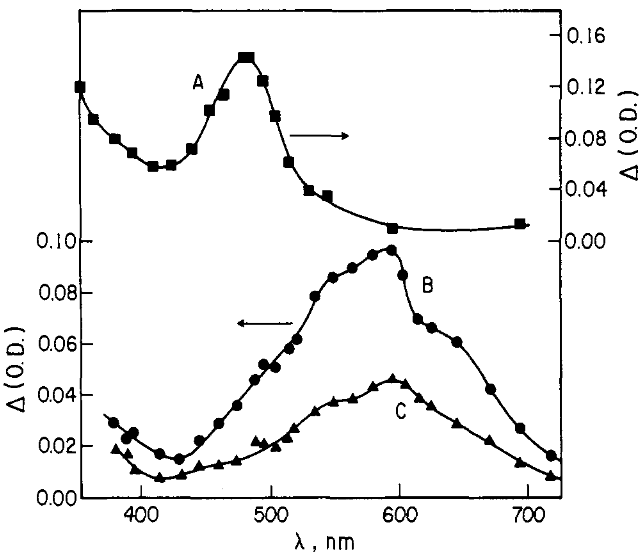

Figure 2. Transient spectra due to triplet benzil (A) in the absence of TEA; in the presence of TEA, 250 ns after the pulse (B); and 10 ns after the pulse (C), i.e., "jump" spectrum.

at 570 nm (where the radical anion absorbs), we observe a growth with a lifetime of 55 ns, preceeded by a "jump", which occurs within the first few nanoseconds following excitation (Figure 1). Further addition of amine does not change the lifetime associated with the buildup process or the "plateau" to "jump" ratio, but a decrease in the total signal, as measured by the "plateau" level, can be observed. Roughly, 0.4 M TEA will decrease the total signal to one half of the value for a 0.1 M concentration, where typical "plateau" absorbances were around 0.08. We assign the lifetime of 55 ns mentioned above to the exciplex formed between triplet benzil and TEA. Figure 2 shows the spectra observed 250 ns after the pulse (radical anion) and 10 ns after the pulse (i.e., the "jump" spectrum) and also the T-T absorption of triplet benzil. The spectrum after 10 ns is tentatively assigned to the exciplex; it clearly resembles that of the radical anion, except for a lower extinction coefficient and a slightly wider band. On the basis of this assignment, we conclude that the structure of the exciplex approaches II, rather than I. Similar observations have been carried out for some singlet exciplexes (e.g., *sym*-tetracyanobenzene-toluene).[2,12]

$$\begin{array}{cc} [\mathrm{B}^{*}\cdots\mathrm{TEA}] & [\dot{\mathrm{B}}^{-}\cdots\mathrm{TEA}^{+}\cdot] \\ \mathrm{I} & \mathrm{II} \end{array}$$

Benzil fluoresces in solution with λ_{max} 496 nm. This fluorescence can be quenched by TEA with $k_q\tau_s \sim 6\ M^{-1}$. The decrease in signal intensity (due to $B^{-}\cdot$) observed upon addition of TEA is presumably due to a decrease in the triplet input, reflecting singlet quenching.[13] The constancy of the "jump" to "growth" ratio observed in our experiments rules out the possibility of the "jump" being due to a singlet-state process.

No luminescence that could be attributed to the triplet exciplex was detected; perhaps this is not surprising, since our evidence indicates that the exciplex structure resembles II rather than I. A recent report by Fang and Singer[14] has suggested that exciplex formation by benzil in poly(methyl methacrylate) matrices is responsible for nonradiative decay processes.

In *n*-heptane, where $k_q = 7.2 \times 10^8\ M^{-1}\ s^{-1}$, the behavior of the system does not resemble that observed in polar media; that is, no "delayed" product formation could be detected, even if the traces do indicate that some photoreduction takes place. These results could reflect a shorter exciplex lifetime or, alternatively, different properties (spectroscopic and kinetic)[12] from those observed in wet acetonitrile.[15]

Further research on the effects of the medium, structure, and temperature on the properties of triplet exciplexes is currently in progress.

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(9) The pK_a of benzil radical anion is 5.7.[8b]
(10) In fact ground-state complexation is not likely to have a large effect on exciplex behavior.
(11) The samples were irradiated with the pulses (8 ns, 337.1 nm, 3 mJ) from a nitrogen laser. For details on the experimental setup, see Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979,** *101*, 2146-2152.
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(17) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2017 from the Notre Dame Radiation Laboratory.

