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Received March 29, 1976

Kinetics of the Oxidation of Some Unsaturated Compounds by Sodium Ruthenate

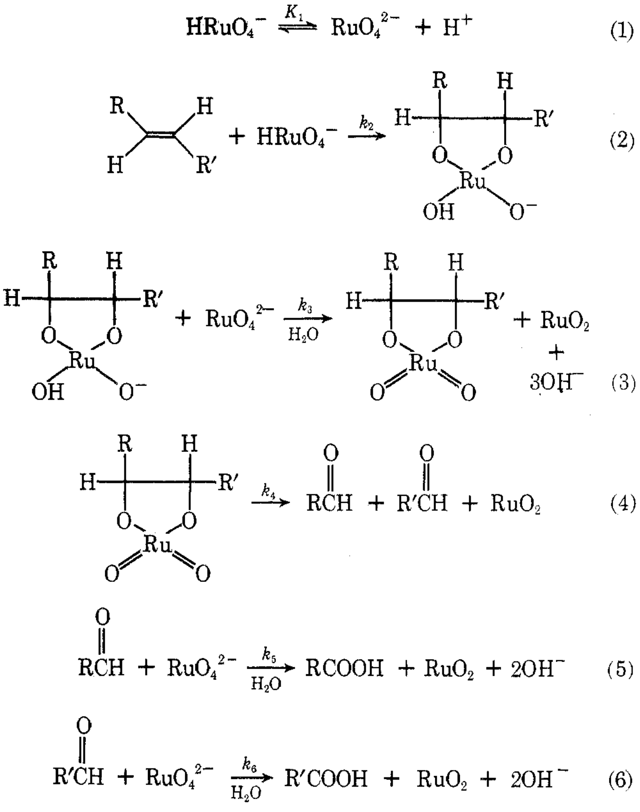
Summary. A kinetic study of the oxidation of a number of unsaturated carboxylic acids by sodium ruthenate suggests that the reaction proceeds by way of a complex mechanism which involves both ruthenium(IV) and ruthenium(VI) diesters as intermediates.

Sir: An investigation of the oxidative cleavage of carbon–carbon double bonds by sodium ruthenate (Na_2RuO_4) is of interest because ruthenium(VI) oxides may be involved as intermediates in ruthenium tetroxide oxidations.[1] We have found that the results obtained from a kinetic study of the oxidation of a large number of unsaturated carboxylate ions by sodium ruthenate can all be accommodated by the reaction mechanism outlined in Scheme I. Aqueous sodium hydroxide was used as the solvent for these experiments because ruthenate ion is not stable in neutral or acidic solutions.[2]

Sodium ruthenate[3] was found to react at easily measurable rates with unsaturated carboxylate ions in aqueous base at 85 °C. The rates were determined by removing aliquots at appropriate intervals and estimating the concentration of ruthenate ion using a Perkin-Elmer 356 dual wavelength, double beam spectrophotometer which has previously been described.[4] The absorbance at 460 nm (maximum) was compared with that at 570 nm (minimum) and the concentration of ruthenate ion obtained from a previously prepared calibration curve.

Initial rate studies indicated that the reaction was first order in both ruthenate and carboxylate ions. However, good second-order kinetics were not maintained throughout the entire course of the reaction, and subsequent studies revealed that the experimental data could not be satisfactorily fitted to any integral rate expression. Consequently, a computer program which simulates reaction kinetics by numerical integration was used to define the rate law.[5] The program generates data for a particular scheme starting from an initial set of rate constants, compares the generated data with the experimental data, adjusts the rate constants, and repeats the process until the differences between calculated and experimental absorbance values have been minimized. When approximately 30 different possible reaction schemes were investigated in this way, Scheme I was found to give the best agreement with all of the available data.

Scheme I



The approximate values for k_2 were first obtained from initial reaction rates, and k_3, k_5, and k_6 were assumed to be large relative to k_2 and k_4. Since step 3 involves the transfer of electrons between two oxy anions, it is not unlikely that k_3 would be relatively large.[6] Test tube experiments indicated

Table I. Rate Constants for the Oxidation of Unsaturated Carboxylic Acids by Sodium Ruthenate in Aqueous Sodium Hydroxide[a]

Carboxylate ion	Concn, M	[NaOH], M	$k_2 \times 10^3$, $M^{-1} s^{-1}$ [b]	$k_4 \times 10^5$, $M^{-1} s^{-1}$ [b]
Acrylate	0.00820	0.717	25.1 ± 1.2	23.0 ± 7
Crotonate	0.00780	0.717	11.9 ± 0.6	3.3 ± 0.9
Crotonate	0.00798	0.628	16.8 ± 0.1	3.6 ± 1.1
Crotonate-β-*d*	0.00798	0.628	28.4 ± 0.7	5.5 ± 1.6
Methacrylate	0.00796	0.717	9.1 ± 0.2	1.7 ± 0.5
α-Methylcrotonate	0.0177	0.717	8.8 ± 0.1	4.7 ± 1.4
β-Methylcrotonate	0.00795	0.717	3.4 ± 0.1	0.76 ± 0.23
Cinnamate	0.00121	0.532	59.2 ± 1.5	1.9 ± 0.6
Cinnamate-α-*d*	0.00121	0.532	73.3 ± 0.9	1.4 ± 0.4
Cinnamate-β-*d*	0.00121	0.532	70.2 ± 2.0	1.7 ± 0.5
p-Methylcinnamate	0.00462	0.516	48.6 ± 0.4	7.2 ± 2.2
m-Methoxycinnamate	0.00462	0.516	45.5 ± 0.7	5.2 ± 1.6
m-Nitrocinnamate	0.00462	0.516	42.4 ± 0.4	4.8 ± 1.4

[a] Temperature 85.0 ± 0.1 °C. Initial ruthenate concentration was 4.3×10^{-4} to 5.0×10^{-4} M. [b] k_2 and k_4 are defined in Scheme I.

that aldehydes rapidly reduce ruthenate ion at room temperature, thus confirming that k_5 and k_6 must also be large at 85°. Using these initial assumptions the program then generated the values of k_2 and k_4 summarized in Table I.

