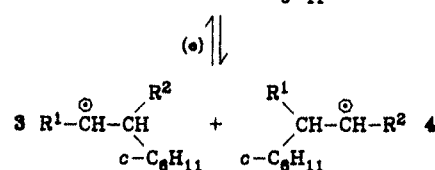
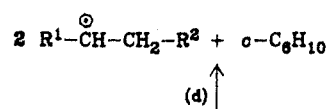


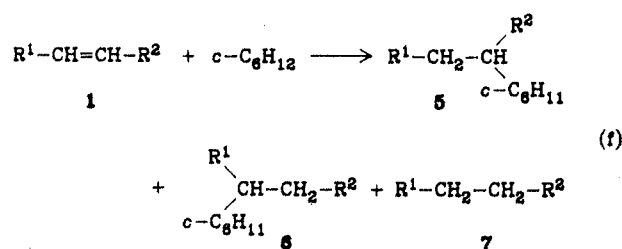
known.^[2] The first experimental example of reaction (d) is reported here.

Reaction (d) should be possible to observe as a reaction competing with the addition (e) of an alkyl radical to the CC double bond of an alkene.



a, R¹ = R² = COOMe; b, R¹ = Ph; R² = COOMe

As an example, the addition of cyclohexane to dimethyl fumarate **1a** and to methyl cinnamate **1b** was studied. This radical chain reaction (f) can be carried out above 250°C under mainly thermodynamic control with respect to the addition (e).^[3]



Besides the addition products **5** (via **3**) and **6** (via **4**), the dihydro product **7** is formed from **1a** and **1b** in a reaction that is first order with respect to alkene **1b**. This may be readily explained by the exothermic reaction (d) and subsequent stabilization of the radical **2** by H abstraction from the solvent cyclohexane. The complementary product, cyclohexene, was identified in the reaction mixture (**7a**:cyclohexene, ca. 1.2:1) as the dibromo adduct.

The experimental results (Table 1) are easily understandable. The metathesis (d), as a "closed-shell" reaction, has a higher activation energy than the "open-shell" reaction (b). Accordingly, the amount of the dihydro product **7** increases relative to the amounts of addition products **5** and **6** with increasing temperature (experiments 1-5). The reaction rate of (d) is independent of the concentration of H donor in contrast to that of (b). Therefore, the relative amount of **7** increases with lower concentrations of cyclohexane: **7** can even become the main product (experiments 5-9). The addition of radical formers such as 2,3-diphenylbutane^[4] increases the rate of formation of both competitive products equally (experiment 4). Activated

Metathesis of Alkyl Radicals and Alkenes— a Novel Elementary Reaction of Alkyl Radicals

By Jürgen O. Metzger*

A notable gap exists in the series of known elementary reactions (a)-(c) of alkyl radicals in which a hydrogen atom is transferred: the thermochemically possible transfer (d) of a β-hydrogen atom of an alkyl radical to an alkene with the formation of a new alkyl radical and a new alkene.

The search for an example of the frequently postulated^[1] reaction (d) appeared promising since corresponding reactions in analogous oxygen-containing systems are

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Table 1. Reactions of cyclohexane with dimethyl fumarate **1a** and methyl cinnamate **1b** [a]. **5a = 6a**.

No.	T [°C]	[c-C ₆ H ₁₂] [b]	Conversion 1a [c]	[5a] [c]	[7a] [c]	5a/7a	Conversion 1b [c]	[5b] [c]	[6b] [c]	[7b] [c]	Σ 5b, 6b/7b
1 [d]	250	5.76	> 99	71	3.1	22.9	11	4.2	1.3	0.4	13.7
2	360	5.56	> 99	78	5.3	14.7	46	22.7	8.8	8.0	3.9
3	390	5.13	> 99	75.6	6.4	11.8	25 [e]	9.5	3.8	4.7	2.8
4	390	5.13	—	—	—	—	56 [e, f]	18.9	7.7	9.5	2.8
5	400	5.00	> 99	70.1	6.2	11.3	55	20.7	8.3	11.4	2.5
6	400	3.65	> 99	65.5	7.1	9.2	44	14.6	5.9	9.5	2.2
7	400	2.44	97	62.9	7.6	8.3	30	8.2	3.4	6.8	1.7
8	400	0.90	79	40.7	9.1	4.5	10	1.7	0.7	2.3	1.0
9	400	0.40	49	14.1	7.7	1.8	4	0.4	0.2	0.9	0.7

[a] With the exception of No. 1, the reactions were carried out in a high-pressure, high-temperature flow reactor [3,7] in a stainless steel capillary; reaction time 2–3 min; molar ratio cyclohexane : **1** = 1000 : 1. The concentration of cyclohexane was adjusted by variation of the pressure. The addition products are stable under the reaction conditions. Under the same conditions at 400 °C, less than 1% of **5b** decomposes to **7b**. [b] mol/L. [c] Yields and conversion in mol-% based on unreacted **1**. [d] Reaction in duran glass ampules; reaction time 10 min. Upon addition of activated charcoal (1 mg/mL reaction solution) as radical trap, only traces of the products were formed. [e] Reaction time 1 min. [f] Addition of 10 mol-% 2,3-diphenylbutane based on **1b**.

charcoal as a radical trap inhibits the formation of both products (experiment 1). The kinetic chain length is estimated to be 100 from the amount of chain-terminating product cyclohexylcyclohexane (ca. 1 mol-% based on reacted starting material **1a**).

Alternative explanations for the formation of the dihydro product **7**, such as the frequently postulated pericyclic H transfer^[5] or the symproportionation of alkene and alkane to give two alkyl radicals (a),^[3,6] are clearly ruled out on the basis of the experimentally confirmed radical chain reaction. A conceivable β-cleavage of the cyclohexyl radical (c) and addition of the H atom to the alkene **1** would be a reaction of zero order with respect to **1** and thus is also ruled out.

The unequivocal experimental proof of the metathesis of alkyl radicals and alkenes (d) and the reaction conditions required for it to occur show that chain transfer during polymerization^[1a] via this reaction, which has been frequently postulated, is unlikely. A thermal pericyclic hydrogenation of alkenes with alkanes^[5] is also kinetically unlikely.

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