# Reaction of Hydrogen Atoms with Cyclopropane in the Temperature Range from 628 to 779 K

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The reaction between cyclopropane and hydrogen atoms has been investigated in the temperature range from 628 to 779 K at a total argon pressure between 5.3 and 13.2 Torr using a discharge-flow system with gas-chromatographic product analysis. The measured products, methane, ethane, ethene, propane and propene, are shown to be consistent with a mechanism

$$\begin{array}{l} H+c-C_{3}H_{6}\longrightarrow H_{2}+c-C_{3}H_{5} & (1) \\ H+c-C_{3}H_{5}\longrightarrow C_{3}H_{6} (propene) \\ H+C_{3}H_{6}\longrightarrow products \\ H\xrightarrow{wall} 0.5H_{2}. & (w) \end{array}$$

Measurement of  $k_w$  permits evaluation of the rate constant for the abstraction process

 $\log(k_1/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = (13.6 \pm 1.0) - (48.5 \pm 13.0 \text{ kJ mol}^{-1}/2.3 \text{RT})$ 

which is similar to that for the corresponding reaction of methane on account of the almost identical C—H bond strengths in the molecules.

A composite function of the rate constants for addition to the two positions in propene is evaluated. It is shown that the flow rate of hydrogen atoms as measured by our previously described ethene titration technique gives values which are consistently only 80% of those evaluated by summation of the products of reaction with cyclopropane.

Over the past few years we have investigated the reactions of hydrogen atoms with various alkenes<sup>1-5</sup> and alkanes<sup>6-8</sup> using flow-discharge systems equipped either for gas-chromatographic analysis of final stable products or for mass-spectroscopic measurement of reactants and products. The latter method permits the 'direct' measurement of the rate constants for the primary reactions involved,<sup>5, 6</sup> whereas the former has permitted only 'indirect' measurements<sup>7, 8</sup> involving curve-fitting *via* computer integration of the coupled differential equations describing the overall reactions.

The present paper describes a study using a flow-discharge system equipped for gas-chromatographic analysis but used in such a way as to make a 'direct' measurement of a rate constant. The particular reaction chosen for this study is that between hydrogen atoms and cyclopropane. This reaction does not appear to have been investigated at other than room temperature. Early studies<sup>9, 10</sup> suggested that there was no reaction, but Schiff and Steacie<sup>11</sup> were able to show that there was a slow reaction with a collision yield of *ca*.  $10^{-8}$ , *i.e.* a rate constant of *ca*.  $10^{6}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>.

The lack of any previous detailed investigation provides the main justification for

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this work, especially as the reaction is of some interest given the unusually strong C—H bond in cyclopropane.<sup>12</sup> Moreover, it has been suggested<sup>13</sup> that the initial step could be an addition process giving n-propyl, although this may not be relevant to the present gas-phase study since it was based on experiments at 77 K in a solid matrix of cyclopropane and hydrogen iodide.

### **EXPERIMENTAL**

All experiments were carried out using a conventional discharge-flow system. The flow reactor was constructed of quartz tubing of 1.76 cm internal diameter. A heated zone, 40 cm long, was achieved using a furnace consisting of Nichrome wire wound with suitable insulation and lagging on a copper tube around the flow reactor. The temperature along the heated reactor tube was constant to  $\pm 2$  K with very sharp temperature gradients at both ends of the heated zone.

Hydrogen atoms were generated by passing dilute mixtures of hydrogen in argon through a microwave discharge. Hydrocarbon reactants were added to the atom flow in the heated zone via a probe which was moveable along the axis of the reactor. The temperature of the reactor was measured using a chromel-alumel thermocouple mounted in the tip of the moveable probe. All the quartz surfaces in the region of the heated zone were 'poisoned' with 10 mol dm<sup>-3</sup> nitric acid using our previously described procedure<sup>14</sup> to minimise the heterogeneous loss of hydrogen atoms. All flow rates were determined from measurements of the rate of pressure change (via an electrical transducer) in calibrated volumes.

