Investigation of Strained Transition States in Free Radical Copolymerizations by means of High-pressure Kinetics

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Summary Increasing substitution of the comonomer in high-pressure, free-radical copolymerizations of maleic anhydride with multisubstituted olefins involves greater pressure acceleration and hence more negative activation volumes and later transition states.

The basic concept of activation volume ($\Delta V^{\ddagger}$), arising from transition state theory, has been widely used in organic[1] and macromolecular chemistry[2] in order to distinguish between mechanistic alternatives, to detect secondary orbital interactions,[3,4] and to optimize high-pressure organic synthesis.[5] The activation volume was shown to be a useful parameter when the individual volumetric contributions in the activated step are understood and interpreted correctly.

Recently we were interested in the high-pressure copolymerization of weak charge-transfer complexes[6] involving maleic anhydride (MA) as the common monomer and mono- or multi-substituted olefins (with alkyl and aryl substituents) as the second comonomer. We observed that when MA is allowed to react with ethylenes substituted with bulky groups, the pressure acceleration and hence the overall activation volume for the copolymerization may change significantly with the increasing size of the substituent and the degree of substitution. This was attributed to steric effects and prompted us to look more closely at the influence of substitution by highly compressing groups, such as phenyl and t-butyl groups, on the activation volume of the copolymerization of MA with hindered olefins.

Copolymerizations were performed in $CHCl_3$ under nitrogen in PTFE capsules in the presence of purified lauroyl peroxide (LP) at pressures up to 150 MPa. To determine the reaction rate in the linear portion of the kinetic curve, conversions were kept to 5—20% according to the comonomer. Polymers were recovered by precipitation with anhydrous light petroleum, and were purified twice by reprecipitation, filtered, dried *in vacuo*, and finally weighed. The reproducibility of the data was fair (2—5% depending on the system).

The Table reports the values of $\Delta V^{\ddagger}$ and some selected high pressure kinetic values. The usual range of $\Delta V^{\ddagger}$ values for copolymerizations showing unhindered and neutral transition states is -14 to $-20\ \mathrm{cm^3\ mol^{-1}}$.[7] Our results clearly demonstrate that the greater the hindrance, the greater the pressure acceleration. Particularly noticeable is that increased crowding of the ethylenic monomer leads to higher absolute values for $\Delta V^{\ddagger}$ according to the sequence:

$$|\Delta V^{\ddagger}|_{\text{monosubst.}} < |\Delta V^{\ddagger}|_{1,2\text{-disubst}} < |\Delta V^{\ddagger}|_{1,1\text{-disubst}}$$

Such results are not completely unexpected as shown by the Menshutkin reaction.[8,9] However, this reaction is characterized by a highly polarisable transition state with appreciable electrostriction and therefore cannot be considered a proper example, since it is rather difficult to separate the steric from the electrostatic contribution in the $\Delta V^{\ddagger}$ expression. Two explanations for the pressure acceleration of hindered reactions have been proposed: interpenetration of compressing groups with a subsequent decrease in volume of the activated complex[8] or a simple consequence of the Hammond postulate.[10]

TABLE.[a] High pressure copolymerization of maleic anhydride (MA) with olefins (M) substituted by compressing groups.

			v_p/v_0[b]				$\Delta V^{\ddagger}$[c]
Entry	Comonomer	v_0[b]	0	50	100	150[d]	/cm³ mol⁻¹
	$CH_2{=}CHPr$	1·86	1	1·28	1·65	2·18	−16·5
1	$CH_2{=}CHPh$	3·00[e]	1	1·38	1·82	2·31	−18·5
2	*trans*-$PhCH{=}CHPh$	3·13	1	1·54	2·20	2·80	−25
3	$CH_2{=}CMePh$	2·05	1	1·86	3·81	4·21	−35
4	$CH_2{=}CPh_2$	0·03[f]	1	2·31	4·46	7·15	−52
5	$PhCH{=}CPh_2$	—		No reaction			—
6	$Ph_2C{=}CPh_2$	—		No reaction			—
7	$CH_2{=}CHBu^t$	0·64	1	1·75	2·45	3·06	−31
8	*cis*-$MeCH{=}CHBu^t$	1·94	1	2·24	3·91	5·76	−45
9	$CH_2{=}CMeBu^t$	0·15	1	2·69	6·60	15·1	<−55

