

Figure 4.23 The E2 energy surface.

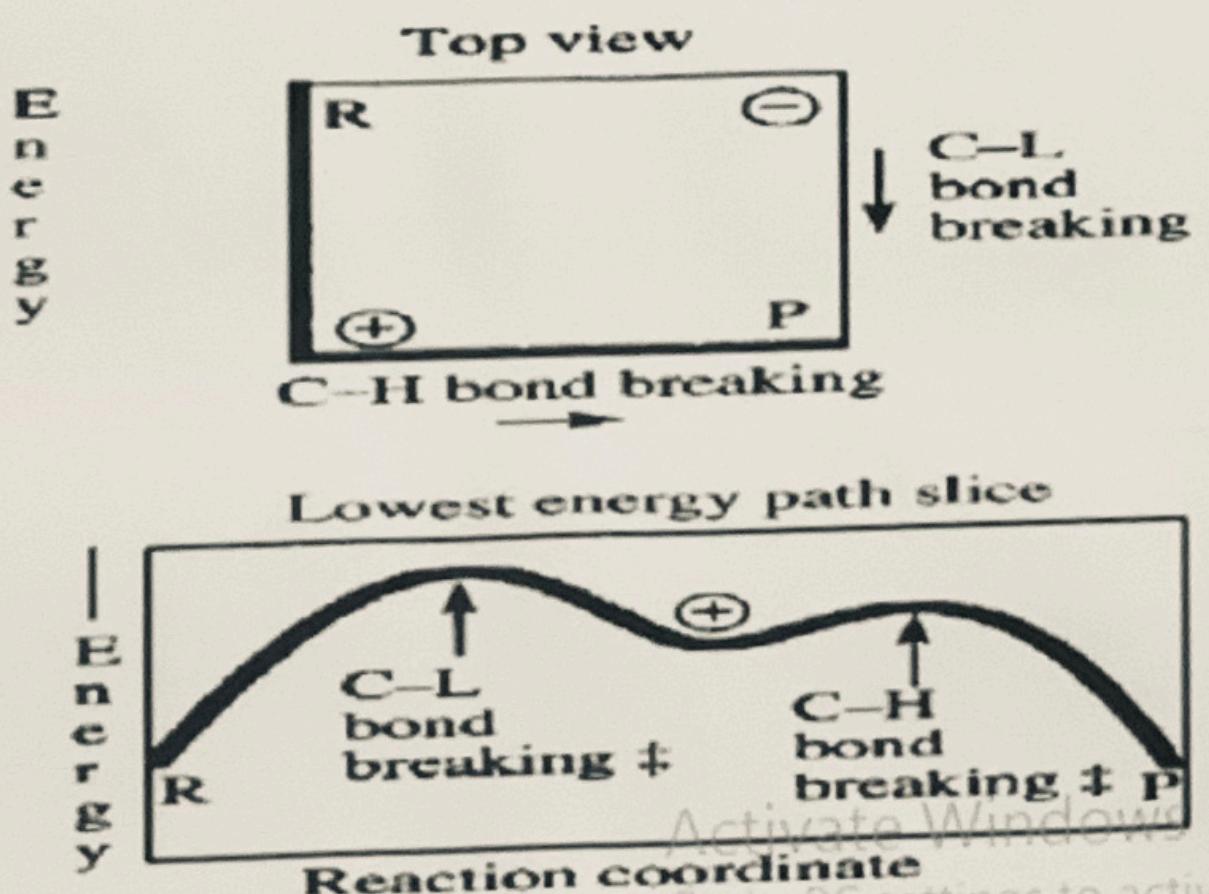
