

38. *The Role of Surface in the Pyrolysis of 2-Chlorobutane.*

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The pyrolysis of 2-chlorobutane to hydrogen chloride and a mixture of isomeric n-butenes has been studied under a variety of conditions of vessel surface and temperature.

In a clean Pyrex vessel packed with Pyrex glass wool at 210° heterogeneous elimination occurs producing a low yield of but-1-ene (~12.0%) and a low ratio of *trans/cis*-but-2-ene (0.68). Isomerisation of but-1-ene in the presence of hydrogen chloride also takes place readily at the same temperature yielding a similar ratio of but-2-enes.

In a clean silica vessel at higher temperatures (~350°) both homogeneous and heterogeneous reactions occur with the yield of but-1-ene increased (~25.0%), but *trans/cis*-but-2-ene ratios (1.12) are still low when compared with equilibrium values. The product distribution and reaction rate are considerably altered when the vessel surface is modified by (a) carbon coating with the products of ethyl chloride pyrolysis, (b) carbon coating with *cis*-but-2-ene at high temperature, and (c) the presence of excess of ammonia after *cis*-but-2-ene treatment. Under conditions where the surface is believed to be inactive, homogeneous elimination produces but-1-ene (43%) and a *trans/cis* ratio (1.89) which is higher than the equilibrium ratio.

A common mechanism for surface elimination and olefin isomerisation in the presence of hydrogen chloride is suggested. Dewar-type complexes between olefins and surface protons are believed to be important intermediates in determining preferential formation of *cis*-but-2-ene in these reactions. The general significance of similar complexes in elimination reactions and in isomerisation of olefins on a variety of acidic and metallic catalysts is briefly discussed.

MANY studies of the pyrolysis of alkyl halides have been made in recent years, particularly by Barton and his co-workers¹ and by Maccoll and his co-workers.² It has been demonstrated that once the reaction vessel has been seasoned by prolonged contact with a halogenated hydrocarbon such as allyl bromide or ethyl chloride, many of these reactions appear to be unimolecular homogeneous processes producing simply olefin and hydrogen chloride.



¹ Barton and Howlett, *J.*, 1949, 155; Barton, Head, and Williams, *J.*, 1951, 2039; Barton and Head, *Trans. Faraday Soc.*, 1950, **46**, 114.

² Maccoll, *J.*, 1955, 965; Agius and Maccoll, *J. Chem. Phys.*, 1950, **18**, 158; Maccoll and Thomas, *ibid.*, 1951, **19**, 977; Green, Harden, Maccoll, and Thomas, *ibid.*, 1953, **21**, 178.

Seasoning in this manner causes the deposition through heterogeneous cracking and polymerisation processes of a thin carbonaceous film. Knispel and Swinbourne³ have studied the films produced from ethyl chloride pyrolysis and have shown that these differ from graphite in having a high electrical resistance. This would be consistent with the presence of a high concentration of "foreign" atoms, groups, and/or molecules at the intercrystal boundaries.

The pyrolysis of 2-chlorobutane was studied by Maccoll and Stone⁴ in a reaction vessel seasoned with the products of the decomposition of allyl bromide. They concluded that in the temperature range 330—390° the decomposition was of the first order and unimolecular with a rate constant given by

$$k = 10^{13.62} \exp(-49,600/RT) \text{ sec.}^{-1}$$

The reaction produced hydrogen chloride and a mixture of isomeric *n*-butenes (but-1-ene, 40 ± 2%; *cis*-but-2-ene, 22.8%; *trans*-but-2-ene, 37.2%). *cis*- and *trans*-But-2-ene were found to be present always in equilibrium proportions (as defined by the thermodynamic values published by the American Petroleum Institute¹²).

Heydtmann and Rinck⁵ used a vessel coated with potassium chloride to suppress heterogeneous reactions. At temperatures between 316 and 393° they found a first-order rate constant given by

$$k = 10^{14.00 \pm 0.25} \exp [(-50,600 \pm 650)/RT] \text{ sec.}^{-1}$$

which is in good agreement with that of Maccoll and Stone.⁴ Although obtaining similar values for the composition of the butenes, these authors conclude that the homogeneous reaction leads to preferential formation of *trans*-but-2-ene. The analyses given are but-1-ene, 43.5 ± 2%; *cis*-but-2-ene, 19.5 ± 4%; *trans*-but-2-ene, 37.5 ± 3%. These figures were unaffected by temperature in this range or by duration of an experiment.

