

Peroxometalate Catalyzed Oxidations with Hydrogen Peroxide in Biphasic Reaction Media: Reactions in Inverse Emulsions

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Summary: Transition metal catalyzed oxidations carried out in liquid-liquid biphasic reaction media using aqueous hydrogen peroxide as oxygen donor and quaternary ammonium cations are shown to be reactions in inverse emulsions and not typical phase transfer catalyzed reactions.

Over the last 30 years the use of processes mediated by quaternary ammonium salts in catalytic two-phase reactions or what is more commonly termed phase transfer catalysis has become an important and general method in synthetic organic chemistry.¹ At first the method was almost exclusively applied to the transfer of anionic reactants into an apolar phase. Basically, two mechanisms have been widely accepted. For reactions under neutral conditions, it has been shown that the reactions take place in the organic phase after extraction of the reactive anion.² Additionally, it was shown that even with quaternary ammonium salts such as hexadecyltrimethylammonium bromide, known also as effective surfactants, formation of inverted micelles has been discounted as an explanation of the catalytic effects observed.^{2,3} Under basic conditions, especially in the presence of aqueous hydroxide, the situation is somewhat more complicated,⁴ with interactions of the hydroxide anion at the water-organic interphase becoming of greater significance.

More recently, the concepts and scope of phase transfer catalysis have been extended to new areas such as extraction of hydrophilic *neutral* compounds into organic phases by quaternary ammonium salts. An important example in this field pertains to the use of 30% aqueous hydrogen peroxide in catalytic oxidations of organic substrates in biphasic media. Catalysts include manganese porphyrins,⁵ RuCl₃,⁶ and peroxometalates or polyanions.⁷ In all cases, it is thought that the quaternary ammonium salts are used either to solubilize the anionic catalyst in the organic phase and/or extract hydrogen peroxide. It is intriguing to notice, however, that most of the reactions were performed using quaternary ammonium salts that could be considered surfactants. Thus, the most commonly cited effective cations include hexa-

decylpyridinium, hexadecyltrimethylammonium, didecylmethylammonium, or dioctadecyldimethylammonium cations. This observation led us to inquire on the phase transfer mechanism of such biphasic reactions. Therefore, using the well described {PO₄[W(O)(O₂)₂]₄}³⁻, **1**, anion⁸ as a model for a biphasic catalytic oxidation with hydrogen peroxide, the effect of the quaternary ammonium cation was investigated. A significant advantage in the use of these catalysts is that there is no dismutation of hydrogen peroxide to dioxygen and water which would complicate measurements.⁷ We found that the reaction system is best described as a water in oil or inverse emulsion and not a typical phase transfer catalyzed reaction taking place in the organic phase.

Various catalysts, Q₃PO₄[W(O)(O₂)₂]₄, Q-1, were prepared by the published procedure⁸ using the following quaternary ammonium cations (Q): tetrahexylammonium (THA), trioctylmethyl (TOMA), (-)-dodecyl-*N*-methylephedrinium (DME), and hexadecyltrimethyl ammonium (HTMA). The activity of the catalysts was tested using the epoxidation of 1-octene to 1-octene oxide as a probe. Thus, 0.58 mmol of 1-octene and 0.03 mmol of Q₃PO₄[W(O)(O₂)₂]₄ in 1 mL of 1,2-dichloroethane were stirred magnetically in a 5 mL round bottom flask with 3 mmol of 30% H₂O₂ (pH = 3) at 25 °C. Aliquots from the organic phase were periodically removed to measure the rate of reaction. The reactions were all zero order in 1-octene, Figure 1, and the initial rates, V₀, are summarized in the Table 1 along with other pertinent information.⁹ The symmetric THA-1 catalyst was less active by 1 order of magnitude than the surfactant type DME-1 and HTMA-1 catalysts having a hydrophobic tail and a hydrophilic head. The TOMA-1 catalyst was of intermediate activity. It may be added that there is no correlation between the activity of the catalyst and

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(9). The reactions are first order in catalyst and in H₂O₂ as can be seen from the slopes of log[rate] vs log[DME-1] and log [rate] vs log-[H₂O₂] plots, Figure 1 inserts. This means that the rate determining step of the reaction is the formation of the epoxidizing agent Q-1 and not the epoxidation reaction itself.

