Transport Limitations during Phase Transfer Catalyzed Ethyl-Benzene Oxidation: Facts and Fictions of "Halide Catalysis"

Vera P. Santos,* Jasper J.W. Bakker, Michiel T. Kreutzer, Freek Kapteijn, and Jorge Gascon*

Catalysis Engineering-Chemical Engineering Dept, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

S *Supporting Information*

ABSTRACT: The mechanistic interpretation of the catalytic effect of phase transfer catalysts in the selective oxidation of ethyl benzene is hampered by mass transfer effects. We demonstrate that proper experiments lead to a more correct interpretation of the role of the quaternary ammonium salt (QAS) and its counterion. Specifically, experiments unequivocally show that the main action of the counterion is to enhance physical mass transfer processes, while its catalytic effect is limited to a shift in selectivity, not activity. The QAS as a whole accelerates the induction process in the ethyl benzene (EB) oxidation by degenerate branching of its hydroperoxide (EBHP). Proper mechanistic understanding of these phenomena in QAS catalysts is especially crucial under industrially relevant conditions

KEYWORDS: *ethyl benzene oxidation, hydroperoxide, quaternary ammonium salts, phase transfer catalysis*
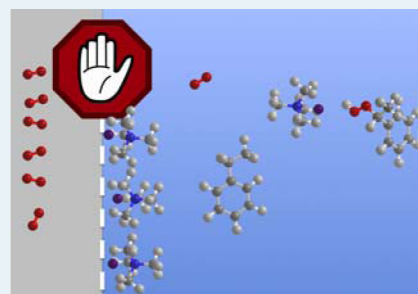
Liquid phase oxidations of different petroleum feed-stocks into chemicals are among the most important industrial processes. The selective oxidation of ethyl benzene (EB) to its hydroperoxide (EBHP) is the first crucial step in the SM/PO (styrene monomer/propylene oxide) process, that coproduces propylene oxide (PO) and styrene monomer (SM) by the epoxidation reaction between EBHP and propylene.[1−3] Shell, Lyondell, Sumitomo, and Repsol are the main users of the SM/PO process.[1] Industrially, this autocatalytic oxidation of EB to obtain EBHP is performed using air, in the absence of solvents and catalyst, at ~150 °C. Usual product composition is 12−14 wt % EBHP in EB. To improve yields, several catalysts have been proposed as alternative to the auto-oxidation of EB. These include transition metal ions,[4−6] alkali and alkaline-earth metal bases,[7] *n*-hydroxyimides,[8,9] and quaternary ammonium salts (QAS).[10,11]

The concept of "halide catalysis" was coined in the early 1960s after the seminal work of Brederec et al.[12] In general -onium salts (e.g., ammonium, phosphonium, sulfonium) can be defined as catalysts that facilitate the migration of a reactant from one into another phase where reaction occurs.[13] Investigations on the role of phase-transfer catalysts suggest that these compounds have a strong influence on the oxidation rate of hydrocarbons by O$_2$, either beneficial or detrimental.[11,13−15] In addition to the type of hydrocarbon, the nature of the cation R$_4$N$^+$ (effective charge and volume) and the catalyst concentration,[11] several studies have since been reported that the catalytic activity of -onium salts in selective oxidation reactions strongly depends on the nature (size and polarizability) of their counterions. Two different theories have been postulated to explain the role of these catalysts in the oxidation of hydrocarbons. One theory supports that O$_2$ is activated by the onium salt via interaction between the vacant *d*-orbital of the central atoms from the salt.[16] This hypothesis was first

introduced by Fukui et al.,[16] but it is not supported experimentally.[17] The other theory proposed that the onium salts promote the decomposition of the initiators into radicals, increasing the rate of the initiation step.[11,13,15] The decomposition of the initiator is promoted by the electrostatic interaction with the onium cation, and its efficiency depends on the effective charge density of the quaternary cation, which is controlled by the nature and size of the counteranion.[15] This theory is supported both theoretically and experimentally, although the major part of these studies were performed in polar solvents, far from the industrial process, where no solvent is used. Solvent effects can play a major role on the mechanistic action of QAS because of specific solute−solvent interactions (dissociation effects). Considering the relative permittivity of ethyl benzene ($\varepsilon_r \approx 2$),[18] no dissociation of QAS may be expected in a solvent-free system. On the contrary, when polar solvents are present, dissociation of the QAS takes place, leading to a different interaction between the onium cation and the initiator.[18]

