Catalytic Alkane Activations in Reverse Microemulsions Containing Iron Salts and Hydrogen Peroxide

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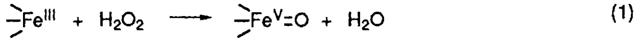
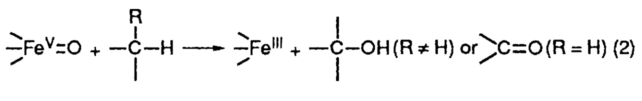
A microemulsion system generated from two reverse microemulsions containing respectively an aqueous solution of iron salts and 30% H_2O_2 dispersed in liquid alkanes catalyses the oxidation of C–H bonds.

We describe here the first example of the catalytic oxidation of alkanes in water/oil reverse microemulsions. In such a liquid–liquid dispersion, the substrate (in the present case the alkane to activate) is the solvent of an aqueous solution containing the other reagents (iron salts and hydrogen peroxide). These systems offer many advantages over homogeneous catalysis: (i) no ligands or solvent degradations; (ii) stabilization of reactive intermediates within the swollen micelles.[1,2] We demonstrate that in thermodynamically stable liquid–liquid dispersions, microemulsions, the catalytically active species can only be generated within the aqueous microdroplets.

Our studies were performed in the well-known microemulsion system[2] consisting of water–hydrocarbon–anionic surfactant (sodium bis-2-ethylhexyl sulphosuccinate, Aerosol OT). Thus, two microemulsions containing respectively an aqueous solution of 30% H_2O_2 and an aqueous solution of Fe^{II} or Fe^{III} salts† were prepared and mixed at $t = 0$ to form the 'active microemulsion' because the droplets fuse instantaneously.[2] The catalytic system must be generated *in situ* and we have observed that oxidation does not occur in the biphasic system nor in the microemulsion obtained by dispersion of a previously prepared aqueous solution containing both hydrogen peroxide and iron salts.‡ The microemulsions were allowed to stand at room temperature under nitrogen and the composition of the oil phase was studied by gas chromatography (Table 1). Our microemulsion system is active for the oxidation of C–H bonds to ketones and secondary and tertiary alcohols with a fairly high yield approaching 10% *per* H_2O_2 and a turnover number of 10. Cyclo-octane is specifically and directly oxidized into cyclo-octanone. This result seems to be in agreement with the conclusions drawn recently on the homogeneous iron–pyridine–acetic acid system[3] (Gif system). A minor influence on pathways going through alcohols or alkyl radicals intermediates is inferred.§ When the substrates contain both tertiary and secondary carbons (*e.g.*, in *cis*- or *trans*-decalin) the oxidation leads to a mixture of ketones and tertiary alcohols.¶ The secondary carbons α or β are oxidized at the same rate for a given substrate. The ratio of *cis*- and *trans*-9-decalols is approximately 25 : 75 in each instance. The greater amount of 9-decalols produced from *cis*-decalin is in agreement with the higher reactivity of the equatorial C–H bonds.[4] This lack of stereoselectivity makes our system different from the previously described stoicheiometric proce-



$$\mathrm{{-}Fe^{III} + H_2O_2 \longrightarrow {-}Fe^{V}{=}O + H_2O} \qquad (1)$$



$$\mathrm{{-}Fe^{V}{=}O + {-}\overset{R}{C}{-}H \longrightarrow {-}Fe^{III} + {-}C{-}OH\,(R \neq H)\ or\ {>}C{=}O\,(R = H)} \qquad (2)$$

Table 1.

Hydrocarbon[a] = oil phase	Product (s)	Reaction time/h (% conversion)			
		1	4	6.5	24[b]
Cyclo-octane	Cyclo-octanone	0.18	0.30	0.35	0.51
		0.7	4	7	24[b]
cis-Decalin	*cis*-1-Decalone	0.02	0.04	0.05	0.06
	cis-2-Decalone	0.02	0.03	0.05	0.05
	trans-9-Decalol	0.04	0.10	0.15	0.24
	cis-9-Decalol	0.02	0.03	0.04	0.06
		1	3	7	24[b]
trans-Decalin	*trans*-1-Decalone	0.06	0.08	0.10	0.13
	trans-2-Decalone	0.06	0.08	0.10	0.13
	trans-9-Decalol	0.02	0.03	0.05	0.07
	cis-9-Decalol	—	0.01	0.01	0.02
		1	4	7	24[b]
Tetralin	α-Tetralol	0.5	0.7	1.0	1.6
	α-Tetralone	0.5	0.7	1.0	1.6

