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THE FORMATION OF CATION-RADICALS BY THE ACTION OF CHLORINE DIOXIDE ON p-SUBSTITUTED STYRENES AND OTHER ALKENES

Ehud Choshen (Goldstein), Rudi Elits and Chaim Rav-Acha*
The Environmental Health Laboratory
The Hebrew University-Hadassah Medical School
POB 1172, Jerusalem 91010, Israel

Abstract: *The Hammett plot for the reaction of ClO_2 with p-substituted styrenes, the solvent effect, and the order of reactivity of several alkenes towards ClO_2, indicate that the alkene-ClO_2 reaction proceeds via the formation of cation-radicals.*

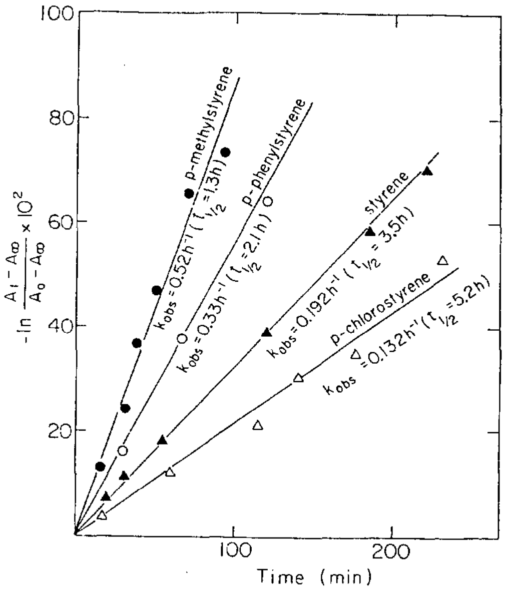
Chlorine dioxide has recently become a viable alternative to chlorine for the disinfection of drinking water. One of the main reasons for this is the fact that it does not form trihalomethanes in water,[1] and as compared to chlorine, it produces fewer and less chlorinated organic products. In spite of its growing environmental importance, knowledge on the organic reactions of ClO_2 is surprisingly limited.[2] Whereas it has been proven that ClO_2 functions as an electron oxidant towards amines[3] and phenols,[4] an allylic radical mechanism has been proposed for the reactions of ClO_2 with olefins.[5,6] The findings reported in this paper refute this radical mechanism, and show that alkenes react with ClO_2 by an electron transfer mechanism - the alkene is oxidised to a cation radical and ClO_2 is reduced to chlorite (ClO_2^-):

$$\text{olefin} + ClO_2 \text{ --------> } [\text{olefin}]^{+\cdot} + ClO_2^-$$

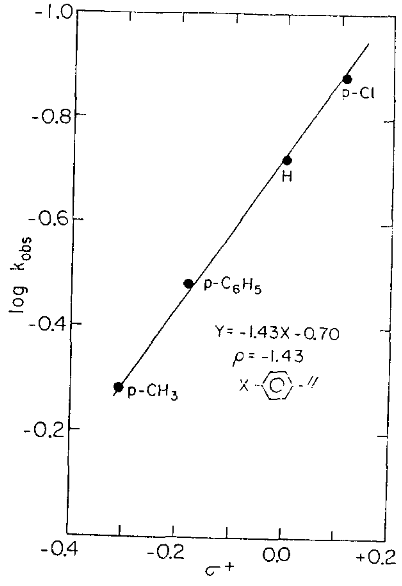
Stock solutions of olefins were prepared in 0.05 M phoshphate buffer at pH 7.0, employing purified water.[7] ClO_2 was generated from sodium chlorite and acetic anhydride and was devoid of all traces of chlorine.[8] The final concentrations of ClO_2 and olefins were 9×10^{-4} M and 5×10^{-5} M, respectively. Olefin concentrations were followed spectrophotometrically at T=25±1°C. As shown in Figure 1, the reaction of p-substituted styrenes in the presence of excess ClO_2 gave rise to pseudo-first order rate constants (k_{obs}). A plot of these rate constants against σ^+, as described by Brown and Okamoto,[9] was linear with a slope, ρ, of -1.43 (Figure 2).

Similar Hammett plots have been described for other reactions which proceed via the formation of benzylic cations (for example, the acid-catalyzed hydration of styrene,[10] and the dehydration of β-phenyl-β-hydroxyproprionic acid to cinnamic acid [11]). The finding that the reaction is markedly accelerated by electron-donating substituents and inhibited by electron-withdrawing substituents indicates that a positive charge is generated on the carbon atom at the reaction center. This hypothesis is also supported by the solvent effect as the rate of reaction decreases as the ratio of isopropanol:water is increased. Thus, the k_{obs} values, 0.19, 0.14, 0.09 and 0.05 h^{-1}, were obtained for styrene with aqueous solutions containing 0%, 25%, 35% and 50% of isopropanol, respectively.