Downstream of the reactor was a sampling system allowing direct injection of samples of reacted gases into the gas chromatograph, which was fitted with a flame ionisation detector. The column used for analysis consisted of a 2 m length of 5 mm o.d. copper tubing packed with a 1:1 w/w mixture of benzene-washed F.20 alumina coated with 6.76% w/w of squalane and Chromosorb G (120 mesh). To improve the separation of ethane and ethene a 2.5 cm long column packed with uncoated alumina was connected in series with the main column. The column was operated at 37 °C using nitrogen carrier gas at an inlet pressure of 5 p.s.i.g.

All hydrocarbon reactants contained no significant impurities and were always thoroughly outgassed before use.

### THEORY

### MECHANISM

Following previous workers<sup>11</sup> we will assume that the initial reaction of H with cyclopropane is an abstraction process

$$H+c-C_3H_6 \rightarrow H_2+c-C_3H_5$$

presumably followed by

$$H+c-C_{3}H_{5} \rightarrow (c-C_{3}H_{6})^{*}$$

which, since the excited state contains ca. 425 kJ mol<sup>-1</sup> excess energy,<sup>12</sup> will isomerise to propene, cf. the activation energy for the thermal isomerisation of cyclopropane to propene<sup>15</sup> is around 270 kJ mol<sup>-1</sup>. Thus one would predict the sole, primary, stable product to be propene. However, the rate constant for reaction of H with propene, an addition process, is several orders of magnitude greater than for an abstraction process by H from a hydrocarbon on account of an activation energy difference which may be as high as 30–40 kJ mol<sup>-1</sup>. Thus, the primary product, propene, except under conditions of a vast excess of cyclopropane over hydrogen atoms, will react with hydrogen atoms generating the products characteristic of that reaction. The reaction of propene with hydrogen atoms at room temperature has been discussed in detail by us in a previous publication<sup>2</sup> and a comprehensive mechanism was suggested. We assume that this mechanism applies in the present study and, where appropriate, we will also use relevant numerical values given in our earlier paper.

Note that we can neglect the unimolecular isomerisation of c-C<sub>3</sub>H<sub>5</sub> to allyl in comparison with its bimolecular reaction with H. A recent measurement of the rate constant<sup>16</sup> of the isomerisation shows it to be at least an order of magnitude slower in the conditions of the present experiments if we assume a rate constant of  $4 \times 10^{13}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> for the radical-radical reaction.

### DETERMINATIONS OF RATE CONSTANT $k_1$

In our reaction system there is competition for hydrogen atoms between heterogeneous loss and reaction with cyclopropane. Thus we can write a mechanism

$$H+c-C_3H_6 \xrightarrow{k_1} \text{ products}$$
 (1)

$$H \xrightarrow{k_w} 0.5 H_2$$
 (w)

where  $k_1$  is the rate constant for the initial abstraction reaction, which is indubitably the rate-determining step in the reaction with cyclopropane. Of course, subsequent reactions of the initially produced c-C<sub>3</sub>H<sub>5</sub> will use up more H atoms. Let us define then a stoichometry number, n, as the total number of hydrogen atoms used per molecule of cyclopropane used, *i.e.* the overall reaction is

$$nH + c - C_3H_6 \rightarrow products$$

with a rate determined by the rate of reaction (1).

From the above two-step mechanism, assuming that all H atoms react in the heated zone of the reactor, we derive

$$f =$$
 fraction of H atoms reacting with c-C<sub>3</sub>H<sub>6</sub>  
=  $nk_1F_{\Delta}/(nk_1F_{\Delta}+k_w)$ 

where  $F_{\Delta}$  is the flow rate of cyclopropane. Thus, if  $F_{\Delta con}$  is the flow rate of cyclopropane converted to products, we have

$$F_{\Delta \mathrm{con}} = f F_{\mathrm{H}} / n$$

where  $F_{\rm H}$  is the initial flow rate of hydrogen atoms. Combination of these two equations followed by rearrangement gives

$$\frac{1}{nF_{\Delta \text{con}}} = \frac{1}{F_{\text{H}}} + \frac{k_{\text{w}}}{k_1 F_{\text{H}}} \frac{1}{nF_{\Delta}}.$$
 (I)

Note that we have implicitly assumed that  $F_{\Lambda}$  is constant, *i.e.* that only a small fraction of the cyclopropane is converted into products.

