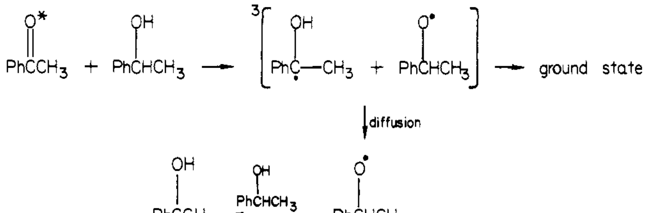
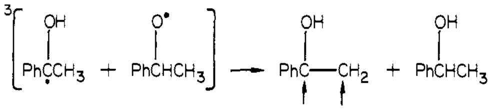
require ketyl–ketone hydrogen exchange for AP and $(PH)_2$ formation.

Since the pinacol experiments demonstrate that triplet ketones can abstract hydrogen atoms fairly efficiently from OH of benzyl alcohols, we must address the question as to how this process in eq 9 can lead to efficient overall quenching. One must conclude that in-cage disproportionation of the α-hydroxy–alkoxy radical pair is highly efficient, since any alkoxy radicals which escape the cage would eventually react with more alcohol to produce the thermodynamically more favorable α-hydroxy radicals[24] (eq 5).



We suggest that in-cage disproportionation of the triplet radical pair is unusually rapid because formation of triplet acetophenone enol can proceed exothermically. Abstraction at OH by triplet ketone must be nearly thermoneutral;[26] styrene's triplet energy is some 10 kcal/mol lower than that of acetophenone.[27] Therefore, there are no spin restrictions to prevent the efficient cage reactions always observed with singlet radical pairs.[28] The phenomenon of efficient in-cage collapse of triplet radical ion pairs when energetic requirements are met has recently been postulated to explain unusual CIDNP spectra.[29]



It is also possible that the free spin on oxygen promotes rapid spin relaxation in the radical pair. Whatever the exact nature of the quenching process, it is clear that the photoreduction of ketones still provides mechanistic surprises.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(23) Ingold and Griller[17] also observed β cleavage as evidence for alkoxy radical formation.

(24) At a typical absorbed light intensity of 10^{-5} einstein L^{-1} s^{-1}, the steady-state radical concentration is 10^{-7} M. H-abstraction by alkoxy radicals is known to be fast enough[25] that even diffusion controlled radical–radical reactions could not compete.

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Received April 11, 1980

Importance of Mass Transfer and Intraparticle Diffusion in Polymer-Supported Phase-Transfer Catalysis

Sir:

Insoluble polymer-supported quaternary ammonium[1] and phosphonium[2] salts catalyze reactions between water-soluble anions and organic substrates under triphase (aqueous, organic, polymer) conditions.[3] The catalysts can be separated from reaction mixtures by simple filtration and can be reused. Their activity, however, is often less than that of soluble phase-transfer catalysts. To obtain more active polymer-supported catalysts, it is vital to know what experimental parameters control rates of reactions. We present evidence here that mass transfer, intraparticle diffusion, and the structure of the active site can all limit the rate of reaction between aqueous sodium cyanide and 1-bromooctane in toluene (eq 1).

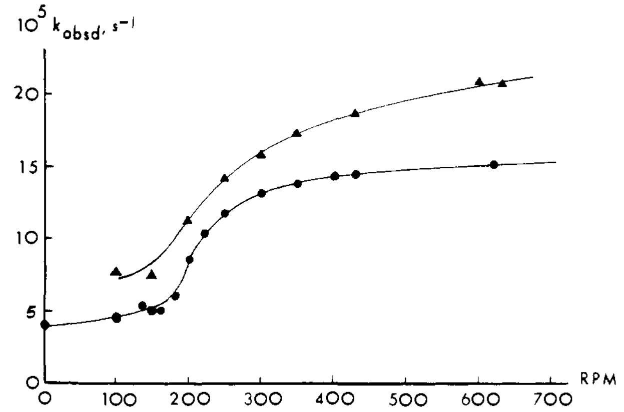

Figure 1. Dependence of the observed pseudo-first-order rate constants on the stirring speed: $C_8H_{16}Br$, 0.02 mol; toluene, 20 mL; 0.02 molar equiv of the catalyst cross-linked by 2% divinylbenzene; 90 °C; swollen particle size 150–300 μm (●) or 100–200 μm (▲).

