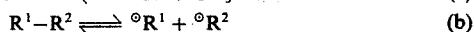
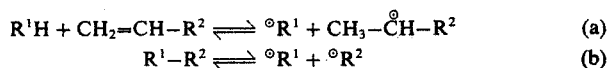


Formation of Alkyl Radicals by Thermal Bimolecular Reaction of Alkanes and Alkenes

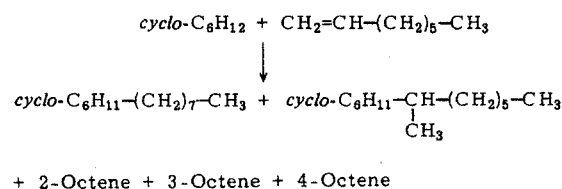
By Jürgen O. Metzger*

The symproportionation (a) of an alkane and an alkene to give two alkyl radicals is a thermodynamically feasible elementary reaction that has long been sought^[1]. It is the reverse of the disproportionation of alkyl radicals. In contrast to the intensively investigated homolysis of single bonds (b)—the reversal of the recombination of alkyl radicals—the symproportionation has so far never been unequivocally demonstrated^[2].



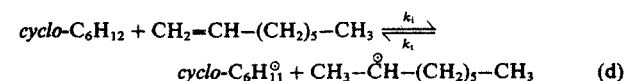
The activation enthalpy of the bimolecular reaction (a) is substantially lower than that of the monomolecular homolysis (b); it is equal to the negative reaction enthalpy of the radical disproportionation and is thus easy to evaluate by thermochemical methods^[3]. In some special cases a knowledge of the symproportionation was considered essential for interpreting the course of a reaction: A classical example is the initiation reaction of the spontaneous polymerization of styrene. However, recent findings by Pryor would appear to contradict such an initiation reaction^[1b].

We have already shown in earlier experiments that alkanes can be added to alkenes in a thermally initiated reaction^[10]. Kinetic studies on the addition of cyclohexane to 1-octene clearly revealed that a radical chain reaction is involved.



Cyclohexane was allowed to react with 1-octene (molar ratio 100:1) at 360–450°C and 200 bar with total exclusion of oxygen until ca. 90% conversion. 1-Octene reacts in two parallel reactions with formation of the adducts 1-cyclohexyloctane and 2-cyclohexyloctane (total yield of adducts ca. 50% referred to 1-octene; ratio of the two regioisomers 94.9:5.1) as well as isomeric octenes. In addition, *n*-octane and cyclohexylcyclohexane are also detected in the product mixture. The kinetics of the initiation reaction can be described in terms of equation (c).

$$v_{\text{start}} = k_i[1\text{-octene}][\text{cyclohexane}] \quad (\text{c})$$



The experimentally determined value of $\lg(k_i/k_t)^{1/2} = -6.89$ yields the quasi steady-state radical concentration $[\text{cyclohexyl}]_{\text{exp}} = 5.82 \times 10^{-8}$ mol/L at 450°C and 200 bar. This value is in good agreement with the radical concentration of $[\text{cyclohexyl}]_{\text{calc}} = 5.83 \times 10^{-8}$ mol/L obtained on

calculation of the equilibrium (d) from the thermochemical data.

The results of the kinetic investigation can only be satisfactorily explained in terms of the initiation reaction (d). Other initiation reactions such as homolysis of CC bonds of the alkane and of the alkene, bimolecular disproportionation of alkene, or intermediary formation of a 1,2-diradical combined with an H-abstraction from the alkane, lead to other rate equations, other activation energies, or completely different A factors.

A two-step reaction path *via* a 1,2-diradical can be confidently ruled out; it would be orders of magnitude slower than the observed reaction. This means that the thermal formation of radicals from alkane and alkene must proceed in one step as bimolecular metathesis, *i. e.* indeed as a reversal of the disproportionation of alkyl radicals with the same transition state^[1a]. Thus, the kinetics and thermodynamics are consistent with an initiation reaction as depicted in equation (a). This can be used for the investigation of radical reactions over a wide range of temperatures and without the addition of special radical initiators. This type of reaction obviously plays an important role in cracking processes^[2b]; it must also proceed intramolecularly and is possibly of significance in thermal intramolecular reactions such as the retro-ene reaction.

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cyclo-C₆H₁₂, 110-82-7; CH₂=CH(CH₂)₅CH₃, 111-66-0.

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