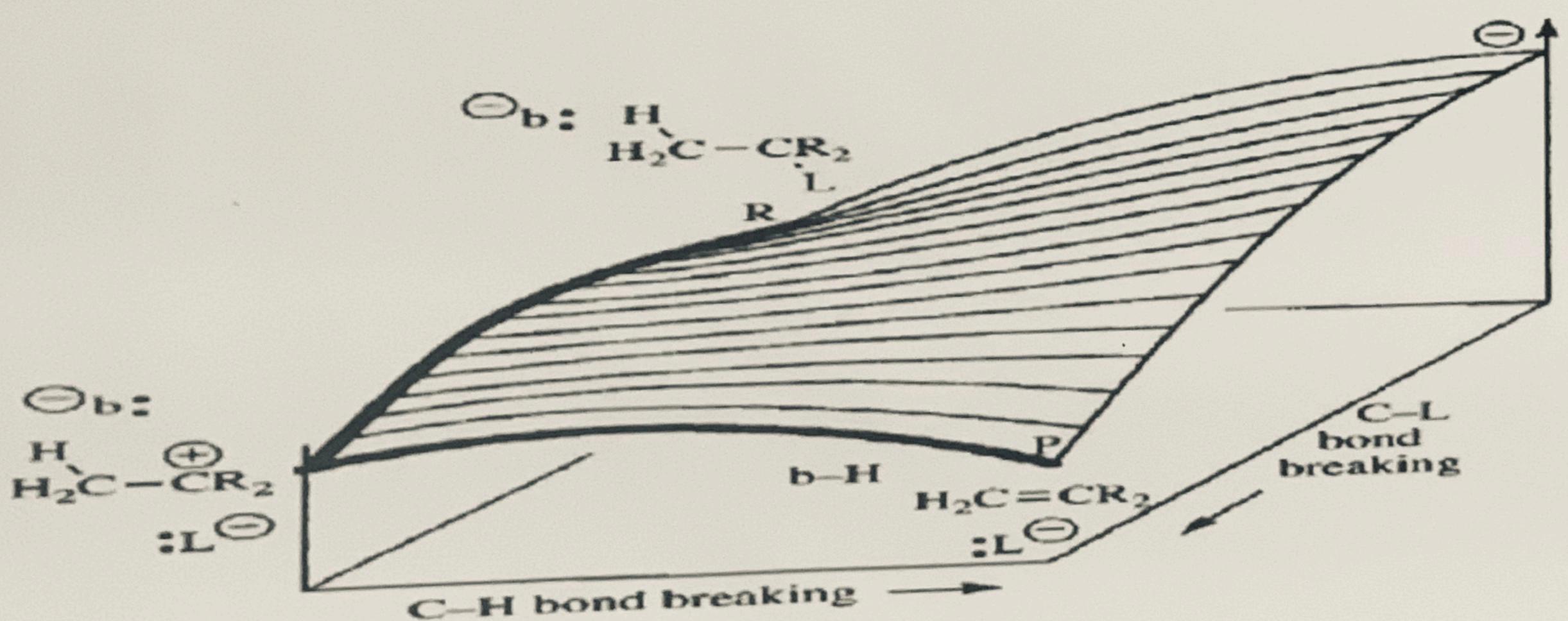
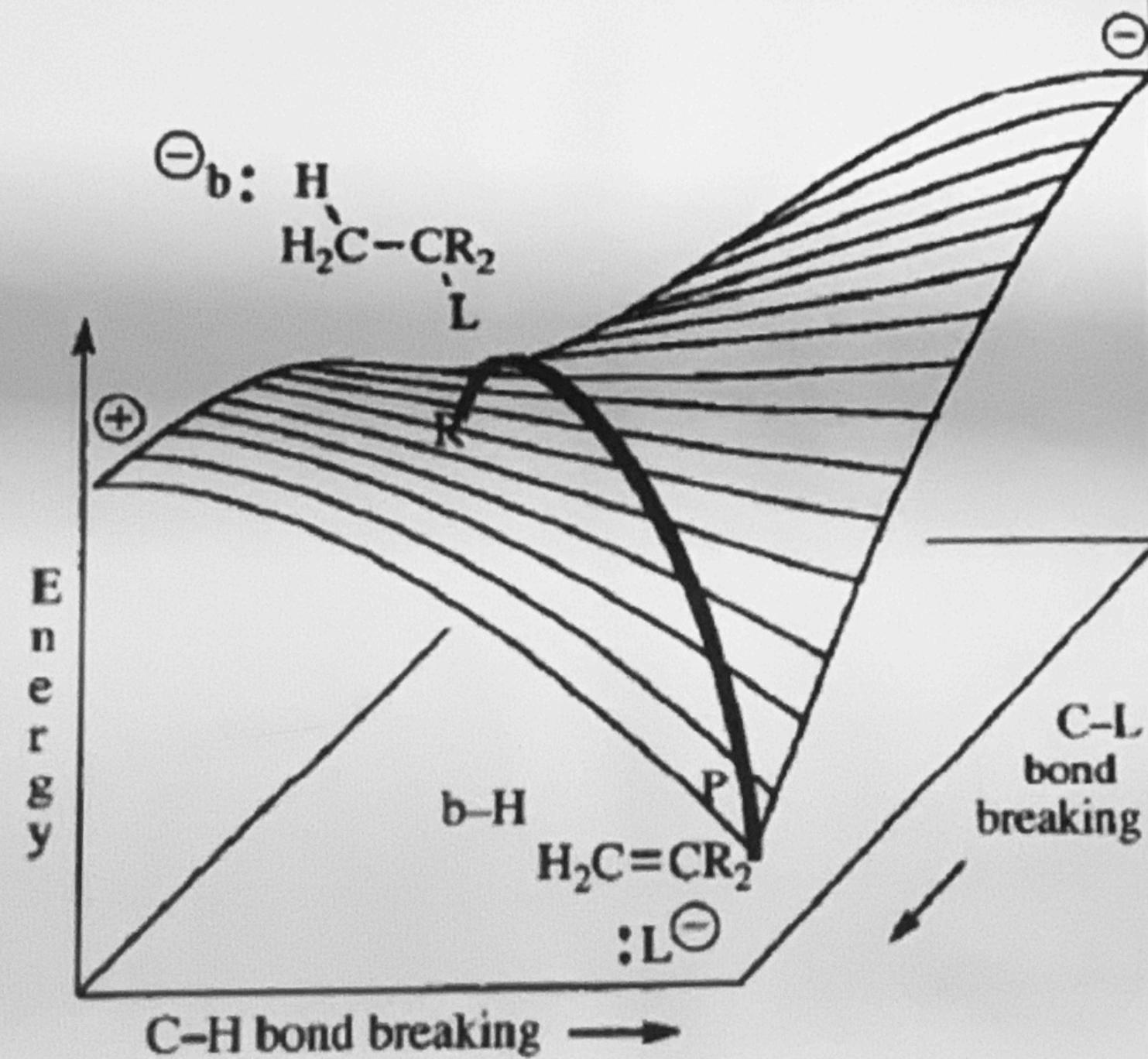
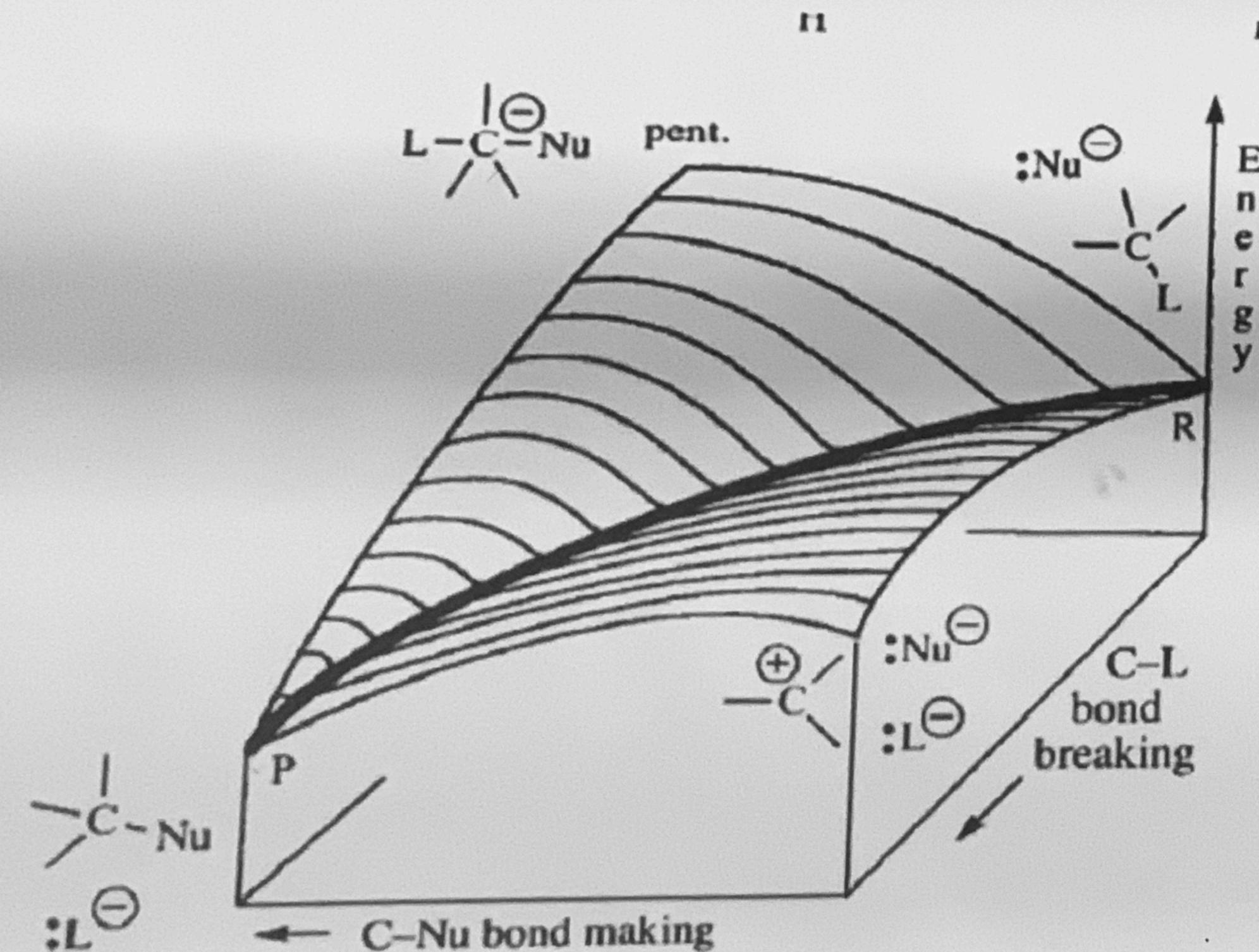
