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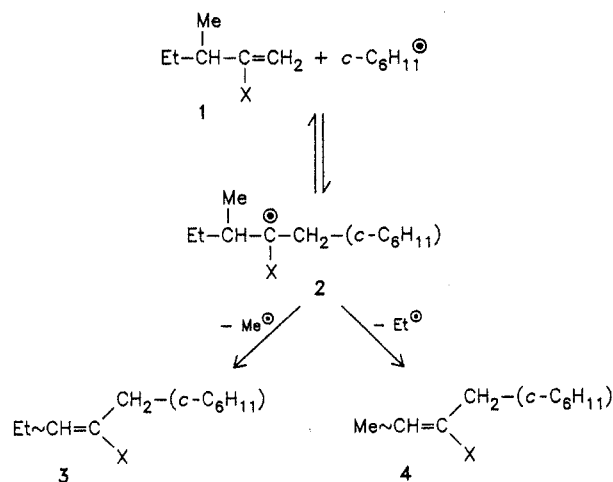
Bei der Wiedergabe von Gebrauchsnamen, Handelsnamen, Warenbezeichnungen und dgl. handelt es sich häufig um gesetzlich geschützte eingetragene Warenzeichen, auch wenn sie nicht als solche mit \* gekennzeichnet sind.

### The Influence of Polar and Steric Effects on the Selectivity of the $\beta$ -Cleavage of Alkyl Radicals\*\*

By Kurt Klenke, Jürgen O. Metzger,\* and Stefan Lübben

The  $\beta$ -cleavage of radicals plays an important role in the complex reaction mechanisms of pyrolysis, combustion, photooxidation, the thermal degradation of polymers,<sup>[1]</sup> and increasingly also in preparatively useful reactions.<sup>[2]</sup> The selectivity of the  $\beta$ -cleavage has been the subject of very few studies. We have therefore carried out experiments aimed at demonstrating the influence of polar and steric effects on the  $\beta$ -cleavage of alkyl radicals.

The radicals **2** were generated by addition of cyclohexyl radicals ( $c\text{-C}_6\text{H}_{11}^\bullet$ ) to the alkenes **1**. These fragment in an intramolecular competition reaction to give the products **3** and **4** with cleavage of methyl and ethyl radicals, respectively.<sup>[3]</sup> The polar effect of X on the selectivity of the radical cleavage can be investigated by variation of the substituents X on the radical carbon atom.<sup>[5]</sup> The products **3** and **4** are each formed as (*E*)- and (*Z*)-isomers, so that also the polar effect of X on the stereoselectivity can be measured.



a, X = COOMe; b, X = Ph; c, X = *p*-MeO-C<sub>6</sub>H<sub>4</sub>; d, X = *p*-Cl-C<sub>6</sub>H<sub>4</sub>

The results (Table 1) are in many respects surprising. The benzyl radical **2b** fragments more slowly than the methoxycarbonylalkyl radical **2a**, since **2b** is about 15 kJ/mol more stable than **2a**.<sup>[6]</sup> The selectivity of the cleavage of the more reactive radical **2a** is, however, clearly greater. The stereoselectivity is also greater. This reversal of the reactivity-selectivity principle can be explained, in analogy to the radical addition to alkenes, in terms of the polar effect of

the leaving radical and of the substituents X in the alkyl radical **2**.<sup>[7]</sup> The cleavage of the more nucleophilic ethyl compared to the methyl radical is accelerated by the electron-withdrawing substituent X = COOMe. This polar effect is especially evident on considering the difference in the activation energies, which amounts to ca. 18 kJ/mol for the fragmentation of **2a** to **3a** and **4a**. The difference in the stability of the products is only ca. 8 kJ/mol.<sup>[8]</sup> The polar effect of the methoxycarbonyl group is thus about 10 kJ/mol referred to the two leaving groups in question and increases the selectivity. The converse is true in the case of the nucleophilic radical **2b**, which gives the more electron-

Table 1.  $\beta$ -Cleavage of the radicals **2** to give the products **3** and **4** at 350°C [3].

