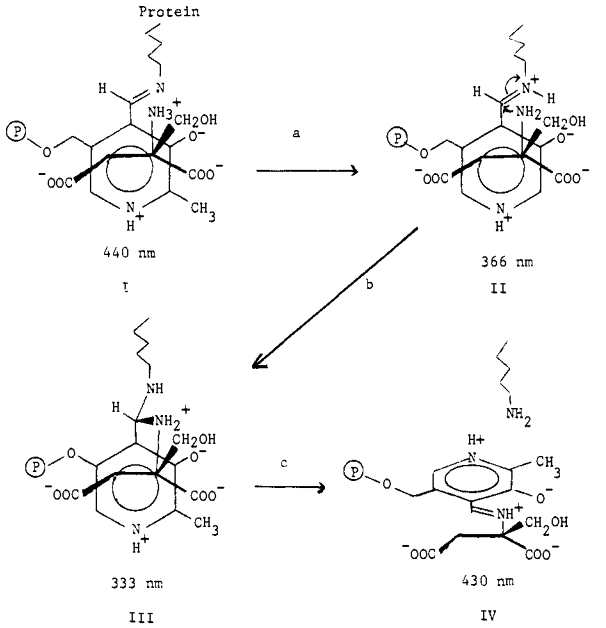

Figure 2, but the 430-nm band is devoid of CD. The absence of CD seem characteristic of substrate Schiff bases such as IV. Therefore, we suggest that the 440-nm band with a positive CD observed with 2-(hydroxymethyl)aspartate is the first ES complex I rather than IV. A smaller amount of II may be present and absorbing at 366 nm while the 330-nm band may be the adduct III. It is also possible that 2-(hydroxymethyl)aspartate binds in a different conformation than do the normal, less sterically hindered substrates. Thus the 440-nm complex may not be strictly analogous to a Michaelis complex with a substrate and may therefore not go on to give IV.

The dissociation constant 1.4 mM for the L-2-(hydroxymethyl)aspartate complex with the enzyme is substantially lower than the 5–10 mM reported for L-2-methylaspartate.[5,15] Thus, the presence of the hydroxyl group in some way enhances the binding of this inhibitor.

(Hydroxymethyl)aspartate has been cocrystallized with aspartate aminotransferase, as has been described for 2-methylaspartate.[14] The crystals have the same morphology as those of the 2-methylaspartate crystals, indicating that they are probable isomorphous with the native enzyme whose structure is being determined by Arnone et al.[16]

Acknowledgment. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Assistant Secretary for Energy Research, Office of Basic Energy Sciences, WPAS-KC-02-03, and by Grant AM-01549 from the National Institutes of Health. We thank Carol M. Metzler for crystallization of the complex of (hydroxymethyl)aspartate with aspartate aminotransferase.

Supplementary Material Available: Tables I, II, and III listing structural parameters and observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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Received July 7, 1980

Quenching of Triplet Ketones by Alcohol OH Bonds

Sir:

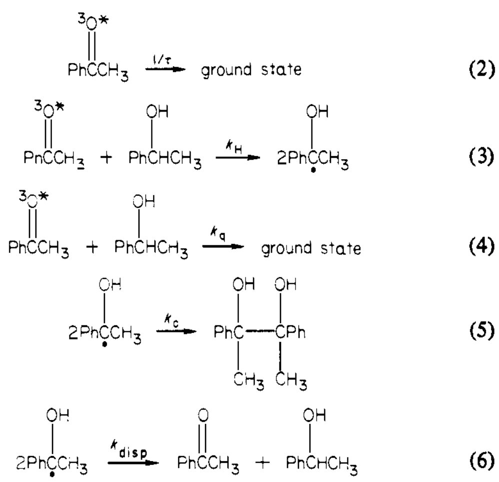
The photoreduction of ketones by alcohols is one of the oldest[1] and best known[2] photoreactions. It has long been known to involve hydrogen atom abstraction by triplet ketones.[3] We have now found that in the photoreduction of acetophenone (AP) by 1-phenylethanol (PE),[4] half of the ketone triplets are quenched by the OH bond rather than react with the α-C–H bond. This conclusion results from several independent experimental findings.

