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Kinetic study of the ruthenium catalysed oxidation of styrene and substituted styrenes

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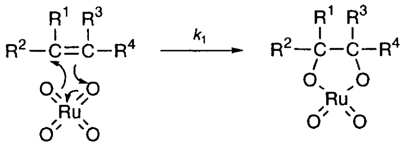
The kinetics of ruthenium catalysed oxidation of styrene and substituted styrenes by sodium hypochlorite solution was investigated using gas chromatography. The substituted styrenes used were *p*-methoxystyrene, *p*-methylstyrene, *p*-bromostyrene and *m*-nitrostyrene. It was found that the reaction rates increased from *p*-methoxystyrene to *m*-nitrostyrene. The rate constants showed that an electron donating group slowed the rate of reaction while an electron withdrawing group increased the rate of the reaction. The rate constants did not give a good linear relationship with the Hammett substituent constants when correlation with the Hammett equation was attempted. On the other hand, this trend was consistent with the results of analysis by the frontier molecular orbital theory, in which the activation energy of a reaction was correlated with the energy difference between the HOMO of the substituted styrenes and the LUMO of ruthenium tetroxide.

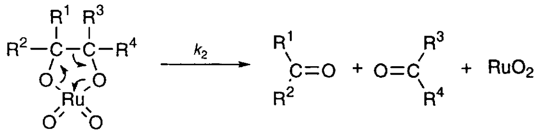
It is well known that the carbon–carbon double bonds can be cleaved by many types of inorganic oxidants to give ketones or aldehydes, and that the aldehydes in turn are usually oxidized to give carboxylic acids.[1–8] Among many such oxidants, ruthenium tetraoxide (RuO_4) was one of the first to be discovered as a vigorous oxidizing agent[9] and is known to convert olefins directly into the corresponding carbonyl compounds under mild conditions such as low temperature and neutral solvents.[10] One of the striking properties of RuO_4 is that it can be regenerated[11] *in situ* from its reduced products by other less expensive oxidants such as sodium periodate and sodium hypochlorite (NaClO). Thus, it can act as a catalyst for the oxidation of olefins with sodium periodate or sodium hypochlorite serving as the consumed oxidant. A number of studies have been made on the synthetic application of stoichiometric or catalytic amounts of RuO_4. However, to the best of our knowledge, so far only one report on the study[12] of the kinetics of oxidation by stoichiometric quantity of RuO_4 has been made and no reports are yet available on the kinetics of oxidation of olefins using RuO_4 as a catalyst.

The present work was initiated to study the kinetics of olefinic oxidation using RuO_4 as a catalyst. The reaction rate of a redox reaction system containing a catalytic amount of the ruthenium compound, substituted styrenes, excess sodium hypochlorite and solvent was experimentally studied. Four substituted styrenes were chosen to be the double bond substrates for the kinetic study. These provide several advantages: (*i*) any steric effect will be constant for all *para*- and *meta*-substituted styrenes because the reaction site is on the ethylene double bond; (*ii*) any substituent effect can be correlated with the well known Hammett substituent constant and (*iii*) the overall rate of styrene oxidation in the presence of sodium hypochlorite to give products such as benzoic acid and carbonic acid can be thermodynamically favoured and is considered to be an irreversible process.

Based on the kinetic data, Lee and Spitzer[12] suggested that the reaction between olefin and RuO_4 proceeds by two steps as follows:



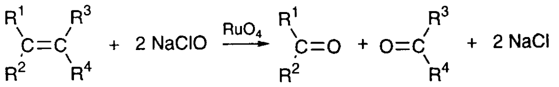
(1)



(2)

$$RuO_2 + 2\,NaClO \longrightarrow RuO_4 + 2\,NaCl \qquad (3)$$

The first step is a concerted pericycloaddition followed by decomposition of the cycloaddition product. The rate constants of these reactions are designated as k_1 and k_2 respectively. This mechanism is exactly identical to the well established mechanism by which permanganate or osmium tetraoxide reacts with a carbon–carbon double bond because RuO_4, osmium tetraoxide and permanganate ion have the same tetrahedral structure,[13,14] and these central atoms all have a high oxidation number. If the carbonyl product is an aldehyde, it will be further oxidized to a carboxylic acid or to carbonic acid in the case of formaldehyde. In the presence of sodium hypochlorite, RuO_2 (*i.e.*, the reduced product of RuO_4) can be oxidized back to RuO_4 [eqn. (3)]. This regenerated RuO_4 can go back to reaction (1) and begin the reaction sequences again. In this way, RuO_4 acts as a catalyst, and the reactants actually consumed are the olefin and the sodium hypochlorite. By combining reactions (1)–(3) the overall reaction can be presented as:



$$R^1R^2C{=}CR^3R^4 + 2\,NaClO \xrightarrow{RuO_4} R^1R^2C{=}O + O{=}CR^3R^4 + 2\,NaCl \qquad (4)$$