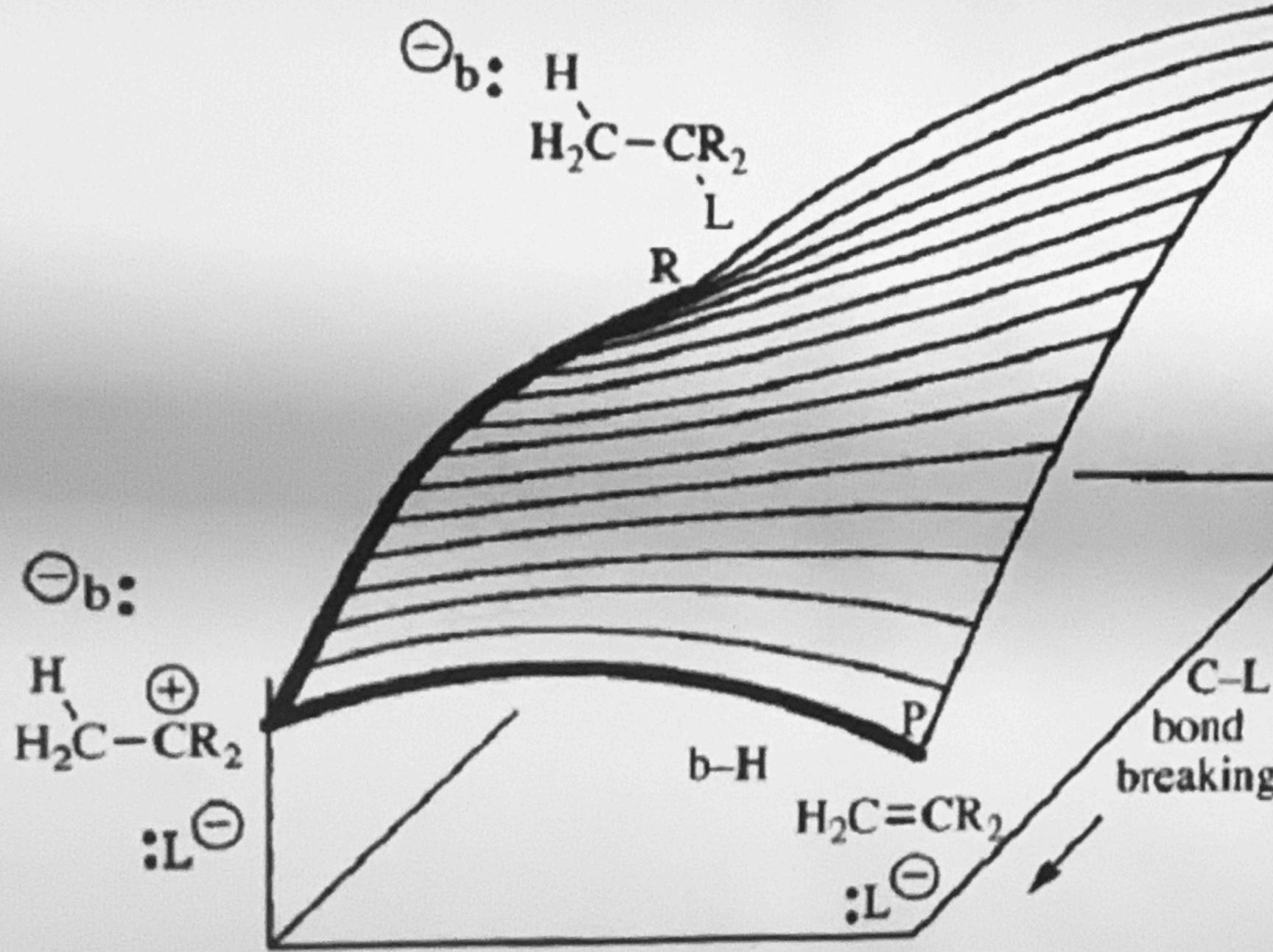
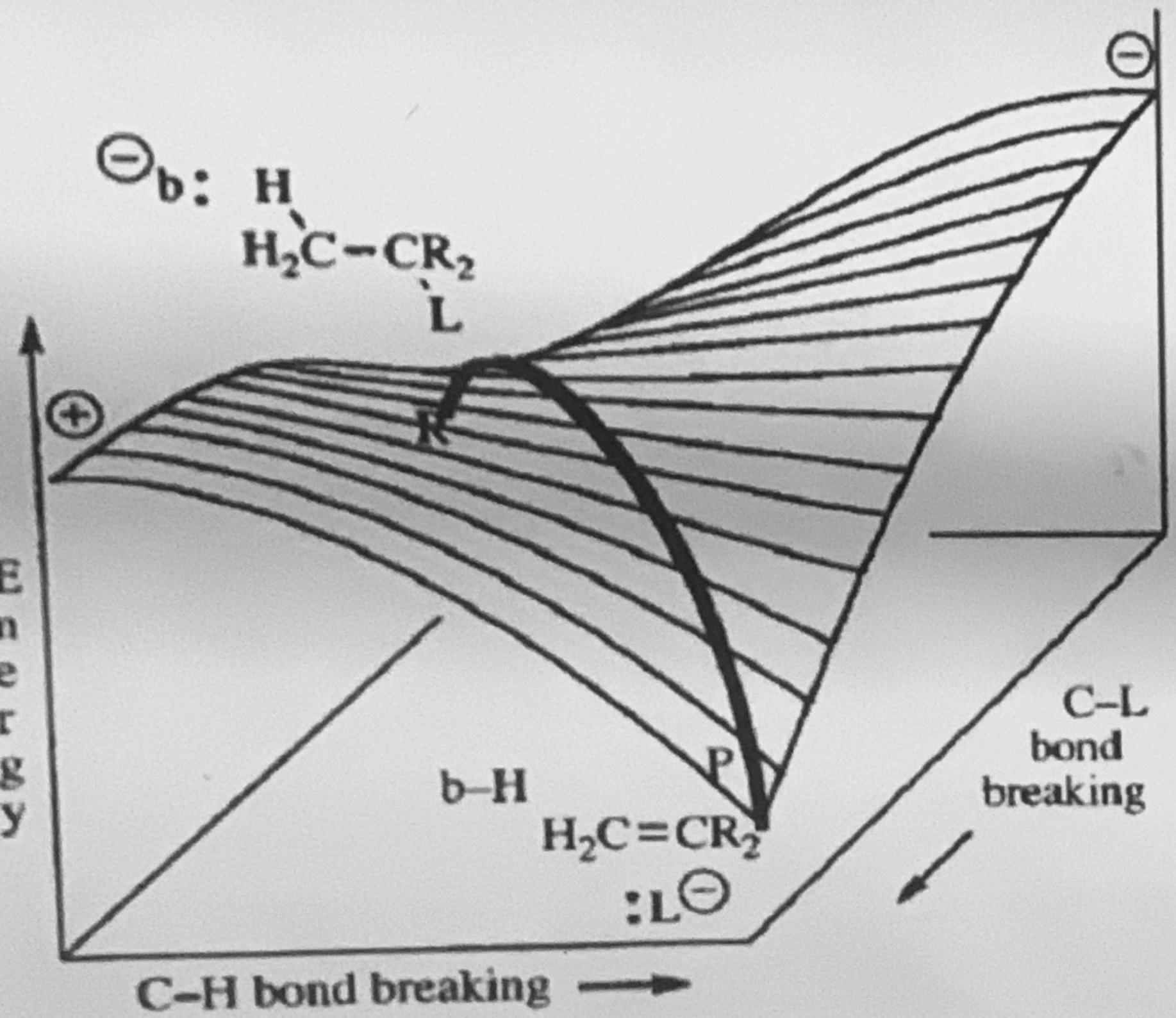


