

Liquid-phase oxidation of hydrocarbons in the presence of different types of phase-transfer reagents

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Abstract

The autoxidation of cyclohexene, tetralin and cumene was investigated in the presence of non-ionic, anionic and cationic surfactants and it was found that all three types of phase-transfer reagents are able to influence the rate of oxidation. If their HLB values are not too low (> 3) or not too high (< 15) all the non-ionic surfactants increase the rate of oxidation, otherwise they exert a slight inhibitory effect. If present in acid form, anionic surfactants all increase the rate of oxidation, while their Na-salts slightly inhibit the oxidation. Cationic surfactants all increase the autoxidation rate, but their catalytic efficiencies depend strongly on the experimental conditions. It was shown that the phosphonium ion-type surfactants are quickly oxidized by hydroperoxide present, but their catalytic and phase-transfer capabilities are not detectably reduced. In biphasic systems, the catalytic activities of cationic surfactants are strongly reduced by the presence of water as a separate phase. Light scattering measurements demonstrated that all three types of surfactants are prone to self-association when their concentrations are increased, and this limits their influence on the rate of oxidation. The oxidation rate is strongly reduced when non-ionizing but strongly solvating solvents are simultaneously applied in the reaction mixture. The rate-diminishing effect seems to correlate with the sequence of solvating ability of the solvents. It was pointed out that the presence of hydroperoxide is essential for the PTC-catalyzed oxidation of hydrocarbons. It is thought that the cationic and the anionic surfactants interact with the more nucleophilic (the inner one) and the more electrophilic (the outer one) O-atom of hydroperoxide, respectively, whereby homolysis of the O–O bond is facilitated. The non-ionic surfactants exert their rate-influencing effects through H-bond formation. In the PTC-catalyzed oxidation of hydrocarbons, the rate changes linearly only in a narrow range of PTC, hydroperoxide and substrate concentrations, and consequently the turnover number is not suitable to characterize the oxidation.

Keywords: Hydrocarbon; Autoxidation; Phase-transfer catalysis; Self-association of surfactants

1. Introduction

It was first reported by Brederec et al. [1] that the autoxidation of oleic acid and tetralin was accelerated by quaternary ammonium salts. This effect was called ‘halide catalysis’. Some years later, the oxidation reactions of tetralin, cumene and *p*-xylene were investigated by Fukui et al. [2–5] in the

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presence of sulfonium, phosphonium, selenonium and arsonium salts. These authors confirmed the finding of Brederer et al. that the catalytic efficiencies of onium salts depend on the nature of their counterions, and they attributed the catalysis to the activation of O₂ by an interaction with the vacant d-orbitals of the central sulfur, phosphorus, etc. atoms. They later proposed that the homolysis of hydroperoxide present into radicals is promoted by onium ion catalysts [3]. This idea was accepted by van Tilborg [6] when he rejected the O₂ activation concept as arising from the interpretation of an experimental artifact. Hronec et al. [7,8] recently returned to the 'halide catalysis' concept when they concluded that the role of onium ions in the oxidation of hydrocarbons is simply to promote the transfer of bromide and complex Co–bromo anions into the organic phase.

During the past decade, phase-transfer catalysts (PTCs) have been widely used in the liquid-phase oxidation of hydrocarbons. In spite of the increased interest, little is known as yet as concerns the characteristics and appropriate application of PTCs as direct oxidation catalysts. This paper is a contribution to this topic.

2. Experimental

The hydrocarbons and the solvent chlorobenzene were purified by methods usual for liquid-phase oxidation reactions [10]. Phase-transfer agents and other chemicals of c.p. grade were applied without any purifications.

The oxidations of tetralin (T), cyclohexene (Ch) and cumene (C) were investigated at 70°C in a magnetically stirred batch reactor (fitted with a reflux condenser cooled with water at 10°C) in the absence or in the presence of PTC, in the dark, by measuring the O₂ uptake with an automatic syringe type gas burette (a modified Metrohm Dosimat E415P) with temperature control as a function of time. After a net conversion time of 120 min, the reaction products were determined by iodometry and gas chromatography: a 2 m long 4 mm i.d. column filled with Chromosorb W coated with 10% Carbowax 20 M carrier gas: N₂ at 30 cm³ min⁻¹; FID detector.

The light scattering measurements were done with a SEMATech SEM 663 apparatus fitted with an RTG photon-correlator.

3. Results

At the beginning detailed investigations were done on how the oxidation of the mentioned hydrocarbons is influenced by the experimental conditions. Because all the three hydrocarbons behaved similarly, only the results obtained with tetralin is presented here.

3.1. Oxidation of tetralin in the absence of phase-transfer reagents

The extent of oxidation of tetralin exhibited a dependence on the stirring rate below 350 rpm, the O₂ uptake being partially controlled by diffusion. All measurements were carried out at a stirring rate of 750–800 rpm in the kinetically controlled regime. The rate of oxidation displayed a linear dependence on the initial substrate concentration up to ca 5 M; from then on, the extent of oxidation approached a limiting value. The O₂ uptake was found to increase linearly with the concentration of hydroperoxide initiator up to 0.02 M. Above this, a further increase of the concentration resulted in

Table 1
Dependence of oxidation of tetralin on concentrations of substrate and initiator

| Tetralin (M) | Tert-BHP (M) | Time lag (min) | O ₂ uptake (mmol) | O _{act} ^{corr} (mmol) ^a |
|--------------|--------------|----------------|------------------------------|--|
| 0.920 | 0.0125 | 51 | 0.024 | 0.021 |
| 1.839 | 0.0125 | 45 | 0.036 | 0.033 |
| 2.759 | 0.0125 | 25 | 0.048 | 0.041 |
| 2.759 | 0.0125 | 24 | 0.047 | 0.041 |
| 3.678 | 0.0125 | 24 | 0.051 | 0.041 |
| 4.599 | 0.0125 | 26 | 0.055 | 0.041 |
| 5.519 | 0.0125 | 28 | 0.063 | 0.049 |
| 6.439 | 0.0125 | 25 | 0.074 | 0.070 |
| 7.359 | 0.0125 | 18 | 0.079 | 0.070 |
| 2.759 | 0.000 | 88 | 0.011 | 0.012 |
| 2.759 | 0.005 | 59 | 0.015 | 0.013 |
| 2.759 | 0.005 | 63 | 0.014 | 0.018 |
| 2.759 | 0.010 | 48 | 0.020 | 0.015 |
| 2.759 | 0.013 | 36 | 0.057 | 0.056 |
| 2.759 | 0.013 | 34 | 0.053 | 0.055 |
| 2.759 | 0.020 | 24 | 0.096 | 0.095 |
| 2.759 | 0.027 | 19 | 0.166 | 0.160 |
| 2.759 | 0.040 | 14 | 0.265 | 0.240 |
| 2.759 | 0.054 | 3 | 0.390 | 0.392 |
| 2.759 | 0.054 | 3 | 0.385 | 0.376 |
| 2.759 | 0.067 | 4 | 0.505 | 0.481 |
| 2.759 | 0.087 | 0 | 0.749 | 0.637 |
| 2.759 | 0.134 | 0 | 0.945 | 0.806 |
| 2.759 | 0.161 | 0 | 0.947 | 0.917 |

Conditions: the reaction mixture contained the given concentration of tetralin and tert-BHP as initiator in chlorobenzene solution. Net conversion time: 120 min.

$$^a \Delta O_{act}^{corr} = (\Delta O_{act})_{found} - [tert-BHP]_0.$$

only a moderate rate increase due to the H-bond association of hydroperoxide [14]. The relevant data are compiled in Table 1.

It was previously reported [9,10] that the rate of oxidation is also influenced by the water content of the hydrocarbons.

