Temperature Dependence of the Disproportionation/ Combination Ratio for H+t-C₄H₉ and of the Orientation of H Atom Addition to iso-C₄H₈

BY ROGER M. MARSHALL* AND CARLOS E. CANOSA

Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA2 8PP

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The reaction between hydrogen atoms and isobutene has been investigated under conditions where $[H] \leq [i-C_4H_8]$ in the temperature range 20-328°C at an argon pressure of 6.6 Torr in a discharge-flow apparatus. Two ratios of rate constants have been determined,

 $\log(k_2/k_1) = 0.47 \pm 0.33 - 16.6 \pm 2.6 \text{ kJ mol}^{-1}/(2.3 \text{ RT})$

and $k_s/k_6 = 3.55 \pm 0.24$, independent of temperature. (Error limits are 95% confidence limits.)

 $H+i-C_4H_8 \rightarrow t-C_4H_9^* \tag{1}$

 $H+i-C_4H_8 \rightarrow CH_3+C_3H_6 \tag{2}$

 $H+t-C_4H_9 \rightarrow H_2+i-C_4H_8 \tag{5}$

$$H+t-C_4H_9 \rightarrow i-C_4H_{10}^* \tag{6}$$

The stoichiometry of the overall reaction is discussed.

In a previous publication ¹ from this laboratory, we reported a detailed mechanistic study of the reaction of hydrogen atoms with isobutene in a discharge-flow system at 290 ± 3 K. Inter alia we were able to derive values for the ratio (=0.0014) of non-terminal to terminal H atom addition to isobutene and for the disproportionation/ combination ratio (=3.73) for H+t-C₄H₉.

We have recently become interested in measuring the temperature dependence of the rate constant for the reaction

$$H+i-C_4H_8 \rightarrow t-C_4H_9^* \tag{1}$$

using a discharge-flow system with mass spectrometric monitoring of reactants and products. To obtain values of k_1 working in the usual pseudo-first-order conditions it is necessary to assume values for the stoichiometry of the overall reaction. Thus, for the conditions [H] \leq [i-C₄H₈], where one monitors the decay of H with time, one must measure (or just assume) the overall number of hydrogen atoms reacting per hydrogen atom consumed in reaction (1). Our previous work shows this number to be close to 2, as was assumed by Knox and Dalgleish in their study.² For the conditions [H] \geq [i-C₄H₈], where one monitors the decay of i-C₄H₈ with time, the situation is made more complex because most (> $\frac{3}{4}$) of the isobutene removed by reaction (1) is reformed in the subsequent reaction

$$H+t-C_4H_9 \rightarrow H_2+i-C_4H_8. \tag{5}$$

Thus the decay with time of $i-C_4H_8$ is substantially lower than the actual rate of reaction (1).

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All the appropriate stoichiometric calculations can be done based on the information contained in our earlier study. However, this information applies only to 290 K and it is, therefore, desirable to make similar measurements over a range of temperatures so that the results may be applied to the measurement of values of k_1 over the same temperature range. The present paper presents the results of such a study.

EXPERIMENTAL

The experiments were carried out in a discharge-flow apparatus under the conditions $[i-C_4H_8] \ge [H]$. Details of the apparatus, materials and procedure have been published previously.^{1, 3, 4} Gas chromatographic analysis of the products was *via* a 1.6 m× $\frac{1}{4}$ in. column of alumina poisoned with 5 % w/w silicone oil, operated at 400 K. Unlike our previous study ¹ the sample for analysis was not compressed in a gas burette before injection into the column.

RESULTS

Experiments were carried out in the range 293-601 K. Total pressure, M, was 6.6 Torr which corresponded to an argon flow rate $\approx 540 \ \mu \text{mol s}^{-1}$. The flow rates of hydrogen atoms, F_{H} , and of isobutene, $F_{C_4H_8}$, were both $\approx 4 \ \mu \text{mol s}^{-1}$. Because of the high number (≈ 10) of hydrogen atoms lost for every isobutene molecule lost,¹ these flow rates effectively correspond to a substantial excess of i-C₄H₈ over H. Moreover, following our earlier work,¹ we can assume that the reaction with isobutene removes all of the hydrogen atoms and that any new olefin produced stays, unreacted, in the system.