We have reconfirmed[4b] that the maximum quantum yield for photoreduction in degassed solvents is only 0.59 in benzene and 0.50 in acetonitrile. The double reciprocal plot in Figure 1 is described by eq 1 with the rate constants appropriate to the reactions in Scheme I.

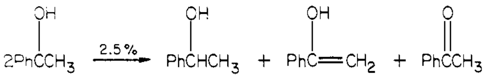
$$\Phi^{-1}(\text{pinacol}) = \left(\frac{k_c + k_{\text{disp}}}{k_c}\right)\left(1 + \frac{1}{(k_H + k_q)\tau[\text{PE}]}\right)\left(\frac{k_H + k_q}{k_H}\right) \tag{1}$$

Since the photoreduction of benzophenone by benzhydrol proceeds in close to 100% quantum efficiency,[5] and hemibenzpinacol radicals are known not to disproportionate at room temperatures,[6] inefficiency in similar photoreductions is usually assumed to involve disproportionation of radical intermediates back to ground-state reactants rather than quenching of triplet ketone.

Scheme I



In this case, a 50:50 disproportionation/coupling ratio of the 1-phenyl-1-hydroxyethyl radicals would explain the entire inefficiency. Such a large fraction of disproportionation is unusual for a benzylic radical, but might be favored by formation of acetophenone enol.[7] However, we have shown that the actual percentage of disproportionation is only 2.5% (eq 7).



$$2\mathrm{Ph\dot{C}(OH)CH_3} \xrightarrow{2.5\%} \mathrm{PhCH(OH)CH_3} + \mathrm{PhC(OH){=}CH_2} + \mathrm{PhC(O)CH_3} \tag{7}$$

The experimental basis for the above conclusion comes from irradiation of 0.15 M AP in benzene containing 0.2 M 1-phenyl-1-propanol, which yields PE and acetophenone pinacol as the only significant products in a ratio of 0.025/1, as measured by GC analysis at low conversions. At the relatively high AP

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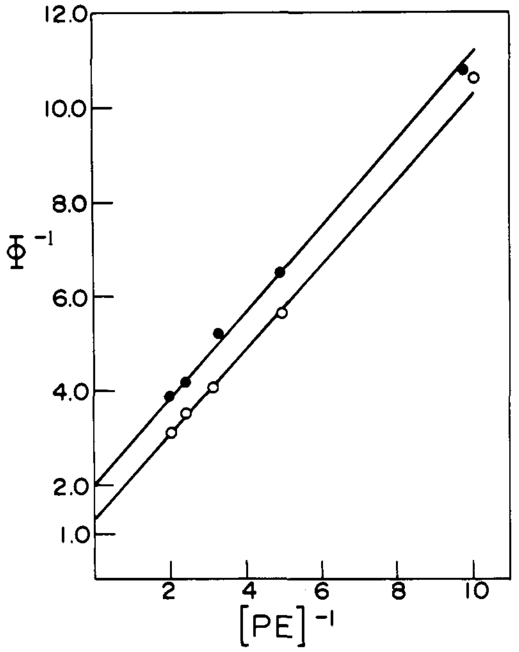
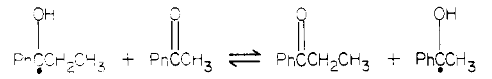


Figure 1. Double-reciprocal plot describing how the quantum yield of pinacol formation in acetonitrile depends on 1-phenylethanol (PE) concentration; (●) PE OH; (○) PE OD. Each point represents the average of four runs with ±5% precision.

concentration used, rapid hydrogen atom exchange occurs[8] such that the $\mathrm{PhC(OH)CH_3}$ radical is the only one present in sufficient concentration to give radical–radical products. At lower initial ketone concentrations, ketyl–ketone hydrogen exchange is slower such that larger fractions of the products are derived from phenylpropanol (eq 8).



$$\mathrm{Ph\overset{OH}{\underset{\bullet}{C}}CH_2CH_3 + Ph\overset{O}{\overset{\|}{C}}CH_3 \rightleftarrows Ph\overset{O}{\overset{\|}{C}}CH_2CH_3 + Ph\overset{OH}{\underset{\bullet}{C}}CH_3} \qquad (8)$$