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Hydrogen Evolution from the Photolysis of Alcoholic Benzophenone Solutions via Redox Catalysis

Sir:

It has been shown recently that a number of noble metals or their oxides, when dispersed in aqueous solutions, are capable of mediating water oxidation[1] and reduction[2] by agents which have the appropriate thermodynamic potential. Platinum proved to be suitable for H_2 evolution while colloidal ruthenium(IV) oxide is an appropriate choice for O_2 formation from water.[1d] Apart from the possible employment of these systems to achieve water splitting from solar light, one can envisage a wide scope of other applications. In particular, through judicious selection of the redox catalyst, photoinduced processes may be directed in a way to give novel and desirable products. In the present paper, we shall illustrate how the pathway of a classical photochemical reaction, i.e., the reduction of benzophenone to benzopinacole, is altered drastically in the presence of catalytic amounts of colloidal platinum.

This catalyst was developed earlier[3] in the search for materials suited to mediate efficiently H_2 production from H_2O and reduced methyl viologen (MV^{+}). It is prepared[3] by pre-

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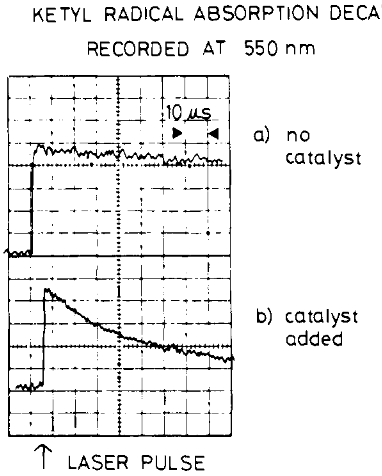
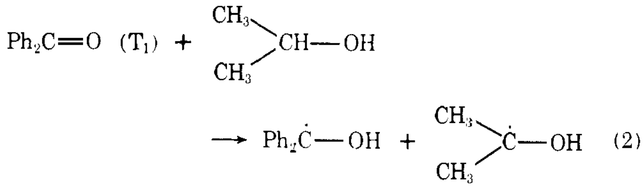


Figure 1. Oscilloscope traces from the laser photolysis of 10^{-3} M benzophenone in 2-propanol-water (50:50), pH neutral; samples were deoxygenated by bubbling with Ar. Catalyst concentration: 8 mg/100 mL.

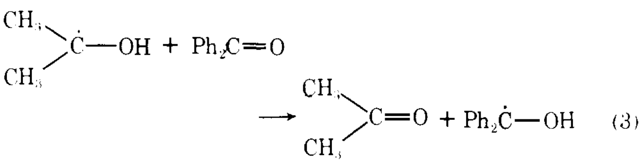
cipitating Pt in colloidal form from an aqueous solution of hexachloroplatinate (pH 8) in the presence of polyvinyl alcohol (mol wt 60 000, 2% solution) through reduction by hydrogen. Crucial to the catalytic activity is the subsequent centrifugation over 8 h at 50 000 *g*. This removes heavier particles leaving a Pt sol with a mean particle size of 120 Å in the supernatant solution, as determined by quasi-elastic light-scattering techniques. Even in dilute solutions of this catalyst, the reaction of MV^+ with water to produce H_2 requires only a few microseconds. This fact encouraged us to apply the same Pt sol to systems where other reducing radicals appear as intermediates in photochemical reactions.

Consider, for example, the photoinduced reduction of benzophenone[4a] in a 2-propanol-water mixture which leads to the formation of ketyl radicals via the reaction sequence[4b] shown in eq 1-3. At the concentrations of benzophenone and 2-pro-

$$\mathrm{Ph_2C{=}O}\quad (\mathrm{S_0}) \xrightarrow{h\nu} {}^{\prime}\mathrm{Ph_2C{=}O}\quad (\mathrm{T_1}) \tag{1}$$



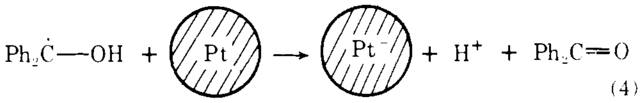
$$\mathrm{Ph_2C{=}O}\quad (\mathrm{T_1}) + {}^{\mathrm{CH_3}}_{\mathrm{CH_3}}\!\!>\mathrm{CH{-}OH} \longrightarrow \mathrm{Ph_2\dot{C}{-}OH} + {}^{\mathrm{CH_3}}_{\mathrm{CH_3}}\!\!>\mathrm{\dot{C}{-}OH} \tag{2}$$



$${}^{\mathrm{CH_3}}_{\mathrm{CH_3}}\!\!>\mathrm{\dot{C}{-}OH} + \mathrm{Ph_2C{=}O} \longrightarrow {}^{\mathrm{CH_3}}_{\mathrm{CH_3}}\!\!>\mathrm{C{=}O} + \mathrm{Ph_2\dot{C}{-}OH} \tag{3}$$

