Abstraction Reaction of the Allyl Radical with Toluene

By R. J. AKERS and J. J. THROSSELL

(*Department of Chemistry, Westfield College, Hampstead, London, N.W.3*)

THERE have been relatively few determinations of the rates of abstraction reactions of allyl radicals. Activation energies for abstraction from cyclopentane,[1] 4-methylpent-1-ene,[2] and toluene[3] have been reported as $31\cdot8 \pm 3\cdot6$, 12, and 12—17 kcal./mole, respectively. In the course of a detailed study of toluene–carrier pyrolyses in a stirred-flow reactor system, the rate of abstraction by allyl radicals from toluene has been determined relative to the rate of combination of allyl + methyl radicals. Allyl radicals were generated by pyrolysis of 4-phenylbut-1-ene between 850 and 950°K. Some experiments were also carried out using hexa-1,5-diene. The main products from the 4-phenylbut-1-ene were propene and hexa-1,5-diene, with hydrogen, methane, ethane, ethylene, allene, and but-1-ene as the more important minor products.

Although the system is fairly complex, it seems clear that the main reaction producing propene is

$$C_3H_5 + C_6H_5{\cdot}CH_3 \rightarrow C_3H_6 + C_6H_5{\cdot}CH_2 \qquad (1)$$

Another possible source, the disproportionation of allyl radicals, may be neglected since the allene/propene ratio $\leqslant 0{\cdot}03$. The rate constant k_1 was estimated from the steady-state condition in the reactor, *i.e.*,

$$f_{C_3H_6} = Vk_1[C_3H_5][C_6H_5{\cdot}CH_3]$$

where $f_{C_3H_6}$ = flow rate of propene from the reactor, in mole sec.$^{-1}$ The allyl radical concentration was determined from the flow rate of but-1-ene, formed by the combination of allyl radicals with methyl radicals,

$$CH_3 + C_3H_5 \rightarrow C_4H_8 \qquad (2)$$

via the methyl radical concentration determined from the flow rate of methane formed by the reaction

$$CH_3 + C_6H_5{\cdot}CH_3 \rightarrow CH_4 + C_6H_5{\cdot}CH_2 \qquad (3)$$

Thus,

$$\frac{k_1}{k_2} = \frac{f_{C_3H_6}}{f_{C_4H_8}} \frac{[CH_3]}{[C_6H_5{\cdot}CH_3]}$$

A detailed discussion of the possible mechanisms of minor product formation, and hence the justification for basing the allyl radical concentration on reaction 2, will be given in a subsequent report.

An Arrhenius plot gave $\log (k_1/k_2) = -0{\cdot}55 - 17{,}200/4{\cdot}574T$.

The cross-combination ratio k_2^2/k_4k_5, where k_4 refers to

$$2C_3H_5 \rightarrow C_6H_{10} \qquad (4)$$

and k_5 to

$$2CH_3 \rightarrow C_2H_6, \qquad (5)$$

was estimated assuming that the contribution to the total ethane production of the dimerization of CH_3 radicals was given by $f'_{C_2H_6} = Vk_5[CH_3]^2$, the remainder of the ethane coming from the sequence

$$H + C_2H_4 \rightarrow C_2H_5 \qquad (6)$$

$$C_2H_5 + C_6H_5{\cdot}CH_3 \rightarrow C_2H_6 + C_6H_5{\cdot}CH_2 \qquad (7)$$

Then

$$k_2^2/k_4k_5 = f^2_{C_3H_8}/f'_{C_2H_6}{\cdot}f_{C_6H_{10}}$$

Taking $k_5 = 5 \times 10^{12}$ cm.^{3} mole^{-1} sec.$^{-1}$, the mean value of the ratio was about 4, although there was some scatter among the individuals. A reasonable value for k_2 would be $k_2 = 10^{12}$ cm.^{3} mole^{-1} sec.$^{-1}$ whence $\log k_1 = 11{\cdot}45 — 17{,}200/4{\cdot}574T$ cm.^{3} mole^{-1} sec.$^{-1}$ and $k_4 = 5 \times 10^{10}$ cm.^{3} mole^{-1} sec.$^{-1}$ Using this value for k_4, reasonably good agreement was obtained between the allyl radical concentrations determined from but-1-ene and from the hexa-1,-5-diene. Nothing is known at present about rates of recombination of allyl radicals, but it may be that a low value of k_4 relative to corresponding values for alkyl radicals should be expected from a consideration of the configuration of the transition state. For the reverse, unimolecular decomposition, reaction (-4)

$$C_6H_{10} \rightarrow 2C_3H_5 \qquad (-4)$$

a relatively low *A*-factor would be expected on the basis that two degrees of internal rotation are lost in the transition state as compared to the normal molecule since the π-electron system in the allyl radical will prevent rotation about the C(2)–C(3) axis. Unpublished work by the present authors indicates that $A_{-4} = 10^{13{\cdot}4}$ sec.$^{-1}$ Similar conclusions in regard to "stiff" transition states have recently been reached by Rabinovitch *et al.*,[5,6] from studies of the decomposition of chemically activated olefins which produce allyl radicals.

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