No kinetic data are available for reaction (3), but from our observations, the black solid RuO_2 will dissolve instantaneously into sodium hypochlorite solution. Thus, the reaction (3) can be believed to be very fast, *i.e.*, faster than reaction (1) or (2). It can be assumed that reaction (3) is always in equilibrium and the overall rate of reaction (4) is approximately equal to the rate of reaction (1) or (2), depending upon which one is slower.

Experimental

Synthetic method

All the solvents and materials used are high purity reagent grade materials. Before the kinetic experiments, styrene and the substituted styrenes were subjected to oxidation to isolate the corresponding substituted benzoic acids. These synthetic

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experiments were carried out at higher concentrations and with larger amounts. A typical reaction procedure for the oxidation of *m*-nitrostyrene is described below.

In a three-necked round bottom flask fitted with the condenser, 1 g of *m*-nitrostyrene, 10 ml of acetonitrile, 55 ml of sodium hypochlorite solution (12%) and *ca.* 50 mg of RuO_4 were placed. To this biphasic solution, 7 drops of conc. hydrochloric acid were added to adjust the pH value of the solution to between 6 to 8, and then the reaction mixture was stirred for about 8 h. The reaction was stopped and 10% of sodium hydroxide solution was added to the black solution until the pH exceeded 11. The reaction mixture was filtered and the filtrate was acidified with hydrochloric acid. About 30 ml of dichloromethane was used to extract this aqueous solution. The yellow organic phase obtained was washed with 30 ml of 5% solution of sodium bisulfite several times until it became colourless. The dichloromethane was then removed under vacuum until the volume of the solution was reduced to about 3 ml. This residue was cooled with ice–water to precipitate the product. The precipitate was filtered and dried under an infrared lamp. The weight of the solid product was 0.78 g (68%). The product was identified by melting point and IR and NMR spectral measurements. The remaining substituted styrenes and the styrene were oxidized by the same procedure. These results are summarized in Table 1.

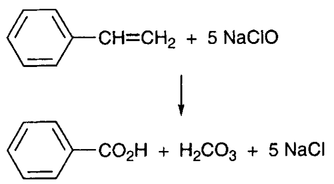
The relatively low product yields may be due to loss in the isolation processes. Since the goal of the experiment was to only make sure that the ultimate oxidation products were the corresponding substituted benzoic acids, little effort was put into maximizing these yields.

Kinetic experiment

For the kinetic experiment the reaction was carried out in a three-necked round bottom flask fitted with a condenser. One neck of the flask was used for the thermometer to monitor the temperature and the other for sampling. A magnetic stirrer was used to agitate the mixture. A typical reaction system consisted of 10 ml each of carbon tetrachloride and acetonitrile, 0.5 ml of styrene (or substituted styrenes), 0.3 ml of *tert*-butylbenzene (a GC internal reference compound), 50 ml of 12% of NaClO solution. The mixture was stirred for 2 min and the stirring was stopped to take the first sample. Conc. hydrochloric acid (7 drops) was added dropwise until the pH value was between 6 and 8. The organic layer was allowed to settle completely, and then 2 ml of ruthenium solution (50 mg of RuO_4 dissolved in 200 ml of NaClO solution) was added carefully to avoid disturbance of the organic layer. The magnetic stirrer was turned on quickly and the time was recorded at this moment.

The first sample was taken before start of the reaction. The second sample was taken at 3.5–7.0 min after start of the reaction. During sampling, the magnetic stirrer was stopped completely and in 2 s, the organic phase had settled to the bottom. A long dropper was used to draw *ca.* 0.1 ml of the organic layer, and the magnetic stirrer was turned on immediately to continue the reaction. At the same time, 2–3 drops of the sample in the dropper was discharged into a separatory funnel containing 10 ml sodium bisulfite solution (5%), and the mixture was shaken thoroughly to quench the reaction. Any excess sample resting in the dropper was put back quickly into the reaction system. About 3–5 ml of dichloromethane was added to the separatory funnel to extract the organic compounds for gas chromatographic (GC) analysis. The sampling was designed using the rule that the next time interval was twice the previous one. All the samples were subjected to GC analysis and every sample was analysed by three injections. Each injection produced a chromatogram with numeric peak areas for the substituted styrenes (S_a) and the internal reference compound (S_r). The area ratio, (S_a/S_r) of the injections was calculated and the average ratio was used to calculate the concentration ratio, ([A]/[A_0]) as per the method suggested below.

