# Characteristic Reactions of the Cyclohexadienyl Radical below 200°C

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EXTENSIVE delocalization in the π-electron system of the cyclohexadienyl radical is revealed by its electron spin resonance spectrum,[1] and an associated stabilization energy of 24 ± 1 kcal./mole has recently been estimated for this radical.[2] Such a degree of stabilization should be sufficient to suppress the normal radical reactions of metathesis and addition between room temperature and 200° C, but may be insufficient to ensure that the cyclohexadienyl radical is thermally stable against aromatization by loss of a hydrogen atom throughout this range. The characteristic reactions of the cyclohexadienyl radical should therefore be limited to bimolecular combination and disproportionation and unimolecular thermal dissociation. We have recently confirmed this hypothesis, and have investigated the patterns of some typical bimolecular interactions and the energetics of the unimolecular dissociation.

Gaseous mixtures of azomethane and cyclohexa-1,4-diene were photolyzed with 3660 Å radiation, when cyclohexadienyl radicals were generated by metathesis between the primary methyl radicals and cyclohexa-1,4-diene:

$(E_a = 5\cdot5$ kcal./mole)
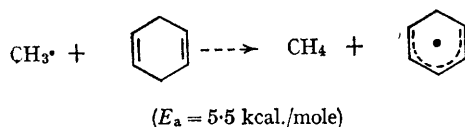
The majority of methyl radicals escaped this scavenging process when the ratio of cyclohexadiene to azomethane was low and the intensity of illumination high. Cross interaction of methyl and cyclohexadienyl radicals could then be studied by analysis of the products, and was found to conform to the pattern:
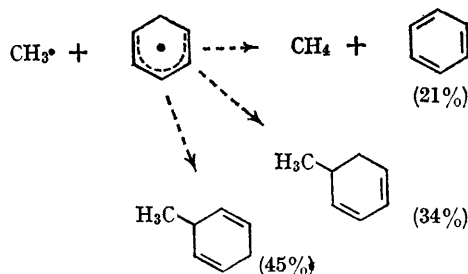

between 23 and 117°. Conversely, exhaustive scavenging of the methyl radicals by cyclohexadiene occurred when the ratio of cyclohexadiene to azomethane was high and the intensity of illumination very low, and was confirmed by the absence of peaks for the methylcyclohexadienes from the chromatogram. Mutual interaction of cyclohexadienyl radicals then occurred exclusively, and conformed to the pattern:
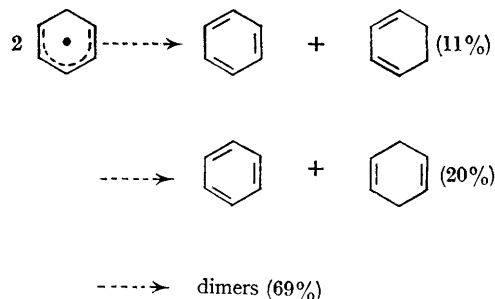
between 63 and 101°. These patterns are in general agreement with the less complete results obtained for these systems in the liquid phase at room temperature,[3,4] and imply a correlation between reactivity and spin density[1] at the ortho- and para-sites of the cyclohexadienyl radical.

At 136° cyclohexene appeared among the products of this system under conditions of exhaustive scavenging. Furthermore, the relative abundance of both cyclohexene and benzene increased rapidly as the reaction temperature was raised, until at 186° the rate of formation of each exceeded the rate of the primary generation of cyclohexadienyl radicals, indicating a chain mechanism. The results are consistent with the sequence:

$(E_a = 31$ kcal./mole)
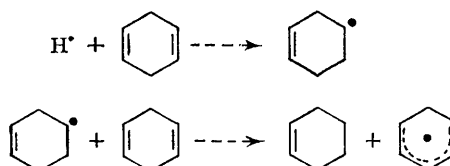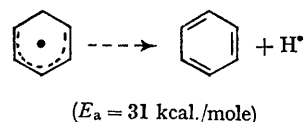
The Arrhenius activation energy for the addition of the hydrogen atom to benzene is 3·8 kcal./mole.[5] Combining this with our value for the reverse process, we may derive the values of 45 kcal./mole for the enthalpy of formation of the cyclohexadienyl radical, 70 kcal./mole for the enthalpy of dissociation of the methylenic carbon–hydrogen bond of cyclohexa-1,4-diene, and 24 kcal./mole for the stabilization energy of the cyclohexadienyl radical, in complete agreement with an independent estimate.[2]

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