Interpretation of these two sets of results obviously requires very careful assessment of the equilibrium values for the isomeric butenes and unfortunately the published data show some divergences (see Table 5). It is, however, clear that *cis-trans* equilibration is promoted on a carbon surface derived from allyl bromide and the question arises whether such a surface is also active in the elimination itself.

Wojciechowski and Laidler⁶ have pointed out that alkyl halides could pyrolyse by a free-radical mechanism if the surface initiates chains as well as stopping them. The absence of any acceleration of the reaction by increased surface area would not then in itself exclude a free-radical mechanism.

Although reasons exist for believing that free radicals do not participate in many simple alkyl chloride pyrolyses, it is more difficult to be certain that molecular surface processes do not occur. Little attention has been given to the heterogeneous decomposition of alkyl halides on glass surfaces apart from the work of Barton and Onyon⁷ on *t*-butyl chloride and the equilibrium studies of Howlett.⁸

The present work was undertaken in order to understand more fully the role of the surface in alkyl halide pyrolyses. The production of a mixture of butenes from 2-chlorobutane makes this molecule suitable since the relative proportions of the butenes obtained may be expected to be influenced by the surface if this is active for elimination. Although the carbon coating used by Maccoll and Stone promotes *cis-trans* equilibration, this is not true of all carbon coatings. The gas-phase isomerisation *cis*-but-2-ene \rightleftharpoons *trans*-but-2-ene

³ Knispel and Swinbourne, *Austral. J. Chem.*, 1958, **11**, 433.

⁴ Maccoll and Stone, *J.*, 1961, 2756.

⁵ Heydtmann and Rinck, *Z. phys. Chem. (Frankfurt)*, 1961, **30**, 250; 1963, **36**, 75.

⁶ Wojciechowski and Laidler, *Trans. Faraday Soc.*, 1963, **59**, 369.

⁷ Barton and Onyon, *Trans. Faraday Soc.*, 1949, **45**, 725.

⁸ Howlett, *J.*, 1951, 1409.

is relatively slow and has been studied in silica vessels seasoned with *cis*-but-2-ene at high temperatures.⁹

It was therefore of interest to pyrolyse 2-chlorobutane in a silica vessel seasoned in this way, and to make a general study of the influence of different conditions of temperature and surface treatment on the reaction products.

EXPERIMENTAL

Materials.—2-Chlorobutane. Samples from various commercial sources were used. The purification procedure was initially that described by Barton *et al.*¹ for alkyl halides but later samples were simply dried (Na_2CO_3) and fractionally distilled through a column of the type described by Naragon and Lewis.¹⁰ The physical constants of one such sample were b. p. $68.0^\circ/764$ mm.; $n_D^{25} = 1.3930$ (lit.,¹¹ b. p. $68.25^\circ/760$ mm.; $n_D^{25} = 1.3946$). Hydrogen chloride, prepared by the action of concentrated sulphuric acid on concentrated hydrochloric acid, was bubbled through concentrated sulphuric acid and stored in a bulb having a tap lubricated with "Florube" grease. Ammonia from a cylinder (I.C.I.) was stated to be $>99.9\%$ pure. Samples of *cis*- and *trans*-but-2-ene and -but-1-ene were supplied by the Matheson Company and stated to be $>99.0\%$ pure.

Apparatus.—Low-temperature pyrolyses were studied in an apparatus of the type described by Howlett.⁸ The Pyrex reaction vessel of approximately 200 ml. volume was packed with Pyrex glass wool and enclosed in a vapour jacket. Nitrobenzene was used as the reflux liquid and a thermometer in the vapour showed no variation in boiling point other than that due to variations in atmospheric pressure. High-temperature pyrolyses were studied in a conventional static apparatus. Reaction vessels were housed in an electrically wound horizontal furnace controllable to -0.2° . A temperature variation of about 2° over the length of the reaction vessel was noted. Pressure changes were measured using a spoon type Bourdon gauge which together with the inlet tubing was heated to about 50° to prevent condensation. Reactants were admitted by vaporising directly from storage bulbs and the vessel was closed by a greaseless stopcock incorporating a fluorocarbon rubber diaphragm. Several different reaction vessels were used. Vessel 1 was of silica, of volume 178 ml., which had been seasoned by prolonged contact with ethyl chloride at high temperatures ($\sim 480^\circ$). Vessel 2 was of silica, of volume 162 ml., which was seasoned by admitting *ca.* 30 mm. of *cis*-but-2-ene at 480° for 30 min. and then cooling to *ca.* 350° . Vessel 3 was of clean silica, of volume 174 ml. This was later packed with short (2 cm.) lengths of silica tubing having flame-polished ends. Packing increased the surface: volume ratio by a factor of 7.8. For runs after Run 58 the packed vessel 3 was seasoned similarly to vessel 2 with *cis*-but-2-ene. Vessel 4 was of Pyrex, of *ca.* 200 ml. volume, packed with Pyrex wool.