In this work, we make a crucial step in resolving the mechanistic action of the counterion (under solvent-free conditions) by careful exclusion of physical transport phenomena to reveal the chemical processes. Specifically, we demonstrate that slow oxygen transfer limits most high-temperature, solvent-free reaction data reported in the literature on the partial oxidation of EB to EBHP. Most experimental studies on the partial oxidation of hydrocarbons in the presence of onium salts are performed under low O$_2$ concentrations, low temperatures, and in the presence of solvents. Surprisingly, very little has been reported on the catalytic effect of QAS under

industrial conditions (no solvent added and high temperatures) and in these cases the effect of possible oxygen diffusion limitations has not been carefully studied.[10,11] Although some studies classify the rate of hydrocarbon oxidations as slow, the autocatalytic nature of this reaction, with speed-up as the reaction progresses, makes such a conclusion erroneous for a broad conversion range.[19,20] Mass-transfer gradients may lead to lower yields and change the chemistry of the process (i.e., promoting dimerization reactions).[21] These effects can be particularly important in phase transfer catalysis.[22]

Figure 1(a) shows the reaction results obtained during the partial oxidation of ethyl benzene in the presence of different
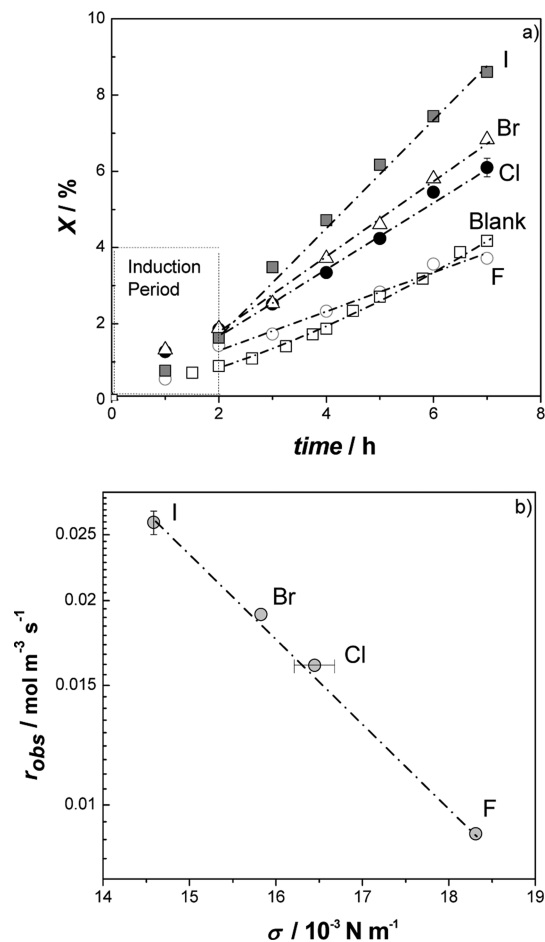

Figure 1. (a) Ethyl benzene oxidation in the presence of tetramethyl ammonium halides (TMAH) (F, Cl, Br, I) under mass transfer control. Conditions: 125 °C, 50 g of EB, 1 mM TMAH, 150 STP cm^3/ min flow (6%O$_2$ in N$_2$) and 800 r.p.m (magnetic bar). For comparative purposes, the oxidation of ethyl benzene without catalyst is also presented ("blank"). (b) Correlation between the observed EBHP production rate and surface tension obtained by pendant drop method.

quaternary ammonium salts (QAS) at 125 °C. Similar conditions as those reported in literature were used (800 rpm, 150 STP cm^3/min flow 6 vol % O$_2$ in N$_2$).[11]

In the absence of an initiator, a linear relationship between conversion and time is observed for all different catalysts after an induction period of ~2 h. In good agreement with other studies,[11] the activity of QAS strongly depends on the type of counteranion, with TMAI being the most active catalyst, followed by TMABr, TMACl, and TMAF. The conversion–

time relations after the induction period match very well those reported in literature.[10,11]

We now test the hypothesis that the rate at which oxygen is dissolved into the reaction mixtures depends on the counterion. The counterion has surface-active properties and strongly affects the surface tension of the liquid. Along the surface of moving air bubbles, gradients in surface tension develop that induce flow near the surface and enhance mass transfer.[23] Additionally, surface-active species greatly reduce the rate of bubble coalescence, thus increasing the interfacial area, maximizing the GL interfacial area.[24−26] Figure 1b depicts a clear correlation (log−linear scale) between surface tension of the different QAS and the observed reaction rate, suggesting that the surface-active properties of the counterion determine the reaction rate by affecting the oxygen mass-transfer rate.