3.2. Influences of non-ionic surfactants on the autoxidation of hydrocarbons

In our experience, non-ionic surfactants influenced the oxidation of hydrocarbons (Table 2) in different ways. It was found that the rate-influencing effects of non-ionic PTCs did not depend on the nature of the hydrocarbon to be oxidized. It seems that there is some approximate relationship between the HLB (hydrophile–lipophile balance) value of the PTC [12,13] and the catalytic activity. When the HLB value was high (< 15) or low (> 3), i.e. the given PTC was rather hydrophilic or significantly lipophilic in character, the surfactant hardly influenced the rate of autoxidation, or even inhibited the reaction, especially for lipophilic PTCs. In such cases, the time lag is lengthened considerably. The PTCs with intermediate HLB values (7 < HLB < 13) all increased the rate of autoxidation (see last column in Table 2) and the time lags dropped to zero.

3.3. Influences of anionic surfactants on the autoxidation of hydrocarbons

Protonated anionic surfactants such as capric, lauric, myristic, palmitic, stearic and oleic acids all moderately increased the rate of autoxidation of hydrocarbons (Table 3). On the other hand, their

Table 2
Effects of non-ionic surfactants on the oxidation of hydrocarbons

| Hydrocarbon (M) | <i>Tert</i> -BHP (M) | PTC (mg) | Time lag (min) | ΔO_2 (mmol) | ΔO_{act}^{corr} (mmol) | $(\Delta O_2)_{PTC} / \Delta O_2$ |
|-----------------|----------------------|----------|----------------|---------------------|--------------------------------|-----------------------------------|
| 2.759 T | 0.0125 | — | 17 | 0.333 | 0.264 | — |
| 2.759 T | 0.0125 | 30 TR | 12 | 0.958 | 0.769 | 2.88 |
| 2.759 T | 0.0125 | 30 TR | 11 | 1.051 | 0.829 | 3.26 |
| 2.759 T | 0.0125 | 30 Plu | 0 | 0.772 | 0.789 | 2.12 |
| 2.759 T | 0.0125 | 30 Plu | 0 | 0.683 | 0.668 | 2.05 |
| 2.759 T | 0.0125 | 30 Sp | 41 | 0.054 | 0.045 | 0.16 |
| 2.759 T | 0.0125 | 30 Sp | 38 | 0.058 | 0.049 | 0.17 |
| 2.759 T | 0.0125 | 30 Bri | 3 | 0.274 | 0.264 | 0.82 |
| 2.759 T | 0.0125 | 30 Tw | 2 | 1.193 | 1.132 | 3.58 |
| 2.759 T | 0.0125 | 30 Tw | 0 | 1.244 | 1.221 | 3.74 |
| 2.759 T | 0.0125 | 30 Trg | 0 | 0.492 | 0.486 | 1.48 |
| 2.468 Ch | 0.0125 | — | 3 | 0.534 | 0.506 | — |
| 2.468 Ch | 0.0125 | 30 Tw | 0 | 1.085 | 0.748 | 2.03 |
| 2.468 Ch | 0.0125 | 30 Tw | 0 | 1.158 | 0.849 | 2.17 |
| 2.468 Ch | 0.0125 | 30 Trg | 0 | 0.902 | 0.829 | 1.69 |
| 2.468 Ch | 0.0125 | 30 Trg | 0 | 1.008 | 1.225 | 1.88 |
| 2.468 Ch | 0.0125 | 30 Plu | 0 | 0.962 | 0.849 | 1.80 |
| 2.468 Ch | 0.0125 | 30 Sp | 35 | 0.099 | 0.082 | 0.18 |
| 2.468 Ch | 0.0125 | 30 Bri | 7 | 0.310 | 0.284 | 0.58 |
| 2.468 Ch | 0.0125 | 30 TR | 0 | 1.310 | 1.132 | 2.45 |
| 2.468 Ch | 0.0125 | 30 TR | 0 | 1.331 | 1.254 | 2.49 |
| 2.669 C | 0.0125 | — | 22 | 0.049 | 0.021 | — |
| 2.669 C | 0.0125 | 30 Tw | 8 | 0.310 | 0.284 | 6.33 |
| 2.669 C | 0.0125 | 30 Trg | 15 | 0.084 | 0.054 | 1.71 |
| 2.669 C | 0.0125 | 30 TR | 13 | 0.099 | 0.070 | 2.02 |
| 2.669 C | 0.0125 | 30 Plu | 8 | 0.063 | 0.062 | 1.29 |
| 2.669 C | 0.0125 | 30 Sp | 71 | 0.026 | 0.021 | 0.53 |
| 2.669 C | 0.0125 | 30 Bri | 28 | 0.028 | 0.021 | 0.57 |

Conditions: 8.00 cm³ chlorobenzene solution containing the hydrocarbon, the initiator in the given concentration and 30 mg PTC (if any). Net conversion time: 120 min. Notations: Bri – Brij 30, HLB: 15 (polyoxyethylene(4)lauryl ether), Plu – Pluronic L92, HLB: 7 (block copolymer of polyethylene and polypropylene glycol), Sp – Span 65, HLB: 2.1 (sorbitan tristearate), TR – Triton X-100, HLB: 9.8 (octylphenol polyethylene glycol ether), Trg – Tergitol NP 35, HLB: 14 (nonylphenol polyethylene glycol ether), Tw – Tween 65, HLB: 10.5. (polyoxyethylenec(20)sorbitantristearate).

sodium salts all slightly inhibited the oxidation. It should be emphasized that sodium salts dissolve only poorly in the non-polar hydrocarbon and chlorobenzene solution. Ca-stearate, which is a more soluble salt, promotes the oxidation. AOT (Aerosol OT, sodium bis(2-ethylhexyl)sulfosuccinate) demonstrated rather special behavior. When AOT was added to a reaction mixture at the start, the oxidation took place more slowly than in the absence of PTC. In contrast, when AOT was introduced into an otherwise similar reaction mixture after a 120 min conversion, a definite rate increase was observed. This rate enhancement was greater than would be expected due to the increase in the hydroperoxide concentration during the 120 min run. When Aliquat 336 was simultaneously applied in equivalent quantity besides AOT, a slower oxidation, but still faster than the uncatalyzed process, was observed.

3.4. Influences of cationic surfactants on the autoxidation of hydrocarbons

Phosphonium, pyridinium and ammonium-type cationic surfactants exert a strong catalytic effect on the oxidation of hydrocarbons by dioxygen. The catalytic efficiencies were found to depend

Table 3
Effects of anionic surfactants on oxidation of hydrocarbons

| Hydrocarbon (M) | <i>Tert</i> -BHP (M) | PTC (M) | Time-lag (min) | ΔO_2^a (mmol) | ΔO_{act}^{corr} (mmol) ^a | $(\Delta O_2)_{PTC} / \Delta O_2$ |
|-----------------|----------------------|---------------------------|----------------|-----------------------|---|-----------------------------------|
| 2.468 Ch | 0.0125 | — | 41 | 0.025 | 0.023 | |
| 2.468 Ch | 0.0125 | H-Pal 0.01 | 8.5 | 0.090 | 0.073 | 3.60 |
| 2.468 Ch | 0.0125 | H-Stea 0.01 | 24 | 0.054 | 0.032 | 2.08 |
| 2.468 Ch | 0.0125 | H-Ol 0.01 | 9 | 0.127 | 0.107 | 5.48 |
| 2.468 Ch | 0.0125 | H-Cap 0.01 | 53 | 0.031 | 0.022 | 1.24 |
| 2.468 Ch | 0.0125 | H-Lau 0.01 | 29 | 0.045 | 0.040 | 1.80 |
| 2.468 Ch | 0.0125 | H-My 0.01 | 27 | 0.034 | 0.030 | 1.36 |
| 2.468 Ch | 0.0125 | Na-DBSO ₃ 0.01 | 53 | 0.016 | 0.018 | 0.64 |
| 2.468 Ch | 0.0125 | Na-DSO ₄ 0.01 | 52 | 0.015 | 0.004 | 0.60 |
| 2.468 Ch | 0.0125 | NaOl 0.01 | 48 | 0.015 | 0.002 | 0.60 |
| 2.468 Ch | 0.0125 | AOT 0.01 | 41 | 0.023 | 0.014 | 0.92 |
| 2.468 Ch | 0.0125 | Ca-Stea 0.01 | 38 | 0.041 | 0.032 | 1.64 |
| 2.759 T | 0.0125 | — | 42 | 0.023 | 0.021 | — |
| 2.759 T | 0.0125 | H-Pal 0.01 | 17 | 0.033 | 0.026 | 1.43 |
| 2.759 T | 0.0125 | H-Stea 0.01 | 22 | 0.031 | 0.024 | 1.35 |
| 2.759 T | 0.0125 | H-Ol 0.01 | 2.5 | 0.145 | 0.079 | 6.30 |
| 2.759 T | 0.0125 | H-Lau 0.01 | 8.5 | 0.059 | 0.030 | 2.56 |
| 2.759 T | 0.0125 | Ca-Stea 0.01 | 32 | 0.026 | 0.019 | 1.13 |
| 2.759 T | 0.0125 | Na-DSO ₄ 0.01 | 41 | 0.017 | 0.010 | 0.72 |
| 2.759 T | 0.0125 | Na-DBSO ₃ 0.01 | 39 | 0.013 | 0.002 | 0.55 |
| 2.759 T | 0.0125 | AOT 0.01 | 37 | 0.021 | 0.016 | 0.91 |
| 2.759 T | 0.0125 | H-My 0.01 | 20 | 0.034 | 0.032 | 1.47 |
| 2.759 T | 0.0125 | H-Cap 0.01 | 17 | 0.039 | 0.038 | 1.69 |
| 2.759 T | 0.0125 | Na-Ol 0.01 | 32 | 0.017 | 0.017 | 0.76 |