It is to be anticipated that n will vary with conditions. For example, n = 2 when there is a vast excess of cyclopropane over H, since then there is no secondary reaction with the propene produced initially. Conversely n > 2 when the latter reaction does occur. Thus eqn (I) implies that we should plot  $1/nF_{\Delta con}$  against  $1/nF_{\Delta}$ , thereby obtaining a straight line of intercept  $1/F_{\rm H}$  and slope  $k_{\rm w}/k_1F_{\rm H}$ . Thus from the measured value of the ratio of intercept to slope, and knowing the value of  $k_w$ , we can obtain the value of  $k_1$ .

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#### DETERMINATION OF n

In order to generate the plot required by eqn (I) for the determination of  $k_1$  we must derive the value of *n* from the experimental results. A simple consideration of the rate of reacting hydrogen atoms gives the result

$$n = 2 + [2F_{\text{sat}} + 1.438(1 + 1.304/P)F_{\text{C}_{2}\text{H}_{2}}]/F_{\text{Acon}}$$

where  $F_{\text{sat}}$  is the total flow rate of saturated products,  $F_{C_3H_8}$  is the flow rate of propane product and P is the total pressure (predominantly argon). This expression is essentially made up of three terms which account for the various ways in which H atoms are lost. The first term accounts for the 2H atoms used in converting cyclopropane to propene and the other two terms account for H atoms lost in reaction with propene, the term in  $F_{\text{sat}}$  accounting for those H atoms which end up in observable products, *i.e.* the alkanes, and the term in  $F_{C_3H_8}$  accounting for those H atoms lost by disproportionation with i-C<sub>3</sub>H<sub>7</sub> forming H<sub>2</sub> and thus unobservable directly. The numerical values appearing in this latter term are taken from our previous paper,<sup>2</sup> and since they involve rate constants for reactions of excited C<sub>3</sub>H<sub>8</sub> molecules and the disproportionation to combination ratio for H+i-C<sub>3</sub>H<sub>7</sub> it is reasonable to assume values which are independent of temperature. Indeed, the validity of this assumption has been demonstrated for the very similar reaction of H with isobutene.<sup>4</sup>

The expressions for the quantities required to plot eqn (I) are

$$F_{\text{sat}} = F_{\text{CH}_4} + F_{\text{C}_2\text{H}_6} + F_{\text{C}_3\text{H}_8}$$
  
$$F_{\Delta \text{con}} = [F_{\text{CH}_4} + 2(F_{\text{C}_2\text{H}_6} + F_{\text{C}_2\text{H}_4}) + 3(F_{\text{C}_3\text{H}_8} + F_{\text{C}_3\text{H}_6})]/3.$$

### **REACTION WITH PROPENE**

The initial steps of the reaction may be represented by

$$H + c - C_3 H_6 \rightarrow c - C_3 H_5 + H_2 \tag{1}$$

$$H + c - C_3 H_5 \rightarrow C_3 H_6 \text{ (propene)} \tag{2}$$

$$H + C_3 H_6 \rightarrow i - C_3 H_7^* \tag{3}$$

$$H + C_3 H_6 \rightarrow n - C_3 H_7^* \rightarrow C H_3 + C_2 H_4.$$
<sup>(4)</sup>

The value of the rate constant for reaction (1) is much lower than those of reactions (2)–(4) and so the steady-state approximation may be applied to  $c-C_3H_5$  and to  $C_3H_6$ . We thus obtain

$$k_{1}[H][c-C_{3}H_{6}] = k_{2}[H][c-C_{3}H_{5}]$$
  
=  $(1-\alpha)k_{3}[H][C_{3}H_{6}] + k_{4}[H][C_{3}H_{6}]$ 

where  $\alpha$  is the fraction of the propene reacting *via* reaction (3) which is reformed in the subsequent reactions of i-C<sub>3</sub>H<sub>7</sub><sup>\*</sup> (by disproportionation of H and i-C<sub>3</sub>H<sub>7</sub>). Our previous work<sup>2</sup> gives  $\alpha \approx 0.42$ 

for the conditions of the present work and so, in terms of flow rates, we have

$$F_{C_3H_6} = F_{\Delta} k_1 / (0.58k_3 + k_4). \tag{II}$$

Thus a plot of  $F_{C_3H_4}$  against  $F_{\Delta}$  should be a straight line of slope  $k_1/(0.58k_3+k_4)$  passing through the origin.



