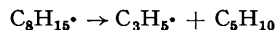
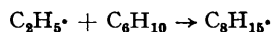


Disproportionation Reactions of The Allyl Radical

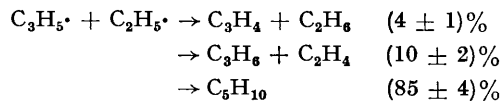
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ALLYL radicals are important intermediates in the pyrolysis, photolysis, and radiolysis of many hydrocarbon systems, and are commonly consumed by interaction with alkyl radicals. For want of data, the ratio of disproportionation to combination is often assumed to be negligibly small in such interactions. To test this assumption we have generated allyl radicals in the presence of a large excess of ethyl radicals by illuminating a gaseous mixture of diethyl ketone and diallyl with 3130 Å radiation between 134 and 175° c. Allyl radicals are formed by a sequence of addition and dismutation:



Allyl radicals react only with ethyl radicals under our conditions; two modes of disproportionation yield allene and propene, respectively, and combination gives pent-1-ene. The only other source of these products is the dismutation, which yields one molecule of pent-1-ene for each allyl radical. We can therefore calculate the relative rates:



These are consistent with the corresponding

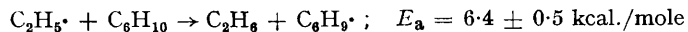
$$E_a = 6.9 \pm 0.3 \text{ kcal./mole}$$

$$E_a = 17 \pm 4 \text{ kcal./mole}$$

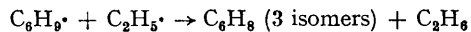
values of 3, 8, and 89% calculated from the equation:¹

$$\log k_{\text{dis}}/k_{\text{com}} = 0.131(\sum S^{\circ}_{\text{dis}} - S^{\circ}_{\text{com}}) - 5.47$$

Disproportionation between allyl and ethyl radicals is clearly not negligibly small. In contrast, the α -allyl-allyl radical shows little tendency to disproportionate. This radical is generated by metathesis:



Product analysis indicates that disproportionation occurs:



but only 0.4% of the α -allyl-allyl radicals react in this way.

¹R. A. Holroyd and G. W. Klein, *J. Phys. Chem.*, 1963, **67**, 2273.

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