Conditions: 8.00 cm³ chlorobenzene solution containing the hydrocarbon, the initiator in the given concentrations and 0.01 M PTC (if any). Net conversion time: 60 min. Notations: H-Cap – capric acid (decanoic acid), H-Pal – palmitic acid, H-Lau – lauric acid (dodecanoic acid), H-Stea – stearic acid, H-My – myristic acid, H-Ol – oleic acid, Na-DBSO₃ – Na-dodecylbenzenesulfonate, Na-DSO₄ – Na-dodecylsulfate (Na-lauryl sulfate), Na-Ol – Na-oleate, Ca-Stea – Ca-stearate, AOT – Aerosol OT.

^a Arithmetic mean of parallel measurements, $\Delta O_{act}^{corr} = (O_{act})_{found} - added \text{ } tert\text{-BHP}$.

strongly on the experimental conditions (on the concentrations of hydrocarbon, the initiator and PTC (see Tables 4 and 5).

When AOT was added after a 120 min conversion to a reaction mixture catalyzed by Aliquat 336, the oxidation rate suddenly dropped almost to zero and the reaction subsequently proceeded at that minimum value.

3.5. Influences of the aqueous phase on the autoxidation of hydrocarbons catalyzed by cationic surfactants

In catalytic oxidation, the phase-transfer agents are generally used in a biphasic system. Accordingly, the onium-type catalysts were also checked under biphasic conditions. The data in Table 6 indicate that all three hydrocarbons were oxidized to smaller extents when the aqueous phase was present during the runs. when the aqueous phase was removed before the oxidation (i.e., only the homogeneously dissolved water remained present in the organic phase), considerably higher rates were observed.

In both cases, the pH of the aqueous phase exerted a small influence on the oxidation rate: at lower pH, the oxidation proceeded at a higher rate.

Table 4
Effects of cationic surfactants on oxidation of hydrocarbons

| Hydrocarbon (M) | <i>Tert</i> -BHP (M) | 9.09×10^{-3} M PTC | ΔO_2 (mmol) | ΔO_{act}^{corr} (mmol) | Time-lag (min) | $(\Delta O_2)_{PTC} / \Delta O_2$ |
|-----------------|----------------------|-----------------------------|---------------------|--------------------------------|----------------|-----------------------------------|
| 6.69 T | 0.0175 | — | 0,198 | 0,197 | 4 | — |
| 6.69 T | 0.0175 | — | 0.196 | 0.192 | 4 | — |
| 6.69 T | 0.0175 | A | 4.860 | 4.268 | 0 | 24.67 |
| 6.69 T | 0.0175 | A | 4.831 | 4.240 | 0 | 24.52 |
| 6.69 T | 0.0175 | B | 4.548 | 3.948 | 3 | 23.09 |
| 6.69 T | 0.0175 | B | 4.718 | 4.226 | 1 | 23.95 |
| 6.69 T | 0.0175 | C' | 4.687 | 3.934 | 0 | 23.79 |
| 6.69 T | 0.0175 | C' | 4.105 | 3.461 | 0 | 20.84 |
| 6.69 T | 0.0175 | D | 2.649 | 2.669 | 1 | 13.45 |
| 6.69 T | 0.0175 | D | 2.777 | 2.516 | 0 | 14.10 |
| 6.69 T | 0.0175 | E | 2.604 | 2.405 | 0 | 13.22 |
| 6.69 T | 0.0175 | E | 2.839 | 2.655 | 0 | 14.41 |
| 6.69 T | 0.0175 | F | 1.145 | 0.946 | 6 | 5.81 |
| 6.69 T | 0.0175 | F | 1.009 | 1.015 | 9 | 5.12 |
| 8.97 Ch | 0.0184 | — | 0.653 | 0.653 | 0 | — |
| 8.97 Ch | 0.0184 | — | 0.646 | 0.653 | 0 | — |
| 8.97 Ch | 0.0184 | A | 3.296 | 3.295 | 0 | 5.07 |
| 8.97 Ch | 0.0184 | A | 3.206 | 3.152 | 0 | 4.94 |
| 8.97 Ch | 0.0184 | B | 2.933 | 3.012 | 0 | 4.52 |
| 8.97 Ch | 0.0184 | B | 3.098 | 3.150 | 0 | 4.77 |
| 8.97 Ch | 0.0184 | C' | 0.558 | 0.565 | 0 | 0.86 |
| 8.97 Ch | 0.0184 | C' | 0.571 | 0.593 | 0 | 0.88 |
| 8.97 Ch | 0.0184 | D | 3.012 | 3.041 | 0 | 4.64 |
| 8.97 Ch | 0.0184 | D | 3.286 | 3.317 | 0 | 5.06 |
| 8.97 Ch | 0.0184 | E | 2.823 | 2.902 | 0 | 4.35 |
| 8.97 Ch | 0.0184 | E | 2.891 | 2.902 | 0 | 4.45 |
| 8.97 Ch | 0.0184 | F | 3.284 | 3.324 | 0 | 5.06 |
| 8.97 Ch | 0.0184 | F | 3.226 | 3.268 | 0 | 4.97 |
| 6.534 C | 0.0181 | — | 0.114 | 0.095 | 27 | — |
| 6.534 C | 0.0181 | — | 0.110 | 0.094 | 31 | — |
| 6.534 C | 0.0181 | A | 0.695 | 0.734 | 11 | 6.20 |
| 6.534 C | 0.0181 | A | 0.836 | 0.901 | 8 | 7.46 |
| 6.534 C | 0.0181 | B | 0.095 | 0.045 | 16 | 0.85 |
| 6.534 C | 0.0181 | B | 0.086 | 0.067 | 20 | 0.77 |
| 6.534 C | 0.0181 | C' | 0.341 | 0.348 | 11 | 3.04 |
| 6.534 C | 0.0181 | C' | 0.359 | 0.372 | 11 | 3.20 |
| 6.534 C | 0.0181 | D | 0.735 | 0.605 | 11 | 6.56 |
| 6.534 C | 0.0181 | D | 0.530 | 0.539 | 12 | 4.73 |
| 6.534 C | 0.0181 | E | 3.164 | 2.263 | 0 | 28.25 |
| 6.534 C | 0.0181 | E | 3.216 | 2.374 | 0 | 28.71 |
| 6.534 C | 0.0181 | F | 0.029 | 0.020 | 35 | 0.26 |
| 6.534 C | 0.0181 | F | 0.036 | 0.025 | 41 | 0.32 |

Conditions: 5.50 cm³ chlorobenzene solution containing the hydrocarbon, initiator and PTC in the given concentrations. Net conversion time: 120 min. Notations: A – MeO₃NCl, B – Hex₄NCl, C' – benzylEt₃NCl, D – benzylBu₃NCl, E – hexadecylBu₃PBr, F – hexadecylIPyCl.