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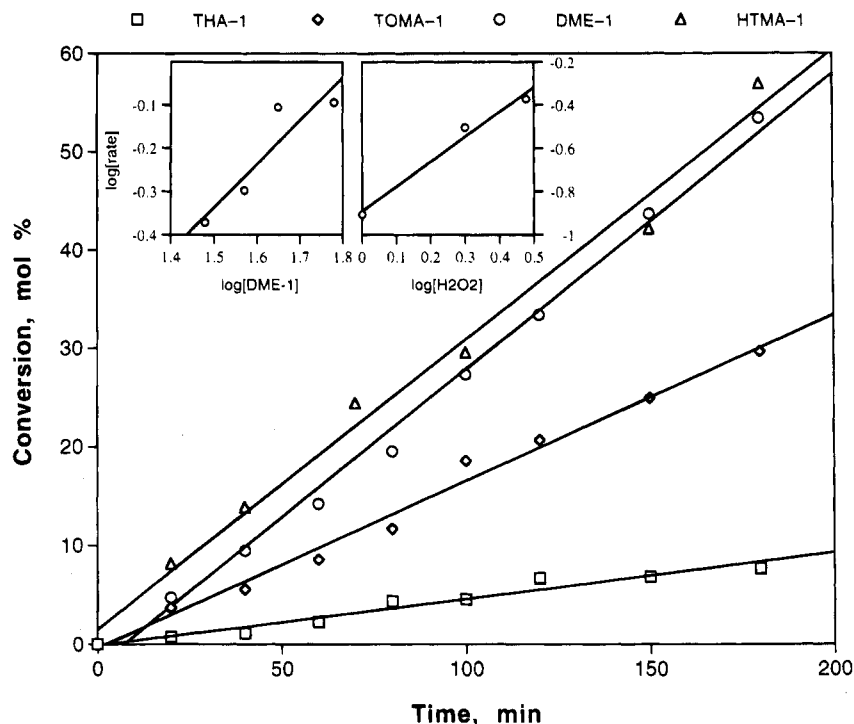


Figure 1. Reaction profiles of the oxidation of 1-octene with 30% H_2O_2 catalyzed with different Q-1. Reactions were carried out by magnetically stirring in a 5 mL flask 0.58 mmol of 1-octene and 0.03 mmol of $\text{Q}_3\text{PO}_4[\text{W}(\text{O})(\text{O}_2)_2]_4$ in 1 mL of 1,2-dichloroethane with 3 mmol of 30% H_2O_2 at 25 °C. Aliquots were taken from the organic phase and the conversion was measured by GLC analysis on a 15 m long 0.25 mm i.d. capillary silica column bonded with 0.25 μm coating of methyl silicone. Inserted graphs are $\log[\text{rate}]$ vs $\log[\text{DME}-1]$ and $\log[\text{H}_2\text{O}_2]$ plots under similar conditions where the amount of DME-1 was varied from 0.03 to 0.06 mmol and 30% H_2O_2 was varied from 1 to 3 mmol.

Table 1. Summary of Results on the Hydrogen Peroxide Biphasic Oxidation System

parameter	catalyst			
	THA-1	TOMA-1	HTMA-1	DME-1
V_0^a (mM/s $\times 10^3$)	4.7 ± 0.7	16.9 ± 1.3	30.0 ± 2.2	29.5 ± 3.0
conversion ^a (mol % at 180 min)	5.8	29.4	56.6	57.2
no. of carbons in Q	24	25	19	23
extraction ^b (mol H_2O_2 /mol Q)	0.93 ± 0.2	0.55 ± 0.2	0.30 ± 0.2	0.28 ± 0.2
E_a^c (kcal/mol)	10.9 ± 1.2		9.6 ± 1.1	
$\Delta H^{\ddagger c}$ (kcal/mol)	10.3 ± 1.2		9.0 ± 1.1	
$\Delta S^{\ddagger c}$ (eu)	-47.4 ± 4.6		-47.7 ± 4.1	

