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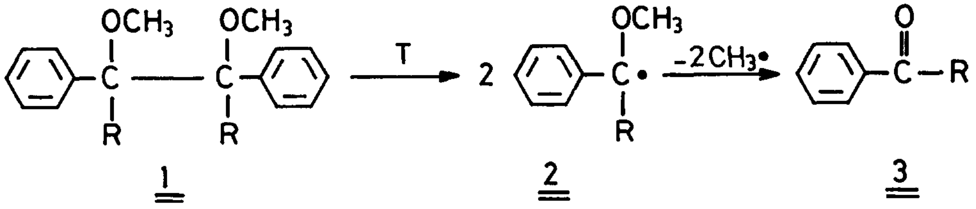
ON THE STABILIZATION ENERGY OF α-METHOXYALKYL RADICALS[1)]*

Hermann Birkhofer, Hans-Dieter Beckhaus and Christoph Rüchardt[+)]
Chemisches Laboratorium, Universität Freiburg, Albertstr. 21, D-7800 Freiburg

Abstract: A stabilization energy of 1.5-2.0 kcal·mol^{-1} is estimated for α-methoxyalkyl radicals from the strain enthalpies and the free enthalpies of thermal decomposition of three glycol ethers **1**.

The influence of α-methoxy groups on the rates of formation of free radicals is strongly variing from reaction to reaction[2)]. It can exert a rate enhancing factor of 10^5, when polar effects are dominating[3)], but only a factor of 10 or less in other reactions e.g. two step thermal rearrangements[4)] or azo thermolyses[5)]. A stabilization energy of ∿ 5 kcal·mol^{-1} can be estimated from bond strength data determined by kinetic procedures[6)].

We recently were successful in separating steric substituent effects from electronic stabilization effects on the rates of formation of carbon radicals in CC-cleavage reactions[7,8)] which are free from polar effects[8)]. Therefore, we investigated now the thermal decomposition of three glycol ethers **1**[9)] into radicals **2** and ketones **3** and determined their strain enthalpies H_s from heats of combustion data[1b)] and by molecular mechanics calculations[10)].



$R = CH_3, C_2H_5$

Table Thermal Stability[a] and Strain Enthalpy[10] of 1

R	Konfig.	$\Delta G^{\ddagger}$(300°C) kcal·mol^{-1}	$\Delta H^{\ddagger}$ kcal·mol^{-1}	$\Delta S^{\ddagger}$ e.u.	H_s[b] kcal·mol^{-1}	yield 3[c] %
CH_3	D,L	39.0±0.5	47.3±0.3	14.5±0.6	7.6[d]	77(m),80(t)
CH_3	meso	39.2±0.7	46.2±0.6	12.3±0.9	7.0	64(m)
C_2H_5	meso	34.5±0.7	44.0±0.5	16.6±1.0	15.9	68(m),67(t)

a) The activation parameters are derived from 4-5 kinetic runs over a temperature range of 45-50°C with statistical error analysis[1b,8].

b) See Lit.[7-8] and [10] for definition and calculation of H_s by molecular mechanics.