[a] Reaction conditions: [MA] = [M] = 0·50 mol l⁻¹, [LP] = 0·01 mol l⁻¹, solvent $CHCl_3$, T 70·2 °C. [b] v_p/v_0: ratio of reaction rates (calculated from gravimetric data) at pressures P and 0, respectively (v_0 is given in $10^{-5}\ \mathrm{mol\ l^{-1}\ s^{-1}}$). [c] Precision is *ca.* 0·5 cm³ mol⁻¹ for the lowest absolute values, but is estimated as $\geqslant 5$ cm³ mol⁻¹ for the most negative values, since it is difficult to make precise measurements of $\Delta V^{\ddagger}$ in reactions that are strongly accelerated by pressure. [d] Pressure in MPa. [e] 50·0 °C. [f] 90·0 °C.

The present investigation concerns polymerization reactions carried out in an inert medium *via* a radical mechanism. The reactions are assumed to involve neither electrostriction (this is made plausible on the basis of the independence of $\Delta V^{\ddagger}$ of the solvent[11]), nor other particular effects† (*e.g.*, resonance, hyperconjugation, penultimate effects), so that the activation volume roughly reflects only volume variations in the geometry of the molecules (bond formation), in the transition state. The volumetric term $\Delta V^{\ddagger}$ is ascribed to the formation of the less crowded transition state and the additional volume contribution to $\Delta V^{\ddagger}$ is believed to be related either to an internal change of volume of the activated complex (Gonikberg's hypothesis) or to a displacement of the transition state towards the final state (the Hammond postulate).

Supplementary information can be gained from inspection of the Table. The t-butyl group is confirmed as a particularly compressing group (entries 7—9). It is interesting to note that neither tri- (entry 5) nor tetra-phenylethylene (entry 6) reacts with MA even at very high pressure (experiments were performed with both comonomers up to 1000 MPa at which pressure a small amount of polymeric material was produced with the triphenylethylene monomer, but it could not be analysed). With these comonomers very high pressures would be needed to overcome steric hindrance and the $|\Delta V^{\ddagger}|$ value would probably be $> 50\ \mathrm{cm^3\ mol^{-1}}$. Finally, we found high negative values for $\Delta V^{\ddagger}$ in three cases (entries 4, 8, and 9). We do not know any other example showing such pressure accelerated reactions.‡

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† Resonance and hyperconjugation may affect the absolute value of the rate constant. However, as they are purely electronic effects, pressure does not modify their magnitude (at least in the 0–500 MPa region), so that the pressure coefficient $\delta \ln k/\delta P$ is unaffected.

‡ A value of $-50\ \mathrm{cm^3\ mol^{-1}}$ has been reported for the iododestannylation of tetramethyltin (N. Isaacs and K. Javaid, *Tetrahedron Letters*, 1977, 3073).

[1] For a recent review, *cf.* T. Asano and W. Le Noble, *Chem. Rev.*, 1978, **78**, 407.
[2] G. Jenner, in 'High Pressure Chemistry,' ed. H. Kelm, Reidel, Dordrecht, 1978, p. 365—420.
[3] R. Grieger and C. Eckert, *J. Amer. Chem. Soc.*,, 1970, **92**, 7149.
[4] G. Jenner and J. Rimmelin, *Tetrahedron*, 1976, **32**, 1107.
[5] G. Jenner, *Nouveau J. Chim.*, 1979, **3**, 329.
[6] M. Kellou and G. Jenner, *Makromol. Chem.*, 1979, **180**, 1687.
[7] W. Dellsperger and K. Weale, *Amer. Chem. Soc., Polymer. Pre P.*, 1970, **11**, 645.
[8] M. Gonikberg, *Russ. J. Phys. Chem.*, 1963, **37**, 247.
[9] W. Le Noble and Y. Ogo, *Tetrahedron*, 1970, **26**, 4119.
[10] W. Le Noble and T. Asano, *J. Amer. Chem. Soc.*, 1975, **97**, 1778.
[11] M. Kellou and G. Jenner, *European Polymer J.*, 1977, **13**, 9.