Fig. 1. Plots of  $F_{\text{prod}}$  against  $F_{\Delta}$  for experiments at 677 K and 10.6 Torr total pressure with a measured  $F_{\text{H}}$  (ethene titration) of 5.84  $\mu$ mol s<sup>-1</sup>. Key to products: (a) methane, (b) ethane, (c) ethene, (d) propene and (e) propane.

## **RESULTS AND DISCUSSION**

The reaction of hydrogen atoms with cyclopropane has been investigated in the temperature range 628–779 K at total argon pressures in the range 5.3–13.2 Torr with contact time in the heated reactor *ca.* 10–15 ms. The flow rate of hydrogen atoms,  $F_{\rm H}$ , measured using our previously described ethene titration technique,<sup>1, 7</sup> was in the range 1.8–6.6  $\mu$ mol s<sup>-1</sup>, corresponding to a concentration of *ca.*  $5 \times 10^{-10}$  mol cm<sup>-3</sup>. For each value of  $F_{\rm H}$  experiments were conducted with *ca.* 15 different flow rates of cyclopropane,  $F_{\Delta}$ , in the approximate range 0.2–65  $\mu$ mol s<sup>-1</sup>. The value of the first-order rate constant,  $k_{\rm w}$ , for the heterogeneous loss of hydrogen atoms was measured by monitoring the decay of the hydrogen-atom concentration along the reactor using the ethene titration technique.<sup>2</sup> Values of  $k_{\rm w}/s^{-1}$  were in the range 65–194, *i.e.* the walls of the reactor are not as inactive as in some of our previous work<sup>8</sup> but they are suitable for the present purposes. Complete tables of results are available.<sup>17</sup>

### MECHANISM

Fig. 1 shows a typical set of results in the form of a plot of product flow rate  $F_{\text{prod}}$  against  $F_{\Delta}$  for a constant initial  $F_{\text{H}}$  at constant temperature and pressure. The general dependence of  $F_{\text{prod}}$  on  $F_{\Delta}$  was independent of conditions and may be summarised thus: (i) plots of  $F_{\text{CH}_4}$  pass through broad maxima and decline at high  $F_{\Delta}$ , (ii)  $F_{\text{C}_2\text{H}_4}$ ,  $F_{\text{C}_2\text{H}_6}$  and  $F_{\text{C}_3\text{H}_8}$  all appear to level out at high  $F_{\Delta}$  and (iii)  $F_{\text{C}_3\text{H}_6}$ , in contrast, constantly increases as  $F_{\Delta}$  increases.

There is a temperature dependence of the relative amounts of the products, the most significant change being the increase in the yield of ethene as the temperature increases.

All of these observations are in agreement with the mechanism assumed above. Thus the dependences of the flow rates of methane, ethane, ethane and propane on reactant flow rate at constant temperature, pressure and  $F_{\rm H}$  are broadly similar to those observed in our study of the H+propene reaction,<sup>2</sup> whilst the dependence of  $F_{C_3H_4}$ on  $F_{\Delta}$  is in accord with that predicted from eqn (II). The enhanced yield of ethene



Fig. 2. Plot of  $1/nF_{\Delta con}$  against  $1/nF_{\Delta}$  for the results shown in fig. 1.

at higher temperatures is in line with the prediction based on the higher activation energy of reaction (4) in comparison with that of reaction (3).<sup>18</sup>

The significant difference between the shapes of the plots for ethene and propene yields against  $F_{\Delta}$  implies that reaction of ethene with H is insignificant since, otherwise, the shape of the plot for ethene would be similar to that for propene. However, even if it were significant it would make no difference to the interpretation of the present results since the reaction of H with ethene generates only alkanes as products<sup>1</sup> and thus any H atoms that had reacted in this way would be included in the calculation of *n via* the term in  $F_{sat}$ .