$$n\text{-}C_8H_{17}Br + NaCN(aq) \rightarrow n\text{-}C_8H_{17}CN + NaBr(aq) \quad (1)$$

Rates of polymer-supported phase-transfer-catalyzed reactions could be influenced by (1) mass transfer of reactant from bulk liquid to catalyst surface; (2) diffusion of reactant through polymer matrix to active site; (3) intrinsic reaction rate at active site; (4) diffusion of product through polymer matrix and mass transfer of product to external solution; (5) rate of ion exchange at active site. Previous reports of kinetics of polymer-supported phase-transfer catalysis have mentioned that mass transfer and diffusion could be important, but these factors have not been studied directly.[4,5] The intrinsic reaction rate was assumed to be limiting in an earlier investigation of the reaction of 1-bromooctane with sodium cyanide employing polystyrene-supported quaternary ammonium salt catalysts.[1b]

All catalysts used in this study were synthesized in our laboratory by suspension copolymerization of styrene, chloromethylstyrene (60/40 *m*/*p*), and a cross-linker and displacement of the chloride with tri-*n*-butylphosphine or trimethylamine. Particles of different sizes were separated with sieves at the copolymer stage. Each catalyst had 14–18% of the polymer repeat units substituted as onium salts. In a standard kinetic run a 100-mL three-neck flask was charged with 0.02 molar equiv of the catalyst (based on 1-bromooctane), 20 mL of toluene, 9.8 g (0.20 mol) of sodium cyanide, 30 mL of water, and 0.5 g of *o*-dichlorobenzene (internal standard for GC). The mixture was stirred mechanically at 100 rpm with a standard 45 × 18 mm curved Teflon blade at 90 °C for 60 min to condition the catalyst. The stirring rate was changed, 1-bromooctane (0.02 mol) was added, and small samples of the organic phase were analyzed periodically by gas chromatography. Rates were pseudo first order in 1-bromooctane up to at least 50% conversion,[6] demonstrating

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(6) The catalysts decomposed slightly under the reaction conditions. Observed rate constants decreased gradually with increasing reaction time in the slower reactions.

0002-7863/80/1502-7140$01.00/0

Table I. Dependence of Observed Pseudo-First-Order Rate Constants on Method of Stirring[a]

method of stirring[b]	swollen particle size, μm	$10^5 k_{\mathrm{obsd}}$, s^{-1} [e]
mechanical, 600 rpm	150-300	15
	100-200	21
vibromixer, upward[c]	150-300	15
vibromixer, downward[c]	150-300	14
	100-200	19
ultrasonic wave[d]	150-300	11

[a] $C_8H_{17}Br$, 0.02 mol; toluene, 20 mL; 0.02 molar equiv of the catalyst cross-linked by 2% divinylbenzene; 90 °C. [b] Photographs of the agitated reaction mixtures show that mechanical stirring breaks the organic phase into drops 0.5-3 mm in diameter dispersed in the aqueous phase, vibromixing produces much smaller but still visible organic droplets, and ultrasound produces an emulsion. [c] Two kinds of vibromixing were used. The disk with holes tapering upward forces the mixture to flow rapidly upward around the stirrer shaft. The disk with holes tapering downward forces the mixture to flow rapidly downward from the bottom of the disk. The vibrational amplitude was adjusted to prevent the catalyst from splashing out of the reaction mixture. [d] A 21-kHz probe was placed directly in the reaction mixture. Many of the catalyst particles formed large clusters. We suspect reduced activity of the clusters is responsible for the slower rate. [e] Rate constants are reproducible to ±5% with mechanical stirring and ±10% with vibromixing and ultrasonic mixing.

Table II. Dependence of Observed Pseudo-First-Order Rate Constants on Particle Size of Catalyst[a]

swollen particle size, μm	$10^5 k_{\mathrm{obsd}}$, s^{-1}
150-300	15
100-200	21
50-90	31
20-50	38
5-35	40

[a] $C_8H_{17}Br$, 0.02 mol; toluene, 20 mL; 0.02 molar equiv of the catalyst cross-linked by 2% divinylbenzene; 90 °C; 600-640 rpm mechanical stirring.

that the rate of ion exchange does not limit the kinetics. Rates were linearly dependent on the amount of catalyst from 0 to 4 mol %. With no catalyst, no reaction was observed in 24 h. Rate constants were reproducible to ± 5%.