The flow rate of hydrogen atoms was determined by reaction with excess ethene as described previously.^{3, 4} The full results obtained for the reaction of hydrogen atoms with excess isobutene are given in table 1. We could not measure the minor products, ethene and neopentane. Otherwise, the results are broadly comparable

| T/°C | 0.5 F _H | F _{CH4} | $F_{C_2H_6}$ | $F_{C_3H_8}$ | $F_{C_3H_6}$ | $F_{i-C_4H_{10}}$ | k5/k6 | k_2/k_1 | S_1 | S_2 |
|------|--------------------|------------------|--------------|--------------|--------------|-------------------|-------|-----------|-------|-------|
| 20 | 53.25 | 1.53 | 0.31 | 0.29 | 0.41 | 8.47 | 5.04 | 0.004 3 | 2.04 | 0.18 |
| 22 | 38.42 | 1.61 | 0.26 | 0.32 | 0.70 | 7.85 | 3.62 | 0.013 6 | 2.05 | 0.24 |
| 34 | 43.10 | 1.05 | 0.08 | 0.44 | 0.43 | 9. 79 | 3.24 | 0.003 67 | 2.03 | 0.25 |
| 43 | 38.50 | 1.21 | 0.08 | 0.40 | 0.55 | 10.48 | 2.51 | 0.007 56 | 2.03 | 0.30 |
| 55 | 44.48 | 2.41 | 0.26 | 0.47 | 0.66 | 8.50 | 3.86 | 0.008 61 | 2.07 | 0.24 |
| 58 | 48.33 | 1.93 | 0.17 | 0.75 | 0.56 | 8.98 | 4.06 | 0.001 64 | 2.06 | 0.22 |
| 108 | 41.83 | 1.96 | 0.26 | 0.62 | 0.75 | 8.66 | 3.50 | 0.008 34 | 2.06 | 0.25 |
| 130 | 37.27 | 1.93 | 0.68 | 0.33 | 0.88 | 7.43 | 3.62 | 0.019 4 | 2.07 | 0.26 |
| 185 | 30.71 | 1.69 | 0.38 | 0.34 | 1.03 | 6.82 | 3.15 | 0.028 6 | 2.05 | 0.28 |
| 200 | 30.55 | 1.98 | 0.43 | 0.32 | 1.14 | 6.08 | 3.58 | 0.033 5 | 2.06 | 0.27 |
| 203 | 32.50 | 1.93 | 0.78 | 0.13 | 1.25 | 6.56 | 3.52 | 0.039 3 | 2.06 | 0.27 |
| 255 | 34.72 | 2.46 | 1.30 | 0.35 | 2.40 | 5.90 | 4.19 | 0.071 0 | 2.05 | 0.27 |
| 257 | 22.03 | 1.77 | 0.52 | 0.28 | 1.47 | 4.97 | 2.92 | 0.066 2 | 2.05 | 0.33 |
| 308 | 37.47 | 2.90 | 1.82 | 0.50 | 3.89 | 6.28 | 4.14 | 0.111 | 2.02 | 0.30 |
| 315 | 19.02 | 1.93 | 0.83 | 0.17 | 1.97 | 4.16 | 2.87 | 0.116 | 2.05 | 0.36 |
| 328 | 33.43 | 3.27 | 2.03 | 0.54 | 5.14 | 6.20 | 3.45 | 0.174 | 1.99 | 0.37 |

| TABLE | 1 | R | FSI | пля |
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with our previous work.¹ It should be noted that the flow rates given in table 1 are in arbitrary units. This is immaterial for our present purposes since we are interested solely in ratios of product yields but, for the purposes of comparison, we estimate 1 arbitrary unit $\equiv 0.062 \ \mu \text{mol s}^{-1} \equiv 0.76 \ \text{mTorr}$ in the reaction zone at 295 K.

INTERPRETATION AND DISCUSSION

We may interpret our results in terms of the mechanism given below which we have previously shown¹ to account for the room temperature results.

$$H + i - C_{4}H_{8} \rightarrow t - C_{4}H_{9}^{*}$$
⁽¹⁾

$$H+i-C_4H_8(\rightarrow i-C_4H_9^*) \rightarrow CH_3+C_3H_6$$
(2)

$$M + t - C_4 H_9^* \rightarrow t - C_4 H_9 + M \tag{3}$$

$$\mathrm{H} + \mathrm{t-C_4}\mathrm{H_9^*} \to \mathrm{CH_3} + \mathrm{C_3}\mathrm{H_7} \tag{4}$$

$$H+t-C_4H_9 \rightarrow H_2+i-C_4H_8 \tag{5}$$

 $H+t-C_4H_9 \rightarrow i-C_4H_{10}^* \tag{6}$

$$M + i - C_4 H_{10}^* \rightarrow i - C_4 H_{10} + M$$
 (7)