The overall RuO_4 catalysed reaction of the substituted styrenes by sodium hypochlorite can be represented as:



(5)

where H_2CO_3 will decompose into H_2O and CO_2, depending on the pH value of the solution. According to the reaction mechanism, k_2 is assumed to be much larger than k_1 *i.e.*, the first step is the rate determining step and hence, the rate law can be written as

$$d[A]/dt = -k_1[A][RuO_4] \qquad (I)$$

where [A] is the concentration of substituted styrene, t is the reaction time and $[RuO_4]$ is the concentration of ruthenium tetraoxide. At the beginning of the reaction, RuO_4 was added in catalytic amount and NaClO was added in excess (20 times the stoichiometric amount of the substituted styrene). The ruthenium tetraoxide, generated instantly by NaClO from its reduced state, is considered constant and integration of eqn. (I) gives

$$\ln\{[A]/[A]_0\} = -k_1[RuO_4]t \qquad (II)$$

where $[A]_0$ is the initial concentration of the substituted styrene and k_1 is rate constant. Substituted styrenes are volatile and can therefore be quantitatively measured by GC with a FID detector. According to eqn. (II), only the ratio of $[A]/[A]_0$, not the absolute values of [A] and $[A]_0$ are required, and this ratio can be obtained easily using an internal reference compound. The equation then represents the relationship between the concentration of the substituted styrene and the peak areas on the gas chromatograms.

$$[A]/[A]_0 = (S_a/S_r)/(S_{a0}/S_{r0}) \qquad (III)$$

Here, S_a and S_r are the peak areas from the GC for the substituted styrenes and reference compound respectively, in a sample; the S_{a0} and S_{r0} are the peak areas of the GC in the first sample which was sampled when the reaction time was zero.

The basic experimental procedure was designed to be a

Table 1 Oxidation of styrene to benzoic acids

starting compound	product	yield (%)	m.p./°C (obs.)	m.p./°C (ref. 17)
styrene	benzoic acid	65	122–123	122–123
p-methylstyrene	*p*-methylbenzoic acid	40	181–182	180–182
p-bromostyrene	*p*-bromobenzoic acid	47	254–255	252–255
p-methoxystyrene	*p*-methoxybenzoic acid	59	180–182	182–185
m-nitrostyrene	*m*-nitrobenzoic acid	68	139–141	140–142

reaction system containing one substituted styrene, one reference compound, catalytic amount of ruthenium compound, excess amount of sodium hypochlorite and solvent. Samples were taken in a series of time intervals and each sample was quenched with sodium bisulfite solution immediately when it was removed from the flask and the samples were analysed by GC. A plot of $\ln\{[A]/[A]_0\}$ *vs.* t was drawn, and a specific rate constant k (equal to $k_1[RuO_4]$) was deduced from the slope of the best fitted straight line. In the blank reaction, all the chemicals and procedures remained the same as the kinetic experiment involving styrene, except that there was no ruthenium catalyst in the sodium hypochlorite solution.

Results and Discussion

The kinetic data are given in Table 2. A plot of $\ln\{[A]/[A]_0\}$ *vs.* t is shown in Fig. 1 for styrene and all the substituted styrenes. In the blank experiment, the slope of the straight line is -0.0011 which indicates that this reaction is about 70 times slower than the counterpart catalytic reaction, which was the styrene catalytic reaction with a slope of -0.0734. So this uncatalysed reaction was insignificant in contrast to the catalysed reaction and it was considered negligible in the analysis of the catalysed reaction data. All the plots for styrene and substituted styrenes show that there is an approximate linear relation between $\ln\{[A]/[A]_0\}$ and time for each reaction. These data fitted the kinetic reaction described by eqn. (II).

Table 2 Sampling time and GC analysis of styrene and substituted styrenes

	p-methoxystyrene				
time/min	4	11.5	26.5	63	120
$\ln\{[A]/[A]_0\}$	−0.182	−0.230	−0.647	−1.37	−2.83
	p-methylstyrene				
time/min	4	13	28	55	
$\ln\{[A]/[A]_0\}$	−1.924	−0.699	−1.204	−2.090	
	styrene				
time/min	3	7	14	21	
$\ln\{[A]/[A]_0\}$	−0.221	−0.511	−1.122	−1.480	
	p-bromostyrene				
time/min	3	9.5	22.5		
$\ln\{[A]/[A]_0\}$	−0.432	−1.11	−2.63		
	m-nitrostyrene				
time/min	1.5	4	6.5		
$\ln\{[A]/[A]_0\}$	−0.74	−1.48	−2.36		
	blank reaction				
time/min	60				
$\ln\{[A]/[A]_0\}$	−0.0672				