Product Analyses.—Products were analysed by gas-liquid chromatography. They were condensed into a trap through a short tube packed with a mixture of soda lime and magnesium perchlorate which effectively removed hydrogen chloride.

The butenes were separated on a 20 ft. column of 35% acetylacetone on 30/60 mesh firebrick at room temperature. The percentages of the various products were calculated from peak heights after calibration, and six analyses on a standard mixture showed that analyses were accurate to within 2%. Calculation then showed that an average value of the ratio *trans/cis*-but-2-ene was subject to an error of not more than 5%.

Results.—*Vessel 1.* The pyrolysis of 2-chlorobutane was found to proceed in a first-order manner. The overall stoichiometry of the reaction $\text{C}_4\text{H}_9\text{Cl} \rightarrow \text{Butenes} + \text{HCl}$ was confirmed (a) by measurements of total pressure which rose to twice the initial value and (b) by occasional analyses by gas chromatography (using a silicone-polyethylene glycol column at 79°) which showed the equivalence of butene produced and 2-chlorobutane decomposed.

First-order rate constants were derived from the pressure measurements which show good agreement with the results of other workers. Thus at 367° the following values of the rate constants were obtained, $4.73 \times 10^{-4} \text{ sec.}^{-1}$ (this work), $4.27 \times 10^{-4} \text{ sec.}^{-1}$ (Maccoll and Stone¹), $1.70 \times 10^{-4} \text{ sec.}^{-1}$ (Heydtmann and Rinck⁵). Product analyses were carried out after a number

⁹ Rabinowitch and Michel, *J. Amer. Chem. Soc.*, 1959, **81**, 5065.

¹⁰ Naragon and Lewis, *Ind. Eng. Chem.*, 1946, **18**, 448.

¹¹ Timmermanns, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, Netherlands, 1950.

of runs at 348° for varying lengths of time. Various mixtures of 2-chlorobutane with hydrogen chloride or 2-chloropropane (which produces hydrogen chloride by pyrolysis) were also left in the reaction vessel for similar periods. The results are shown in Table 1.

Vessel 2. Experiments were carried out to test the activity of the surface for isomerisation of but-1-ene and *cis*-but-2-ene both in the absence and presence of hydrogen chloride.

TABLE 1.*

Vessel 1 at 348°.

| Run | Time of sampling (hr.) | Reactant | Pressure (mm.) | B-1 (%) | <i>trans/cis</i> |
|----------------------------------|------------------------|----------|----------------|---------|------------------|
| 74 | 0.75 | 2Cl-B | 90.4 | 41.5 | 1.79 |
| 75 | 17.5 | 2Cl-B | 85.5 | 44.3 | 1.84 |
| 74 | 19.0 | { 2Cl-B | 53.2 | 39.6 | 1.92 |
| | | { HCl | 56.0 | | |
| 77 | 46.0 | { 2Cl-B | 67.4 | 38.9 | 1.84 |
| | | { HCl | 111.6 | | |
| 78 | 19.25 | { 2Cl-B | 68.7 | 42.9 | 2.00 |
| | | { HCl † | 76.8 | | |
| Equilibrium values ¹² | | | | 14.9 | 1.64 |

* In all Tables, 2-Cl-B is 2-chlorobutane, B-1 is but-1-ene, B-2 is but-2-ene, *c* and *t* being *cis* and *trans*. † Derived from 76.8 mm. 2-chloropropane.

