

RELATIVE RATES OF ADDITION REACTIONS

Ronald E. Erickson and Robert L. Clark

Department of Chemistry, University of Montana, Missoula, Montana 59801

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Recently Awasthy and Roček reported rate studies on the oxidation of olefins by chromic acid and made several reasonable inferences as to the nature of the transition state for this reaction (1). One section of their argument was concerned with the relative reactivities of cyclohexene, cyclopentene, and norbornene in reactions involving cyclic transition states. Specifically, they noted that for reactions leading to a three-membered cyclic intermediate, the relative reactivities with respect to cyclohexene are 1.25-2.0 for cyclopentene and 1.2-17.0 for norbornene, whereas for reactions with larger membered cyclic transition states the values are 9.4-110 for cyclopentene and 450-8000 for norbornene. Their data for Cr(VI) oxidations (cyclopentene:cyclohexene 1.29, norbornene:cyclohexene 5.5) correlated well with the three-membered ring transition state data and they argued accordingly against a five-membered ring transition state. Qualitatively, the rate differences observed in such comparative rate studies are due to relief in strain in going from the alkene to the transition state, and the idea that less strain is relieved in going to a three-membered transition state is reasonable.

In this communication we report experimental data for ozone and osmium tetroxide additions which show that comparable rates are considerably smaller than those for previously studied reactions. Both ozone and osmium tetroxide are generally conceded to react with alkenes to yield initial products containing five-membered rings (2). We have found, however, that both reagents are less selective within the norbornene:cyclohexene pair than any reagent leading to a five-membered ring investigated in the past. Ozone selectivity for the cyclopentene:cyclohexene pair is also considerably lower than that found for

other reactions involving similar transition states. Table I lists the relative rates we have determined for ozone and osmium tetroxide addition to the compounds in question. Other workers' results for diimide reductions and chromic acid oxidations are included for comparative purposes (1,3).

TABLE I  
Relative Rates of Addition Reactions

Reaction	Size of Transition State	Reactivity Rate cyclopentene: cyclohexene	norbornene: cyclohexene	Ref.
O <sub>3</sub> <sup>a</sup>	5	3.9	4.3	this work
OsO <sub>4</sub> <sup>b</sup>	5	21.9	72.3	this work
diimide	6	15.5	450.0	3
CrO <sub>3</sub>	3	1.29	5.5	1

<sup>a</sup>Determined at -78° in ethyl acetate.

<sup>b</sup>Determined at 25° in pyridine.

Relative rates of ozonation were determined competitively by gas chromatography as in previous studies (4). Osmium tetroxide data were determined in a similar manner, but because relative rates were too large to be determined by direct competition, a series of compounds (e.g., cyclopentene vs cycloheptene; cycloheptene vs cyclohexene) was used and the rates were determined indirectly.

We also wish to point out that theoretical calculations do not support the use of data from such a limited number of compounds for the determination of ring size for cyclic transition states. Relative rates of reactions can be correlated semiquantitatively with strain effects as has been shown by Garbisch *et al.* (3) in their study of diimide reductions of a large series of cyclic and acyclic alkenes. They made use of one adjustable parameter ( $\chi$ , the percentage progression along the reaction coordinate), in their calculations. This term, which is of major importance to this communication, corresponds to the normal qualitative concept of a transition state being product-like or reactant-like. Variation of this term can have a large effect on calculated relative rates. Using  $\chi = 0.34$ , Garbisch *et al.* obtained excellent agreement between experimental

and calculated relative rates for a very large number of acyclic, cyclic, and exocyclic alkenes including cyclopentene:cyclohexene 16 and norbornene:cyclohexene 450. However, use of the value  $\chi = 0.07$  (i.e., transition state is 93% reactant-like) in Garbisch's equations, leads to calculated values for cyclopentene:cyclohexene 2.0 and norbornene:cyclohexene 3.5. These calculated values which are based on the diimide six-membered ring transition state and are merely illustrative of Garbisch's method, are in fact quite close to the results for the Cr(VI) oxidations found by Awasthy and Roček which were explained on the basis of a three-membered ring transition state.

Thus, very small rate differences for a series of cyclic alkenes may be due, in a qualitative sense, either to a small membered ring transition state in which little strain has been removed, or to a transition state which is very reactant-like.

We believe that the study of relative rates as carried out by Garbisch may be quite useful in helping to unravel mechanistic problems, and are continuing our studies with ozone and osmium tetroxide. However, both the experimental results reported here and a recognition of the variation of relative rates with  $\chi$  would indicate that transition state analogies based on a limited set of data should be treated with caution.

#### ACKNOWLEDGMENT

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#### REFERENCES

1. A. K. Awasthy and J. Roček, J. Am. Chem. Soc. 91, 991 (1969).
2. There have been suggestions in the literature (e.g., P. S. Bailey and A. G. Lane, J. Am. Chem. Soc. 89, 4473 [1967], R. W. Murray, R. D. Youssefyeh, and P. R. Story, ibid. 89, 2429 [1967]) that ozonolyses of highly hindered *cis* olefins may proceed through three-membered ring transition states. The cyclic alkenes studied here would be expected to form the normal five-

membered molozonide and we (R. E. Erickson and G. D. Mercer, unpublished results) have some evidence from low temperature nmr studies that they do s

3. E. W. Garbisch Jr., S. M. Schildcrout, D. B. Patterson, and C. M. Sprecher, J. Am. Chem. Soc. 87, 2932 (1965).
4. R. E. Erickson, R. T. Hansen, and J. Harkins, J. Am. Chem. Soc. 90, 6777 (1968).