Plots of pseudo-first-order rate constant vs. stirring speed are shown in Figure 1. The rate constants attained with 600 rpm mechanical stirring were as high or higher than those attained by turbulent mixing with a vibromixer or with an ultrasonic probe (Table I). Dependence of reaction rate on speed of stirring and method of mixing indicates that mass transfer contributes to rate limitation in the mechanically stirred mixtures at <600 rpm. Similar dependence of rate on magnetic stirring speed was reported for reactions of 1-bromooctane with iodide ion[4] and 1-decyl methanesulfonate with chloride ion.[5]

Particle size of a heterogeneous catalyst may strongly affect its activity.[7] Table II shows increasing rates with decreasing particle sizes of otherwise identical 2% cross-linked phosphonium salt catalysts. All of these catalysts are spherical particles obtained by suspension polymerization, not ground powders.[8] Their sizes were measured during microscopic examination of catalysts recovered from the reaction mixtures. If mass transfer limits reaction rates, smaller particles will be more active catalysts because of their greater surface area per catalytic site. If diffusion through the polymer matrix limits the rates, smaller particles will be more active because they offer shorter diffusion paths to the active sites. The particle size effect with mechanical stirring at 600 rpm, where mass transfer no longer limits the reaction rate, indicates that intraparticle diffusion contributes to rate limitation.

Table III. Effect of Structure and Content of the Cross-Linker on Observed Pseudo-First-Order Rate Constants[a]

cross-linker	wt % (mol %)	$10^5 k_{\mathrm{obsd}}$, s^{-1}
divinylbenzene	2	21
divinylbenzene	4	17
divinylbenzene	6 (5.3)	16
divinylbenzene	10	9.1
1,6-hexanediol dimethacrylate	(5.3)	18
1,10-decanediol dimethacrylate	(5.3)	18

[a] $C_8H_{17}Br$, 0.02 mol; toluene, 20 mL; 0.02 molar equiv of the catalyst; 90 °C; 600-650 rpm mechanical stirring. The catalysts were prepared from copolymers of particle size 75-150 μm.

With benzyltri-*n*-butylphosphonium chloride catalysts prepared from copolymers containing 2-10% divinylbenzene, the observed rate decreases as the degree of cross-linking increases (Table III). When aliphatic bis(methacrylates) instead of divinylbenzene are used in the copolymers, reaction rates increase slightly. These results also indicate that diffusion of reactant through the polymer matrix limits the reaction rates.

The structure of the active catalytic site also affects rates in our experiments, as it has in many previous studies.[1-5,9] Use of a 150-300-μm 2% divinylbenzene-cross-linked benzyltrimethylammonium chloride catalyst gave $k_{\mathrm{obsd}} = 1.26 \times 10^{-5}\ s^{-1}$ with 600 rpm mechanical stirring compared with $k_{\mathrm{obsd}} = 15 \times 10^{-5}\ s^{-1}$ for the benzyltri-*n*-butylphosphonium chloride catalyst made from the same copolymer.

In summary, mass transfer and intraparticle diffusion as well as the catalyst structure influence the rate of phase-transfer reaction of cyanide ion with 1-bromooctane when benzyltri-*n*-butylphosphonium salt catalysts bound to 2-10% cross-linked polystyrene are employed. Studies of the key experimental parameters affecting rates of other phase-transfer reactions and use of other polymer-supported catalysts are in progress.

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(8) A fine powder (<45 μm) produced by *grinding* showed very low activity ($k_{\mathrm{obsd}} = 2.4 \times 10^{-5}\ s^{-1}$). Similar decreases in rate with ground powders have been observed by Regen.[3] Spherical catalyst particles settle quickly to the phase interface when mixing stops, but irregular particles obtained by grinding remain suspended in the organic phase much longer. We attribute the slower rate with ground powder to insufficient contact between the catalyst and the aqueous phase.

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Received April 14, 1980

Structure and Stereochemistry of Novel Endoperoxides Isolated from the Sensitized Photooxidation of Methyl Linoleate. Implications for Prostaglandin Biosynthesis

Sir:

Evidence continues to accumulate supporting the involvement of singlet molecular oxygen ($^1O_2$) during lipid oxidation in vegetable oils[1,2] and complex biological systems.[3] Although the reaction of $^1O_2$ with polyunsaturated fatty acids to yield allylic hydroperoxides[4] is well documented, we are unaware of any study

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