3.6. Dependence of the rate of oxidation of hydrocarbons on the concentration of cationic surfactants

It was interesting to learn how the oxidation rate depends on the concentration of the onium ion catalysts. To this end, the oxidation of the above hydrocarbons was investigated in the presence of different initiators. Secondary tetralyl (THP) and cyclohexenyl hydroperoxide (ChHP) proved as active as tertiary tert-butyl and cumyl hydroperoxides (CHP) as initiators. The O₂ uptake versus PTC

Table 5
Effects of cationic surfactants on oxidation of hydrocarbons

| Hydrocarbon (M) | <i>Tert</i> -BHP (M) | 0.0125 M PTC | ΔO_2 mmol | ΔO_{act}^{corr} (mmol) | Time-lag (min) | $(\Delta O_2)_{PTC} / \Delta O_2$ |
|-----------------|----------------------|--------------|-------------------|--------------------------------|----------------|-----------------------------------|
| 2.759 T | 0.0125 | — | 0.356 | 0.342 | 10 | — |
| 2.468 Ch | 0.0125 | — | 0.534 | 0.506 | 3 | — |
| 2.695 C | 0.0125 | — | 0.049 | 0.021 | 26 | — |
| 2.759 T | 0.0125 | A | 3.448 | 1.831 | 0 | 9.70 |
| 2.468 Ch | 0.0125 | A | 2.849 | 1.408 | 0 | 5.30 |
| 2.695 K | 0.0125 | A | 0.279 | 0.222 | 4 | 5.69 |
| 2.759 T | 0.0125 | B | 1.251 | 0.905 | 4 | 3.5 |
| 2.468 Ch | 0.0125 | B | 2.106 | 1.316 | 0 | 3.94 |
| 2.695 C | 0.0125 | B | 0.374 | 0.282 | 11 | 7.63 |
| 2.759 T | 0.0125 | C' | 0.794 | 0.624 | 13 | 2.20 |
| 2.468 Ch | 0.0125 | C' | 1.441 | 1.308 | 0 | 2.70 |
| 2.695 C | 0.0125 | C' | 0.486 | 0.443 | 13 | 9.92 |
| 2.759 T | 0.0125 | D | 1.645 | 1.195 | 2 | 4.60 |
| 2.468 Ch | 0.0125 | D | 1.405 | 1.139 | 0 | 2.63 |
| 2.695 C | 0.0125 | D | 0.135 | 0.189 | 6 | 3.77 |
| 2.759 T | 0.0125 | E | 1.799 | 1.179 | 0 | 5.10 |
| 2.468 Ch | 0.0125 | E | 1.261 | 0.909 | 0 | 2.36 |
| 2.695 C | 0.0125 | E | 0.951 | 0.632 | 9 | 19.41 |
| 2.759 T | 0.0125 | F | 0.075 | 0.061 | 26 | 0.21 |
| 2.468 Ch | 0.0125 | F | 0.992 | 0.712 | 4 | 1.86 |
| 2.695 C | 0.0125 | F | 0.045 | 0.037 | 46 | 0.92 |

Conditions: 8.00 cm³ chlorobenzene solution containing the hydrocarbon, initiator and PTC in the given concentrations. Net conversion time: 120 min. Notations: A–F as in Table 4.

concentration relationships gave two different types of curves. The more general type exhibited a steep, linearly rising section, which soon fell away (Fig. 1, curves a and b). The other type was a maximum curve (Fig. 1, curve c). The data in Table 7 show that the maximum or the intersection points are situated at fairly low concentrations of PTC, in spite of the fact that ample hydroperoxide is present, which could be activated further by the addition of phase-transfer agent. The above phenomenon is not limited only to the cationic surfactants. Fig. 2, curves a, b and c show the similar dependences of the catalytic efficiencies on the concentration of surfactant for non-ionic and anionic tensides.

Table 6
Influence of water and pH of the aqueous phase on oxidation of hydrocarbons catalyzed by onium ion phase-transfer catalyst

| O ₂ uptake and (ROOH) formed values in mmol when aqueous phase is | | | | | | | |
|--|----|---------------|---------------|--------------------------------|---------------|---------------|---------------|
| (A) present during oxidation | | | | (B) removed prior to oxidation | | | |
| PTC | pH | tetralin | cyclohexene | cumene | tetralin | cyclohexene | cumene |
| MeOct ₃ NCl | 7 | 0.624 (0.705) | 0.371 (0.444) | 0.024 (0.027) | 4.654 (3.705) | 2.512 (2.512) | 1.339 (1.438) |
| MeOct ₃ NCl | 3 | 0.973 (0.968) | 0.389 (0.463) | 0.047 (0.047) | 5.032 (3.981) | 2.711 (2.254) | 2.170 (2.122) |
| CetBu ₃ PBr | 7 | 2.296 (2.101) | 1.156 (1.162) | 0.049 (0.149) | 3.342 (3.207) | 2.288 (2.244) | 2.435 (1.933) |
| CetBu ₃ PBr | 3 | 2.247 (2.059) | 1.250 (1.204) | 0.038 (0.125) | 3.470 (2.100) | 2.083 (2.100) | 1.992 (1.631) |
| CetPyCl | 7 | 0.140 (0.152) | 0.122 (0.188) | 0.015 (0.060) | 0.165 (0.261) | 0.771 (0.837) | 0.025 (0.056) |
| CetPyCl | 3 | 0.153 (0.166) | 0.159 (0.188) | 0.021 (0.060) | 0.184 (0.281) | 1.133 (1.196) | 0.027 (0.048) |

Conditions: (A) Aqueous phase: 2.50 cm³ water adjusted to the given pH; organic phase: 5.50 cm³ containing 36.7 mmol hydrocarbon, 0.05 mmol phase-transfer catalyst and 0.10 mmol tert-butyl hydroperoxide as initiator and the necessary quantity of chlorobenzene. (B) The aqueous phase was removed by centrifugation and the organic phase was filtered on silicone-treated filter paper.

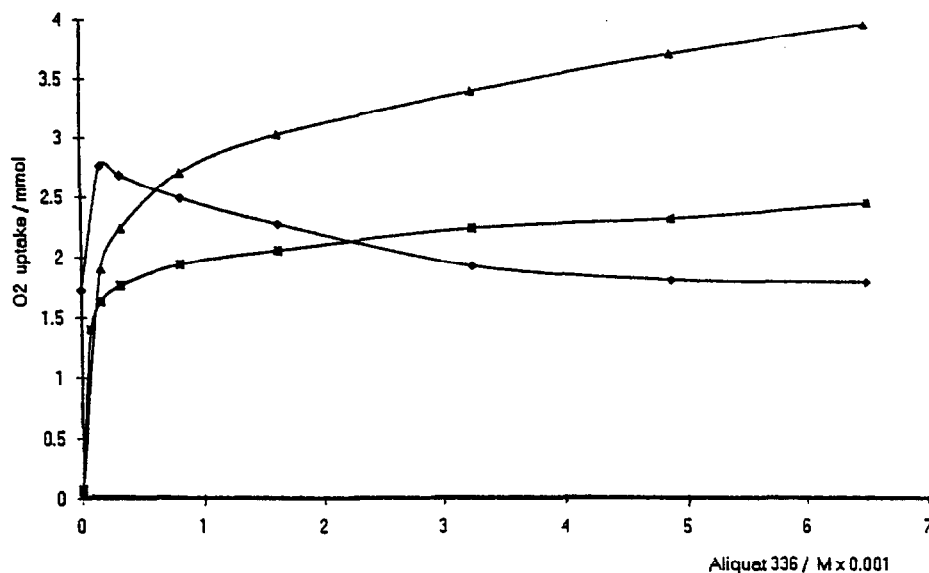


Fig. 1. Dependence of O₂ uptake on concentrations of cationic PTC. Compositions: 8.00 cm³ reaction mixtures contains (▲) 22.08 mmol T + 0.02 mmol *tert*-BHP + chlorobenzene + Aliquat 336, (■) 9.74 mmol Ch + 0.02 mmol ChHP + chlorobenzene + Aliquat 336, (◆) 21.56 mmol Ch + 0.02 mmol CHP + chlorobenzene + Aliquat 336, ordinate value × 0.01. Net conversion time: 120 min.