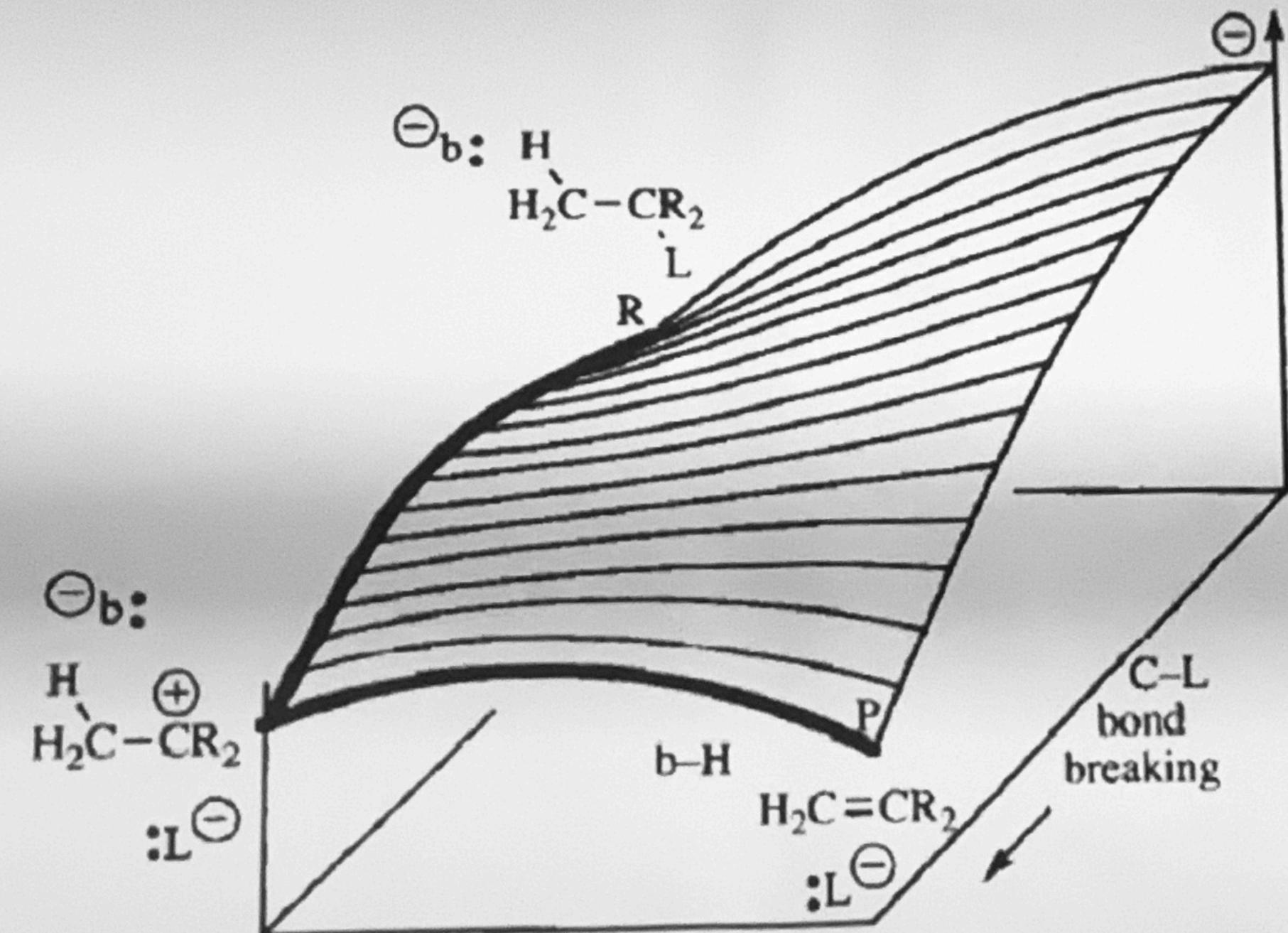
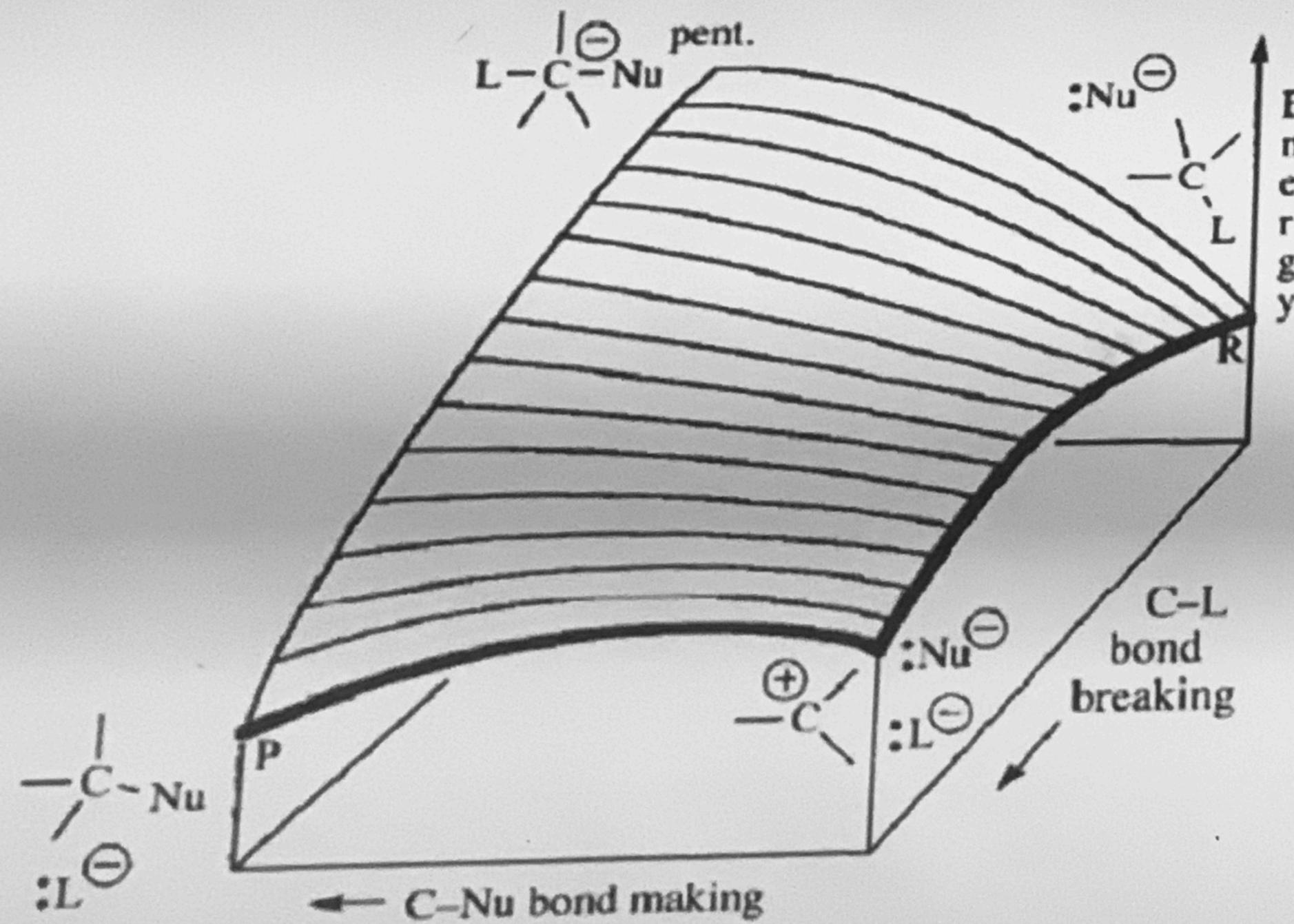
Figure 4.24 The E1 energy surface.

