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A NEW PHYSICO-CHEMICAL ASPECT IN ORGANIC PIEZO-CHEMISTRY,
HIGH PRESSURE SYNTHESIS INVOLVING CONGESTIONED SYSTEMS

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Résumé - Le nouveau concept de volume d'activation lié à un état contraint permet d'expliquer l'effet accélérateur de la pression dans les réactions affectées par des contraintes géométriques (contraintes stériques, de tension, de torsion...). Dans ces réactions, l'effet de contrainte a tendance à déplacer l'état de transition vers le produit en vertu du postulat de Hammond. Les conséquences synthétiques sont mises en lumière.

Abstract - The new concept of volume of activation related to a strained state is a reasonable explanation of the accelerating effect of pressure in reactions involving geometrical and conformational strain (steric, tension, torsional strain...). In such reactions, the strain effect shifts the transition state toward the product by virtue of the Hammond postulate. Synthetic applications of the concept are given.

1. - INTRODUCTION

The success of high pressure syntheses in liquid phase is intimately dependent on the value of the volume of activation ΔV^\ddagger . The "later" or more "product-like" the transition state, the more pressure-accelerated the reaction rate. Stated in other words, if the transition state shifts far toward the final state, then pressure may be a determining parameter in achieving syntheses which would otherwise occur only hardly if not at all.

One possibility to create high negative volumes of activation is to apply high pressure on systems involving very compressive groups or considerable strain in the transition state /1/. The object of this contribution is to consider this important piezochemical phenomenon.

2. - PRESSURE EFFECT ON CONGESTIONED SYSTEMS

Some twenty years ago, Gonikberg /2/ found a strong pressure acceleration effect in Menshutkin reactions when comparing reaction rates for crowded 2,5-disubstituted pyridines vs. unhindered ones. Since the size of groups substituting the reaction centers involves conformational and geometric concepts, one may associate the pressure parameter. As a matter of fact, steric effects are large when adjacent parts of molecules are forced into close neighbourhood by rigid groups and the possibility of evasion are reduced to a minimum; this should have an effect on the volume of activation. Former studies from our laboratory /1,3/ have shown how steric demands of substituents and enhanced strain energy are measurable as activation volume components. Unless other effects (polarity or resonance) act in the opposite way, steric congestion produces "late" transition states, justifying the use of very high pressures to overcome steric inhibition to reaction.

The volume of activation is actually a complex quantity and one may distinguish two essential kinds of volume contributions for a non-polar reaction:
- those generated by the establishment of the activated complex

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- those related to the specific structure of the transition state (e.g. the volume modifications created within the transition state).

The former volume contributions act on the position of the transition state, while the latter do not. Considering strained transition states, we are interested in knowing what kind of volume changes will be involved in a strained or a hindered reaction compared to an unhindered standard.

Let us consider the additional volume components and formulate the overall volume of activation as a sum :

$$\Delta V^\ddagger = \Delta V_O^\ddagger + \Sigma \Delta V_Z^\ddagger$$

ΔV_O^\ddagger is the volume of activation of the standard reaction, ΔV_Z^\ddagger is a volume of activation relative to strain (steric, ring, ...), since a strained state may originate not only from bulkiness considerations, but also from ring strain, deformation, torsion, etc...

In the case of steric strain ($\Delta V_Z^\ddagger = \Delta V_\sigma^\ddagger$), ΔV_σ^\ddagger was approximated as /1/ : $\Delta V_\sigma^\ddagger = -\omega \psi_\sigma$ where ω is a substitution parameter (depending on the mode and the degree of substitution) and ψ_σ a steric parameter representing the total value of the individual steric effects exerted by each substituent.

The concept of steric volume of activation has been extended for ring strain /4/ with an additional volume term ΔV_τ^\ddagger :

$$\Delta V^\ddagger = \Delta V_\sigma^\ddagger + \Delta V_\tau^\ddagger + \Delta V_I^\ddagger$$

Thus the pure structural component in the formulation of the volume of activation may reflect the steric effects operating in the transition state. The additional volume contributions ΔV_σ^\ddagger , ΔV_τ^\ddagger are dynamic terms, e.g. when the steric demand of the reaction increases, the transition state shifts gradually toward the product along the reaction coordinate. An important consequence of this phenomenon is its application to organic synthesis, since high pressure synthesis of crowded molecules is more accelerated with stronger steric interactions, due to the existence of ΔV_Z^\ddagger .

3. - SYNTHETIC APPLICATIONS

Some recent relevant investigations in this field are listed in table I just as illustrations. They concern reactions which occur only at high pressures (500-1200 MPa, 20-100°C).

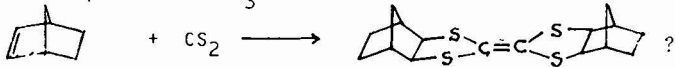
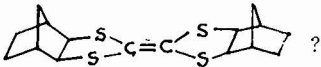


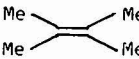
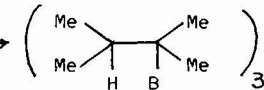
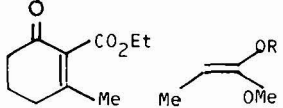
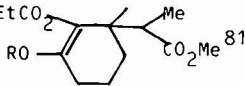
Entries 1 and 2 describe the high pressure quaternization reaction of sterically hindered alkaloids. The addition of CS_2 to norbornene (entry 3) is an example of a strained system imposed by ring strain. At high pressure reaction occurs, leading to an unusual adduct. This reaction should be compared to the high pressure addition of CS_2 to the very strained quadricyclane molecule (entry 4) which yields another type of adduct (thietane). The hydroboration reactions involving olefins substituted by compressive groups (entry 5) reveal that high pressures promote the formation of trialkylborane, whereas at atmospheric pressure, usually the monoborane is alone formed.

The last example (entry 6) is provided by the addition of o-silylated ketene acetals to enones /9/ $R = Si(Me)_2(tBu)$. There is a dramatic pressure effect on such sterically hindered addition.

In conclusion, the results demonstrate the utility of the pressure variable offering an exceptional mild strategy for obtaining new compounds by accelerating sluggish bond-forming reactions on sterically crowded or strained substrates.

Table I

High pressure synthesis involving strained or congested systems

Entry	Reaction	Yield	Ref.
1	α -isolupanine + $\text{CH}_3\text{I} \longrightarrow$ Menshutkin salt	99	15/
2	15-oxosparteine + $\text{CH}_3\text{I} \longrightarrow$ Menshutkin salt	100	15/
3	 + $\text{CS}_2 \longrightarrow$  ?		16/
4	 + $\text{CS}_2 \longrightarrow$ 	20	17/
5	 + $\text{BH}_3 \longrightarrow$  ?		18/
6	 \longrightarrow 	81	19/

$\text{R}=\text{Si}(\text{Me})_2(\text{tBu})$

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