[a] The reaction medium was obtained by mixing two microemulsions. For instance, in the case of cyclo-octane, the compositions were respectively: 5 ml of cyclo-octane containing 1.2 g of AOT, 0.5 ml of a 5% aqueous solution of $[FeSO_4, (NH_4)_2SO_4, 6H_2O]$ (microemulsion 1) and 5 ml of cyclo-octane containing 1.2 g of AOT, 0.5 ml of an aqueous solution of H_2O_2 (30%) (microemulsion 2). [b] All the H_2O_2 is consumed. The reaction starts again upon further addition of H_2O_2.

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† The presence of H_2O_2 or an iron salt slightly modifies the tertiary-phase diagram of the water–hydrocarbon–Aerosol OT mixture. The amount of water which can be incorporated within the microemulsions increases in the presence of H_2O_2 and decreases in the presence of iron salts. In all instances the final (after mixing the two primary microemulsions) ratio of H_2O_2 : Fe 157 has been used.

‡ The same procedure was performed starting from two macroemulsions [with a lower amount (5%) of Aerosol OT], which leads to a less efficient oxidation system: the yield for cyclo-octane oxidation is five times less. The catalytic activity seems to be related to the diameter of the aqueous droplets.

§ Cyclo-octanol cannot be an intermediate in the oxidation process because when it is added to the microemulsion system it remains unchanged. Alkyl radicals do not seem to be involved: the addition of radical scavengers like propan-2-ol (in the aqueous phase) or carbon tetrachloride (in the hydrocarbon phase) does not affect the catalytic reaction. When CCl_4 is added a very small amount of chlorocyclo-octane is produced initially.

¶ Characterized by comparison with authentic samples. 1-Decalone and 2-decalone are commercially available; *cis*- and *trans*-9-decalol have been prepared and purified according to the previously described procedure.[5]

dures[4—6] involving peracids or dioxiranes in organic solvents and implies that isomerisation occurs during the oxidation presumably *via* 9-decalyl radical intermediates.[7] The oxidation of tetralin is much more rapid and occurs at the activated benzylic position giving rise to an almost equimolar mixture of the expected ketone and alcohol.

According to these results, our microemulsion system does not act like a Fenton-type reagent[8]‖ but is more analogous to homogeneous iron catalyst–oxidant systems[3] for which the intervention of an iron(v) oxene intermediate has been proposed [equation (2)]. Such iron(v) oxene species could be produced in our microemulsion system by reaction of Fe^{III} with hydrogen peroxide within the confined aqueous droplets according to the mechanism proposed by Kremer[10] for a Fe^{III}/Fe^{V} redox system [equation (1)]. Because of the pH range, polynuclear iron species like colloidal hydrous ferric oxide $Fe_2O_3.nH_2O$ can be produced[11] and stabilized by electrostatic and steric repulsions within the microemulsion aqueous droplets.[1,2,12]**

The use of a microemulsion as a reaction medium is essential for the generation and the stabilization of the catalytically active species. These systems hold promise in performing catalytic reactions such as alkane oxidations.

We thank CNRS ('Groupe de Recherche Nouveaux Matériaux Tensioactifs') and ATOCHEM for financial support.

Received, 20th December 1989; Com. 9/05419G

‖ The catalytic oxidation can be performed starting either from Fe^{II} or Fe^{III}. Moreover, experiments performed with 1 : 1 and 1 : 8 $Fe^{II} : H_2O_2$ molar ratio show that alkane oxidation does not occur under Fenton's conditions. According to Barton,[9] with 1 : 1 $Fe^{II} : H_2O_2$ Fenton chemistry is the dominant process, but when the molar ratio of $Fe^{II} : H_2O_2$ is 1 : 10 or less, the major part of the chemistry does not involve oxyradicals nor reduced iron.

** A colloidal dispersion of Fe_2O_3 in water, prepared by the procedure previously described,[13] incorporated within a microemulsion can be used as a catalyst precursor: upon addition of a microemulsion containing H_2O_2 30%, catalytic C–H bond oxidation occurs at the same rate.

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