We therefore conclude that eqn (I) and (II) derived above on the basis of the assumed mechanism are valid descriptions of the present results.

### VALUE OF $k_1$

Fig. 2 shows a typical plot of  $1/nF_{\Delta con}$  against  $1/nF_{\Delta}$  to be an excellent straight line, as was observed for all our sets of results. Note that for these plots we used only results derived at sufficiently high values of  $F_{\Delta}$ , in order to ensure that effectively all the H atoms reacted in the hot zone. Table 1 records the values of the slope, S, and intercept, I, of these plots. Also recorded in table 1 are the values of  $k_w$ ,  $k_1$ (calculated via  $k_1 = k_w I/S$ ),  $F_H$  (calculated both from the ethene titration and as the value of 1/I and Z, the numerical factor converting a flow rate in  $\mu$ mol s<sup>-1</sup> into a concentration in mol cm<sup>-3</sup> (obtained from measurement of the flow rate of argon for a measured argon pressure in the flow tube). The error limits of the quoted values for  $k_1$  are difficult to estimate but are inevitably large since the value arises via two independent plots of gas-chromatographic data, one of the plots involving a particularly complex function of experimental results. The existence of wide error limits is born out by the observed scatter of the results,  $\pm 50\%$  about the mean value (ignoring the slight difference in temperatures) at the lowest temperature, but, rather better,  $\pm 25\%$ at the other temperatures. A least-squares treatment of the data yields log  $(A/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 13.6 \pm 1.0$  and  $E_1 = 48.5 \pm 13.0 \text{ kJ} \text{ mol}^{-1} (95\% \text{ confidence})$ limits), which data are remarkably similar to those for H attack on methane<sup>8</sup> which vielded

$(0.58k_3 + k_4)$ $/10^2 \text{ cm}^3$ $\text{mol}^{-1} \text{ s}^{-1}$		3.2	1.5	1.5	3.4	2.0	2.6	4.0	1.9	2.0	3.7	2.3	2.2
$k_1 / 10^9  { m cm}^3 { m mol}^{-1}  { m s}^{-1}$		5.4	2.5	3.0	11.6	6.9	9.5	19.8	11.5	12.7	26.8	17.9	18.5
	$10^{10} Z^{b}$	2.92	2.18	1.99	2.70	1.99	1.86	2.52	1.93	1.75	2.40	1.76	1.68
$F_{ m H}/\mu{ m mol}~{ m s}^{-1}$	(ii) <sup>a</sup>	2.48	6.94	8.77	2.44	6.41	7.81	2.56	5.88	6.94	2.51	5.88	7.19
	(i) <sup>a</sup>	1.83	5.88	6.47	2.03	5.84	6.57	2.14	4.35	5.41	1.99	3.78	5.17
	$I/\mu$ mol <sup>-1</sup> s	0.404	0.144	0.114	0.409	0.156	0.128	0.391	0.170	0.144	0.398	0.170	0.139
	S	25.3	17.5	28.9	11.2	10.3	12.1	9.7	8.7	10.9	9.9	9.2	8.7
	$k_{\rm w}/{\rm s}^{-1}$	96	65	154	86	16	167	123	114	168	160	171	194
	P/Torr	5.3	10.6	13.2	5.3	10.6	13.2	5.3	10.6	13.2	5.3	10.6	13.2
	T/K	628	631	638	676	677	683	739	737	738	617	778	773

<sup>*a*</sup> The two values quoted are those obtained (i) from the ethene titration and (ii) by taking the value of 1/I. <sup>*b*</sup> Z is the numerical factor to multiply flow rates in  $\mu$ mol s<sup>-1</sup> to give concentrations in mol cm<sup>-3</sup>.

