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THE NATURE OF THE ACTIVATED COMPLEX IN THE CHROMYL CHLORIDE OXIDATION OF CYCLOALKENES[1]

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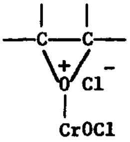
The chromyl chloride oxidation of unsaturates has been extensively investigated by a large number of workers (1,3-7). In order to account for the variety of products, several intermediates (I-IV) have been proposed. However, these deductions have been drawn from product studies, under nonidentical conditions, instead of kinetic data. We have therefore investigated the chromyl chloride oxidation of cyclopentene (V), cyclohexene (VI), and norbornene (VII) spectrophotometrically (415 mμ) in a stopped-flow reactor. All experiments were performed under pseudo-first order conditions with a large excess of cycloalkene (8-9).



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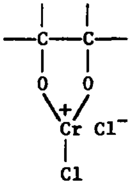

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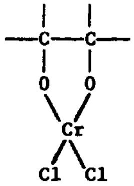

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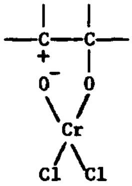


IV

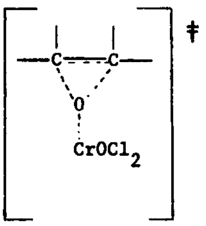
V, VI, and VII were selected for comparison of relative rates because of the influence of the ring size of the activated complex on the rates of reaction (10-11). In typical 1,3-dipolar cycloadditions, which involve five-membered cyclic activated complexes, VII reacts 10^3 to 10^4 times faster than VI. Relief of strain is the driving force for the high reactivity of VII. In epoxidation and dibromocarbene addition reactions (three-membered cyclic activated complexes) the rate differences between V and VI are small (Table I) (10-12).

TABLE I. RELATIVE RATES FOR CYCLOALKENE REACTIONS INVOLVING CYCLIC ACTIVATED COMPLEXES AT 25°

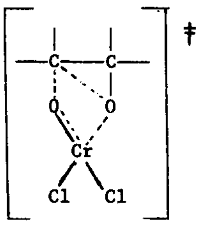
Reaction	Size of Activated Complex	Ratio of Relative Rates					
		VII/V	Δ[a]	V/VI	Δ[a]	VII/VI	Δ[a]
Chromyl chloride oxidation, 5°	3	63		4.9		312	
Chromic acid oxidation[11]	3	4.3	15	1.29	3.8	5.5	57
Epoxidation[10]	3	0.6	105	2.0	2.5	1.2	260
Dibromocarbene[12]	3			1.25	3.9		
Phenyl azide addition[13]	5	103	1.6	64	13	6500	20.8
Picryl azide addition[14]	5	189	3.0			8000	25.6

[a] Δ is a comparison ratio of the chromyl chloride oxidation ratio and the ratio for the respective reaction.

Comparison of the $\frac{V}{VI}$ values for chromyl chloride with those for the reactions with three-membered activated complexes gives the values 2.5, 3.8, and 3.9. On the other hand, comparison with phenyl azide cycloaddition gives a value of 13. Therefore, the values for the chromyl chloride oxidation of V and VI are closer to those for the three-membered activated complex than the five-membered activated complex. In contrast, in comparing the $\frac{VII}{VI}$ values for chromyl chloride with those for the reactions with three-membered activated complexes, the values are 56.7 and 260. The five-membered activated complexes give ratios of 20.8 and 25.6. Clearly, the values for the chromyl chloride oxidation of VII are closer to those for the five-membered activated complex. It is therefore likely that the activated complex for the oxidation of V or VI can be represented by VIII or IX, while the activated complex for the oxidation of VII can be formulated as X or XI (15).



VIII



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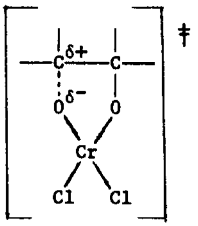
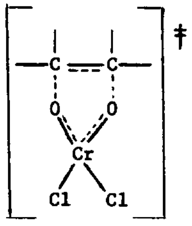


X



XI

Great care must be exercised in drawing qualitative conclusions concerning the nature of activated complexes from relative rates. The unusually large entropies of activation (Table II) are indubitably greatly influenced by bond angle bending strain, torsional strain, and non-bonded interactions in the cycloalkene as well as the rigid orientation requirements for the activated complex. However, there is a remarkable similarity between the entropies of activation for the epoxidation and the chromyl chloride oxidation of V and VI. In contrast, the value for VII is more like 1,3-dipolar cycloaddition reactions. We are investigating the influence of relative rates and of thermodynamic parameters on the nature of activated complexes in the chromyl chloride oxidation of various cycloalkenes.

TABLE II. THERMODYNAMIC PARAMETERS FOR CYCLIC ACTIVATED COMPLEXES

Reaction	Size of activated complex	$\Delta H^\ddagger$, kcal/mole			$\Delta S^\ddagger$, e.u.			Ref.
		V	VI	VII	V	VI	VII	
Chromyl chloride oxidation	3	8.9	10.3	1.97	-23.5	-21.6	-40.2	a
Epoxidation[b]	3		12.7			-24.0		16
Picryl azide addition	5	12.3	-	9.8	-35.5	-		13

[a] This work. [b] -21 to -26 e.u. is usually the range for styrenes and stilbenes.

ACKNOWLEDGEMENT

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