Comparison of S_N2 and $E2$ PES's



Comparison of E2 and E1 PES's

Activate Wi
Go to PC setting



Comparison of S_N1 and E1 PES's

Activate Windo
Go to PC settings to

Select & Zoom

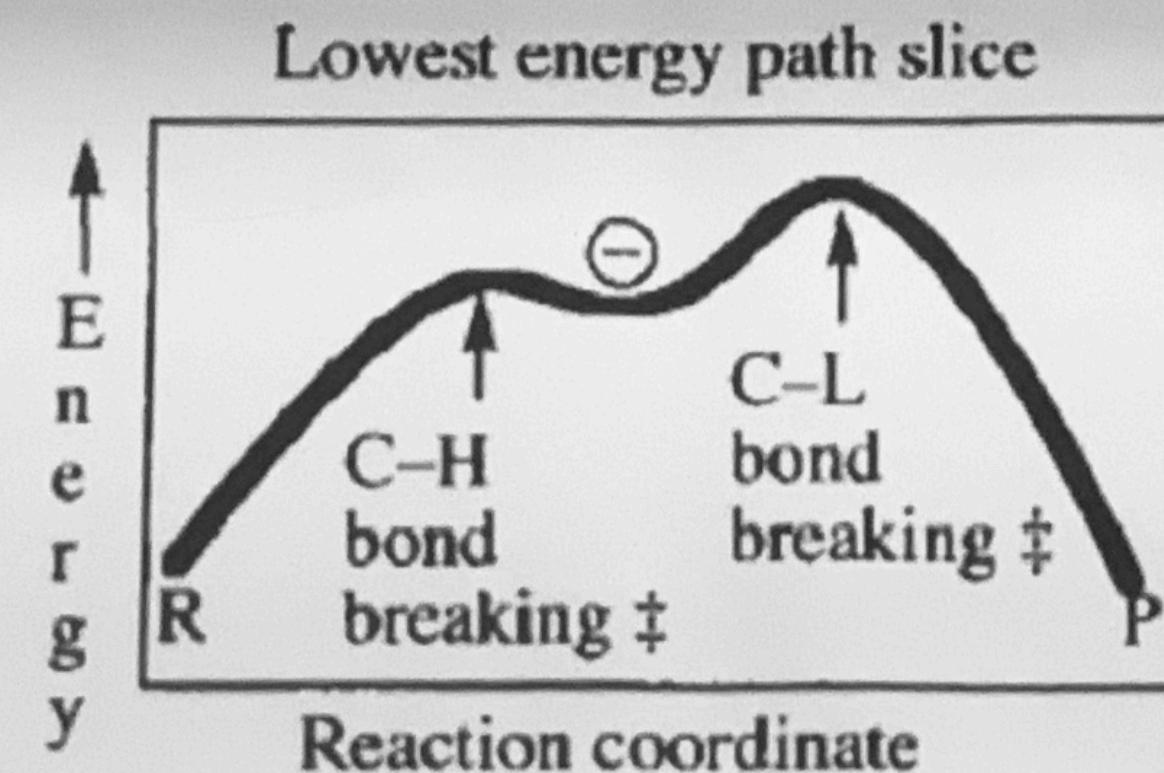
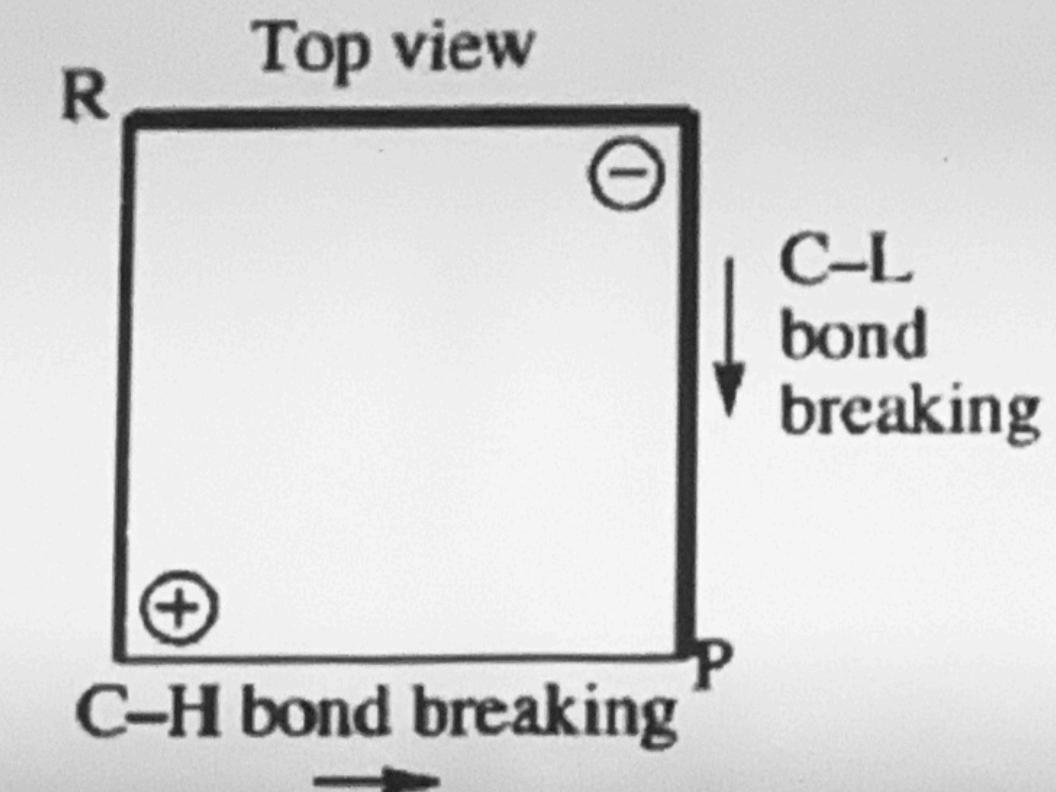
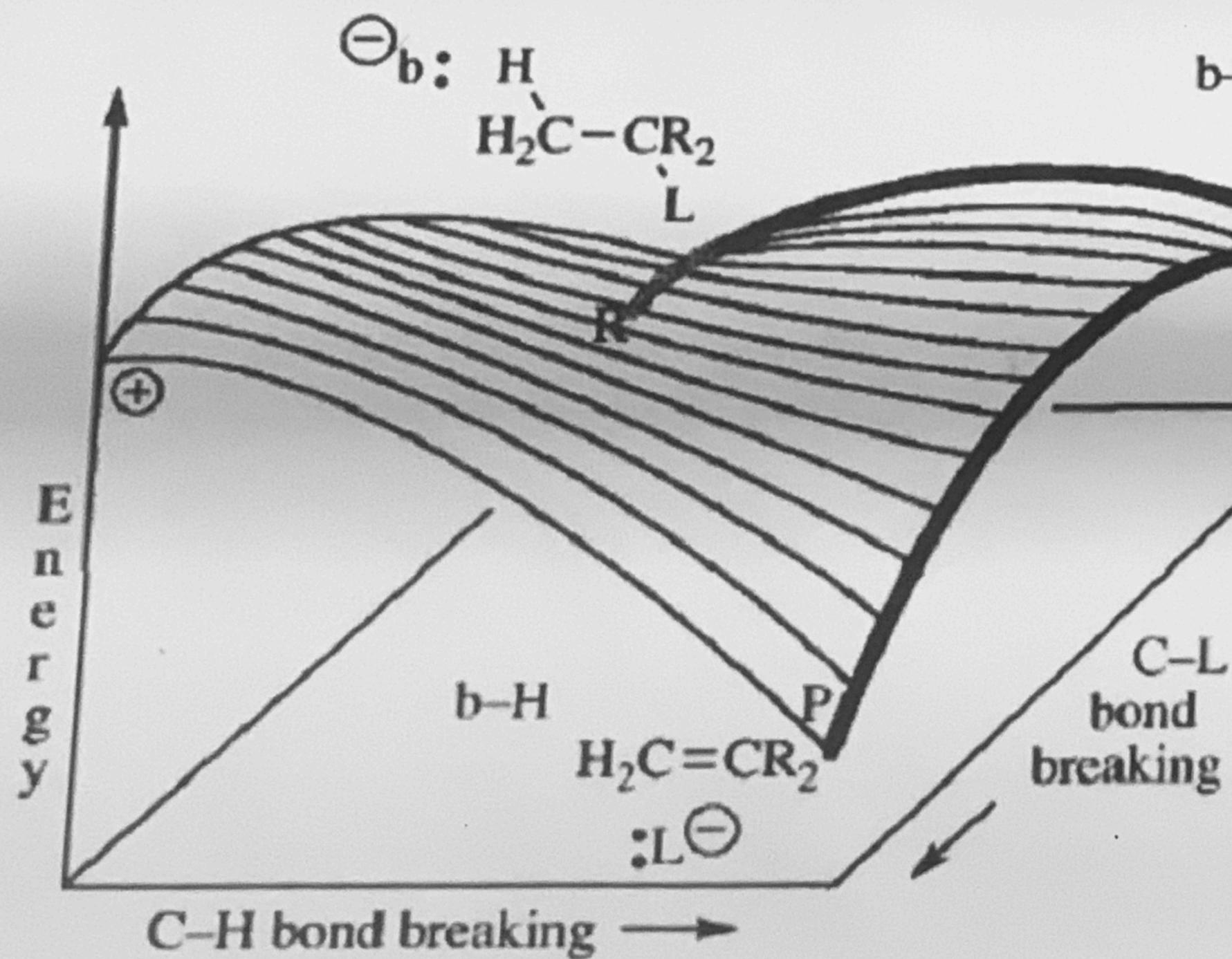


