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The Penultimate Unit Effect of Radical Copolymerization

B. Giese and R. Engelbrecht

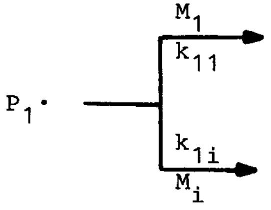
Institut für Organische Chemie und Biochemie, Technische Hochschule Darmstadt,
Petersenstraße 22, 6100 Darmstadt, Federal Republic of Germany

SUMMARY

The effect of polar β- and γ-substituents on the selectivity of alkyl radical additions to alkenes has been measured. Although these substituents don't influence the nucleophilicity of radicals they reduce the rate of addition to diethyl fumarate. It is concluded that the penultimate unit effect is a through space repulsive interaction of polar substituents between the radicals and the alkenes.

INTRODUCTION

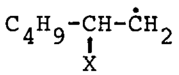
In radical copolymerization reactions of alkenes M_1 with different monomers M_i the copolymerization parameters r_1, that are the selectivities of polymeric radicals $P_1\cdot$ in competition reactions between M_1 and M_i, can be correlated with addition rates of alkyl radicals to alkenes (JENKINS 1974; GIESE and MEIXNER 1980).



$$r_1 = \frac{k_{11}}{k_{1i}}$$

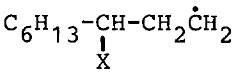
If steric effects are small (TEDDER 1982; GIESE 1983) substituents at radical C-atoms influence the selectivity of radicals mainly by polar effects, which can be described by the frontier molecular orbital theory (FLEMING 1976; GIESE 1983).

Since copolymerization reactivity ratios r_1 sometimes depend on the nature of the penultimate unit of the polymeric radical $P_1\cdot$ (JENKINS 1974), remote substituents at radicals should effect addition rates. To proof this we have measured the selectivities of radicals **1** and **2** with substituents X at β- and γ-carbon atoms.



$C_4H_9\text{-}\underset{X}{CH}\text{-}\dot{C}H_2$

1



$C_6H_{13}\text{-}\underset{X}{CH}\text{-}CH_2\dot{C}H_2$

2

The rel. rates where measured by the recently developed "mercury method" (GIESE, KRETZSCHMAR and MEIXNER 1980): Reduction of alkyl mercuric chloride **3** with $NaBH_4$ generates alkyl radicals **6** (HILL and WHITESIDES 1974) that react with alkenes **7** via adduct radicals **8** to yield products **9** and the alkylmercury radical **5** that carries the chain.

$$\underset{\mathbf{3}}{RHgCl} \xrightarrow{NaBH_4} \underset{\mathbf{4}}{RHgH} \xrightarrow{-H\cdot} \underset{\mathbf{5}}{RHg\cdot} \xrightarrow{-Hg} \underset{\mathbf{6}}{R\cdot}$$

$$\underset{\mathbf{4}}{R\cdot} + \underset{\mathbf{7}}{YCH{=}CHZ} \longrightarrow \underset{\mathbf{8}}{R\text{-}CHY\text{-}\dot{C}HZ} \longrightarrow \underset{\mathbf{9}}{R\text{-}CHY\text{-}CH_2Z} + \underset{\mathbf{5}}{RHg\cdot}$$

The precursors **10** and **11** of the radicals **1** and **2** were synthesized by mercuration of alkyl halides and solvomercuration of alkenes and cyclopropanes [ZELLER, STRAUB and LEDITSCHKE 1974].

$$\underset{\mathbf{10}}{C_4H_9\text{-}CHX\text{-}CH_2HgCl} \xrightarrow{NaBH_4} \mathbf{1} \xrightarrow[k_1]{\mathbf{7}} C_4H_9\text{-}CHX\text{-}CH_2\text{-}CHY\text{-}\dot{C}HZ$$

$$\underset{\mathbf{11}}{C_6H_{13}CHXCH_2CH_2HgCl} \xrightarrow{NaBH_4} \mathbf{2} \xrightarrow[k_2]{\mathbf{7}} C_6H_{13}CHXCH_2CH_2CHY\dot{C}HZ$$

EXPERIMENTAL

About 0.3 mmol of organomercuric salts **10** and **11** and 3.0 to 30 mmoles of the alkene pairs methyl α-chloroacrylate/methyl acrylate or diethyl fumarate/methyl acrylate were dissolved in 10-20 ml CH_2Cl_2. At 20°C 0.5-1.5 mmol $NaBH_4$ in 0.5-2.0 ml H_2O was added. After 5-30 min the mixture was filtered and analyzed by gas chromatography. From the ratio of the products rel. rates k_1 and k_2 of additions are calculated according to pseudo-first order kinetics (TABLE 1).

RESULTS AND DISCUSSION

To proof whether remote substituents X influence the nucleophilicity of radicals **1** and **2** rel. rates in a methyl chloroacrylate/methyl acrylate competition system were measured. The chorine atom at the alkene lowers the energy of the LUMO (lowest unoccupied molecular orbital) of the acrylate and, therefore, enhances the rate of addition of nucleophilic radicals (GIESE 1983). The data of TABLE 1 show for substituted and unsubstituted radicals **1** and **2** a rate increase with methyl chloroacrylate of 11±2. Therefore, remote substituents X at radicals **1** and **2** exert no effect on the nucleophilicity of these radicals.

TABLE 1

Rel. rates of radicals **1** (k_1) and **2** (k_2) with methyl chloroacrylate and diethyl fumarate at 25°C in CH_2Cl_2 (mean error ± 5%). The rel. rate of methyl acrylate ($H_2C{=}CHCO_2CH_3$) is defined to 1.0.

	$CH_2{=}CClCO_2CH_3$		$H_5C_2O_2CCH{=}CHCO_2C_2H_5$	
X	k_1	k_2	k_1	k_2
H	9.0	9.0	2.8	2.8
C_2H_5	12		2.2	
OCH_3	11	13	1.1	2.0
$O{-}\overset{\overset{O}{\|}}{C}{-}CH_3$	9.5	10	0.73	1.6

On the other hand, in a diethyl fumarate/methyl acrylate competition system remote substituents X influence the rate of radical attack. An OCH_3 and OAc group at the β-position of radical $\underline{\underline{1}}$ reduces the selectivities by factors of 2.5 and 3.8, respectively. This can not be explained by steric effects because an ethyl group ($X=C_2H_5$) has nearly no effect. It is more likely that this rate decrease reflects a repulsive through space interaction between the polar substituents X and the ester group at the attacked C-atom of the diethyl fumarate. With X=OAc this leads to a reversal of the selectivity of radical $\underline{\underline{1}}$, so that diethyl fumarate now reacts slower than methyl acrylate (TABLE 1). The repulsive interaction between X and the ester group of the fumarate is smaller with γ-substituted radicals $\underline{\underline{2}}$, but an OAc substituent still has a rate reducing effect of 1.7.

The penultimate unit effect can, therefore, be explained by a through space repulsive interaction of polar substituents at the radicals and the alkenes.

ACKNOWLEDGEMENT

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