 $i-C_4H_{10}^* \to C_3H_7 + CH_3$ (8*a*)

$$i-C_4H_{10}^* \to C_3H_6 + CH_4 \tag{8b}$$

 $H+C_{3}H_{7} \rightarrow H_{2}+C_{3}H_{6}$ (9) $H+C_{3}H_{2} \rightarrow C_{3}H_{6}$ (10)

$$H + C_3 H_7 \to C_3 H_8^* \tag{10}$$

$$M + C_3 H_8^* \to C_3 H_8 + M \tag{11}$$

$$C_3H_8^* \to CH_3 + C_2H_5 \tag{12a}$$

$$C_3H_8^* \to CH_4 + C_2H_4 \tag{12b}$$

$$H+C_2H_5 \to 2CH_3 \tag{13}$$

$$CH_3 + H \to CH_4 \tag{14}$$

$$2CH_3 \to C_2H_6 \tag{15}$$

$$CH_3 + t - C_4H_9 \rightarrow \text{neo-}C_5H_{12} \text{ or } CH_4 + i - C_4H_8$$
 (16)

$$H + t - C_4 H_9^* \rightarrow 2C_2 H_5 \text{ or } CH_3 + C_3 H_7$$
 (17)

The only reactions whereby hydrogen atoms react without appearing as an observable product are reactions (5) and (9). Thus, if

$$F_{\rm sat} = (F_{\rm CH_4} + F_{\rm C_2H_6} + F_{\rm C_3H_8} + F_{\rm i-C_4H_{10}}),$$

 $(0.5F_{\rm H}-F_{\rm sat})$ is the yield of hydrogen from reactions (5) and (9). Now at the lower temperatures of this study, the total yield of propene is very much less (by a factor ≈ 30) than $(0.5F_{\rm H}-F_{\rm sat})$ and hence we may set $(0.5F_{\rm H}-F_{\rm sat})$ equal to the yield of hydrogen from reaction (5). As the temperature increases the yield of propene increases substantially until, at 601 K, it is comparable to the yield of isobutane. Conversely, the yield of propane does not increase to anything like the same extent and, since the propane yield must be comparable to the yield of propene from reaction (9) (cf. the low temperature results), we conclude that the increase in the propene yield with increasing temperature is due to the increasing importance of reaction (2). Thus, even at the higher temperatures, we conclude that $(0.5F_{\rm H}-F_{\rm sat})$ is equal to the yield of hydrogen from reaction (5). Thus, since hydrogen and isobutane are the

predominant products, other than those derived from reaction (2), at all temperatures, we conclude that

$$(0.5 F_{\rm H} - F_{\rm sat})/F_{\rm i-C_4H_{10}} = k_5/k_6.$$
 (I)

Values for k_5/k_6 , the disproportionation/combination ratio for H+t-C₄H₉ calculated *via* this equation are shown in table 1. Clearly, there is no significant trend with temperature. We thus conclude that, in the range 293-601 K, k_5/k_6 is independent of temperature and the mean value (ignoring the obviously discrepant results for 20 and 43°C) is

$$k_5/k_6 = 3.55 \pm 0.24$$

where the error limits, here and subsequently, are 95 % confidence limits calculated by statistical methods. This value is in agreement with the value (3.73 ± 0.12) obtained previously ¹ for 290 K.

In our previous publication we derived the equations

$$\frac{MF_{C_{3}H_{8}}}{F_{i-C_{4}H_{10}}} \left(1 + \frac{k_{12a} + k_{12b}}{k_{11}M}\right) = \frac{k_{10}}{k_{9} + k_{10}} \left[\frac{k_{8a}}{k_{7}} + 0.5 \frac{k_{4}}{k_{3}} \left(1 + \frac{k_{5}}{k_{6}}\right)F_{H}\right]$$

and

$$\frac{F_{C_{3H_6}}}{F_{i-C_{4H_{10}}}} = \frac{k_2}{k_1} \left(1 + \frac{k_5}{k_6}\right) + 0.5 \frac{k_4}{k_3} \left(\frac{k_9}{k_9 + k_{10}}\right) \left(1 + \frac{k_5}{k_6}\right) \frac{F_H}{M} + \frac{k_{8a}}{k_7 M} \left(\frac{k_9}{k_9 + k_{10}}\right) + \frac{k_{8b}}{k_7 M} \frac{F_H}{k_7 M} \frac{F_H}{k_7$$