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Table 1. Results



Fig. 3. Plot of  $F_{C_3H_6}$  against  $F_{\Delta}$  for the results shown in fig. 1.

a reflection, presumably of the near equality of the C—H bond strengths in methane and in cyclopropane.<sup>12</sup> This result confirms that the initial step in the reaction of H with cyclopropane is a hydrogen-abstraction process, as has been assumed in this work.

In a parallel study in our laboratory using a flow-discharge system with massspectroscopic measurement of reactants and products we have obtained<sup>19</sup>

$$\log (k_1/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 14.21 - (49.1 \text{ kJ mol}^{-1}/2.3 \textbf{R}T).$$

The agreement with the present Arrhenius parameters is good but the absolute values of  $k_1$  generated differ by a factor of *ca*. 3 for temperatures of *ca*. 600 K. The reasons for this discrepancy are not known.

#### **REACTION WITH PROPENE**

Fig. 3 shows a typical plot of  $F_{C_3H_6}$  against  $F_{\Delta}$ . The plots are good straight lines but only for the higher temperatures do they pass through the origin, as required by eqn (II). The reason for this is that, for the lower temperatures at low  $F_{\Delta}$ , some hydrogen atoms remain at the end of the hot zone and will then react with propene (and with ethene for that matter) in the cold zone. This is confirmed by calculations using data in table 1. Thus, product propene is removed and there is a small intercept on the abscissa on plots of  $F_{C_3H_6}$  against  $F_{\Delta}$ . We have, however, simply taken the slopes of these plots as estimates of  $k_1/(0.58k_3 + k_4)$  and thus we are underestimating the values of the denominator which are recorded in table 1. This inaccuracy is immaterial given the accumulation of errors up to this point in the calculation.

The only published data which may be compared with the presently obtained values seem to be those of Wagner and Zellner,<sup>18</sup> who obtained for the temperature range 195–390 K

$$\log (k_3/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 12.73 - (5.2 \text{ kJ mol}^{-1}/2.3 RT)$$

 $\log (k_4/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 12.64 - (11.7 \text{ kJ mol}^{-1}/2.3 \textbf{R}T)$ 

and

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from which we calculate  $(0.58k_3 + k_4)/10^{12}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> as 1.6, 1.8, 2.0 and 2.1 at 630, 680, 730 and 780 K, respectively. While the agreement with the present values appears quite reasonable, bearing in mind the very long extrapolation from 390 K, the published data suggest values of  $k_4/k_3$  ranging from 0.24 at 630 K to 0.30 at 780 K, which are, in fact, incompatible with the present results which require values of 2-3 at the higher temperatures if the preponderance of product ethene is to be accounted for. A clue to the possible cause of this discrepancy is given by the observation that larger values of  $k_4/k_3$  are required at the lowest pressure to account for the present results. This is not unreasonable since  $k_3$  must be below its high-pressure limiting value in our reaction conditions. Such a pressure dependence is ignored in the results of Wagner and Zellner and thus the extrapolation to our temperature range is subject to substantial uncertainty. Any quantitative agreement between our results and theirs is thus fortuitous, but it is clear that we are in qualitative accord.

### ETHENE TITRATION

Comparison of the values of  $F_{\rm H}$  obtained by the ethene titration technique and by calculation from the intercepts of plots of eqn (I) (cf. fig. 2) shows that the former is consistently only 80% of the latter (the mean ratio is 0.80, with a standard deviation of the mean of 0.02). We cannot account for a discrepancy of this magnitude. Our previous observation that the ethene titration underestimates  $F_{\rm H}$  by ca. 3%<sup>7</sup> can only account for a minor part of the discrepancy. Fortunately, it does not affect our evaluation of  $k_1$  etc. since the value of  $k_w$  required depends only upon the ratios of values of  $F_{\rm H}$ , which are unaffected because of the consistent nature of the discrepancy.

### CONCLUSION

We conclude that the primary step in the reaction of hydrogen atoms with cyclopropane is an abstraction reaction with a rate constant given by

 $\log (k_1/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 13.6 \pm 1.0 - (48.5 \pm 13.0 \text{ kJ mol}^{-1}/2.3 \textbf{R}T).$ 

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