2	Yield [a] [mol-%]	[4]/[3] [b]	[( <i>E</i> )-4]/[( <i>Z</i> )-4]	$\Delta E_a$ [c] [kJ/mol]	$A_4/A_3$ [c]
a	14.7	17.8 (1.25)	3	-18.2 ± 2	0.6 ± 0.2
b	6.0	7.3 (0.86)	2.5	-4.5 ± 0.5	3.0 ± 0.3
c	7.4	8.9 (0.95)	2.3	-8.4 ± 0.6	1.6 ± 0.2
d	9.0	9.4 (0.97)	2.3	-7.2 ± 0.8	2.4 ± 0.5

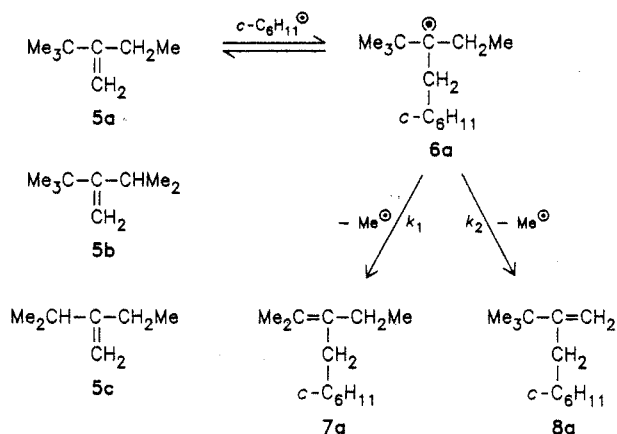
[a] Sum of the  $\beta$ -cleavage products **3** and **4** based on alkene **1** used. [b] In parenthesis: selectivity  $S = \lg([4]/[3])$ . [c]  $\Delta E_a = E_a(4) - E_a(3)$ ; 300-450°C.

rich alkenes **3b** and **4b**. The cleavage of nucleophilic radicals is all the more difficult the more nucleophilic they are. The cleavage of the ethyl radical is more strongly retarded than that of the methyl radical. The difference of 4.5 kJ/mol in the activation energies again makes the polar effect especially noticeable. The transition states lie ca. 3.5 kJ/mol closer together than the ground states of the products that are formed. In this case the polar effect of the phenyl group reduces the selectivity of the  $\beta$ -cleavage.

Smaller but significant effects are observable on comparing the fragmentation of the radicals **2b**, **2c** and **2d** (Table 1). The electron withdrawal by chlorine in **2d** increases the reactivity and the selectivity compared to **2b**. Surprisingly, the *p*-methoxy group in **2c** apparently reacts only through its -I effect. The selectivity of the ethyl/methyl cleavage is increased significantly compared to **2b**. This is understandable only in terms of the *p*-methoxy group having an electron-attracting effect.

The ratios **6** were obtained by the addition of cyclohexyl radicals to the alkenes **5**. These fragment in a competition reaction to give the products **7** and **8** and a methyl radical.<sup>[9]</sup> The relative effect of the substituents attached to the carbon atom at which the C-C bond is ruptured on the cleavage of the methyl radical can be determined from the ratio of the products **7** : **8**.

The fragmentation is remarkably selective (Scheme 2): the thermodynamically more stable alkene **7** is formed in only slight excess at 400°C. Normalized to the number of cleavable methyl groups, the methyl radical is even preferentially cleaved from the lesser substituted alkyl group to give the thermodynamically more unstable alkene **8**.



\*] Priv.-Doz. Dr. J. O. Metzger, Dr. K. Klenke, Dipl.-Chem. S. Lübben, Fachbereich Chemie der Universität Carl-von-Ossietzky-Strasse 9-11, D-2900 Oldenburg (FRG)

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Table 2. Selectivity of the  $\beta$ -cleavage of the radicals **6** at 400°C.

<b>6</b>	[ <b>7</b> ] [mol-%]	[ <b>8</b> ] [mol-%]	$[k_2/k_1]_{\text{norm.}}$ [a]	S [b]
<b>a</b>	57	43	2.3	0.36
<b>b</b>	52	48 [c]	1.4	0.15
<b>c</b>	62 [c]	38	1.2	0.08

[a] Relative rate normalized to one methyl group. [b]  $S = \lg k_2/k_1$ . [c] (*E*)- and (*Z*)-products.

