

183. Chlorine Dioxide as an Electron-Transfer Oxidant of Olefins

Preliminary Communication

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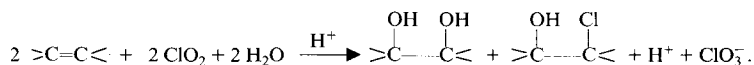
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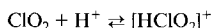
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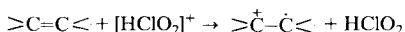
The kinetics and product studies of oxidation of eight olefins **1–8** by ClO_2 in H_2O in the pH range 3–7 are described. The reaction is faster as the pH decreases. At $\text{pH} < 4$, ClO_2 reacts equimolarly with olefins to yield isomeric mixtures of chlorohydrines and 1,2-dioxygenated products, following the equation:



The order of reactivity is: (*E*)-stilbene > indene > β -methylstyrene > acenaphthylene > α -methylstyrene > styrene > cyclohexene > allylbenzene. A multi-stage radical-cation mechanism is proposed, in which an initial reversible protonation:



is followed by an electron-transfer stage (rate-determining):



The cation-radical thus produced, adds rapidly an additional ClO_2 to form dioxygenated products. The chlorohydrines most likely arise from HClO additions to the olefinic double bonds, which, in turn, generate from dismutation of 2 HClO_2 into $\text{HClO} + \text{H}^+ + \text{ClO}_3^-$.

Unlike Cl_2 , the disinfection of drinking water by ClO_2 [1] does not appear to generate mutagenic or suspected carcinogenic trihalomethanes [2] and produces much less toxic chlorinated organic compounds [3]. This prompted the development of ClO_2 as a viable substitute for Cl_2 for the disinfection of drinking water. In spite of its growing environmental importance, there are only a few studies on the nature of the reaction in H_2O between ClO_2 and organic functionalities. Whereas ClO_2 functions as an electron oxidant towards tertiary amines [4] and phenols [5], the reaction with olefins was hitherto viewed to involve free-radical attacks both on the allylic $\text{sp}^3\text{-C}$ -atoms and the olefinic $\text{sp}^2\text{-C}$ -atoms [6]. This brings up the interesting question as to whether the reaction mechanism of ClO_2 varies with the substrate demand. Towards this end, we undertook a study aimed at establishing the mechanisms of the reaction between ClO_2 in H_2O and two types of olefins. One, containing allylic sites such as indene (**1**), α - and β -methylstyrenes (**3** and **5**, respectively), allylbenzene (**8**), and cyclohexene (**7**), and the other one, comprising non-allylic olefins such as acenaphthylene (**4**), (*E*)-stilbene (**2**), and styrene (**6**). The reaction

