The Reactions of Hydrogen Atoms with Isobutane and Isobutene

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THE reactions of hydrogen atoms with isobutane and isobutene have been studied in a fast flow system between 12 and 132°C at total pressures of $\sim$ 2 torr and linear flow rates of $\sim$20 m. sec.$^{-1}$, giving a time resolution of $\sim$ 0·1 msec.

Mixtures of 5—10% H_2 in Ar were passed through an 18 Mc./sec. radiofrequency discharge ($\sim$ 100 w), giving $\sim$ 25% dissociation of H_2 into H. The initial concentration of H atoms, $[H]_0$, was determined by titration with NO_2.[1] However, only relative concentrations of H were generally required, and the decay of $[H]/[H]_0$ as a function of time or distance was obtained by a "catalytic probe" consisting of a small piece of platinum foil attached to one junction of a Pt–Pt/Rh thermocouple: the other junction was about 2 mm. away and was coated with glass. The whole assembly could be moved axially along the flow tube. Pure isobutane or mixtures of isobutane (at 20—200% of $[H]_0$) and isobutene (at 0—5% of $[H]_0$) were added to the H-atom stream. Samples were taken for analysis by gas chromatography through a second probe which could also be moved axially. Analysis showed that the reaction of pure isobutane with H gave isobutene and traces of ethane, ethylene, propane, and propene. No higher hydrocarbons, and in particular no octanes, were detected. The concentrations of olefins, particularly isobutene, rapidly assumed stationary values although the H-atom concentration decreased continuously. The H-atom decay was first order once the stationary concentration of olefin had been attained. Since the total yield of products amounted to only 4% of the consumption of H and since the decay of [H] in the absence of titrant was slight, the removal of H must be catalysed either by olefin or alkane.

In the presence of pure olefin at concentrations comparable to those of alkane, the decay of H was almost instantaneous and the main reaction product was a small quantity of isobutane. Thus the catalytic removal of H occurs *via* reaction with olefin. The following reactions must therefore be considered:

$$\begin{array}{lll}
\mathrm{H + RH} & = \mathrm{H_2 + R}\ (\mathrm{RH} = \text{alkane}) & (1)\\
\mathrm{H + R} & = \mathrm{A + H_2}\ (\mathrm{A} = \text{olefin}) & (2)\\
\mathrm{H + R} & = \mathrm{RH} & (3)\\
\mathrm{H + A} & = \mathrm{R^*} & (4)\\
\mathrm{R^* + M} & = \mathrm{R + M}\ (\mathrm{M} = \text{any molecule}) & (5)\\
\mathrm{R^*} & = \mathrm{CH_3 + A'}(\mathrm{A'} = \text{lower olefin}) & (6)\\
\mathrm{R + R} & = \mathrm{A + RH} & (7)\\
\mathrm{R + R} & = \mathrm{R\text{–}R} & (8)\\
\mathrm{H} + \text{wall} & = \tfrac{1}{2}\mathrm{H_2} + \text{wall} & (9)
\end{array}$$

The catalytic recombination of H results from the cycle (2), (4), (5). Reaction (3) is a minor one since there is little isobutane formed when hydrogen is removed catalytically by reaction with isobutene. Reaction (6) is unimportant since only traces of propene are formed. This does not however necessarily mean that all the R radicals entering into reaction (2) are thermalized: it only implies that they have lost about 5—10 kcal. mole^{-1}, the difference between the C–H and C–C bond strengths in isobutane. The absence of octane implies that reaction (8) is unimportant but because of the uncertain energy of the average R radical this does not imply that (7) is also unimportant: the combination/disproportionation ratio may be very low for the t- or iso-butyl radicals present in this system.

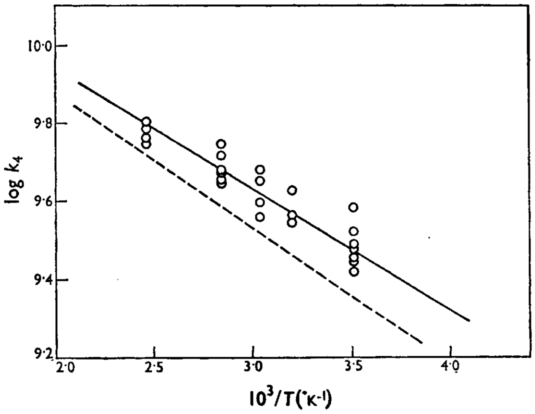

FIGURE. *Arrhenius plot for reaction* (4). *Points and full line, this work*: *broken line, calculated from Kang Yang and Baldwin.*

Since the concentration of A is stationary the rate of removal of H is given to a good approximation by

$$-\mathrm{d}\ \ln[\mathrm{H}]/\mathrm{d}t = 2k_4[\mathrm{A}] + k_9$$

with either isobutane or isobutane + isobutene mixtures added to the H-atom stream. Thus the rate constant k_1 is inaccessible in the present system except in so far as a lower limit can be obtained from the brief time taken to set up the stationary state of A.

From the values of k_4 (l.$^{-1}$ mole sec.$^{-1}$) obtained with various mixtures of titrant gases, and plotted in the Figure, the following Arrhenius equation was derived:

$$\log k_4 = (10{\cdot}56 \pm 0{\cdot}08) - \frac{(1420 \pm 110)(\text{cal.mole}^{-1})}{2{\cdot}303\ \boldsymbol{R}T}$$

The error limits are the 95% confidence limits obtained by the method of least squares. The Figure also gives the line calculated from the data of Kang Yang[2] and Baldwin.[3] Kang Yang competed the reaction of H-atoms with isobutene and propane, and Baldwin gives the Arrhenius equation for reaction (1) with propane as

$$\log_{10}k_1 = (10{\cdot}81 \pm 0{\cdot}2) - \frac{(7800 \pm 500)}{2{\cdot}303\ \boldsymbol{R}T}$$

The formation of isobutane from isobutene implies that either reaction (7) or (3) occurs to a small extent, and indeed some such reactions are necessary if a stationary concentration of A is to be explained. A distinction can be made between the two on the basis of a study of the temperature-dependence of the ratio $[\mathrm{A}]_{\mathrm{SS}}/[\mathrm{RH}]$. If it is assumed that only (3) is important the following Arrhenius equation is obtained:

$$\log(k_2/k_3) = -1{\cdot}17 + 4100/(2{\cdot}303\ \boldsymbol{R}T)$$

If only (7) is important we obtain:

$$\log\,(k_2/k_7^{\frac{1}{2}}) = 5{\cdot}3 + 1100/(2{\cdot}303\ \boldsymbol{R}T)$$

where the 1100 cal.mole^{-1} for $(\frac{1}{2}E_7 - E_2)$ is a maximum value. The first equation seems unlikely since E_3 can hardly be as high as 4000 cal. mole^{-1}. We therefore prefer (7) as the source of the isobutane from isobutene.

(*Received, November* 14*th*, 1966; *Com.* 895.)

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[2] Kang Yang, *J. Amer. Chem. Soc.*, 1962, **84**, 719, 3795.

[3] R. R. Baldwin, D. Jackson, R. W. Walker, and S. J. Webster, "10th International Symposium on Combustion", Combustion Institute, 1965, p. 423.