At first sight this result is surprising. One might expect that the stabler alkene is formed with higher selectivity<sup>[10]</sup> and that the cleavage of the methyl radical preferably occurs at the more substituted alkyl group. However, the result is understandable if the  $\beta$ -cleavage is considered from the point of view of the addition (Fig. 1). Substituents on the C atom that is attacked sterically hinder the addition.<sup>[7, 12]</sup> The free enthalpy of activation for the addition of the methyl radical to the alkene **7** is raised in comparison

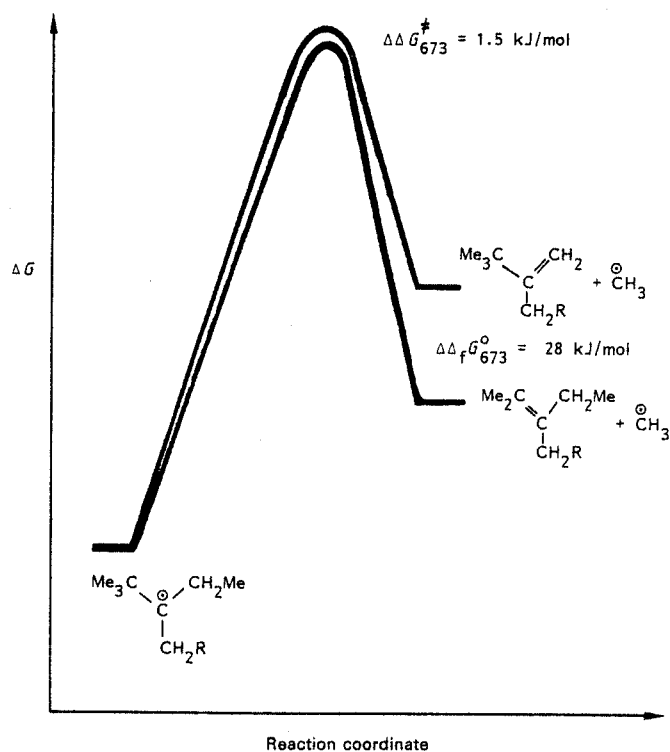


Fig. 1. Reaction coordinate of the  $\beta$ -cleavage of radical **6a**.

to the alkene **8** by the larger number of methyl groups on the C atom that is attacked. This means that the transition state of the  $\beta$ -cleavage is correspondingly also raised and the reaction retarded.<sup>[13]</sup>

The steric effects of substituents in  $\beta$ -cleavages should also play an important role in  $\alpha$ -cleavages. Evidence to this effect is provided, for example, in  $S_H$  reactions of alkyltin<sup>[14]</sup> and alkylboron compounds.<sup>[15]</sup> Our results show that it is essential that polar and steric effects be taken into account as well the generally dominating influences of product stability<sup>[11]</sup> when considering the selectivity of  $\beta$ -cleavage.

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**1a**, 3070-70-0; **1b**, 26452-86-8; **1c**, 115982-37-1; **1d**, 115982-38-2; **2a**, 115982-39-3; **2b**, 115982-40-6; **2c**, 115982-41-7; **2d**, 115982-42-8; **3a**, 115982-43-9; **3b**, 115982-44-0; **3c**, 115982-45-1; **3d**, 115982-46-2; (*E*)-**4a**, 115982-47-3; (*Z*)-**4a**, 115982-51-9; (*E*)-**4b**, 115982-48-4; (*Z*)-**4b**, 115982-52-0; (*E*)-**4c**, 115982-49-5; (*Z*)-**4c**, 115982-53-1; (*E*)-**4d**, 115982-50-8; (*Z*)-**4d**, 115982-54-2; **5a**, 18231-53-3; **5b**, 20442-64-2; **5c**, 7357-93-9; **6a**, 115982-55-3; **6b**, 115982-56-4; **6c**, 115982-57-5; **7a**, 115982-58-6; **7b**, 115982-59-7; (*Z*)-**7c**, 115982-60-0; (*E*)-**7c**, 115982-61-1; **8a**, 115982-62-2; (*Z*)-**8b**, 115982-63-3; (*E*)-**8b**, 115982-64-4; **8c**, 115982-65-5; cyclohexane, 110-82-7; cyclohexyl, 3170-58-9.

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- [9] 0.01 mol/L solutions of the alkene **5** in cyclohexane were heated at 350–450°C and 200 bar for 20 min as described in [3]. The conversions were maximally 4 mol-%.
- [10] As models for examining the stability of the alkenes **7** and **8**, alkenes were chosen in which the  $\text{CH}_2\text{C}_6\text{H}_{11}$  group is replaced by the  $\text{CH}_3$  group. The thermochemical data of these alkenes are tabulated in Ref. [11] (e.g.  $\Delta\Delta G_{600}^\circ = 28$  kJ/mol for 2,3,3-trimethyl-1-butene and 2,3-dimethyl-2-pentene).
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