and thus, since we showed ¹ that the term $k_{8b}/(k_7M)$ was negligible, we derive

$$\frac{F_{C_{3}H_{6}}}{F_{i-C_{4}H_{10}}} = \frac{k_{2}}{k_{1}} \left(1 + \frac{k_{5}}{k_{6}}\right) + \frac{k_{9}}{k_{10}} \left(1 + \frac{k_{12a} + k_{12b}}{k_{11}M}\right) \frac{F_{C_{3}H_{8}}}{F_{i-C_{4}H_{10}}}$$

By analogy with k_5/k_6 one would expect k_9/k_{10} , the disproportionation/combination ratio for H+i-C₃H₇, to be temperature independent in the range 293-601 K. Moreover, one would not expect a strong temperature dependence of $(k_{12a}+k_{12b})/k_{11}$, this being the ratio of decomposition/stabilisation for an excited molecule. This conclusion is borne out by the results shown in table 1. As the temperature goes up there is no substantial increase in the yields of the products, CH₄, C₂H₆, C₃H₈ and C₃H₆, arising from decomposition of excited molecules, other than the increase due to the enhanced importance of reaction (2). Thus we are justified in using the values

$$k_9/k_{10} = 0.54 \pm 0.11$$
,¹ $k_{12a}/k_{11} = 0.72 \pm 0.08$ Torr [M = Ar] ⁵

and

$$k_{12b}/k_{11} = 0.58 \pm 0.05$$
 Torr [M = Ar],⁵

previously obtained by us for 290 K, together with eqn (I) to obtain

$$k_2/k_1 = (F_{C_3H_6} - 0.65 F_{C_3H_8})/(F_{i-C_4H_{10}} + 0.5 F_H - F_{sat}).$$
(II)

At low temperatures, the C_3H_8 term in eqn (II) is $\approx 50\%$ of the C_3H_6 term whereas at the higher temperatures it is <10 % of it. Thus, in the high temperature region, where the assumptions inherent in eqn (II) are open to some doubt, the effect of any error in the assumptions is insignificant. However, in the low temperature region, the $\pm 20\%$ confidence limits (95%) for the value of k_9/k_{10} used lead to possible error limits of the same order for the calculated values of k_2/k_1 . Some scatter of the results on the Arrhenius plot shown in fig. 1 is thus inevitable at the low temperature end. Ignoring the obviously erroneous results for 22 and 58°C (not shown on the diagram), we obtain

$$\log (k_2/k_1) = 0.47 \pm 0.33 - 16.6 \pm 2.6 \text{ kJ mol}^{-1}/(2.3 \text{ RT}).$$

Also shown on the figure are our previous result ¹ and that of Falconer and Sunder ⁶ which seem to be the only previous estimates of k_2/k_1 , the present results seemingly being the only study of its temperature dependence. The agreement with the former result is not good, for reasons which are not at all clear. However, the agreement with the latter result is quite good.

The temperature dependence measured here supports the assertion made by Falconer and Sunder ⁶ that it is predominantly an activation energy difference which determines the relative rates of addition to the two positions of an asymmetric olefin, *i.e.*, that the pre-exponential factors for the two additions are roughly equal. The present measurement seems to be the first direct evidence for this assertion.



FIG. 1.—Arrhenius plot for k_2/k_1 : \bigcirc , present work; \bigcirc , ref. (6); \blacksquare , ref. (1).

A prime aim of this work was to evaluate the overall stoichiometry of the reaction between hydrogen atoms and isobutene over an extended temperature range for the two experimental conditions of a considerable excess of one of the reactants. Consider first the condition $[H] \leq [i-C_4H_8]$. Then the overall number of hydrogen atoms, S_1 , consumed per hydrogen atom reacting in reactions (1) and (2) may be derived thus:

$$S_1 = F_{\rm H} / (C_{\rm i-C_4H_8} + F_{\rm H_2}),$$

where $C_{i-C_{4H_8}}$ is the net consumption (in terms of flow rate) of isobutene, *i.e.*, the amount used up in reactions (1) and (2) less that reformed in reaction (5), the latter being equal to F_{H_2} , which, in turn, is equal to $(0.5F_H - F_{sat})$. Clearly

$$C_{i-C_4H_8} = 0.25 F_{CH_4} + 0.5 F_{C_2H_6} + 0.75 (F_{C_3H_8} + F_{C_3H_6}) + F_{i-C_4H_{10}}$$

and hence we obtain

$$S_1 = F_{\rm H} / (0.5 F_{\rm H} - 0.75 F_{\rm CH_4} - 0.5 F_{\rm C_{2H_6}} - 0.25 F_{\rm C_{3H_8}} + 0.75 F_{\rm C_{3H_6}}).$$