3.7. Self-association of surfactants at increased PTC concentrations

This 'saturation' or maximum dependence on the PTC concentration was attributed to the self-association of the surfactant when its concentration was increased. To prove this assumption, the light scattering of the solution was measured both in the absence and in the presence of hydroperoxide (or water or other polar substances). The resulting data (Table 8) indicated that in the absence of polar substances the solutions did not contain any light scattering particles. In the presence of a polar substance, however, aggregation occurred on increase of the concentration of cationic surfactant, and heterodisperse particles with an average diameter of 2–4 μm could be detected. The occurrence of self-association did not depend on the nature of the counteranions of PTC, as it was also found for Bu₄NI and Bu₄NCl.

As concerns the anionic surfactant, AOT displayed some light scattering even in the absence of a polar component. The addition of water resulted first in an increase in the light scattering; then, when the water concentration was further increased, dissolution of the aggregates was promoted. When the partially aggregated AOT solution was filtered on a filter paper of 0.2 μm porosity, the light-scattering particles were removed, but association set in again when water was added to this solution.

3.8. Products of oxidation of hydrocarbons catalyzed by Aliquat 336

For orientation, the Aliquat 336-catalyzed oxidation products of the above hydrocarbons are listed in Table 9. Tetralin was oxidized mostly to tetralyl hydroperoxide; some tetralone was also formed, but tetralol formation was not detected. In the case of cyclohexene, the main product was cyclohexenyl hydroperoxide, but some cyclohexene oxide (7-oxabicyclo[4.1.0]heptane, in short the epoxide) and cyclohexanol were also formed; cyclohexanone formation was not observed. As regards cumene, products other than the main product cumene hydroperoxide were not identified, although the lack in

Table 7
Characteristics of O₂ uptake versus [PTC] curves

| Hydrocarbon (M) | ROOH (M) | PTC | PTC concentration (M) at | |
|-----------------|-----------------|------------------------|--------------------------------------|----------------------------|
| | | | maximum | intersection |
| 1.839 T | 0.0125 tert-BHP | Hex ₄ NCl | — | 6.70 × 10 ⁻⁴ |
| 1.839 T | 0.0125 tert-BHP | CetBu ₃ PBr | — | 6.70 × 10 ⁻⁴ |
| 1.839 T | 0.0125 tert-BHP | CetPyCl | 1.50 × 10 ⁻³ | — |
| 1.839 T | 0.0125 tert-BHP | MeOct ₃ NCl | — | 1.45 × 10 ⁻³ |
| 2.759 T | 0.0125 tert-BHP | MeOct ₃ NCl | — | 2.50 × 10 ⁻⁴ |
| 2.759 T | 0.0125 ChHP | MeOct ₃ NCl | — | 2.0–3.0 × 10 ⁻⁴ |
| 2.759 T | 0.0025 THP | MeOct ₃ NCl | 1.6 × 10 ⁻³ | — |
| 2.759 T | 0.0025 ChHP | MeOct ₃ NCl | — | 2.0–3.0 × 10 ⁻⁴ |
| 2.759 T | 0.0025 CHP | MeOct ₃ NCl | — | 2.50 × 10 ⁻⁴ |
| 2.759 T | 0.0125 CHP | MeOct ₃ NCl | — | 2.50 × 10 ⁻⁴ |
| 2.468 Ch | 0.0125 tert-BHP | CetPyCl | — | 1.50 × 10 ⁻³ |
| 2.468 Ch | 0.0125 tert-BHP | CetBu ₃ PBr | — | 2.5 × 10 ⁻⁴ |
| 2.468 Ch | 0.0125 tert-BHP | MeOct ₃ NCl | — | 3.5 × 10 ⁻⁴ |
| 2.468 Ch | 0.0025 tert-BHP | MeOct ₃ NCl | 1.62 × 10 ⁻⁴ | — |
| 2.468 Ch | 0.0250 tert-BHP | MeOct ₃ NCl | — | 4.2 × 10 ⁻⁴ |
| 2.468 Ch | 0.0125 tert-BHP | MeOct ₃ NCl | monotonously decreasing ^a | — |
| 2.468 Ch | 0.0125 tert-BHP | MeOct ₃ NCl | — | 1.3 × 10 ⁻⁴ |
| 2.468 Ch | 0.0025 ChHP | MeOct ₃ NCl | — | 2.0 × 10 ⁻⁴ |
| 2.468 Ch | 0.0125 ChHP | MeOct ₃ NCl | — | 2.0 × 10 ⁻⁴ |
| 2.468 Ch | 0.0025 CHP | MeOct ₃ NCl | — | 3.0 × 10 ⁻⁴ |
| 2.468 Ch | 0.0125 ClIP | MeOct ₃ NCl | — | 2.5 × 10 ⁻⁴ |
| 2.669 C | 0.0025 tert-BHP | MeOct ₃ NCl | 1.50 × 10 ⁻⁴ | — |
| 1.797 C | 0.0125 tert-BHP | MeOct ₃ NCl | 1.60 × 10 ⁻³ | — |
| 4.490 C | 0.0125 tert-BHP | MeOct ₃ NCl | 1.50 × 10 ⁻⁴ | — |
| 2.669 C | 0.0025 ChHP | MeOct ₃ NCl | 2.5 × 10 ⁻⁴ | — |
| 2.669 C | 0.0125 ChHP | MeOct ₃ NCl | 2.5 × 10 ⁻⁴ | — |
| 2.669 C | 0.0025 CHP | MeOct ₃ NCl | 1.5 × 10 ⁻⁴ | — |
| 2.669 C | 0.0125 CHP | MeOct ₃ NCl | 1.5 × 10 ⁻⁴ | — |
| 1.797 C | 0.0125 tert-BHP | Hex ₄ NCl | — | 3.0 × 10 ⁻⁴ |
| 1.797 C | 0.0125 tert-BHP | CetBu ₃ PBr | — | 3.75 × 10 ⁻⁴ |
| 1.797 C | 0.0125 tert-BHP | CetPyCl | monotonously decreasing | — |

Intersection relates to the concentration of PTC at the intersection point of the tangents to the steepest rising linear part and the least steep limiting (or saturation) section of the O₂ uptake versus [PTC] curve. Measurements were performed in the range 1.0 × 10⁻⁴–1.0 × 10⁻² M PTC. Notation: Cet = hexadecyl.

^a Measurements were performed in the range 0.0035–0.10 M PTC.

the O₂ balance points to the formation of other products in small quantities (probably acetophenone, α -cumyl alcohol, dicumyl peroxide, etc.).