TABLE 2.

| Run | Reactant | Pressure (mm.) | Temp. | Time (min.) | B-1 | <i>t</i> B-2 (%) | <i>c</i> B-2 (%) | <i>trans/cis</i> |
|-----|----------------|----------------|--------|-------------|------|------------------|------------------|------------------|
| 4 | <i>c</i> B-2 | 28.0 | 480.0° | 30 | 0.7 | 22.5 | 76.8 | — |
| 7 | <i>c</i> B-2 | 30.0 | 333.5 | 30 | 0.0 | 1.0 | 99.0 | — |
| 8 | <i>c</i> B-2 | 30.0 | 318.0 | 1380 | 0.0 | 3.0 | 97.0 | — |
| 9 | { <i>c</i> B-2 | 29.0 | 332.0 | 35 | 0.3 | 2.7 | 97.0 | — |
| | { HCl | 31.0 | | | | | | |
| 11 | 2Cl-B | 35.0 | 332.5 | 35 | 28.6 | 42.1 | 29.3 | 1.44 |
| 13 | 2Cl-B | 51.0 | 316.0 | 71 | 30.8 | 41.8 | 27.4 | 1.53 |
| 14 | { B-1 | 29.7 | 316.0 | 35 | 30.9 | 42.0 | 27.1 | 1.55 |
| | { HCl | 28.8 | | | | | | |
| 15 | B-1 | 30.0 | 338.0 | 120 | 99.5 | — | 0.5 | — |

2-Chlorobutane was also pyrolysed in this vessel and the results of all these experiments are listed in chronological order in Table 2. It will be noted that isomerisation both of but-1-ene and *cis*-but-2-ene is negligible in the absence of hydrogen chloride. In the presence of hydrogen chloride both isomerisations are affected although the *cis-trans* conversion is still small compared with the rate of pyrolysis of 2-chlorobutane.

Ammonia additions. The observed catalysis of isomerisation of but-1-ene by hydrogen chloride made it appear likely that the surface would also be active in the elimination reaction. Ammonia was therefore added to 2-chlorobutane both to remove hydrogen chloride and also to poison the surface and reduce, if possible, surface elimination. The effect of increasing ammonia/2-chlorobutane ratio upon the yield of but-1-ene and upon the ratio of *trans/cis*-but-2-ene is shown in Fig. 1.

In addition to the effect of added ammonia during a run, a permanent effect of ammonia on the vessel surface was noticed. Runs using 2-chlorobutane alone (initial pressure 30.60 mm.) showed a significantly higher yield of but-1-ene after the ammonia treatment than those before it (Runs 11, 13, Table 2). These runs are in Table 3.

TABLE 3.

Vessel 2 after ammonia treatment.

| Run | Temp. | Time (min.) | B-1 (%) | <i>trans/cis</i> | Run | Temp. | Time (min.) | B-1 (%) | <i>trans/cis</i> |
|-----|--------|-------------|---------|------------------|-----|--------|-------------|---------|------------------|
| 20 | 332.0° | 30.0 | 34.6 | 1.60 | 29 | 332.0° | 45.0 | 36.8 | 1.42 |
| 25 | „ | 45.0 | 32.8 | 1.34 | 24 | „ | 1110.0 | 36.0 | 1.71 |

A permanent effect on the activity of the surface towards but-1-ene isomerisation was also observed. An equimolar mixture of but-1-ene and hydrogen chloride was left at 338° for 4½ hr. after the ammonia treatment (Run 28) and showed less than 5% isomerisation (cf. Run 14, Table 2).

Rate measurements. A few measurements were made on the rate of the reaction by following the pressure rise. These showed that runs after the ammonia treatment were slower by a factor of approximately two.

Vessel 3. The results of runs carried out in Vessel 3 are summarised in Table 4. In the initial runs considerable deviation from first-order behaviour was observed after about 25% reaction. However, subsequent runs indicated that first-order behaviour was maintained over longer periods up to 50% reaction. This variation with number of runs is consistent with a gradual seasoning of the vessel surface. The kinetics were not investigated in detail and rate constants were derived from the initial linear portion of first order logarithmic plots or in the case of Runs 48—55 approximate values were derived from initial rates.

Vessel 4. Low-temperature runs, *i.e.*, at 210°, were carried out in a Pyrex reaction vessel packed with Pyrex glass wool. A series of runs at various times show that initially but-1-ene is formed in low yield and the thermodynamically unstable *cis*-but-2-ene predominates. Over a period of 5½ hr. these products tend towards equilibrium values. These results are shown in Table 5.