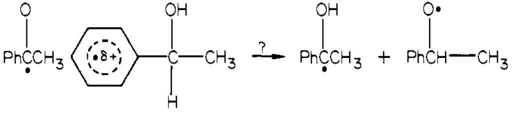
The 50% inefficiency in the photoreduction must involve some hitherto unsuspected triplet quenching process (as measured by k_q in Scheme I) which competes with abstraction of an α hydrogen.[9] To test whether the OH bond is involved in this quenching process, we compared the photoreduction of AP by PE with that by PE-*O-d*. In four separate experiments, quantum yields of pinacol formation were higher for the deuterated PE at all alcohol concentrations; as Figure 1 shows, the extrapolated maximum quantum yield is 0.70. This primary isotope effect[10] confirms the involvement of the OH bond in quenching. Such quenching is probably limited to aromatic alcohols since there is no evidence that *tert*-butyl alcohol is a rapid triplet quencher, and Lewis has reported an extrapolated maximum quantum efficiency of unity for photoreduction of AP by 2-propanol.[11]

Since charge-transfer quenching of triplet ketones by substituted benzene is a general process,[12,13] one appealing mechanism for the quenching by OH is enhanced radiationless decay in a triplet exciplex formed between $^3\mathrm{AP}^*$ and PE. Electronic-to-vibronic energy transfer into high energy O–H stretches is known to accelerate radiationless decay of solvated rare earth ions[14] and of singlet oxygen.[15] Another possible mechanism might be proton transfer from O to C═O in the exciplex, as happens in the benzophenone-promoted photodecarboxylation of phenoxyacetic acid[16] (eq 9).

Table I. Acetophenone and Propiophenone Pinacol Yields upon Irradiation of Propiophenone with 0.1 M Acetophenone Pinacol or 0.1 M 1-Phenylethanol[a]

[PP], M	[AP], 10^{-3} M	$\mathrm{[PH]_2}$, 10^{-3} M
	Acetophenone Pinacol	
0.10	6.1	2.3
0.02	4.9	1.5
	Phenylethanol	
0.10	12.3	10.5
0.02	0.9	4.3

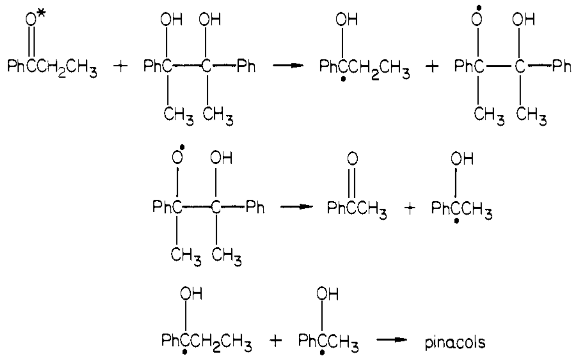
[a] All four samples irradiated in parallel at 313 nm for the same time; benzene solvent; yields average of duplicate samples.



(9)

Given the demonstration that *tert*-butoxy radicals attack both C–H and O–H bonds on several alcohols,[17] it might be expected that triplet ketones would also attack OH bonds. Such behavior has been predicted by semiempirical calculation[18] and observed for benzoquinone[19] and benzophenone with cyclopropanol.[20] Therefore, we have reinvestigated the old, unexplained report that ketones photosensitize the oxidative cleavage of pinacols.[21] Irradiation at 313 nm of 0.02–0.10 M propiophenone (PP) and 0.1 M acetophenone pinacol to 10–15% conversion produces AP, propiophenone pinacol $\mathrm{(PH)_2}$, and mixed pinacol. The quantum yields of AP and $\mathrm{(PH)_2}$ are almost independent of ketone concentration and extrapolate to 0.3 and 0.1, respectively, at infinite pinacol concentration. Table I contrasts these results with those obtained upon irradiation of PP with PE, where the AP yield decreases dramatically at lower initial PP concentrations.