3.9. Influences of coordinating solvents on the oxidation of hydrocarbons catalyzed by Aliquat 336

It is known that the oxidation of hydrocarbons takes place with higher yields in chlorinated polar, but poorly coordinating solvents. In this respect, we checked the extent of the PTC-catalyzed oxidation in the presence of non-ionizing, but strongly solvating solvents. Table 10 convincingly demonstrates that the rate of the catalyzed oxidation was reduced considerably in the presence of strongly coordinating solvents. The rate-diminishing effect relating to unit solvent concentration exhibits the sequence tributyl phosphate (100%) > benzyl cyanide (46%) > ethylene carbonate (18%) > acetonitrile (5%). This activity sequence by and large corresponds to the sequence of solvating

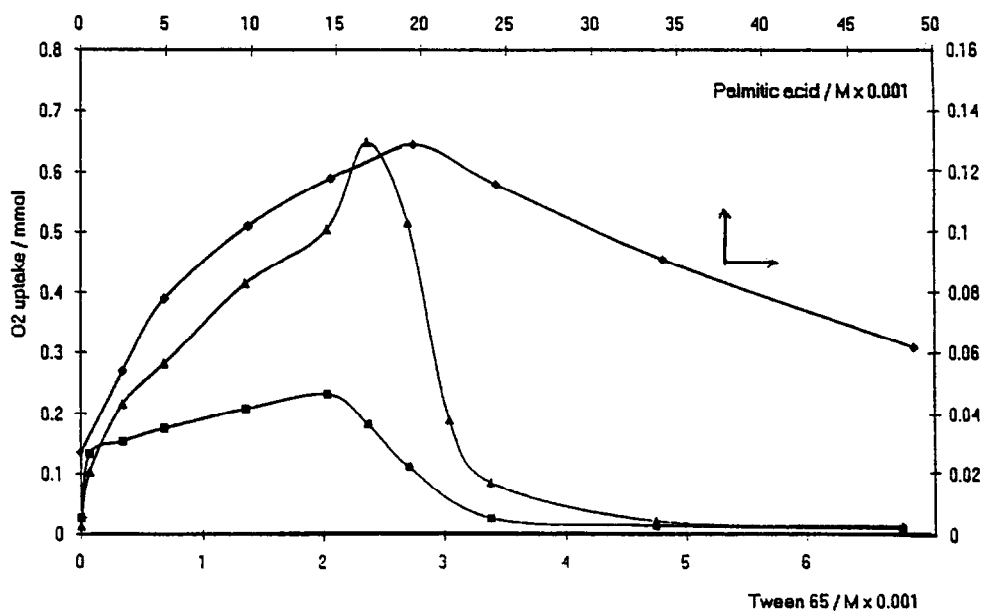


Fig. 2. Dependence of O₂ uptake on concentrations of non-ionic and anionic PTCs. Compositions: 8.00 cm³ reaction mixture contains (▲) 19.74 mmol Ch + 0.01 mmol *tert*-BHP + chlorobenzene + Tween 65, (■) 22.08 mmol T + 0.01 mmol *tert*-BHP + chlorobenzene + Tween 65, (◆) 19.74 mmol Ch + 0.01 mmol *tert*-BHP + chlorobenzene + palmitic acid. Net conversion time: 60 min.

Table 8

Self-association of phase-transfer catalysts according to light-scattering measurements

| Hydrocarbon (M) | 0.0125 M PTC | <i>Tert</i> -BHP (M) | H ₂ O (μl) | Temp (°C) | Viscosity (cP) | Diff. coeff. (cm ² s ⁻¹ × 10 ¹⁰) | Average diameter (μm) |
|-----------------|------------------------|----------------------|-----------------------|-----------|----------------|--|-----------------------|
| 2.759 T | Hex ₄ NCl | 0.000 | 0.00 | 22 | 1.18 | 4.115 | 0.0 |
| 2.759 T | Hex ₄ NCl | 0.0125 | 0.00 | 22 | 1.31 | 86.73 | 0.38 |
| 2.759 T | CetBu ₃ PBr | 0.000 | 0.00 | 22 | 1.04 | 7.468 | 0.00 |
| 2.759 T | CetBu ₃ PBr | 0.0125 | 0.00 | 22 | 1.13 | 13.70 | 2.79 |
| 2.759 T | CetPyCl | 0.000 | 0.00 | 22 | — | — | insoluble |
| 2.759 T | CetPyCl | 0.0125 | 0.00 | 70 | 0.679 | 18.84 | 3.93 |
| 2.695 C | Hex ₄ NCl | 0.0125 | 0.00 | 22 | 0.910 | 8.165 | 5.82 |
| 2.695 C | CetBu ₃ PBr | 0.0125 | 0.00 | 22 | 0.697 | 14.39 | 4.31 |
| 2.695 C | CetPyCl | 0.0125 | 0.00 | 70 | 0.633 | 27.67 | 2.87 |
| 2.468 Ch | Hex ₄ NCl | 0.0125 | 0.00 | 22 | 0.909 | 23.53 | 2.02 |
| 2.468 Ch | CetBu ₃ PBr | 0.0125 | 0.00 | 22 | 0.939 | 15.57 | 2.35 |
| 2.468 Ch | CetPyCl | 0.0125 | 0.00 | 70 | 0.615 | 27.48 | 2.97 |
| 2.759 T | Bu ₄ Nl | 0.0125 | 0.00 | 22 | 1.219 | 22.22 | 1.60 |
| 2.759 T | Bu ₄ NCl | 0.0125 | 0.00 | 22 | 1.180 | 23.41 | 1.57 |
| 2.759 T | Hex ₄ NCl | 0.000 | 5.5 | 22 | 1.18 | 4.115 | 1.99 |
| 2.759 T | CetBu ₃ PBr | 0.000 | 1.8 | 22 | 1.04 | 7.468 | 0.32 |
| 2.759 T | AOT | 0.000 | 0.00 | 25.5 | 1.14 | 22.07 | 1.74 |
| 2.759 T | AOT | 0.000 | 1.60 | 25.5 | 1.14 | 17.58 | 2.18 |
| 2.759 T | AOT | 0.000 | 3.20 | 25.5 | 1.14 | 27.72 | 1.32 |
| 2.759 T | AOT | 0.000 | 8.00 | 25.5 | 1.14 | 80.30 | 0.48 |

Conditions: 8.00 cm³ chlorobenzene solutions containing the given quantities of hydrocarbon, PTC, *tert*-BHP and water. Light scattering was measured at the given temperature; sampling time: 50 μs, cumulative time 300 s. Viscosity was measured with a Rotovisco RV-20 apparatus.