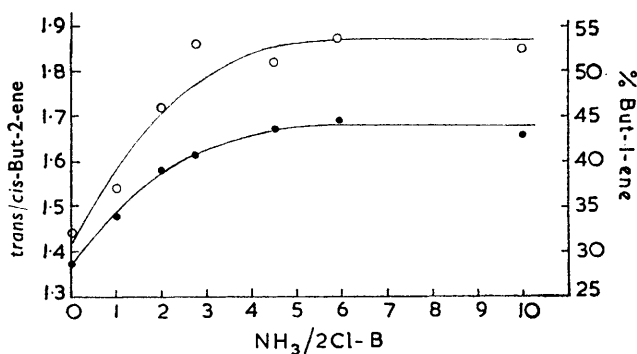


FIG. 1. Effect of ammonia on the pyrolysis of 2-chlorobutane in vessel 2 at *ca.* 350°C.

○ *trans/cis*-But-2-ene. ● But-1-ene (%).

TABLE 4.

| Run | Temp. | $10^4 k_1$ (sec. ⁻¹) | B-1 (%) | <i>trans/cis</i> | Run | Temp. | $10^4 k_1$ (sec. ⁻¹) | B-1 (%) | <i>trans/cis</i> |
|---|--------|-------------------------------------|------------|------------------|---|--------|-------------------------------------|------------|------------------|
| <i>Clean unpacked vessel 3 (s/v = 1.39)</i> | | | | | <i>cis</i> -But-2-ene admitted 4 hr. at 464° | | | | |
| 34 | 347.0° | 29.6 | 25.4 | 1.12 | 62 | 349.0° | 6.0 | 33.1 | 1.25 |
| 36 | 346.5 | 48.8 | 25.1 | 1.14 | <i>cis</i> -But-2-ene admitted 26 hr. at 464° | | | | |
| <i>cis</i> -But-2-ene admitted | | | | | 67 | 350.5 | 4.7 | 35.2 | 1.34 |
| 43 | 351.0 | 1.2 | 31.6 | 1.46 | 70 | 357.0 | 5.4 | 35.4 | 1.37 |
| 46 | 349.0 | 1.3 | 37.3 | 1.63 | <i>cis</i> -But-2-ene admitted 19 hr. at 470° | | | | |
| 47 | 349.0 | 1.6 | 34.6 | 1.52 | 72 | 351.0 | 4.0 | 38.2 | 1.46 |
| <i>Clean packed Vessel 3 (s/v = 10.9)</i> | | | | | 73 | 351.0 | 4.5 | 38.6 | 1.47 |
| 48 | 348.5 | 90 | 28.6 | 1.16 | | | | | |
| 49 | 352.0 | 84 | 27.8 | 1.08 | | | | | |
| 50 | 351.0 | 62 | 24.5 | 1.03 | | | | | |
| 55 | 350.5 | 37 | 23.5 | 1.04 | | | | | |

TABLE 5.

Pyrex vessel at 210°.

| Time (min.) | B-1 (%) | <i>trans/cis</i> | B-1 (%) | <i>trans/cis</i> |
|-------------|---------|------------------|------------------------------|------------------|
| 5 | 12.7 | 0.68 | Equilibrium values at 500° K | |
| 15 | 11.3 | 0.65 | 10.3 | 1.82 (ref. 12) |
| 93 | 14.0 | 0.84 | 14.6 | 1.89 (ref. 13) |
| 330 | 16.2 | 1.30 | 15.2 | 1.61 (ref. 14) |

¹² Selected Values of the Physical and Thermodynamic Properties of Hydrocarbons, Carnegie Press, Pittsburgh, 1953.

¹³ U.S. National Bureau of Standards, Circ. 461, 1947.

¹⁴ Benson and Bose, *J. Amer. Chem. Soc.*, 1963, **85**, 1385.

Isomerisation of *cis*-but-2-ene is slow even in the presence of hydrogen chloride at these temperatures. The isomerisation of but-1-ene in the presence of hydrogen chloride under these conditions was independently checked and it was found that about 10% isomerisation occurred with an equimolar mixture in 45 min. (Run 18). This isomerisation also produced a high *cis* yield and a *trans/cis* ratio of 0.54 (cf. values from elimination reaction in Table 5).