This hypothesis is confirmed by varying the temperature using the most active QAS (TMAI) and presenting the observed reaction rates in an Arrhenius plot (Figure 2). Two
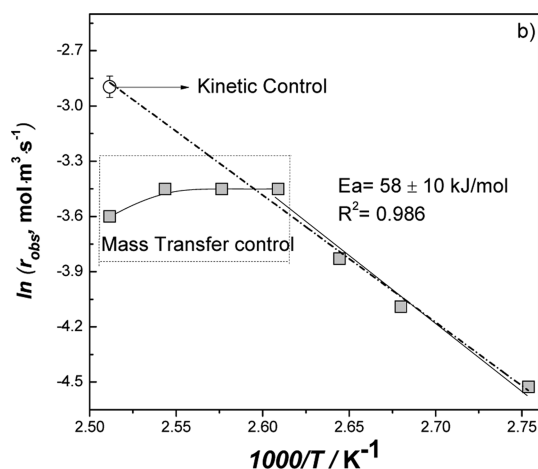

Figure 2. Observed EBHP production rate versus $1/T$ under mass transfer and kinetic control for tetramethylammonium iodide. The open symbol refers to an experiment performed under vigorous agitation, the closed symbols refer to temperature variations of the experimental conditions of Figure 1.

regions are observed in this graph: a linear correlation between $\ln(r_{obs})$ and $1/T$ for the experiments performed at low temperatures, indicating a constant activation energy (E_a) of ~60 kJ/mol. Experiments performed at higher temperatures (T > 100 °C) are mass-transfer limited, as implied by the negligible E_a obtained in this temperature range. These findings prove that GL mass-transfer limitations mask the real catalytic performance of QAS under previously used experimental conditions, and they support our interpretation of the role of the counterion under these conditions.

We now describe experiments in which these mass-transfer limitations were removed to reveal the real catalytic effect of QAS in the selective oxidation of EB. We used a baffled reactor and vigorous mechanical stirring (see Supporting Information).

The results obtained at 125 °C for the different QAS are shown in Figure 3. Experiments performed in this reactor configuration show a different catalytic performance: much higher activities and selectivities are found for all QAS under study. Furthermore, the observed rate at 125 °C is in good agreement with the low temperature data (as shown by the open symbol in Figure 2, top left corner)), demonstrating the absence of diffusion limitations. In contrast to experiments
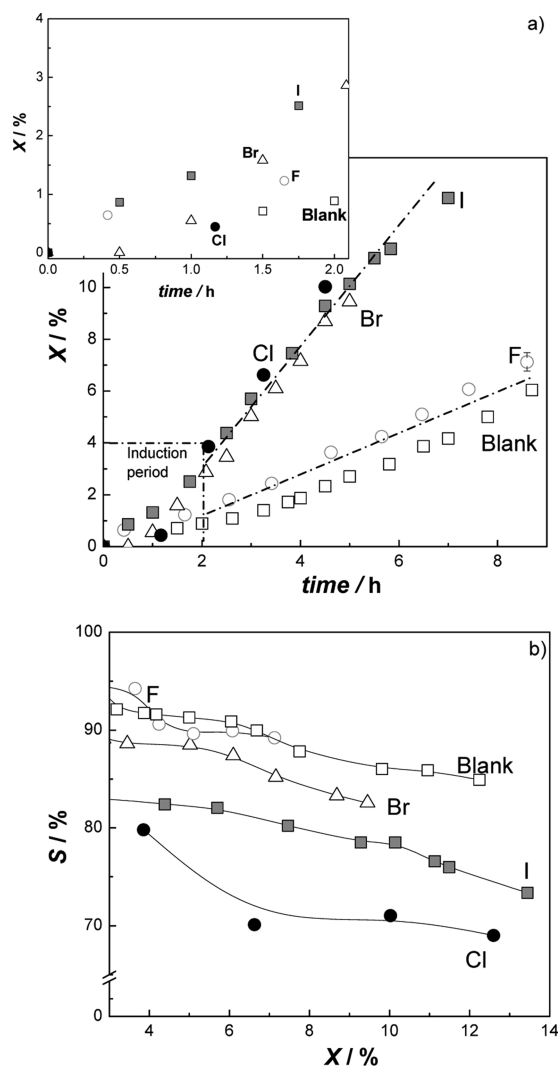
Figure 3. (a) Ethybenzene oxidation in the presence of tetramethyl ammonium halides (F, Cl, Br, I) under kinetic control. Experimental conditions: 125 °C, 50 g of EB, 1 mM tetramethylammonium halides and 800 r.p.m (baffles and mechanical stirrer).