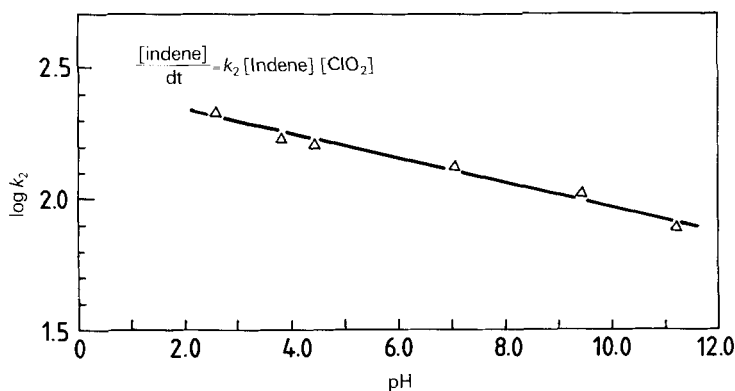


Fig. 1. $\log k_2$ vs. pH for the reaction of indene with ClO_2

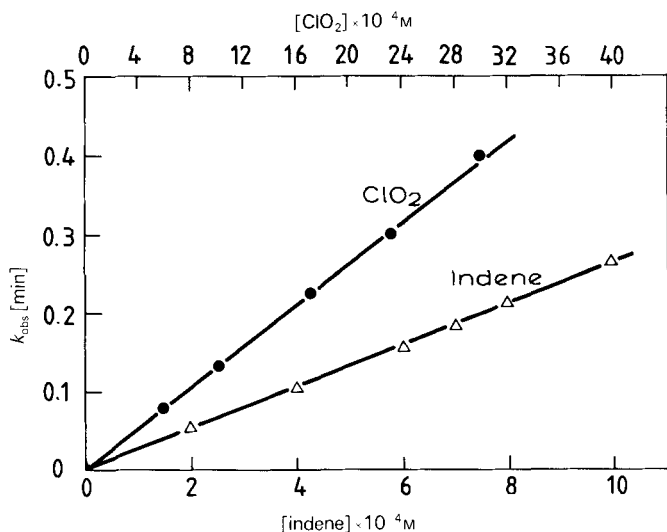
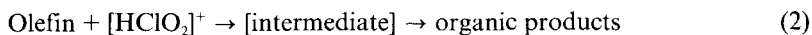
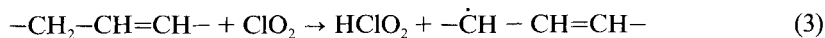


Fig. 2. k_{obs} vs. $[\text{ClO}_2]$, for $2 \times 10^{-5} \text{ M}$ indene with excess ClO_2 , and k_{obs} vs. $[\text{indene}]$ for $5 \times 10^{-5} \text{ M}$ ClO_2 with excess indene. pH 7.0.

between 1 and ClO_2 is shown: *i*) to be faster as the pH decreases [21] (see Fig. 1), suggesting that the conjugate acid $[\text{HClO}_2]^+$ (Eqn. 1), rather than free ClO_2 , initiates the oxidation process; *ii*) the reaction is first-order with respect to ClO_2 , first-order with respect to olefin, and second-order overall (see Fig. 2); *iii*) below pH 4, 2 moles of ClO_2 react with 2 moles of olefin, producing 2 moles of HClO_2 . The reaction could thus be viewed as a multi-stage process, involving first the reversible protonation of ClO_2 (Eqn. 1) at the initial stage, followed by an electron transfer (Eqn. 2) leading to the products:

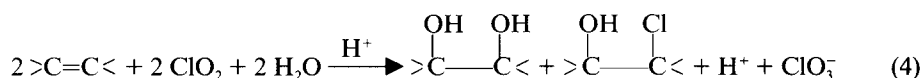


iv) No isotopic effect was observed on exposing $[1,1,3\text{-}^2\text{H}_3]$ indene to the action of ClO_2 in either H_2O or D_2O , indicating that Eqn. 3 is not operating;



v) The reaction of indene with ClO_2 becomes slower as the ratio $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ increases,

suggesting charge development in the rate-determining step. *vi*) The ratio between the reactants indene/ ClO_2 / H_2O at pH 4 was found to be 1:1:1, in accord with *Eqn. 4*:



The ion ClO_3^- is envisaged to arise from disproportionation of HClO_2 at low pH as proposed [7]:



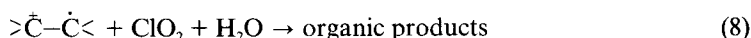
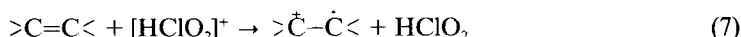
HClO does not accumulate, as it reacts with olefins as soon as formed to produce chlorohydrines.

The second-order rate-constants (k_2) at neutral pH were derived from the equation:

$$-d[\text{ClO}_2]/dt = 2 \times (-d[\text{olefin}]/dt) = k_2[\text{olefin}][\text{ClO}_2] \quad (6)$$

and the reaction rates for eight different olefins in descending order of reactivity are summarized in the *Table*.

This order of reactivity while at variance¹⁾ with the allylic-radical mechanism, proposed earlier by *Lindgren et al.* [6], is consistent with an electron-transfer mechanism leading to a cation radical²⁾ as shown by *Eqns. 7* and *8*.



