Disproportionation Reactions of The Allyl Radical

By D. G. L. JAMES and G. E. TROUGHTON

(*Department of Chemistry, University of British Columbia, Vancouver 8, B.C., Canada*)

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:

$$C_2H_5^{\bullet} + C_6H_{10} \rightarrow C_8H_{15}^{\bullet} \qquad E_a = 6{\cdot}9 \pm 0{\cdot}3 \text{ kcal./mole}$$

$$C_8H_{15}^{\bullet} \rightarrow C_3H_5^{\bullet} + C_5H_{10} \qquad E_a = 17 \pm 4 \text{ kcal./mole}$$

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:

$$\begin{aligned} C_3H_5^{\bullet} + C_2H_5^{\bullet} &\rightarrow C_3H_4 + C_2H_6 && (4 \pm 1)\% \\ &\rightarrow C_3H_6 + C_2H_4 && (10 \pm 2)\% \\ &\rightarrow C_5H_{10} && (85 \pm 4)\% \end{aligned}$$

These are consistent with the corresponding

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

$$\log k_{dis}/k_{com} = 0{\cdot}131(\Sigma S^{o}_{dis} - S^{o}_{com}) - 5{\cdot}47$$

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:

$$C_2H_5{\cdot} + C_6H_{10} \rightarrow C_2H_6 + C_6H_9{\cdot}\ ; \quad E_a = 6{\cdot}4 \pm 0{\cdot}5 \text{ kcal./mole}$$

Product analysis indicates that disproportionation occurs:

$$C_6H_9{\cdot} + C_2H_5{\cdot} \rightarrow C_6H_8 \text{ (3 isomers)} + C_2H_6$$

but only 0·4% of the α-allyl-allyl radicals react in this way.

(*Received, February 15th*, 1965.)

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