

Abstraction Reaction of the Allyl Radical with Toluene

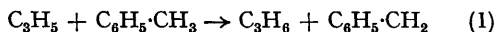
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THERE have been relatively few determinations of the rates of abstraction reactions of allyl radicals. Activation energies for abstraction from cyclopentane,¹ 4-methylpent-1-ene,² and toluene³ have been reported as 31.8 ± 3.6 , 12, and 12–17 kcal./mole, 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.

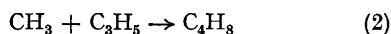
Although the system is fairly complex, it seems clear that the main reaction producing propene is



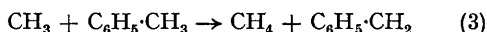
Another possible source, the disproportionation of allyl radicals, may be neglected since the allene/propene ratio ≤ 0.03 . The rate constant k_1 was estimated from the steady-state condition in the reactor, *i.e.*,

$$f_{\text{C}_3\text{H}_4} = V k_1 [\text{C}_3\text{H}_5][\text{C}_6\text{H}_5\cdot\text{CH}_3]$$

where $f_{\text{C}_3\text{H}_4}$ = 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,



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



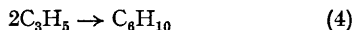
Thus,

$$\frac{k_1}{k_2} = \frac{f_{\text{C}_3\text{H}_4}}{f_{\text{C}_4\text{H}_8}} \frac{[\text{CH}_3]}{[\text{C}_6\text{H}_5\cdot\text{CH}_3]}$$

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 $\log(k_1/k_2) = -0.55 - 17,200/4.574T$.

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

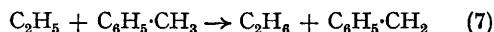
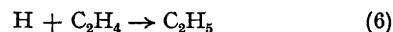


and k_5 to



was estimated assuming that the contribution to

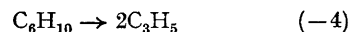
the total ethane production of the dimerization of CH_3 radicals was given by $f'_{\text{C}_2\text{H}_6} = V k_5 [\text{CH}_3]^2$, the remainder of the ethane coming from the sequence



Then

$$k_2^2/k_4k_5 = f_{\text{C}_2\text{H}_6}^2/f'_{\text{C}_2\text{H}_6} f'_{\text{C}_6\text{H}_{10}}$$

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 $\log k_1 = 11.45 - 17,200/4.574T$ 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)



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 $A_{-4} = 10^{13.4}$ 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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¹ A. S. Gordon, S. R. Smith, and J. R. McNesby, *J. Amer. Chem. Soc.*, 1959, **81**, 5059.

² M. Taniowski, *J. Chem. Soc.*, 1965, 7436.

³ M. Szwarc, B. N. Ghosh, and A. H. Sehon, *J. Chem. Phys.*, 1950, **18**, 1142.

⁴ M. F. R. Mulcahy, D. J. Williams, and J. R. Wilmshurst, *Austral. J. Chem.*, 1964, **17**, 1329.

⁵ F. H. Dorer and B. S. Rabinovitch, *J. Phys. Chem.*, 1965, **69**, 1952.

⁶ J. W. Simons, B. S. Rabinovitch, and F. H. Dorer, *J. Phys. Chem.*, 1966, **70**, 1076.