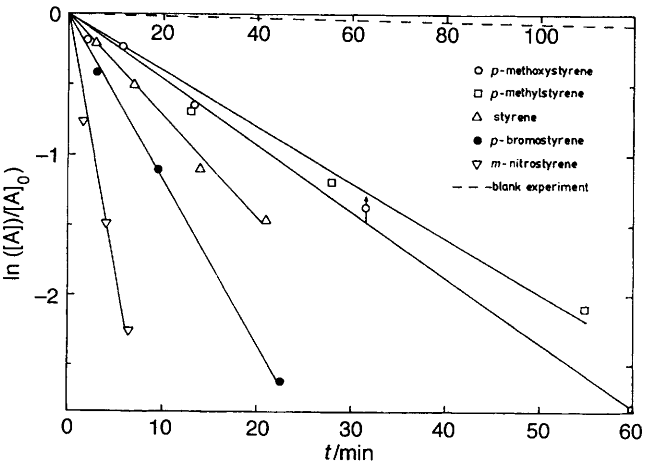


Fig. 1 Kinetic plots of $\ln\{[A]/[A]_0\}$ *vs.* t for styrene and substituted styrenes

Realizing the importance of Hammett equation in the correlation of kinetic data, an attempt was made to evaluate the substituent constants of styrene and its substituted analogues. According to eqn. (II) the reaction rate constant, k_1 should yield the following equation:

$$-k_1[RuO_4] = k(\text{slope}) \qquad (IV)$$

The concentrations of ruthenium tetraoxide in five reactions are assumed to have approximately the same value, then the ratios of reaction rate constants, k_1 can be obtained from the slopes. For example, for styrene and *p*-bromostyrene, the ratio of their rate constants can be calculated as follows:

$$\frac{k_{1b}}{k_{1h}} = \frac{k_{1b}[RuO_4]_b}{k_{1h}[RuO_4]_h} = \frac{\text{slope(b)}}{\text{slope(h)}} = \frac{-0.117}{-0.0734} = 1.59 \qquad (V)$$

where the subscript b stands for *p*-bromostyrene and h for styrene. These ratios of rate constants are correlated using the Hammett[15] relation $\log(k/k_h) = \rho\sigma$, where k_h stands for the unsubstituted compound and k for the substituted compound. These can be either reaction equilibrium constants or reaction rate constants. In the present case, these are the rate constants. The symbol σ is a substituent constant and ρ is the reaction constant. The substituent constants for most substituent groups are known from the literature[15] and these are given Table 3 along with the data on ratio of rate constants. The plot of $\log(k/k_h)$ *vs.* σ is shown in Fig. 2. Obviously, no good linearity exists and the results can be interpreted in terms of electron donating and electron withdrawing groups. The electronic donating groups such as methyl and methoxy decrease the rate of catalytic oxidation reaction while an electronic withdrawing group increases the rate of reaction.

An effort was also made to interpret the kinetic results by frontier molecular orbital theory.[15] From this theory, the interaction energy, E, between two molecules can be calculated as:

$$E = \sum \{q_i q_j/\varepsilon R\} + \sum \{2c_i c_j \beta\}/\Delta E_\psi \qquad (VI)$$

where q_i and q_j are the charges in the molecule i and j respectively, R is the separation distance between these two molecules, ε is the local relative permittivity which is affected by

Table 3 Ratio of reaction rate constants and substitutent constants

styrene	slope	k/k_h	$\log(k/k_h)$	σ
p-MeO	−0.0232	0.316	−0.5	−0.27
p-Me	−0.0442	0.602	−0.216	−0.17
H	−0.0734	1	0	0
p-Br	−0.117	1.59	0.204	0.23
m-NO$_2$	−0.370	5.04	0.702	0.71

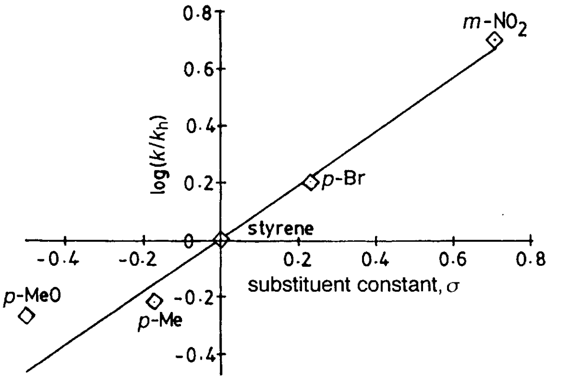


Fig. 2 Plot of $\log(k/k_h)$ *vs.* substituent constant, σ for styrene and substituted styrenes

