

STERIC ACCELERATIONS IN THERMOLYSIS AND SOLVOLYSIS REACTIONS.

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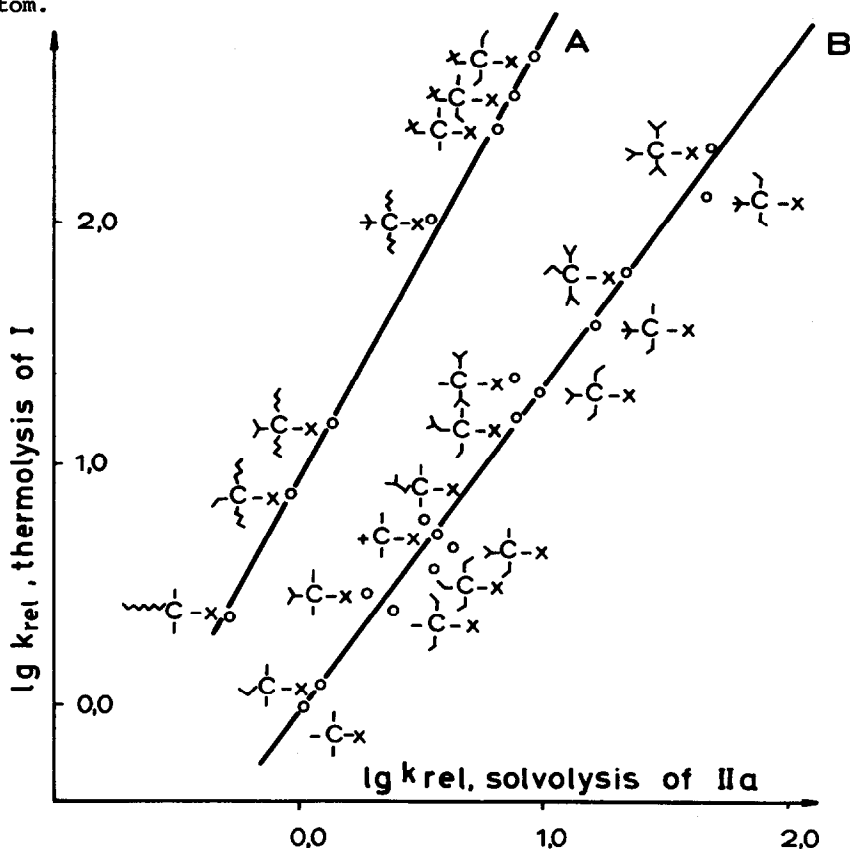
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(Received in UK 11 October 1974; accepted for publication 13 November 1974)

Repulsive interactions between groups, which are relieved, when the central carbon atom passes from tetrahedral bonding to the trigonal bonding of a reactive intermediate, have been recognized as an important factor influencing the rates of solvolysis of tertiary alkyl chlorides and p-nitrobenzoates¹⁾. No systematic investigations of similar effects in thermolysis reactions leading to free radicals have been published²⁾, although there seems to be general agreement, that tertiary alkyl radicals have a planar geometry³⁾. In the table rate constants for the thermal decomposition of t-azo-alkanes are recorded together with solvolysis constants of corresponding p-nitrobenzoates. The thermolysis constants show a 450-fold spread in rate. Therefore these easily available⁴⁾ compounds are an useful new class of radical initiators. Tidwell has recently reported⁵⁾ a 32-fold faster decomposition of t.butyl triisopropyl peracetate than of t.butyl perpivalate. For comparison triisopropyl azomethane decomposes 206 times faster than azoisobutane. Taking the multiplicative effect^{6,7)} of the isopropyl groups on either side of the molecule into account, a rate enhancement factor $\sqrt{206}=14.4$ results. Despite the fact that the transition state of azoalkane decomposition resembles the radicals being generated⁶⁾ and that in contrast only comparatively little C_α-CO-bond stretching has occurred in the transition state of perester fragmentations⁶⁾ a similar steric acceleration factor is found for both reactions. The largest fraction of B- and F-strain apparently is released during the first 10-20% of bond stretching as expected^{2a,6b)}.