Table 9
Products of onium ion-catalyzed oxidation of hydrocarbons

| Hydrocarbon (M) | PTC ($M \times 10^3$) | <i>Tert</i> -BHP (M) | V (cm^3) | ΔO_2 (mmol) | $\Delta\text{O}_{\text{act}}$ (mmol) | $\Delta\text{epoxide}$ (mmol) | $\Delta\text{-ol}$ (mmol) | $\Delta\text{-on}$ (mmol) |
|--------------------|-----------------------------|----------------------|---------------------|---------------------------|--------------------------------------|-------------------------------|---------------------------|---------------------------|
| Tetralin | | | | | | | | |
| 6.69 | 9.09 MeOct ₃ NCl | 0.0175 | 5.5 | 4.860 | 4.190 | 0.00 | 0.00 | 0.540 |
| 6.69 | 9.09 MeOct ₃ NCl | 0.0175 | 5.5 | 4.831 | 4.162 | 0.00 | 0.00 | 0.530 |
| 6.69 | 9.09 MeOct ₃ NCl | 0.0175 | 5.5 | 4.872 | 3.862 | 0.00 | 0.00 | 0.560 |
| 6.69 | 9.09 Hex ₄ NCl | 0.0175 | 5.5 | 4.548 | 3.870 | 0.00 | 0.00 | 0.643 |
| 6.69 | 9.09 Hex ₄ NCl | 0.0175 | 5.5 | 4.814 | 4.079 | 0.00 | 0.00 | 0.730 |
| 6.69 | 9.09 Hex ₄ NCl | 0.0175 | 5.5 | 4.716 | 4.051 | 0.00 | 0.00 | 0.744 |
| 6.69 | 9.09 CetBu ₃ PBr | 0.0175 | 5.5 | 2.803 | 2.507 | 0.00 | 0.00 | 0.344 |
| 6.69 | 9.09 CetBu ₃ PBr | 0.0175 | 5.5 | 2.712 | 2.493 | 0.00 | 0.00 | 0.094 |
| 6.69 | 9.09 CetPyCl | 0.0175 | 5.5 | 1.007 | 0.848 | 0.00 | 0.00 | 0.102 |
| 6.69 | 9.09 CetPyCl | 0.0181 | 5.5 | 1.493 | 1.387 | 0.00 | 0.00 | 0.003 |
| Cyclohexene | | | | | | | | |
| 8.974 | 9.09 MeOct ₃ NCl | 0.0184 | 5.5 | 3.296 | 3.152 | 0.287 | 0.000 | 0.000 |
| 8.974 | 9.09 MeOct ₃ NCl | 0.0184 | 5.5 | 3.205 | 3.069 | 0.261 | 0.000 | 0.000 |
| 2.468 | 1.87 MeOct ₃ NCl | 0.0184 | 8.0 | 2.157 | 1.457 | 0.130 | 0.660 | 0.000 |
| 8.974 | 9.09 Hex ₄ NCl | 0.0125 | 5.5 | 2.933 | 2.656 | 0.256 | 0.000 | 0.000 |
| 8.974 | 9.09 Hex ₄ NCl | 0.0184 | 5.5 | 3.099 | 2.756 | 0.257 | 0.000 | 0.000 |
| 8.974 | 9.09 CetBu ₃ PBr | 0.0184 | 5.5 | 3.073 | 2.832 | 0.017 | 0.051 | 0.000 |
| 8.974 | 9.09 CetBu ₃ PBr | 0.0182 | 5.5 | 3.089 | 2.947 | 0.016 | 0.000 | 0.000 |
| 8.974 | 9.09 CetBu ₃ PBr | 0.0182 | 5.5 | 2.823 | 2.819 | 0.122 | 0.000 | 0.000 |
| 8.974 | 9.09 CetPyCl | 0.0182 | 5.5 | 1.523 | 1.425 | 0.022 | 0.000 | 0.000 |
| 8.974 | 9.09 CetPyCl | 0.0182 | 5.5 | 1.036 | 0.942 | 0.025 | 0.000 | 0.000 |
| Cumene | | | | | | | | |
| 6.534 | 9.09 MeOct ₃ NCl | 0.0183 | 5.5 | 1.557 | 1.462 | — | — | — |
| 6.534 | 9.09 MeOct ₃ NCl | 0.0183 | 5.5 | 0.816 | 0.716 | — | — | — |
| 6.534 | 9.09 MeOct ₃ NCl | 0.0182 | 5.5 | 2.108 | 1.836 | — | — | — |
| 6.534 | 9.09 Hex ₄ NCl | 0.0181 | 5.5 | 0.079 | 0.000 | — | — | — |
| 6.534 | 9.09 Hex ₄ NCl | 0.0181 | 5.5 | 0.065 | 0.000 | — | — | — |
| 6.534 | 9.09 CetBu ₃ PBr | 0.0181 | 5.5 | 2.381 | 1.728 | — | — | — |
| 6.534 | 9.09 CetBu ₃ PBr | 0.0182 | 5.5 | 1.992 | 1.449 | — | — | — |
| 6.534 | 9.09 CetBu ₃ PBr | 0.0182 | 5.5 | 1.989 | 1.437 | — | — | — |
| 6.534 | 9.09 CetPyCl | 0.0182 | 5.5 | 0.025 | 0.000 | — | — | — |
| 6.534 | 9.09 CetPyCl | 0.0182 | 5.5 | 0.027 | 0.000 | — | — | — |

ability (donor number [11]) of these solvents and points to the interaction of the solvent with the onium ion-type catalyst.

3.10. Fundamental role of hydroperoxide during the PTC-catalyzed oxidation of hydrocarbons

The oxidation of hydrocarbons was also investigated when the hydroperoxide content of the substrate was removed just before the oxidation. In the absence of any catalyst, the oxidations of tetralin and cyclohexene started with a long time lag: 65 and 57 min, respectively (Table 11). It should be emphasized that under such experimental conditions (no initial hydroperoxide present) the oxidation proved to be very sensitive to any contamination arising from the surroundings; the time lag and the conversion varied much more sensitively than when the system was somewhat stabilized by the presence of hydroperoxide.

When Aliquat 336 and hexadecyltributylphosphonium bromide were applied, the oxidation was

Table 10
Effects of coordinating solvents on oxidation of hydrocarbons catalyzed by Aliquat 336

| O ₂ uptake and (ROOH) formed values in mmol obtained in presence of | | | | | |
|--|-------------------|------------------------|------------------|------------------------|--------------------|
| hydrocarbon solvents (M) | chlorobenzene (M) | tributyl phosphate (M) | acetonitrile (M) | ethylene carbonate (M) | benzyl cyanide (M) |
| 2.759 T | 3.448 (1.831) | 0.814 (0.664) | 2.809 (1.939) | 1.434 (1.308) | 0.339 (0.282) |
| Chlorobenzene | 6.141 | 2.456 | 2.456 | 2.456 | 2.456 |
| Coordinating solvent | — | 1.378 | 7.180 | 5.625 | 3.429 |
| 2.669 C | 0.279 (0.222) | 0.140 (0.141) | 0.281 (0.272) | 0.227 (0.222) | 0.030 (0.013) |
| Chlorobenzene | 6.141 | 2.456 | 2.456 | 2.456 | 2.456 |
| Coordinating solvent | — | 1.378 | 7.180 | 5.625 | 3.429 |
| 2.468 Ch | 2.849 (1.831) | 0.875 (0.805) | 2.785 (2.192) | 0.943 (0.946) | 0.231 (0.242) |
| Chlorobenzene | 6.141 | 2.456 | 2.456 | 2.456 | 2.456 |
| Coordinating solvent | — | 1.838 | 9.570 | 7.500 | 4.330 |

Conditions: Each sample contains 3.00 cm³ tetralin or 3.00 cm³ cumene or 2.00 cm³ cyclohexene and 0.10 mmol Aliquat 336 and 0.10 mmol *tert*-BHP both dissolved in 2.00 cm³ chlorobenzene, and the mixture is made up to 8.00 cm³ initial volume with the given solvent. For orientation, the donor numbers of the solvents used (DN_{SbCl₅}): are tributyl phosphate, 23.7; ethylene carbonate (1,3-dioxolan-2-one), 16.4; benzyl cyanide, 15.1; acetonitrile, 14.1.

accelerated and the time lags shortened, but the oxidation did not start immediately in the presence of these catalysts. At any event, the fact that the time lag could not be eliminated on the addition of PTC when the reaction mixture did not contain hydroperoxide at the start underlines the decisive role of hydroperoxide. The catalyst promoted the homolysis of hydroperoxide, but the formation of stable oxidation products was also influenced by the catalyst. Because of the latter role of the catalyst, the oxidation time lag usually lengthened on increase of the concentration of the catalyst. In contrast, the ratio $\Delta O_{act}/\Delta O_2$ decreased, because in such cases the formation of the more stable oxidation products became predominant at the expense of the primary product.

The following Arrhenius parameters were found from the temperature dependence of the rate of oxidation of tetralin: $\Delta H^\ddagger = 99.6 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -59.3 \text{ J K}^{-1} \text{ mol}^{-1}$. These values do not differ considerably from those obtained in the presence of $9.09 \times 10^{-3} \text{ M}$ Aliquat 336 catalyst: $\Delta H^\ddagger = 97.7 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -119 \text{ J K}^{-1} \text{ mol}^{-1}$. The higher negative entropy of activation is probably due to the formation of an interaction complex between the initiator hydroperoxide and the catalyst.