Corroboration of this mechanism, based on observations *i* to *vi*, was forthcoming when excess ClO_2 ($9 \times 10^{-4} \text{ M}$) was reacted with *p*-substituted styrenes giving pseudo-first-order rate constants. These rate constants may be correlated with σ^+ [16], with a ρ value

Table. Comparisons of $t_{1/2}$ Values of Oxidation between $1 \times 10^{-4} \text{ mol}$ of Olefin and $3 \times 10^{-4} \text{ mol}$ of ClO_2 at pH 7.0 with Ionization Potentials (I.P.) in eV

Compound	$t_{1/2}$ [h]	I.P. [eV]	Ref.
Indene (1)	0.12	8.20	[9]
(<i>E</i>)-Stilbene (2)	< 0.10	8.00	[10]
β -Methylstyrene (3)	0.42	8.3–8.5	[11]
Acenaphthylene (4)	2.10	8.24, 8.73	[10][12]
α -Methylstyrene (5)	4.20	–	
Styrene (6)	8.4	8.71	[10]
Cyclohexene (7)	18	9.20	[13]
Allylbenzene (8)	54	–	

¹⁾ The expected order of reactivity of alkenes on the basis of the allylic-radical mechanism [6] should have been $1 \sim 8 > 7 > 5 > 3 > -9 \times 9 > 4 \sim 2 \sim 6$ as the allylic H-atoms of molecules such as allylbenzene (8) could be abstracted quite easily [8], whereas compounds such as 2, 4, and 6 do not have any allylic H-atoms and, therefore, according to the allylic-radical mechanism, should not react. This is utterly at variance with the order enumerated in the *Table*.

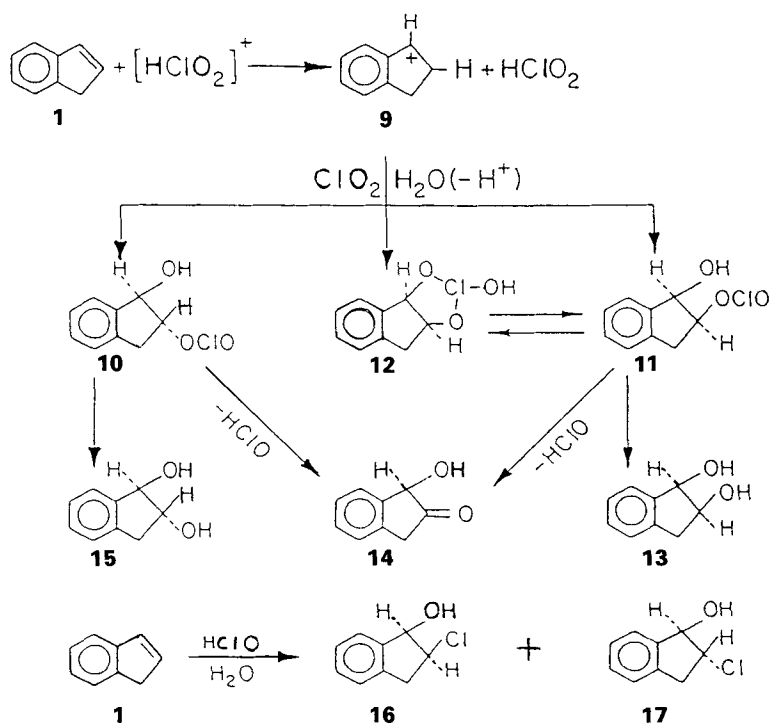
²⁾ According to *McManus* [14], the benzylic cations $\text{Ph}\dot{\text{C}}\text{H}\dot{\text{C}}\text{HPh}$ (I), $\text{Ph}\dot{\text{C}}\text{H}\dot{\text{C}}\text{HMe}$ (II), $\text{Ph}\dot{\text{C}}(\text{Me})\dot{\text{C}}\text{H}_2$ (III), and $\text{Ph}\dot{\text{C}}\text{H}\dot{\text{C}}\text{H}_2$ (IV) are about 20 kcal more stable than the respective aliphatic cations. In the alkene series, secondary free radicals are calculated to be 6 kcal more stable than primary radicals, whereas an α -phenyl group is evaluated to increase the stability of the free radical by an additional 13 kcal. This explains the observed order of reactivity as shown in the *Table*: $2 > 3 > 5 > 6$, which involve the formation of the respective cation-radicals I, II, III, and IV. Similar reasoning implies that $\dot{\text{C}}\text{H}-\dot{\text{C}}\text{H}$ should be formed more readily than $\text{PhCH}_2\dot{\text{C}}\text{H}-\dot{\text{C}}\text{H}_2$, as is the case.

of -1.45 , showing that the electron-donating substituents cause marked acceleration of the reaction, while electron-withdrawing groups slow it down. This indicates that a positive charge is developed on the C-atom at the reaction center [17]. Complementary to these evidences are the results forthcoming from product studies herein described.