under mass-transfer limitations, TMAI, TMABr, and TMACl all display similar activities, while clear differences in selectivity are observed (see Figure 3b). On the other hand, TMAF shows a poor activity, attributed to its strong water solvation capacity that "shields" the active sites, resulting in an almost inert catalyst. These results show that R_4N^+ is responsible for the activity of QAS, which is partially in agreement with the second theory described before. However, the type and size of the counteranion does not affect the activity of QASs. The presence of polar solvents clearly alters the action mechanism of the counteranion, because of dissociation effects. Generally, polar solvents (i.e., acetonitrile) used for this type of reaction have very high relative permittivities ($\varepsilon_r \approx 34.8$)[18] promoting the dissociation of QAS.

Under solvent free conditions, QASs behave as neutral molecules (relative permittivity of ethylbenzene ≈ 2), and the ion pairs will be in the form of higher aggregates.[18]

The differences in selectivity toward EBHP of the different counter-anions deserve special attention. The generally accepted mechanism for the liquid-phase oxidation of hydrocarbons is described as a radical chain mechanism based on three main steps: initiation, propagation, and termination.[21] In the absence of initiator, the thermal activation of ethyl benzene is the main source of radicals, and the rate of this process is generally extremely small, causing long induction periods. Our catalytic data suggest that the presence of specific QAS (TMAI) accelerates this process, because the induction period is shorter in the presence of QAS, in comparison with the uncatalyzed reaction. This leads us to hypothesize that the other initiation process, the degenerate branching of EBHP, is also catalyzed by QAS. If this is the case, then the branching leads to faster decomposition of EBHP, which can explain the observed selectivities in the presence of the QAS. To test this hypothesis, EBPH evolution tests were performed after stopping the O_2 feed. First the catalytic oxidation in the presence of oxygen was carried out, and when the concentration of EBHP was ~0.6 M (10% of conversion), the flow of oxygen was stopped and the concentration evolution of EBHP both in the presence and in absence of QAS was followed (see Supporting Information file). While in the absence of QAS EBHP is fairly stable, it readily decomposes by degenerate branching into the corresponding ketone and alcohol when QAS are present. Decomposition rate increases in the order $Cl^- > I^- > Br^-$, demonstrating that the counteranion plays a crucial role in determining the selectivity of the QAS. However, it cannot be assumed that the counteranion catalyzes the homolytic decomposition of EBHP, since no activity differences were observed during the kinetic experiments.

Summarizing, the theories proposed in the literature to explain the action mechanism of QAS are not valid under solvent-free conditions. The main action of the counterion is to enhance physical mass transfer processes. If this limitation is lifted, the counterion has no effect on the acceleration of the main initiation of the radical chain process, but it does play a role in the initiation of the degenerate branching of EBHP. All-combined, the catalytic action of the counterion manifests itself as a change in selectivity, not activity. The QAS as a whole accelerates the induction process in the EB oxidation by degenerate branching of EBHP. Most experiments published to date (under industrial conditions) on the catalytic effect of QAS suffered from gas–liquid mass-transfer limitations, resulting in a wrong mechanistic interpretation. Special care needs to be devoted to reactor design (hydrodynamics), to decouple transport phenomena and intrinsic catalytic effect.