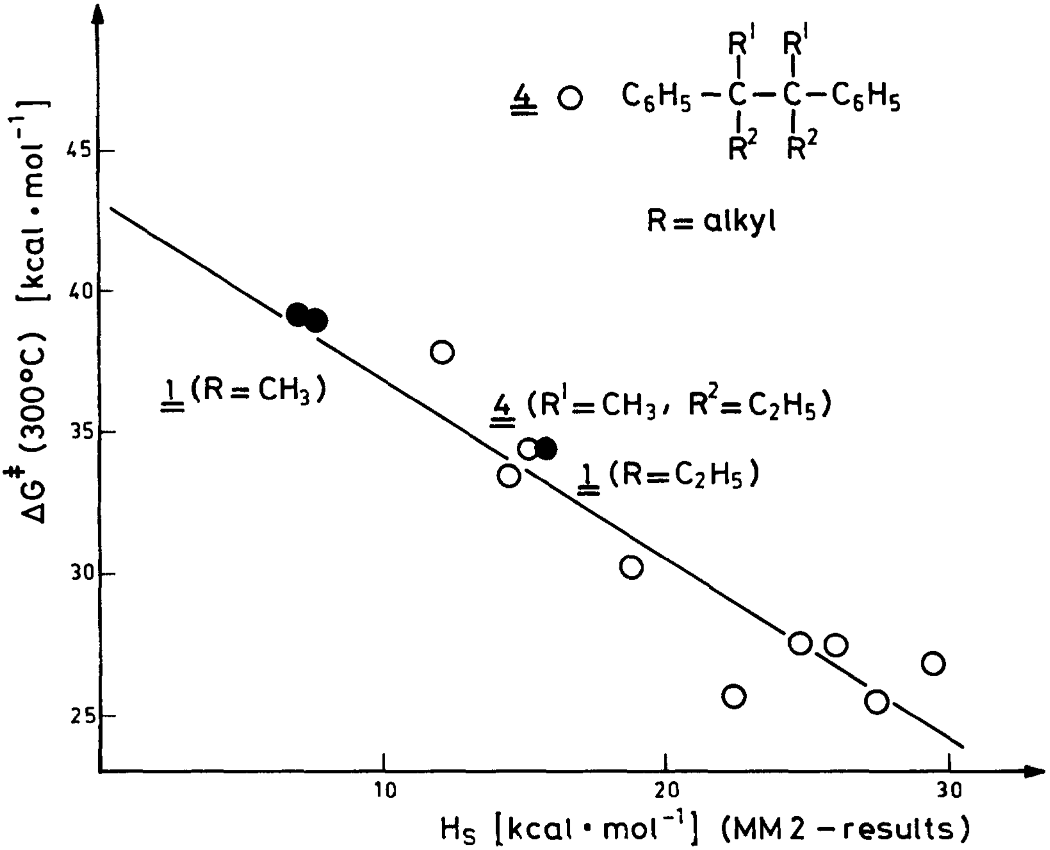
c) 0.05-1.0 m solutions of 1 in mesitylene (m) or tetraline (t) were thermolyzed over 10 half-times and analyzed by quantitative g.c. Besides 3 dimers derived from the solvents were observed.

d) A value 7.9±1.5 kcal·mol^{-1} was determined from the heat of combustion and the heat of sublimation[14].

The results are recorded in the table. For comparison the correlation between the free enthalpy of thermolysis $\Delta G^{\ddagger}$ and the strain enthalpy H_s for the series 4[7,15] is shown in the Figure[16]. Compounds 4 are distinguished from 1 by exchange of two alkyl groups for methoxy. The preliminary results for three compounds of the series 1 fit within the error limits of the experiments the same correlation line as the series of compounds 4 does. Because of the higher average entropy of activation in the series 4 ($\overline{\Delta S}^{\ddagger}$=20.6 e.u.) than 1 an increase in resonance energy H_R of ∿ 1.8 kcal·mol^{-1} for the exchange of methyl- for methoxyl in this type of benzyl radicals is calculated from the Figure[1a]. Almost the same result is obtained by comparing $\Delta H^{\ddagger}$ of 1 (R=C_2H_5; 44.0 kcal·mol^{-1}) and 4 (R^1=CH_3, R^2=C_2H_5; 48.4 kcal·mol^{-1}) which have nearly the same strain enthalpy H_s=15-16 kcal·mol^{-1}. This comparison, of course, depends on the definition of the increments for the strainfree compounds of the two series[10].

The small rate effects of α-methoxy groups in thermal rearrangements[4] and azo decomposition reactions[5] accordingly are in agreement with the small value of the resonance energy of α-methoxyalkyl radicals reported here. Large rate effects of α-methoxy substitution therefore must be due to other reasons, preferentially to polar effects[3,19].

Figure Correlation between Free Enthalpies of Thermolysis $\Delta G^{\ddagger}$ (300°C) and Strain Enthalpies H_s[10].



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*) Dedicated to Prof.W.A.Waters for his 80th birthday.

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