The products from **1** comprise 51% overall yield of 1,2-dioxygenated species **13–15** and 49% of chlorohydrins **16–17** (Scheme 1). Strikingly, the reaction appears to be regiospecific in each group, giving rise to only one of the two possible types of products. Thus, the formation of 1-hydroxyindan-2-one (**14**) and not that of 2-hydroxyindan-1-one is observed in the first group, and the 2-chloro- (**16–17**) rather than the isomeric 1-chloroindan-2-ols, in the second group. To encompass the data produced here, the reaction of **1** with ClO_2 in H_2O is rationalized in terms of a mechanism involving, in the rate-determining step, an electron transfer (**1** $\rightarrow$ **9**) to form a cation radical (Scheme 1), which combines readily with an additional molecule of ClO_2 to yield 1,2-dioxygenated chlorite esters **10–12** leading to products **13** and **15** accompanied by liberation of HClO_2 , and to **14** accompanied by liberation of HOCl . Diols **13** and **15** are proved not to result from hydrolysis of the respective chlorohydrins.

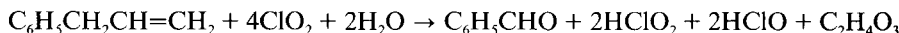
The preponderance of the *cis*-**13** over the *trans*-**15** isomer in the indanediol group is rationalized in terms of a gain in energy by involving a cyclic ortho-ester intermediate **12** in the process **9** $\rightarrow$ **12** $\rightarrow$ **13**³⁾.

Scheme 1



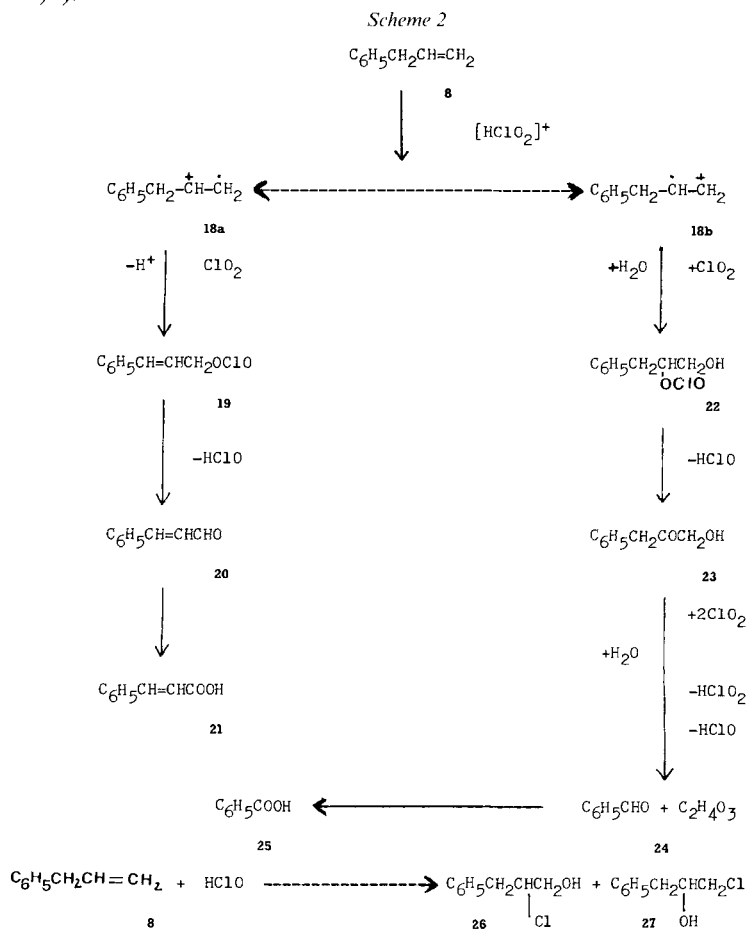
³⁾ Under the reaction conditions, *cis*- and *trans*-isomers were not equilibrated [15], so the *cis*-product most likely resulted from a favored *cis*-attack on **9** [22].