Figure 4.25 The E1cB energy surface.

Select & Zoom

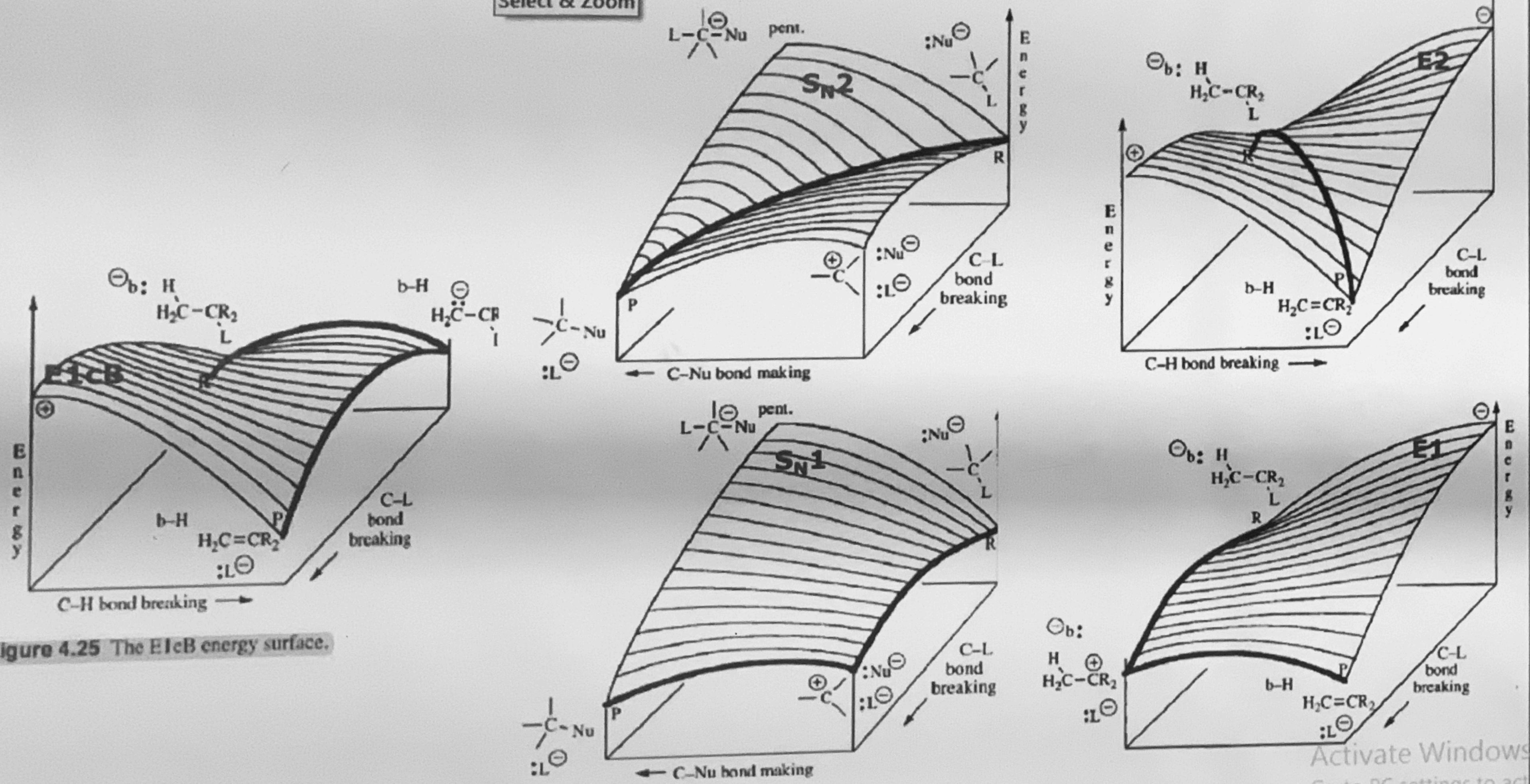


Figure 4.25 The $E1cB$ energy surface.