Ammonia additions. In view of the observed isomerisation of but-1-ene in the presence of hydrogen chloride it was of interest to examine the effect of added ammonia on elimination. Little effect was observed on the but-1-ene yield, but small amounts of ammonia were sufficient to lower the *trans/cis* but-2-ene ratio to a steady value (Table 6).

TABLE 6.

Pyrex vessel at 210°. Analyses at 45 min.

| | | | | | |
|------------------------------|------|------|------|------|------|
| NH ₃ /2Cl-B | 0.10 | 0.33 | 0.74 | 1.39 | 0.0 |
| B-1 (%) | 12.2 | 14.0 | 13.2 | 12.9 | 12.3 |
| <i>trans/cis</i> | 0.50 | 0.51 | 0.50 | 0.47 | 0.69 |

The last run shown in Table 6 was carried out to check for any permanent effect of ammonia on the vessel surface at this temperature. The results agree with the initial values in Table 5. The ability of the surface to isomerise but-1-ene in the presence of hydrogen chloride was again checked after the ammonia treatment. It was found that 14% isomerisation occurred after 45 min. at 210° with an initial ratio of HCl/but-1-ene of 1.1 (Run 19). The *trans/cis* ratio from the isomerisation was 0.57 compared with 0.54 in a similar experiment (Run 18) before the ammonia treatment.

DISCUSSION

The Homogeneous Reaction.—From our results we conclude that under many of the conditions of temperature and vessel surface at which the pyrolysis was studied, homogeneous and heterogeneous processes were occurring simultaneously. This is certainly true in a clean silica vessel (Vessel 3) where the rate is increased by at least a factor of three on increasing the surface : volume ratio by a factor of eight.

Measurements of reaction rates as a criterion of the extent of surface elimination however is not altogether reliable and this work has shown conclusively that where possible, product distributions are a far better indication of the role of the surface. Experiments carried out at 210° in the Pyrex reaction vessel (Vessel 4) where the contribution from homogeneous reaction would be negligible have shown a high percentage of the thermodynamically unstable isomer *cis*-but-2-ene. Possible reasons for this and analogies with other surface processes are examined later, but it is clear that the products of the surface reaction at this temperature differ considerably from those reported for pyrolysis at higher temperatures by Maccoll and Stone⁴ and by Heydtmann and Rinck.⁵

Both of these groups attempted to suppress heterogeneous reactions by coating the walls of the reaction vessel, the former using a Pyrex vessel seasoned with allyl bromide and the latter using a silica vessel coated with potassium chloride. Maccoll and Stone⁴ suggested that if planarity was a requirement of the transition state in the homogeneous gas-phase reaction, then *trans*-but-2-ene would be favoured. Under their conditions however, *cis-trans* equilibration was rapid and no evidence could be obtained on this point. Heydtmann and Rinck⁵ however found a slight preference for *trans*-but-2-ene over the *cis*-isomer in their products.

We believe that we have produced surfaces which are inert towards surface elimination in two cases and that a criterion of the purely gas-phase reaction is the appearance of a preference for *trans*-but-2-ene over *cis*-but-2-ene and a high percentage of but-1-ene in the reaction products. The two cases are in Vessel 1 seasoned by ethyl chloride pyrolysis and in Vessel 2 seasoned by *cis*-but-2-ene treatment when the pyrolysis is subsequently carried out in the presence of ammonia. Thus the products in Vessel 1 show a *trans/cis* ratio of 1.8—1.9 which is unaffected by time of sampling or by pressure of hydrogen chloride (Table 1). This agrees well with the values obtained by Heydtmann and Rinck⁵ and indicates that this surface, like potassium chloride-coated silica, is inactive for butene

isomerisation. For comparison, the *trans/cis* ratio obtained by Maccoll and Stone⁴ is 1.69 which agrees with the published thermodynamic data.¹²

It may therefore be suggested that a carbon coating derived from allyl bromide possesses different activity for butene isomerisation from one produced from ethyl chloride. One must therefore consider the possibility that the activity of these surfaces in elimination may also vary.