Products arising from the reaction of **8** with ClO_2 differ significantly from those of **1**. The conversion after 48 h was not high, and the oxygenated products comprise the unsaturated aldehyde **20** and two carboxylic acids **21** and **25**. No corresponding 1,2-diols or α -ketones were observed. Furthermore, the ratio of oxygenated products/chlorohydrins is 1:2.7 instead of 1:1 in the case of indene. The reaction stoichiometry is thus expressed by the equation:

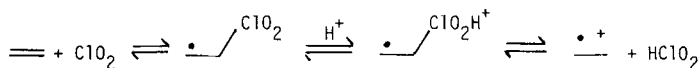


The benzaldehyde is oxidized further to benzoic acid.

To encompass the data presented here a similar radical-cation mechanism is proposed (Scheme 2)⁴⁾.



⁴⁾ In a private communication, Prof. Lennart Eberson suggested a mechanism



which will be further discussed in a forthcoming paper.

Experimental. – The olefins 1–8 (1×10^{-4} M solns. in H_2O) were brought to the desired pH by adding HCl or NaOH in the presence of an appropriate buffer. The reactions were initiated by adding measured volumes from a stock soln. of ClO_2 in H_2O (3×10^{-4} M), and the progress of the reaction was followed spectrophotometrically by monitoring the absorbances at two wave lengths: one for the disappearance of the substrate, and the second at 360 nm for the disappearance of ClO_2 .

Carbonate buffer was used for pH 9–11, phosphate buffer for pH 6–8, acetate buffer for pH 4–6. The buffer concentration in the final solns. was 0.1 M.

ClO_2 was prepared from NaClO_2 and Ac_2O [18]. Unlike other methods, this one provides an aq. ClO_2 soln. devoid of traces of Cl_2 [18].

[1,1,3- $^2\text{H}_3$]Indene (99%) was prepared by allowing indene (1.16 g), D_2O (99.8%, 15 g), 50 ml of pyridine, and Triton B (2 ml in 5 ml of MeOH) to react for 12 h and then chromatographed on a short silica column. This method is a modification of the method described by Bergson [19].

Product Studies. ClO_2 (3×10^{-3} mol), and indene (10^{-3} mol) were added to a 0.05 M acetate buffer solution (1 l, pH 4.0) and the mixture was allowed to stand for 1 h before its passing through *Sap-Pak C-18* cartridge and elution with 1 ml of MeOH. HPLC (250×4 mm column 10 mm *Bondapak RP-18*, linear gradient of 20–100% MeOH/ H_2O) afforded 5 products (100% gradient of 20–100% MeOH/ H_2O) afforded 5 products (100% conversion). First eluted trans-1,2-indanediol (15; 14%), m.p. 161° ([15]: m.p. 160 – 163°); secondly, cis-1,2-indanediol (13; 24%), m.p. 97 – 99° ([15]: m.p. 99 – 101°); thirdly, 1-hydroxyindan-2-one (14; 13%). UV: λ_{max} [nm] 252, 296. MS: 131 (18), 120 (25), 119 (47), 118 (16), 105 (18). Fourth eluted cis-2-chlorindan-1-ol (16; 23%), m.p. 104 – 106° ([20]: m.p. 105 – 108°), and fifth eluted trans-2-chlorindan-1-ol (17; 26%), m.p. 122° ([20]: m.p. 123 – 124°).

The reaction of allylbenzene (8) with ClO_2 in H_2O was carried out in a similar fashion, but terminated after 48 h (48% conversion) by the addition of a 5-fold excess of $\text{Na}_2\text{S}_2\text{O}_3$ (to quench ClO_2). The reaction produced 2-chloro-3-phenylpropan-1-ol (26; 7%) 1-chloro-3-phenylpropan-2-ol (27; 20%), cinnamaldehyde (20; 8%), cinnamic acid (21; 8%), benzoic acid (5%), and unreacted 8 (52%).

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