Table 11
Oxidation of hydroperoxide-free hydrocarbons in absence or in the presence of phase-transfer catalysts

| Hydrocarbon (M) | PTC (M) | ΔO_2 (mmol) | ΔO_{act} (mmol) | Time-lag (min) |
|-----------------|-----------|---------------------|-------------------------|----------------|
| 2.468 Ch | — | 0.367 | 0.362 | 57 |
| 2.468 Ch | 0.0025 AL | 1.925 | 1.367 | 24 |
| 2.468 Ch | 0.0125 AL | 2.066 | 1.448 | 10 |
| 2.468 Ch | 0.0025 CP | 1.041 | 0.897 | 7 |
| 2.468 Ch | 0.0125 CP | 1.092 | 0.925 | 10 |
| 2.759 T | — | 0.094 | 0.088 | 65 |
| 2.759 T | 0.0025 AL | 2.833 | 1.890 | 17 |
| 2.759 T | 0.0125 AL | 1.815 | 1.247 | 41 |
| 2.759 T | 0.0025 CP | 1.787 | 1.388 | 2 |
| 2.759 T | 0.0125 CP | 2.114 | 1.609 | 7 |

Conditions: The hydroperoxide content of the hydrocarbons was previously removed with Al₂O₃ (activated at 250°C for 4 h). 8.00 cm³ samples containing the hydrocarbon and the PTC (if any) in the given concentrations were prepared with chlorobenzene. Net conversion time: 120 min. AL – MeOct₃NCl, Aliquat 336, CP – CetBu₃PBr.

4. Discussion

The presented data reveal that the phase-transfer reagents are all able to influence the rate of oxidation of hydrocarbons, independently of their nature. The non-ionic surfactants with intermediate HLB values (7–13) without exception enhance the rate of autoxidation. When the PTCs are rather lipophilic (HLB < 3), they usually act as inhibitors. (However, most of these PTCs contain weakly acidic OH groups, which may react as radical scavengers, like phenols, independently of their lipophilic character.) The rather hydrophilic non-ionic PTCs (HLB > 15) behave as inactive additives. The anionic and cationic PTCs are active catalysts, although their activities are somewhat individual and differ from one hydrocarbon to another.

The O-atoms in the hydroperoxides are not entirely equivalent: the inner one is more nucleophilic, while the outer one is more electrophilic in character. It is therefore to be expected that an anionic surfactant will attack at the outer (electrophilic) O-atom, whereas a cationic surfactant interacts with the inner O-atom (nucleophilic) of the hydroperoxide, whereby the O–O bond is lengthened, i.e. homolysis (the formation of chain-carrying radicals) is facilitated. It seems probable that the non-ionic surfactants exert their rate-influencing effects through H-bond formation when the polarities of the surfactant and the hydroperoxide are comparable. When the PTC is rather hydrophilic, the H-bond interaction with the hydroperoxide will be weaker and the oxidation will take place at a lower rate than in the absence of the PTC.

The solubility of O₂ in the reacting hydrocarbon solution was not altered to a detectable extent when any type of PTC (non-ionic, cationic or anionic surfactant) was added to the reaction mixture.

In our experience, the nature of the hydroperoxides does not exert any influence on the (non-catalyzed or PTC-catalyzed) oxidation of hydrocarbons, i.e. the secondary and tertiary hydroperoxides proved to be equally effective initiators.

The most noteworthy result of this investigation is that the catalysis with PTCs depends linearly on the concentration of surfactant in only a narrow range. The reason for this is that the surfactant used is prone to self-association. When the concentration is increased beyond the linear range, the rate of oxidation soon reaches its limiting value, or even decreases when the PTC concentration is further increased. The light scattering measurements indicate that the associated PTC forms heterodisperse particles ca. 2–4 μm in size. Aggregation is always facilitated by the presence of the polar components of the reaction mixture (the hydroperoxide formed, stable oxidation products, etc.). The diminishing effects of water (if present as a separate phase) and of the strongly solvating solvents on the oxidation rate can similarly be ascribed to the more effective self-association of the PTCs, promoted by the presence of these polar components.

As concerns the use of quaternary phosphonium ion-type catalysts, it should be borne in mind that tertiary phosphines and their quaternary phosphonium salts are strong reducing agents. Consequently, such catalysts too undergo oxidation during the oxidation of hydrocarbons. The oxidation was checked by means of ¹H and ³¹P NMR resonance measurements. With the hexadecyltributylphosphonium bromide catalyst in excess, it was observed that the characteristic –OOH group ¹H signal of tert-butyl hydroperoxide at 7.71 ppm disappears in a few minutes. On the other hand, in the presence of excess hydroperoxide, the ³¹P signal at 34.12 ppm for the quaternary salt disappears and a new singlet appears at 201.18 ppm, which is assigned to the P=O bond. However, the rapid transformation of the phosphonium cation into tributylphosphine oxide does not mean the disappearance of the phase-transfer activity: the oxidation of the hydrocarbon continues to proceed at a high rate.

Not too much can be said on the dependence of the catalytic activity on the nature of the counteranion of cationic surfactants. It was earlier checked [10] that there is no correlation between

the ionic character (electric conductivity) of the onium catalyst and its catalytic activity. In many cases, the chloride exhibits a higher catalytic activity than the bromide or the iodide, but in other cases the iodide has the highest activity. The most electronegative F- and OH-derivatives of methyltrioctylammonium, tetrahexylammonium and hexadecyltributylphosphonium cations were prepared, but these all proved to be considerably less active catalysts (almost inactive) than the chlorides. These observations contradict the finding of van Tilborg [6] that triphenylsulfonium hydroxide is much more active than the chloride. A possible explanation of this contradiction is that, when the chloride–hydroxide exchange was carried out as usual, by shaking the sulfonium chloride solution with silver oxide, the resulting sulfonium hydroxide remained contaminated by traces of silver ion, which is known to be an effective oxidation catalyst. The explanation that chloride ion can be scavenged by finely-divided CaCO_3 into the hydroxide derivative in the non-polar cumene solution does not seem to be realistic.

The data in Table 1 point to a general feature of the oxidation of hydrocarbons: the rate of O_2 uptake depends on the concentrations of the oxidizable substance and of the initiator hydroperoxide according to curves of a limiting nature. Only in quite narrow ranges of PTC concentration does the rate of the catalyzed oxidation depend linearly on the PTC concentration. Hence, the turnover number (TN), defined as

$$\text{TN} = \frac{\text{O}_2 \text{ uptake (in mmol)}}{[\text{hydrocarbon}] \times [\text{ROOH}] \times [\text{PTC}] \times V_0 \times \text{conversion time (min)}}$$

where V_0 is the volume of the reaction mixture, must not be used to characterize the oxidation of hydrocarbons catalyzed by PTC.

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References

- [1] H. Bredereck, A. Wagner, R. Blaschke, G. Dimetriades and K.G. Kottenhann, *Chem. Ber.* 92 (1959) 2628.
- [2] K. Fukui, K. Ohkubo and T. Yamabe, *Bull. Chem. Soc. Jpn.* 42 (1969) 312.
- [3] K. Ohkubo, T. Yamabe and K. Fukui, *Bull. Chem. Soc. Jpn.* 42 (1969) 1800, 2200.
- [4] K. Ohkubo and T. Yamabe, *Bull. Jpn. Pet. Inst.* 12 (1970) 130.
- [5] K. Ohkubo and H. Kaneda, *Bull. Jpn. Pet. Inst.* 13 (1971) 177.
- [6] W.J.M. van Tilborg, *Tetrahedron* 31 (1975) 2841.
- [7] M. Hronec, M. Haruštíac and J. Ilavský, *React. Kinet. Catal. Lett.* 27 (1985) 231.
- [8] M. Haruštíac, M. Hronec and J. Ilavský, *React. Kinet. Catal. Lett.* 37 (1988) 215.
- [9] L.J. Csányi and K. Jáky, *J. Catal.* 141 (1993) 721.
- [10] L.J. Csányi, K. Jáky and J.T. Kiss, *J. Mol. Catal.* 80 (1993) 353.
- [11] V. Gutmann, *The Donor–Acceptor Approach to Molecular Interactions* (Plenum, New York, 1975).
- [12] N. Schönfeldt, *Surface Active Ethylenoxide Adducts* (Pergamon Press, Oxford–London, 1969).
- [13] J.T. Davies, *Proc. 2nd Int. Congr. on Surface Activity*, London, Vol. 1 (1957) p. 409.
- [14] Ch. Walling and L. Heaton, *J. Am. Chem. Soc.* 87 (1965) 48.