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THE REACTIONS OF OLEFINS WITH PERMANGANATE, RUTHENIUM TETROXIDE, AND OSMIUM TETROXIDE; DEPENDENCE OF RATE ON DEGREE OF SUBSTITUTION

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In spite of the extensive use of the tetraoxotransition metal reagents (MnO_4^-, RuO_4, and OsO_4) for oxidation of olefins in organic synthesis, there has never been a systematic study of the dependence of the rate for these processes on the degree of olefin substitution. Because of our general interest in the reactions of oxometal species with olefins[1] we had occasion to measure the relative rates given in the Table.

Examination of the data in the Table reveals that these oxoreagents are rather insensitive to the extent of alkyl substitution. By comparison it is well known that the reactivity of olefins toward other common electrophilic reagents such as per acids and halogens increases dramatically with increasing alkyl substitution.[2] For both OsO_4 and RuO_4 there are only gradual increases in rate for each additional alkyl substituent. In the case of OsO_4 the relative rate differences are enhanced on going to solvents of poorer coordinating ability (i. e., pyridine → ether → hexane). In hexane, with a rate difference of almost forty, one could hope for fairly selective attack on a tetrasubstituted olefin in the presence of a monosubstituted one.

The most curious results in the Table are those for oxidations by $KMnO_4$ in acetic anhydride.[3] Although the effects are small, the permanganate ion clearly prefers the least substituted olefin 1-undecene. To our knowledge there have been no previous reports[4] of oxidizing agents which exhibit this unusual type of selectivity. Henbest[5] had already discovered another peculiarity of permanganate oxidations of olefins; the oxidations are accelerated by electron-withdrawing substituents ($\rho = +0.65$). By contrast OsO_4 oxidations of the same stilbenes exhibited a ρ of -0.55.

The data given here should be of use in planning selective oxidations of polyenes with these tetraoxoreagents. However, it should be pointed out that all of the substrates in this study are simple acyclic olefins and the situation with complex olefins may be quite different.

Table.[a] Influence of the Extent and the Pattern of Alkyl Substitution on the Relative Rates of Oxidation

Reagent →	OsO_4	OsO_4	OsO_4	RuO_4	$KMnO_4$
Solvent →	hexane	ether	pyridine	CCl_4	Ac_2O
Olefin					
1-undecene	1.0	1.0	1.0	1.0	1.0
2-methyl-1-tridecene		1.3	1.0	1.4	0.2
Z-5-decene		2.0	1.1	3.0	0.4
E-5-decene	5.2	4.2	2.7	4.2	0.8
citronellyl benzoate	8.8	4.7	3.0	6.2	0.6
2,3-dimethyl-2-octene	38	23	9.2	15	0.5

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[a] The relative rates (normalized in each case to 1-undecene) were determined by monitoring the disappearance of starting olefin by glc.

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3. We chose this particular permanganate reagent because the hydrocarbon olefins were soluble in the acetic anhydride and because of our prior experience with this system (ref. 1b).
4. We have recently observed this same type of selectivity with an alkyl imido osmium reagent: K. B. Sharpless, D. W. Patrick, L. K. Truesdale, and S. A. Biller, *J. Amer. Chem. Soc.*, **97**, 2305 (1975).
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