Altogether, the phenomenal rates of QAS that can be achieved make these salts more promising catalysts for the selective oxidation of EB into EBHP than current literature data suggests. The limited stability of the desired hydroperoxide in the presence of QAS might hamper the application of QAS as homogeneous catalysts and suggest immobilization to achieve a fast separation, as the path to follow in the development of a catalytic route for the oxidation of EB to EBPH.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: v.p.santos@tudelft.nl (V.P.S.), j.gascon@tudelft.nl (J.G.).

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Chang, Te. Epoxidation system with fixed bed reactors. Eur. Pat. Appl. 1190770 A1, 2002.

(2) Moulijn, J., Makkee, M., van Diepen, A. *Chemical Process Technology*; John Wiley and Sons Ltd, Chichester, England, 2001.

(3) Buijink, J. K. F.; van Vlaanderen, J. J. M.; Crocker, M.; Niele, F. G. M. *Catal. Today* **2004**, *93–95*, 199.

(4) Matienko, L. I.; Mosolova, L. A. *Kinet. Catal.* **2005**, *46*, 328.

(5) Matienko, L. I.; Mosolova, L. A.; Skibida, I. P. *Russ. Chem. Bull.* **1994**, *43*, 1332.

(6) Raju, G.; Reddy, P. S.; Ashok, J.; Reddy, B. M.; Venugopal, A. *J. Nat. Gas Chem.* **2008**, *17*, 293.

(7) Toribio, P. P.; Campos-Martin, J. M.; Fierro, J. L. G. *J. Mol. Catal. A: Chem.* **2005**, *227*, 101.

(8) Melone, L.; Prosperini, S.; Gambarotti, C.; Pastori, N.; Recupero, F.; Punta, C. *J. Mol. Catal. A: Chem.* **2012**, *355*, 155.

(9) Toribio, P. P.; Gimeno-Gargallo, A.; Capel-Sanchez, M. C.; de Frutos, M. P.; Campos-Martin, J. M.; Fierro, J. L. G. *Appl.Catal. A: Gen.* **2009**, *363*, 32.

(10) Barrio, L.; Toribio, P. P.; Campos-Martin, J. M.; Fierro, J. L. G. *Tetrahedron* **2004**, *60*, 11527.

(11) Toribio, P. P.; Campos-Martin, J. M.; Fierro, J. L. G. *Appl.Catal. A: Gen.* **2005**, *294*, 290.

(12) Bredereck, H.; Wagner, A.; Blaschke, R.; Demetriades, G.; Kottenhahn, K.-G. *Chem. Ber.* **1959**, *92*, 2628.

(13) Csányi, L.; Jáky, K. *J. Mol. Catal. A: Chem.* **1997**, *120*, 125.

(14) Kasaikina, O.; Kartasheva, Z.; Pisarenko, L. *Russ. J. Gen. Chem.* **2008**, *78*, 1533.

(15) Csanyi, L. J.; Jaky, K.; Palinko, I.; Rockenbauer, A.; Korecz, L. *Phys. Chem. Chem. Phys.* **2000**, *2*, 3801.

(16) Fukui, K. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 312.

(17) Ohkubo, K.; Yamabe, T.; Fukui, K. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2200.

(18) Reichardt, C.; Welton, T. In *Solvents and Solvent Effects in Organic Chemistry*; Wiley-VCH Verlag: Weinheim, Germany, 2010; p 7.

(19) Spielman, M. *AIChE J.* **1964**, *10*, 496.

(20) Suresh, A. K.; Sharma, M. M.; Sridhar, T. *Ind. Eng. Chem. Res.* **2000**, *39*, 3958.

(21) Emanuel, N. M.; , Gál, D. *Modelling Oxidation Processes. Prototype: Ethylbenzene Oxidation*; Akadémiai Kiadó: Budapest, Hungary, 1986.

(22) Naik, S. D.; Doraiswamy, L. K. *AIChE J.* **1998**, *44*, 612.

(23) Levich, V. G. *Physicochemical hydrodynamics*; Prentice Hall: Englewood Cliffs, NJ, 1962.

(24) Kremer, H.; Rao, N. *Chem. Ing. Tech.* **1967**, *39*, 1088.

(25) Vázquez, G.; Antorrena, G.; Navaza, J. M. *Ind. Eng. Chem. Res.* **2000**, *39*, 1088.

(26) Lee, J.; Kentish, S. E.; Ashokkumar, M. *J. Phys. Chem. B* **2005**, *109*, 5095.