It is recognized from the figure that two separate correlation lines are observed between the thermolysis rates and the solvolysis rates of the table. The pairs of compounds falling on the two lines are, with two exceptions, charac-

teristically distinguished by the length of the side chain of the central carbon atom.



Correlation between rates of thermolysis of I and rates of solvolysis of II (data from the table)

The compounds falling on curve A are the ones having at least one side chain with a linear arrangement of three carbon atoms⁸⁾. It is suggested that B-strain effects are the main factor responsible for the correlations in the figure, but an overlapping additional effect, which is responsible for the separation into two groups, is recognized. Among several alternatives we discuss presently the interpretation, that solvation of the leaving group is hindered in the compounds of curve A by 1,6-interactions between the carbonyl oxygen and the side chain^{8,9)}. Therefore solvolysis of these compounds is relatively retarded. After correction for the multiplicative effect in the thermolysis reaction a

Table

Rates of thermolysis of azoalkanes I (180°C, ethylbenzene) and of solvolysis of p-nitrobenzoates II (60 vol% dioxane-water; 0.1 M LiClO₄; 100°C)

$R^1R^2R^3C=N=N-CR^1R^2R^3$ I			$R^1R^2R^3C-O-C_6H_4(p)NO_2$ II	
R^1	R^2	R^3	k_{rel}	
			I	II
CH ₃	CH ₃	CH ₃	≡ 1.00 ^{a)}	≡ 1.00 ^{b)}
CH ₃	CH ₃	C ₂ H ₅	1.19	1.28
CH ₃	CH ₃	1-C ₈ H ₁₇	2.30	0.53
CH ₃	CH ₃	1-C ₃ H ₇	3.00	1.93
CH ₃	CH ₃	1-C ₄ H ₉	7.51	3.20
CH ₃	CH ₃	t-C ₄ H ₉	5.30	3.91
CH ₃	CH ₃	neo-C ₅ H ₁₁	247	6.40
CH ₃	C ₂ H ₅	C ₂ H ₅	1.87	2.66
CH ₃	C ₂ H ₅	1-C ₃ H ₇	5.35	4.43
CH ₃	C ₂ H ₅	1-C ₄ H ₉	16.0	7.75
CH ₃	C ₂ H ₅	t-C ₄ H ₉	36.5	17.5
CH ₃	C ₂ H ₅	neo-C ₅ H ₁₁	300	7.89
C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	3.65	3.84
C ₂ H ₅	C ₂ H ₅	1-C ₃ H ₇	20.2	9.80
C ₂ H ₅	C ₂ H ₅	t-C ₄ H ₉	107	50
C ₂ H ₅	C ₂ H ₅	neo-C ₅ H ₁₁	365	9.50
CH ₃	1-C ₃ H ₇	1-C ₃ H ₇	23	7.10
C ₂ H ₅	1-C ₃ H ₇	1-C ₃ H ₇	68.5	18.0
1-C ₃ H ₇	1-C ₃ H ₇	1-C ₃ H ₇	206	49.0
1-C ₄ H ₉	1-C ₄ H ₉	C ₂ H ₅	7.26	0.94
1-C ₄ H ₉	1-C ₄ H ₉	1-C ₃ H ₇	14.4	1.34
1-C ₄ H ₉	1-C ₄ H ₉	t-C ₄ H ₉	107	3.54
CH ₃	1-C ₃ H ₇	neo-C ₅ H ₁₁	453	

a) $k_1 = 1.02 \cdot 10^{-4} \text{ sec}^{-1}$;b) $k_1 = 1.80 \cdot 10^{-5} \text{ sec}^{-1}$;

slope of 0.63 results for curve B; additional front-strain may be responsible for the slope 0.93 of curve A^{1d}). From the figure it is concluded that steric accelerations in solvolysis and thermolysis reactions are not only linearly related but also of a similar order of magnitude. Experiments to obtain a better understanding of these results including the change of leaving group, solvent ionising power and nucleophilicity in the solvolysis reaction of tertiary esters are in progress.

Support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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