Activate Windows
Go to PC settings to act

Where to start?

To stabilize the $\text{TS}^\#$, FIRST, we NEED to know what is 'happening' in the $\text{TS}^\#$.

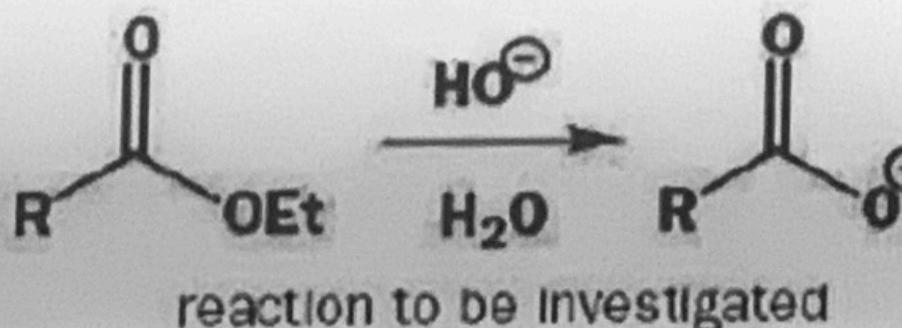
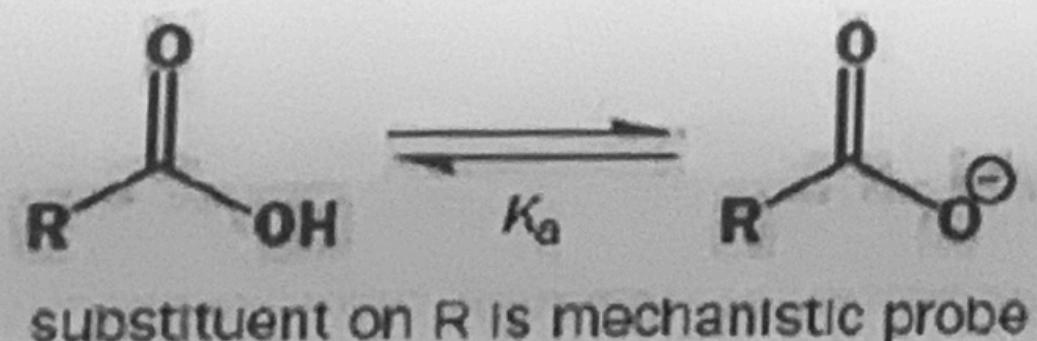
'Happening' = Is electron density increasing or decreasing?

The Hammett Relationship

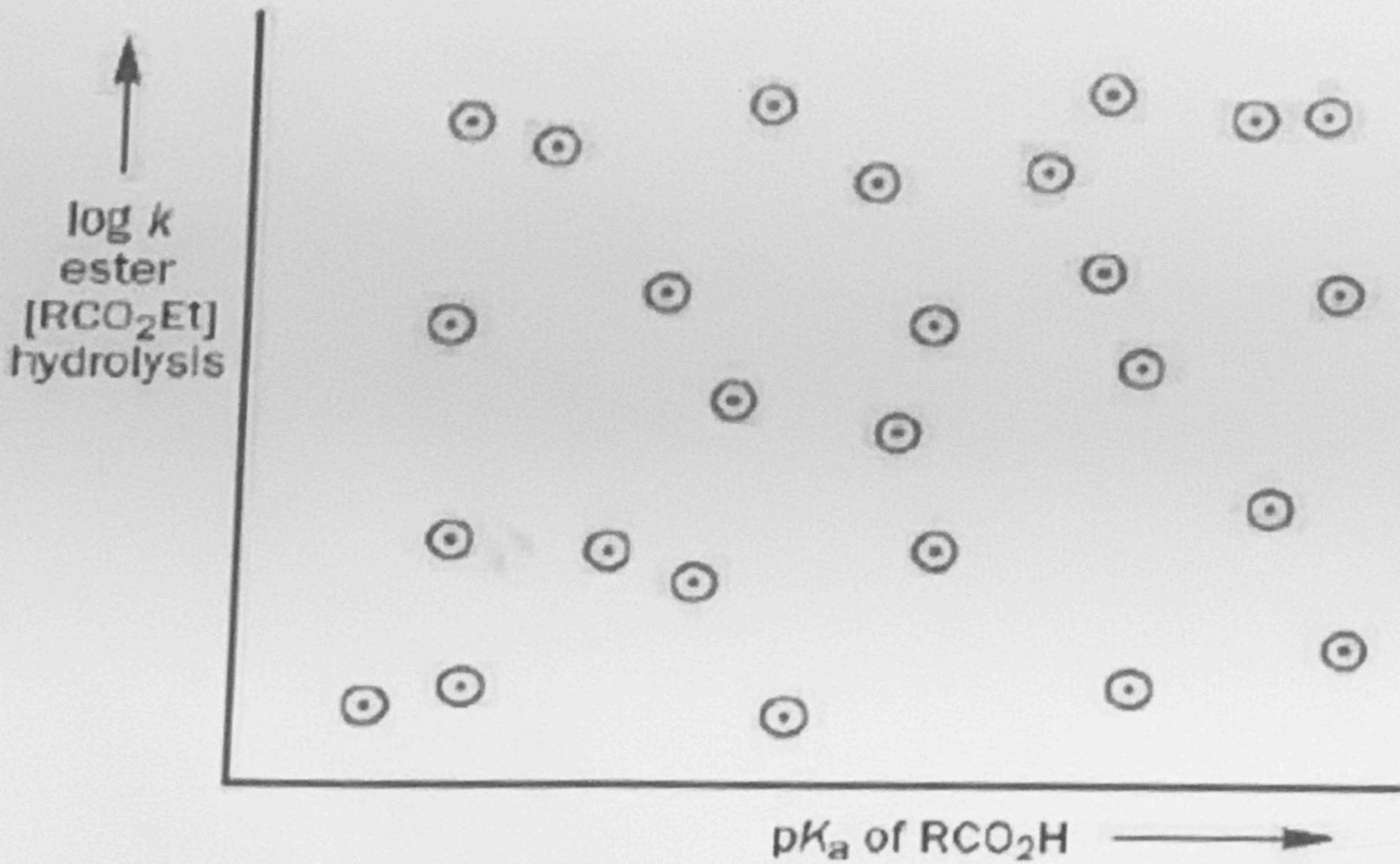
Gives an idea of what the transition state is "really" like

Hammett took the arbitrary [NOT REALLY] decision to use the pK_a of an acid as a guide.