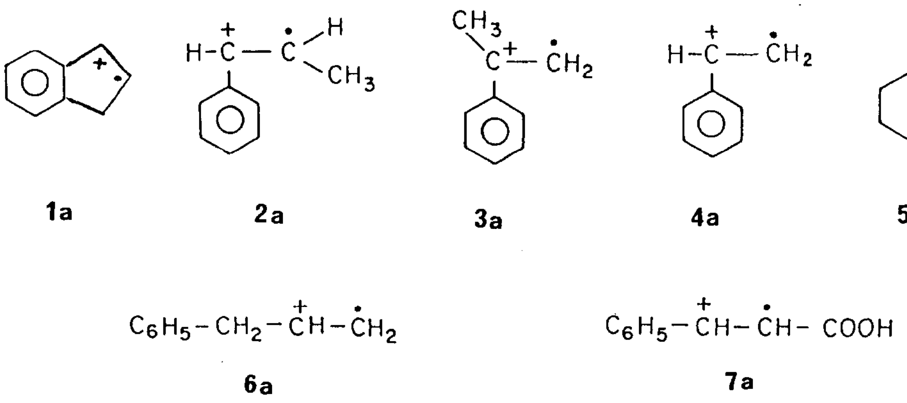
The order of the reactivities of various alkenes towards ClO_2, as shown in Table I, is at variance[12] with the allylic radical mechanism proposed by Lindgren,[5] and may be



<u>Figure 1.</u> Pseuso-first order reactions of p-substituted styrenes with excess chlorine.



<u>Figure 2.</u> Hammett plot for the reactions described in Figure 1.



<u>Figure 3.</u> Cation radicals of various alkenes.

rationalized in terms of stability of the cation-radicals formed by the reaction of ClO_2 as a one-electron acceptor at the π bond. Table I demonstrates that aromatic alkenes, such as indene (**1**), β-methylstyrene (**2**), α-methylstyrene (**3**) and styrene (**4**), which give rise to the cation-radicals, **1a**, **2a**, **3a** and **4a**, respectively, are the most reactive. These benzylic cations are about 20 Kcal more stable than the aliphatic cations (see Figure 3).[13]

In the series of aromatic alkenes, secondary free radicals, such as **1a** and **2a**, are calculated as being more stable than primary radicals, such as **3a** and **4a**, by 6 Kcal. This explains the observed order of reactivity, 1 > 2 > 3 > 4. By similar reasoning, **5a** should be formed more readily than **6a**, and this is indeed the case. Furthermore, cinnamic acid would not be expected to give rise to an unstable radical, such as **7a**, and, therefore, this olefin does not react with ClO_2.

The order of reactivities is also in accord with the ionization potentials of the respective olefins, as shown in Table I.

Table I. Pseudo-first order rate constants of various olefins ($2x10^{-5}M$) with ClO_2 ($9x10^{-4}M$) at pH=7.0, and their ionization potentials (I.P.)

Compound	k_{obs} (h^{-1})	I.P. (e.v.)
indene (**1**)	4.5	8.2,[14] 8.3[15]
trans-β-methylstyrene (**2**)	4.0	8.4[16]
α-methylstyrene (**3**)	1.5	8.5[16]
styrene (**4**)	0.2	8.7[17]
cyclohexene (**5**)	0.07	9.2[18]
allylbenzene (**6**)	0.008	-
cinnamic acid (**7**)	unreactive	

Indene was selected for detailed product analysis becauses, unlike styrene, it possesses allylic hydrogens, and, therefore, a priori, the possibility exists of reaction by either of the two mechanisms - electron transfer or hydrogen abstraction. On reaction of $3x10^{-3}M$ ClO_2 with $10^{-3}M$ indene for one hour at pH 4, the following products were isolated and characterized :[20] *trans*-1,2-indanediol (14%), *cis*-1,2indanediol (23%), 1-hydroxyindan-2-one (14%), *cis*-2-chlorindan-1-ol (23%), and *trans*-2-chloroindan-1-ol (26%). The chlorohydrins were shown to be produced via the action of hypochlorous acid, which is liberated during the course of the reaction. The indene-ClO_2 reaction appears to be regio-specific, and thus leads to the formation of 1-hydroxyindan-2-one and 2-chloro-indan-1-ol, rather than the more common 2-hydroxyindan-1-one and 1-chloro-indan-2-ols, which is consistent with the reaction mechanism proposed above, but not with the hydrogen abstraction mechanism.[5] Furthermore, these products may be explained on the basis of formation of the cation radical (**1a**) in the initial step.

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7. The water used in these experiments was purified by passing it through an ion exchange resin, followed by a Seradest SD 2000 Water Purifier to which a column of activated charcoal and a 0.2μ Millipore filter were attached.
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20. The five products were separated by HPLC. The structures of the two indanediols (eluted first) and the two chlorohydrins (the last two peaks) were confirmed by comparison with authentic samples synthesized by known procedures.[21,22] The 1-hydroxyindan-2-one structure was assigned to the third peak, solely on the basis of mass spectra as it decomposed shortly after isolation (m/z values: 148 (100%), 131 (18%), 120 (25%), 119 (47%), 118 (16%), and 105 (18%)).
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