Seasoning by *cis*-but-2-ene is necessary for the study of the gas-phase isomerisation of *cis*-but-2-ene⁹ and in this work it was shown that at 350° such a surface is inactive towards *cis-trans* isomerisation in the presence of hydrogen chloride (Runs 7 and 8, Table 2). This surface however was found to be more active in promoting but-1-ene isomerisation in the presence of hydrogen chloride (Run 14, Table 2) and this suggested that the surface could also be active in elimination. If a low *trans/cis* ratio and a low % but-1-ene indicates the presence of some heterogeneous elimination (as would be expected from the results in Vessel 4), then the results in Table 2 for Runs 11 and 13 confirm that heterogeneous reaction is occurring since the *trans/cis* ratios and but-1-ene percentages obtained are much lower than those found in Vessel 1 and by other workers.^{4,5}

It is shown in Fig. 1 that in the presence of increasing amounts of ammonia, the percentage of but-1-ene in the products and the *trans/cis*-but-2-ene ratio both rise. Above a molar ratio of ammonia/2-chlorobutane of 5.0 the values obtained are 43.5% but-1-ene, and a *trans/cis*-but-2-ene ratio of 1.87, in good agreement with the values found in Vessel 1 and also those reported by Heydtmann and Rinck.⁵

In view of the close agreement between the results under these widely differing conditions of vessel surface it seems reasonable to postulate that heterogeneous processes have been fully suppressed in these cases and that only the homogeneous gas-phase reaction occurs. The *trans*-but-2-ene preference observed is then support for the idea of a four-centred transition state proposed by Maccoll and Thomas.¹⁵ Further evidence is supplied by the experiments done in a clean silica vessel (Vessel 3). Initially the rate is fast and the kinetics are only of first order in the early stages of the reaction, but subsequent runs cause coating of the vessel surface which decreases the rate and raises the *trans/cis* ratio (Table 4). Packing the vessel increases the rate and lowers the *trans/cis* ratio as would be expected if the heterogeneous contribution is increased. Finally the rate is lowered and the *trans/cis* ratio raised again by coating the packed vessel in a similar manner by *cis*-but-2-ene additions at high temperature.

In order to obtain a truly inert surface for alkyl halide pyrolysis it therefore seems to be better to use a carbon coating derived from ethyl chloride than one from allyl bromide or from *cis*-but-2-ene. More direct evidence is needed on the nature of these carbon coatings but it seems probable that in some cases all the active surface sites are not effectively blocked and that further poisoning, *e.g.*, by ammonia, is necessary to remove their activity. The activity of a surface towards olefin isomerisation in the presence of hydrogen chloride is a good test of whether a surface is also likely to be active towards elimination.

Heterogeneous Reactions.—The remarkable feature of the heterogeneous pyrolysis of 2-chlorobutane on Pyrex at 210° is the preferential formation of the thermodynamically unstable *cis*-but-2-ene. Unlike the reaction on clean silica at higher temperatures (Vessel 3) the formation of *cis*-but-2-ene is not only preferential with respect to thermodynamic equilibrium values, but is preferential in the absolute sense.

Preferential formation of *cis*-olefins in catalysed isomerisations of but-1-ene and pent-1-ene has often been observed. Ratios of *trans/cis*-but-2-ene less than unity have been obtained from but-1-ene on alumina, silica-alumina, silica-magnesia, silicotungstic acid, phosphoric and sulphuric acids,^{16,17} titanium trichloride,¹⁸ and in the presence of hydrogen,

¹⁵ Maccoll and Thomas, *Nature*, 1955, **176**, 392.

¹⁶ Haag and Pines, *J. Amer. Chem. Soc.*, 1960, **82**, 2488.

¹⁷ Brouwer, *J. Catalysis*, 1962, **1**, 22.

¹⁸ Edgcombe, *Tetrahedron Letters*, 1962, **24**, 1162.

on gold.¹⁹ Pent-1-ene behaves in a similar fashion, and *trans/cis* ratios as low as 0.2 have been reported by Brown and his co-workers²⁰ for reaction in excess of hydrogen at room temperature on various nickel catalysts. A similar feature is also observed in elimination reactions, thus the dehydration of butan-2-ol at 340° on alumina²¹ produced 78% but-1-ene, 15% *cis*-but-2-ene, and 7% *trans*-but-2-ene. Several mechanisms have been suggested for isomerisation of olefins on acidic and metallic catalysts and these have been reviewed recently by Ogasawara and Cvetanovic.²² Brouwer,¹⁷ for example, believes that for isomerisations on acidic catalysts, two mechanisms operate, one responsible for *cis-trans* isomerisation and one giving double-bond shift. The first involves acceptance by a gaseous olefin molecule of a surface proton, forming the classical carbonium ion. This then dissociates to a new gaseous olefin regenerating a surface proton. The second is a concerted mechanism involving an allylic complex with simultaneous addition and removal of two protons. Brouwer¹⁷ believes that this second mechanism is responsible for preferential formation of *cis*-but-2-ene on acidic catalysts because the *syn*-configuration of the butenyl complex is favoured on the surface.

