residence times of 600 sec. During several of these runs, as much as 9% of the reactant was allowed to decompose; nevertheless, reaction rates remained reproducible throughout the series of experiments.

The results of the experiments are shown in Fig. 1; the rates of formation of propene lie close to those for methane, and are not shown. Fig. 1 shows that, within experimental error, a four-fold change in the surface : volume ratio of the clean Pyrex vessel had no discernable effect on the average rates of product formation.

Effect of the Nature of the Surface.—In a study of this effect, rates of reaction under fixed conditions were compared in a single cylindrical vessel (270 ml.; area : volume, $A/V = 0{\cdot}9$ cm.$^{-1}$) subjected successively to the treatments (*a*)—(*g*).

The initial rates of product formation at 527° c were determined analytically for residence times of 60 sec. and for initial pressures of n-butane in the range 10—20 mm. Hg.

In the result the proportions of the major products were unaffected by the nature of the treatment of the vessel but the overall rates were so determined. Fig. 2 shows a plot of the initial rate of methane formation, which is synonymous with reaction rate, against initial n-butane pressure for all seven " surfaces." It indicates that, within the limits of accuracy, for fixed experimental conditions, the reaction rate is identical for reactions carried out in " clean Pyrex," " potassium chloride " coated, and " etched " vessels.

Conditioning of the reaction vessel as described in (*e*), (*f*), and (*g*) above resulted in the deposition of a thin layer of carbon on the walls, giving the vessel a " smoked " appearance. Other things being equal, the pyrolysis of n-butane was slower in a conditioned than in a " clean Pyrex " vessel; further, the effect of successive conditionings was cumulative. In a vessel conditioned three times, rates of reaction were 40—45% lower than those measured under comparable conditions for a " clean Pyrex " vessel.

Action of the Magnesium Perchlorate Coating.—The behaviour of the magnesium perchlorate coating was unusual. During the heating of the reaction furnace the freshly deposited coating decomposed, yielding a gas (chlorine and oxygen) which produced a pronounced " tailing " of the mercury in the manometers. Sidgwick[8] has recorded that magnesium perchlorate decomposes above 250°, forming a mixture of the oxide and chloride.

The first reaction carried out in a vessel freshly coated with perchlorate was very rapid indeed, its rate being 10—20 times larger than for a " clean Pyrex " surface. Although the reaction was still very rapid when the vessel was evacuated to terminate the first run, all subsequent reactions took place at rates comparable with those measured for a " clean Pyrex " vessel. When a fresh coating of magnesium perchlorate was deposited on the walls of the vessel this pattern of rates was reproduced again, the first one, or occasionally two, runs being fast and all subsequent ones slow. It is the rate of the slow reaction which is plotted for the perchlorate-coated vessel in Fig. 2; these rates are slightly lower than the comparable ones for the " clean Pyrex " surface.

Although it did not prove possible to estimate accurately the rates of the anomalous " fast "

[8] Sidgwick, " Chemical Elements and their Compounds," Oxford, 1950, p. 240.

reactions, product analyses revealed that two components were present in the products which were not produced during the " slow " reactions or after any of the other surface treatments. Each of these substances constituted about 1% of the total amount of product; one was identified as propane, the other, although not yet positively identified, appears to be allene.

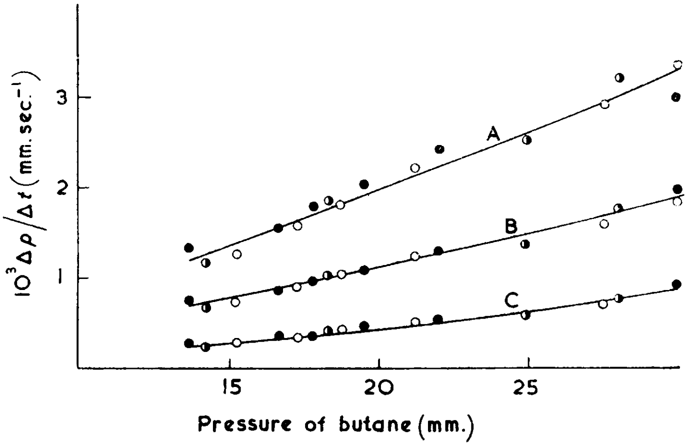

FIG. 1. The effect of initial pressure on the average rates of product formation from the pyrolysis of n-butane at 527° in three different clean Pyrex reaction vessels. ○, A/V = 4·4 cm.$^{-1}$; ◑, A/V = 1·2 cm.$^{-1}$; ●, A/V = 3·7 cm.$^{-1}$. $\Delta p/\Delta t$ were measured for the first 600 sec. A, CH_4; B, C_2H_4; C, C_2H_6.