The values for k_2 could be obtained with good precision (±3% or better) and may be accepted with considerable confidence because they can be verified independently from initial reaction rate studies. Unfortunately, the inherent uncertainties in the k_4 values obtained this way are much greater (about ±30%). Consequently, it is not possible to draw conclusions regarding isotope effects or the effect of substituents on this step of the reaction except to note that a comparison of the rate constants for acrylate, crotonate, and β-methylcrotonate ions seems to indicate that methyl substitution at the double bond decreases the rate of reaction significantly.

The observation that the magnitude of k_2 increases when the vinyl hydrogens are replaced by deuterium indicates that the initial step of the reaction involves a change in hybridization of the α and β carbons from sp^2 to sp^3,[7] and is in agreement with the proposed formation of a cyclic ruthenium(IV) diester.[8] The small effect of ring substituents on the magnitude of k_2 is also similar to that observed in other reactions which involve 1,3-dipolar additions.[9]

The magnitude of k_2 was found to decrease as the basicity of the medium increased during the oxidation of cinnamate ion, presumably because of an equilibrium between RuO_4^{2-} and $HRuO_4^-$ as in step 1 of Scheme I. By comparison with other oxy anions it is not unreasonable to expect that protonation would increase the vigor of the oxidant.[10] At high base concentrations ($[NaOH] \leq 2$ M) the rate of oxidation of crotonate ion increases, indicating that additional reactions may be occurring. However, under all other conditions Scheme I was found to accommodate the experimental results adequately, and, since a large number of other reaction sequences were found to be inadequate, it appears quite probable that the reaction proceeds by this rather logical sequence of reactions. The scheme is also consistent with the observed products of the reaction; the oxidation of cinnamate ion, for example, gave benzoate ion in a 99% yield.

Acknowledgments. The authors gratefully acknowledge the financial assistance of the National Research Council of Canada, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Committee on Higher Education, Imperial Oil Limited, for support of this research.

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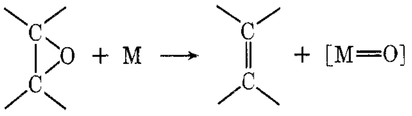
Received March 29, 1976

Deoxygenation of Epoxides by Metal Atom Cocondensation

Summary. Epoxides are converted to alkenes upon cocondensation with first-row transition metal atoms.

Sir: Transition metal atoms are substantially more reactive than the corresponding bulk metals by virtue of the 70–200 kcal/mol required for their formation.[1] This reactivity has been previously used to effect oxidative insertion reactions[2] and π-complex formation.[3] We now report a third reaction type, herein exemplified by the facile deoxygenation of epoxides (1) to alkenes (2). We believe this will be the first in a series of synthetically useful reductive deoxygenations which can be effected by transition metals in their atomic form.[4]



1 2

The relative reactivities of several first row transition metal atoms were determined by high vacuum cocondensation with at least a tenfold excess of cyclohexene oxide at 77 K. Atoms were produced by resistive heating of coated tungsten rods in either a conventional[2] or a new "micro" reactor,[5] the latter suitable for experiments with less than a gram of organic compound. After 1 h, during which time the reactor was allowed to warm to room temperature, the products were pumped into a cold trap and subjected to NMR and GC analysis. The results are presented in Table I. Chromium and vanadium emerged as the most effective (based upon metal), abstracting over 2 equiv of oxygen. Titanium afforded slightly lower yields (epoxide polymer was formed in some runs) and nickel was distinctly less reactive. Cyclohexene production was accompanied by small amounts of benzene (3–10% of product) and varying amounts (0–20%) of 1,3-cyclohexadiene, but cyclohexane could not be detected. With less volatile titanium and vanadium, control experiments indicate a small portion of the observed deoxygenation may be effected by the presence of the hot metal filament per se.

Studies with chromium atoms (Table II) indicate the reaction is general for epoxides. With *cis*-stilbene oxide and allylbenzene oxide, no stable volatile organometallic complexes were noted, although π-complex formation might precede deoxygenation in the matrix. No double-bond migrations were observed, but cis–trans isomerization did take place. In separate experiments, *cis*-4-decene was isomerized

Table I. Cocondensation of Metal Atoms with Cyclohexene Oxide [a]

Metal	Equiv of oxygen removed/ metal[b]	Cyclohexene yield,[c] %
Ti	0.9	8.7
V	2.8	5.6
Cr	2.7	7.8
Co	1.2	6.8
Ni	0.6	2.3

[a] 0.4–1.4 mmol of metal with 10–15 mmol of epoxide. All numbers are corrected for metal reaching the reaction zone. This was determined by depositing a Cr film in the reactor, digestion of the film with 70% $HClO_4$, and titration via standard Fe^{2+}/$Cr_2O_7^-$ methods: G. H. Ayres, "Quantitative Chemical Analysis", 2nd ed, Harper and Row, New York, N.Y., 1968, pp 625–627. [b] These data were obtained in the "micro" reactor and were somewhat lower in the conventional reactor. [c] Absolute yields; those with Cr, Co, and Ni are 70–90% if corrected for recovered starting material.