Comparable mechanisms have been suggested for olefin isomerisation on metals. Interconversion of a monoadsorbed alkyl radical and a 1,2-diadsorbed alkene is known to occur in excess of hydrogen on metals. This mechanism is formally similar to the formation and dissociation of carbonium ions. A concerted mechanism involving an allylic complex with simultaneous addition and removal of hydrogen atoms has also been suggested.²³

We believe that there is a common feature of general importance regarding the nature of the complexes responsible for preferential formation of *cis*-olefins in isomerisations on both acidic and metallic catalysts. The concept of π -bonded olefinic or Dewar complexes seems to meet this requirement and has previously been suggested by Haag and Pines,¹⁶ to account for preferential formation of *cis*-olefin in the isomerisation of but-1-ene on alumina catalysts. It is known that such complexes of *cis*-olefins with silver ions are more stable than those of the corresponding *trans*-isomers,²⁴ and the same is also true of complexes with Pt^{II} ions.

The suggestion has been made that π -bonded complexes play an important role in reactions of hydrocarbons on metal surfaces.²⁵ It is a consequence of this theory that the mechanism of interconversion of monoadsorbed alkyl and 1,2-diadsorbed alkene is more precisely the interconversion of σ -bonded alkyl and π -bonded alkene. This mechanism is important for olefin isomerisation in excess of hydrogen at low temperatures on most metals.

When the catalyst is a transition metal or a transition metal salt (*e.g.*, titanium trichloride) the Dewar-type complex is formed between olefin and metal atom or ion respectively. In the case of acidic catalysts however, these complexes may result from an analogous interaction of olefins with surface protons (*e.g.*, hydrogen chloride on glass). The common feature in all cases is the donation of charge from the filled π -orbital of the olefinic bond to an acceptor σ -bonding orbital of the proton, metal atom, or metal ion.

The ability of a glass surface to eliminate hydrogen chloride from an alkyl chloride was suggested by Knispel and Swinbourne³ to be due to stabilisation of the polarised molecule. The simplest assumption is that this occurs not necessarily in a four-centred transition state as has been suggested for the gas-phase elimination but by a simple attachment of the negative chlorine atom to a positive surface site. In order to explain preferential formation of *cis*-but-2-ene we believe that Dewar complexes are formed in the act of

¹⁹ Webb and Rooney, unpublished work.

²⁰ Brown, *J. Amer. Chem. Soc.*, 1963, **85**, 1003.

²¹ Musaev and Zizin, *J. Appl. Chem. (U.S.S.R.)*, 1956, **29**, 869 (*Chem. Abs.*, 1956, **50**, 15,409 f.).

²² Ogasawara and Cvetanovic, *J. Catalysis*, 1963, **2**, 45.

²³ Turkevitch and Smith, *J. Chem. Phys.*, 1948, **16**, 466.

²⁴ Muhs and Weiss, *J. Amer. Chem. Soc.*, 1962, **84**, 4697.

²⁵ Rooney, *J. Catalysis*, 1963, **2**, 53.

faster in the presence of a carbon coating derived from allyl bromide. Direct *cis-trans*-isomerisation can occur by uncoupling of the π -electrons of the double bond, allowing free rotation. In the gas phase this requires an activation energy of about 63 kcal./mole⁹ but is catalysed by the free radical nitric oxide.²⁶ Surfaces possessing unpaired electrons or electron acceptors may exert a similar effect. Electron spin resonance measurements have shown the presence of free radicals in coked silica-alumina,²⁷ and pyrolytic carbon on glass surfaces may have similar properties.

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²⁶ Cundall and Palmer, 2nd Int. Congr. Catalysis (Paris), 1960, **1**, 573.

²⁷ Rooney and Pink, *Trans. Faraday Soc.*, 1962, **58**, 1632.