the solvent, c_i and c_j are the coefficients of molecular orbitals in contact, permutating all filled/vacant orbital combinations, β is the overlap integral and ΔE_ψ is the energy difference between each pair of highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO). The first term is a electrostatic term which is unimportant because all the reactants are neutral molecules. The second term contains all attractive forces due to overlap of filled orbitals of one molecule with the vacant orbitals of the other of matching symmetry. While all permutations of orbitals of *i* and *j* must be considered, the largest term will come from interactions between the highest occupied molecular orbitals of one molecule and the lowest unoccupied molecular orbitals of the other molecule, because those are the closest in energy, *i.e.*, smallest ΔE_ψ. These HOMOs and LUMOs are referred to as frontier molecular orbitals. The reactivity can thus be predicted by the LUMOs and HOMOs. Obviously, the closer the energy level between the interacting HOMO and LUMO, the faster the reaction. This is because smaller ΔE_ψ gives higher attractive energy and thereby causes a greater decrease in the activation energy. The energy difference, ΔE_ψ is calculated from the absolute energy level of HOMO *i.e.*, E_{HOMO} and the absolute energy level of LUMO *i.e.* E_{LUMO}. The E_{HOMO} is approximately the value of the ionization energy of a molecule which can be measured by photoelectron spectroscopy.[16] Thus, E_{LUMO} is equal to E_{HOMO} plus the electronic transition energy from HOMO to LUMO which can be measured by UV–VIS spectroscopy.

In Table 4 are listed the literature results of the energy levels for all the relevant compounds. Since the energy levels of HOMOs of the substituted styrenes and LUMO of RuO_4 are the closest pairs among all the HOMO–LUMO pair, the interaction between these two orbitals is most important because it will determine the rate of the reaction between two molecules. On the other hand, the LUMOs of substituted styrenes are much higher than HOMO of RuO_4, their interaction is neglected, and the energy levels (LUMOs) of substituted styrenes are not listed. In Fig. 3, the ratio of reaction constants, k/k_h is plotted as a function of energy difference, ΔE_ψ. Obviously, there is a trend between k/k_h and ΔE_ψ. A large k/k_h means a larger reaction rate constant and a small energy difference, ΔE_ψ means a close energy level between HOMO of the substituted styrenes and LUMO of ruthenium tetraoxide. Thus, the results given in Fig. 3 can be interpreted as: the closer these two energy levels, the faster the reaction and this result is in consistent with the frontier orbital theory mentioned above. Furthermore, this analysis gives a more basic understanding of the relationship of reaction rate between the substituted styrenes. The energy level of the HOMO of styrene is higher than the energy level of LUMO of ruthenium tetraoxide. The electron donating power elevates the HOMO, making it futher higher than LUMO, enlarges the energy difference, ΔE_ψ and subsequently, this minimizes its contribution to decrease the activation energy. In other words, styrene substituted with electron donating group will have higher activation energy in its reaction with ruthenium tetraoxide, and consequently have a slower reaction rate.

Table 4 Correlation of energy differences with rate constants

styrene	E_{HOMO}/eV	ΔE_ψ	k/k_h	ref.
p-MeO	−7.92	1.01	0.316	18
p-Me	−8.20	0.73	0.602	18
H	−8.42	0.46	1	19
p-Br	−8.40	0.53	1.59	18
m-NO_2	−9.12	0.19	5.04	18

E_{LUMO} of RuO_4 = − 8.93 eV (ref. 20, 21).

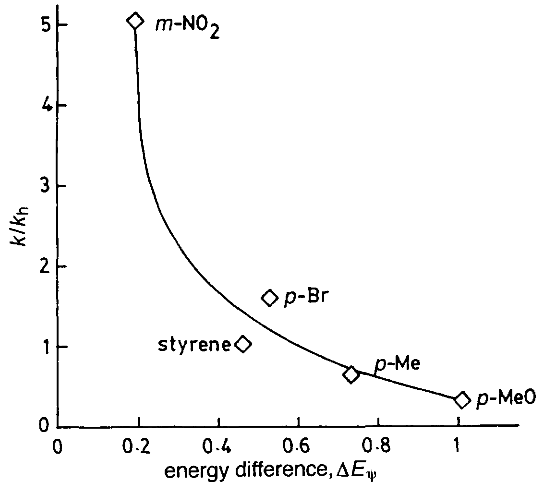


Fig. 3 Plot of k/k_h *vs.* energy difference, ΔE_ψ for styrene and substituted styrenes

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