^a Reactions are essentially completely selective to 1-octene oxide.¹² Values were calculated from two replicate experiments in each case. Errors are given at a 90% confidence interval with r^2 values ranging between 0.96 and 0.99 in all cases. t -values showed significance at a 99.99% significance level. ^b The amount of hydrogen peroxide extracted per mol Q was measured by mixing a 30 mM solution of Q in 1,2-dichloroethane with a 100-fold excess of 30% H_2O_2 at room temperature for 30 min, followed by 10 min settling to separate phases. The analysis of H_2O_2 in the organic phase was done by the published iodometric technique.¹³ It may be noted that no significant amounts of Q-1 (<2%) could be found in the aqueous phase.¹⁴ ^c Calculated from zero order rate constants computed as in *a* above under the conditions described in Figure 1 over a temperature range of 2–50 °C.

the overall hydrophobicity (number of carbon atoms) of the catalyst. Measurement of the extractability of hydrogen peroxide by mixing a 30 mM solution of Q in 1,2-dichloroethane with a hundred fold excess of 30% H_2O_2 at room temperature for 30 min, followed by 10 min settling to separate phases, showed by iodometric titration that the concentration of hydrogen peroxide in the organic phase was significantly lower for the more active catalysts, DME and HTMA, than for the relatively inactive THA. Again the TOMA was in the intermediate range, Table 1. These results are in direct contradiction to the basic tenet of the normal phase transfer mechanism which stipulates that the rate should be a function of the amount of reactant in the organic phase. Although the results at this point indicated that the usual phase transfer type mechanism was not operating for these reactions, it was still possible that due to the different surface activities of the quaternary ammonium salts,

mass transfer effects were an important factor in the epoxidation reaction. In such a case, DME-1 and HTMA-1 could be more active due to the absence of a mass transfer barrier whereas in the case of THA-1 the reaction is diffusion controlled. However, our finding, Table 1, that the activation energy, E_a , for the epoxidation reaction is independent of the identity of the quaternary cation and is not in the range typical for a diffusion controlled reaction, 3–5 kcal/mol, eliminates the possibility of mass transfer effects as a factor in these reactions.¹⁰ This finding is additionally supported by the fact that running reactions at different stirring speeds had no effect on the reaction rate.

Although in the past, inverted micelles or inverse emulsions have been considered as important in PTC

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biphasic systems,^{3,11} they have never been directly observed under catalytic conditions. By homogenizing 10 mL of a 30 mM solution of HTMA-Cl in 1,2-dichloroethane with 10 mL of 30% H₂O₂ and 20 mg of an anionic chromophore, 5,10,15,20-tetraphenyl-21*H*, 23*H*-porphine-tetrasulfonic acid salt, we could directly observe under the microscope the formation of a relatively stable (3–4 h until separation) water in oil emulsion (~5 μm droplets) where the porphyrin anion is observed to dye the internal aqueous phase. Therefore, one assumes that the quaternary ammonium cation is on the organic side and the anions, *i.e.*, the chromophore or in the catalytic system the active catalyst {PO₄[W(O)(O₂)₂]₄}³⁻, are at the internal or dispersed aqueous phase side of the interface; the organic substrate is in the organic (oil) continuous phase.

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(12). No other products could be observed in the GLC analysis. In addition, material balance was satisfactory as the amount of substrate plus product was constant throughout the reaction.

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(14). The concentration of Q-1 in the aqueous phase was measured by quantification of the characteristic absorption of the peroxotungstate at 300 nm in the UV.

In such a configuration the reaction occurs at the water–oil interface. When similarly homogenizing the same phases using instead the THA-1 catalyst, we observed only slight emulsion formation (large droplets of ~100 μm) and then very fast separation within 2 min of the mixture into two homogeneous (water and 1,2-dichloroethane) phases.

Considering the large difference in the rates observed for the HTMA-1 *vs* the THA-1 catalyzed reaction and the fact that only in the former case could stable inverse emulsions be observed, we believe that reactions using aqueous hydrogen peroxide in biphasic systems proceed preferably in inverse or water in oil emulsions and not by the usual phase transfer type catalysis as has been tacitly assumed in the past.

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Supplementary Material Available: Experimental details (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.