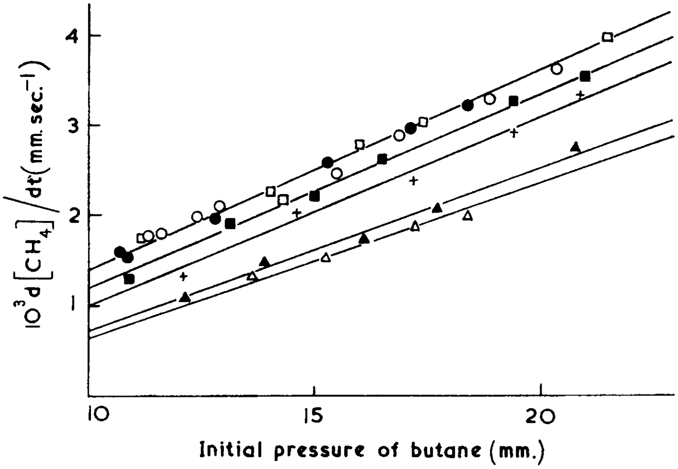

FIG. 2. The effect of initial butane pressure on the initial rate of methane formation at 527° for seven different treatments of the surface of a Pyrex reaction vessel.

○ Potassium chloride.
● Clean Pyrex.
□ Etched.
■ " Slow " magnesium perchlorate.
+ Conditioned once.
▲ Conditioned twice.
△ Conditioned three times.

The chromatographic peak tentatively identified as allene has previously been observed by us in the products of the pyrolysis of n-butane mixed with small quantities of air.

Since the initial activity associated with the perchlorate-treated vessel disappeared during the evacuation rather than during the reaction, it seems likely that the enhanced activity was associated with a homogeneous process. The similarity of the products of the " fast " reaction and of that in the presence of traces of air suggests that during the "fast" reaction found in the present studies, and described by Voevodsky,[3] small quantities of oxygen were released from the "perchlorate" coating and enhanced the rate of pyrolysis by some homogeneous process of the type discussed by Engel *et al.*[7]

DISCUSSION

The reproducibility of reaction rates found here for unconditioned vessels shows a satisfying agreement with the reproducibility found by Voevodsky[3] for clean quartz vessels.

The probable explanation of the irreproducibility reported by Steacie and Puddington[5] is to be found in Fig. 2. These workers carried their reactions to high conversions, and in the earlier runs in a new vessel were almost certainly conditioning the wall by the deposition of carbon. During the conditioning, progressive reductions in reaction rate would be expected, until the wall of the vessel was completely covered with a fine layer of carbon, whereafter further deposition would not affect the rate of the reaction.

The absence of marked effects due to surface : volume ratio with the "clean Pyrex" vessels used in this work, and the finding of identical rates in "clean Pyrex," "KCl-coated," and "etched" vessels, are entirely compatible with a free-radical chain mechanism initiated and terminated homogeneously. The possibility of entirely heterogeneous initiation and termination cannot on this evidence be entirely eliminated, but it must be deemed very unlikely that three surface treatments so markedly different in character would not show any difference in their effect on heterogeneous initiation and termination processes. We therefore conclude that pyrolysis of n-butane in "clean," "KCl-coated" and "etched" Pyrex vessels, is most probably entirely homogeneous.

The fast initial rates obtained with vessels freshly treated with magnesium perchlorate appear to be due to a slow evolution of oxygen, which accelerates the reaction by processes such as those outlined by Engel *et al.*[7] Voevodsky's results,[3] obtained in these conditions, probably have little bearing, therefore, on the mechanism of pyrolysis of paraffins.

The surface remaining when oxygen evolution from the perchlorate is complete is likely to consist, at least in part, of magnesium oxide, which has been shown to be particularly effective for the removal of hydrogen atoms.[9] These are generally believed to be involved in the uninhibited pyrolysis of the lower paraffins, and so the depression of the rate which occurs when a "clean Pyrex" surface is replaced with a "slow" magnesium perchlorate surface may well result from the introduction of a heterogeneous mode of termination of the free-radical chains.

The experimental work described here points also to the occurrence of heterogeneous chain-termination at the surface of carbon-conditioned vessels. This consideration leads us to the view that studies of the pyrolysis are best carried out at low conversions in clean reaction vessels, since only in these conditions may the reaction be said to be completely homogeneous in character. A detailed account of the pyrolysis of n-butane in such conditions is in preparation.

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DEPARTMENT OF PHYSICAL CHEMISTRY,
THE UNIVERSITY, CAMBRIDGE.

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[9] Warren, *Trans. Faraday Soc.*, 1957, **53**, 199.