For example, the rate of hydrolysis of esters might well correlate with the pK_a of the corresponding acid.

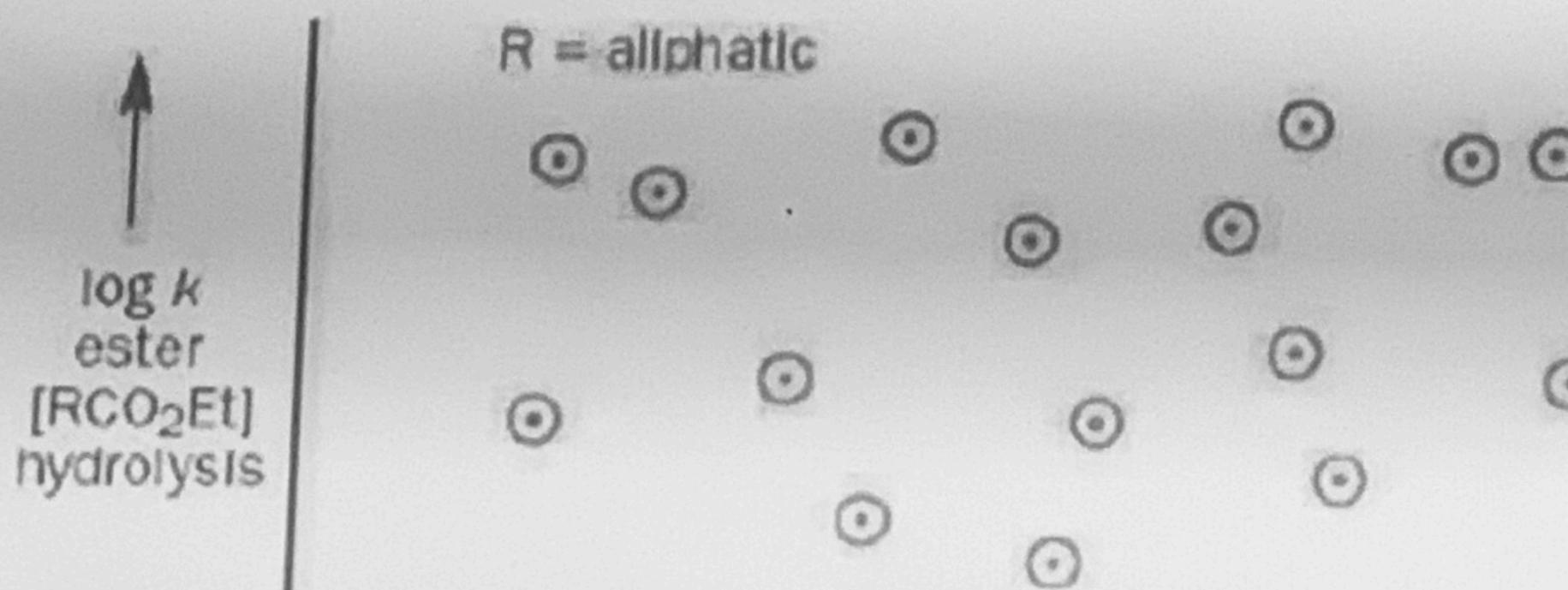


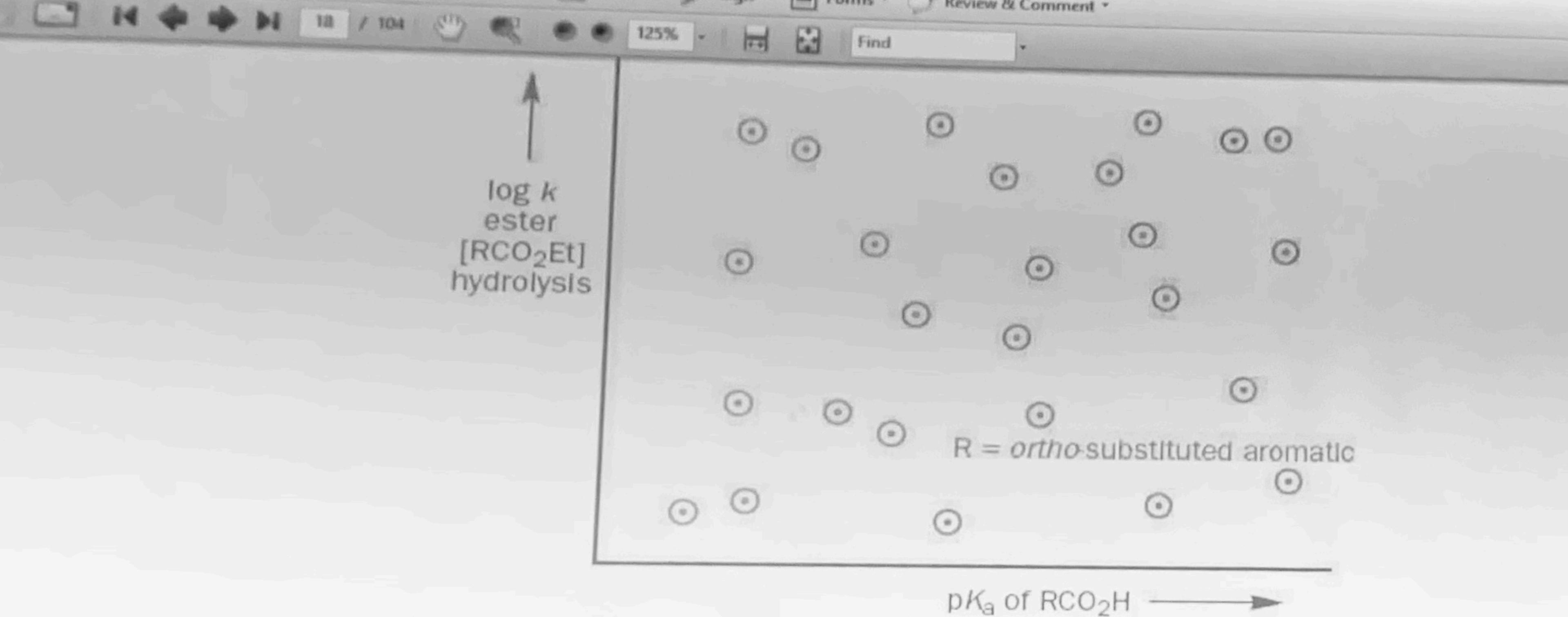
Plotted the rates of ethyl ester hydrolyses (as $\log k$ since pK_a has a log scale) against the $\text{pK}_{\text{a}s}$ of the corresponding acids (both aliphatic and aromatic)



A CLOSER LOOK:

Points towards the top of the graph belonged to the substituted acetic acids





Not a perfect correlation

Hammett had removed the examples where steric hindrance was important *in the reaction being studied*.

What he had discovered was that in a subset of ALL esterification reactions, substituents had a STERIC AD effect to what they had in the ionization o