Values of S_1 calculated *via* this equation are shown in table 1. Within experimental error, the value of S_1 is close to 2.00 over the whole range of our experiments. This is simply a consequence of the fact that the major reaction pathways in all our experimental conditions are

$$2H + i - C_4 H_8 \rightarrow i - C_4 H_{10} \tag{A}$$

and

$$2H+i-C_4H_8 \rightarrow H_2+i-C_4H_8. \tag{B}$$

The occurrence of reaction (2) introduces two other stoichiometries

$$H+i-C_4H_8 \rightarrow C_3H_6 + \frac{1}{2}C_2H_6 \tag{C}$$

and

$$2H+i-C_4H_8 \to C_3H_6 + CH_4. \tag{D}$$

The ratio of stoichiometries (C) and (D) is unknown, but for the purposes of discussing their effect let us assume that they are equal, *i.e.*, we assume that their net effect is

$$1.5H + i - C_4 H_8 \rightarrow C_3 H_6 + 0.5 CH_4 + 0.25 C_2 H_6.$$
 (E)

At the lower temperatures, (E) occurs only to ≈ 1 % of total addition and thus one calculates $S_1 = 2.00$. Even at 601 K, when (E) occurs to the extent of 15 % (since $k_2/k_1 = 0.174$, cf. table 1) of total addition, one calculates $S_1 = 1.92$, in excellent agreement with the direct experimental value shown in table 1. It is clear, therefore, that whatever the method we use to evaluate S_1 , either directly from experiment or from derived data, it is virtually constant, within any reasonable experimental error, at 2.0 over the whole temperature range 20-328°C.

The situation is rather different for the condition $[H] \ge [i-C_4H_8]$. The stoichiometry that we require is the net number of isobutene molecules, S_2 , reacting per molecule of isobutene consumed in reactions (1) and (2). (*N.B.* Even though the present experiments were carried out under conditions such that $[i-C_4H_8] \ge [H]$, we can still derive the relevant stoichiometry.) Values calculated *via* the equation

$$S_2 = C_{i-C_4H_8} / (C_{i-C_4H_8} + F_{H_2})$$

are shown in table 1. Values may be calculated from derived data. Thus at low temperature the effective ratio of stoichiometries is

$$(A):(B):(E) = 0.22:0.77:0.01$$

implying the value $S_2 = 0.23$, whereas at 328° C

$$(A):(B):(E) = 0.19:0.66:0.15$$

implying the value $S_2 = 0.34$.

The calculated values of S_2 are in agreement with those shown in table 1. Clearly, no matter how we evaluate S_2 , it varies substantially (≈ 50 %) with temperature in the range 20-328°C.

Thus, we conclude that it is much preferable, if at all possible, to work in the conditions $[H] \ll [i-C_4H_8]$, where the stoichiometry is essentially constant over a wide temperature range, in order to measure the rate constant for hydrogen atom addition to isobutene.

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- ² J. H. Knox and D. G. Dalgleish, Int. J. Chem. Kinetics., 1969, 1, 69.
- ³ M. P. Halstead, D. A. Leathard, R. M. Marshall and J. H. Purnell, *Proc. Roy. Soc.*, *A*, 1969, **310**, 525.
- ⁴ P. Camilleri, R. M. Marshall and J. H. Purnell, J.C.S. Faraday I, 1974, 70, 1434.
- ⁵ M. J. Lexton, R. M. Marshall and J. H. Purnell, Proc. Roy. Soc., A, 1971, 324, 433.
- ⁶ W. E. Falconer and W. A. Sunder, Int. J. Chem. Kinetics, 1971, 3, 395.

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¹ M. J. Lexton, R. M. Marshall and J. H. Purnell, Proc. Roy. Soc., A, 1971, 324, 447.