A mechanism involving an unprecedented sensitized pinacol C–C bond cleavage to yield two acetophenone ketyl radicals followed by ketyl–propiophenone hydrogen exchange is unlikely; as mentioned above and demonstrated in Table I, such exchange is not efficient enough at low ketone concentration to produce as much AP as is actually observed. The most likely mechanism involves hydrogen abstraction by triplet ketone, possibly via an exciplex, to yield an alkoxy radical which undergoes the expected very rapid β scission[22,23] (eq 10–12). This mechanism does not



$$\mathrm{Ph\overset{O^*}{\overset{\|}{C}}CH_2CH_3 + Ph\overset{OH}{\underset{CH_3}{C}}\text{—}\overset{OH}{\underset{CH_3}{C}}\text{—}Ph \longrightarrow Ph\overset{OH}{\underset{\bullet}{C}}CH_2CH_3 + Ph\overset{\dot{O}}{\underset{CH_3}{C}}\text{—}\overset{OH}{\underset{CH_3}{C}}\text{—}Ph} \qquad (10)$$

$$\mathrm{Ph\overset{\dot{O}}{\underset{CH_3}{C}}\text{—}\overset{OH}{\underset{CH_3}{C}}\text{—}Ph \longrightarrow Ph\overset{O}{\overset{\|}{C}}CH_3 + Ph\overset{OH}{\underset{\bullet}{C}}CH_3} \qquad (11)$$

$$\mathrm{Ph\overset{OH}{\underset{\bullet}{C}}CH_2CH_3 + Ph\overset{OH}{\underset{\bullet}{C}}CH_3 \longrightarrow pinacols} \qquad (12)$$

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[9] Styrene is a likely impurity in the phenylethanol; 0.01% would give an observed quenching rate constant of $10^6\ \mathrm{M^{-1}\ s^{-1}}$. Careful GC comparison of solutions 1 M in phenylethanol and 10^{-4} M in styrene indicated that there is less than 0.0003% styrene in the phenylethanol.

[10] The alcohol was 70–90% deuterated in the different experiments; $k_q^H/k_q^D \sim 3.0$.

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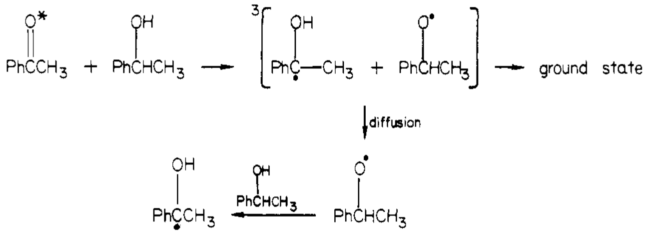
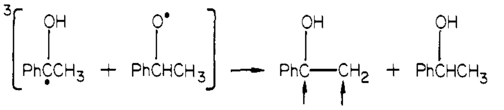
require ketyl–ketone hydrogen exchange for AP and $(PH)_2$ formation.

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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Received April 11, 1980

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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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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).

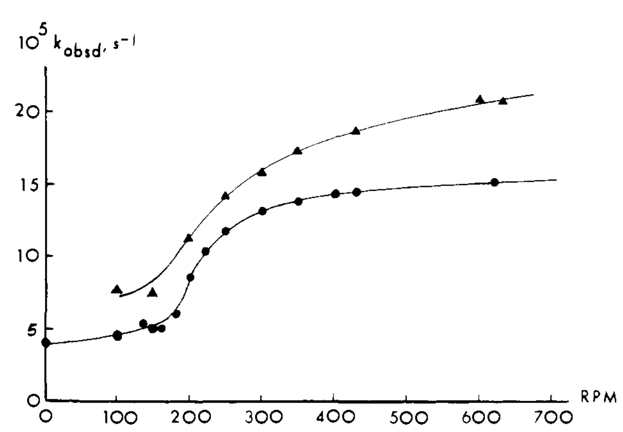

Figure 1. Dependence of the observed pseudo-first-order rate constants on the stirring speed: $C_8H_{16}Br$, 0.02 mol; toluene, 20 mL; 0.02 molar equiv of the catalyst cross-linked by 2% divinylbenzene; 90 °C; swollen particle size 150–300 μm (●) or 100–200 μm (▲).

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

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.

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