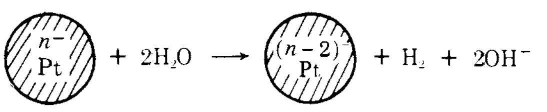
panol employed, these reactions are terminated within 1 µs after the laser pulse ($k_2 = 1 \times 10^6\ M^{-1}\ s^{-1}$; $k_3 = 2 \times 10^9\ M^{-1}\ s^{-1}$). The ketyl radical can readily be identified by its characteristic absorption with a maximum around 550 nm. In the following, we shall scrutinize the ketyl radical reaction in 2-propanol-water mixture (50:50, v/v) in the absence and presence of redox catalyst.

Oscilloscope traces obtained from a 10^{-3} M $Ph_2C{=}O$ solution are displayed in Figure 1. In catalyst-free solution, the 550-nm absorption of the ketyl decays as expected according to a second-order rate law. The rate constant obtained from the kinetic analysis if $8.5 \times 10^8\ M^{-1}\ s^{-1}$ in agreement with published literature values.[5] At the low laser intensity applied, this decay is barely visible on the 10-µs/division time scale in Figure 1a. Addition of catalyst, 8 mg of Pt/100 mL of solution as determined by atomic absorption spectroscopy, sharply enhances the absorption decay. This process follows approximately first-order kinetics, the half-life time being 40 µs. The decay is attributed to the reaction of ketyl radicals with the colloidal Pt particles (eq 4). Consistent with this mechanism



$$\mathrm{Ph_2\dot{C}{-}OH} + \mathrm{Pt} \longrightarrow \mathrm{Pt^-} + \mathrm{H^+} + \mathrm{Ph_2C{=}O} \tag{4}$$

is the observation that the rate of radical disappearance increases with Pt concentration. At 4.0×10^{-4} M Pt concentration the half-life time of MV^+ is 30 µs corresponding to a rate constant of $k_3 = 6 \times 10^7\ M^{-1}\ s^{-1}$ if the analytical Pt concentration is used as a basis for the calculation. However, as the aggregation number of Pt in the colloidal aggregates is at least 1000,[3] it is more appropriate to give for k_3 a lower limit of $6 \times 10^{10}\ M^{-1}\ s^{-1}$. This implies that the charge transfer from MV^+ to the Pt particle occurs essentially at a diffusion-controlled rate. Through multiple electron transfer the Pt microelectrodes become cathodically polarized until water reduction takes place (eq 5). This latter reaction is particularly

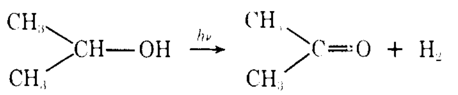


$$\overset{n-}{\mathrm{Pt}} + 2\mathrm{H_2O} \longrightarrow \overset{(n-2)-}{\mathrm{Pt}} + \mathrm{H_2} + 2\mathrm{OH^-} \tag{5}$$

favored by the low overvoltage characteristic for hydrogen evolution on platinum.[6] Hence, instead of recombining to give benzopinacol, ketyl radicals reduce water according to eq 6, followed by the neutralization of H^+ and OH^-. The relatively high reducing capacity of ketyl radicals[7] makes reaction 6 thermodynamically favorable.

$$2\mathrm{Ph_2\dot{C}{-}OH} + 2\mathrm{H_2O} \longrightarrow \mathrm{H_2} + 2\mathrm{OH^-} + 2\mathrm{H^+} + 2\mathrm{Ph_2C{=}O} \tag{6}$$

The overall process catalyzed by the platinum sol is the benzophenone-sensitized dehydrogenation of 2-propanol (eq 7). It should be noted that the standard enthalpy of reaction



$${}^{\mathrm{CH_3}}_{\mathrm{CH_3}}\!\!>\mathrm{CH{-}OH} \xrightarrow{h\nu} {}^{\mathrm{CH_3}}_{\mathrm{CH_3}}\!\!>\mathrm{C{=}O} + \mathrm{H_2} \tag{7}$$

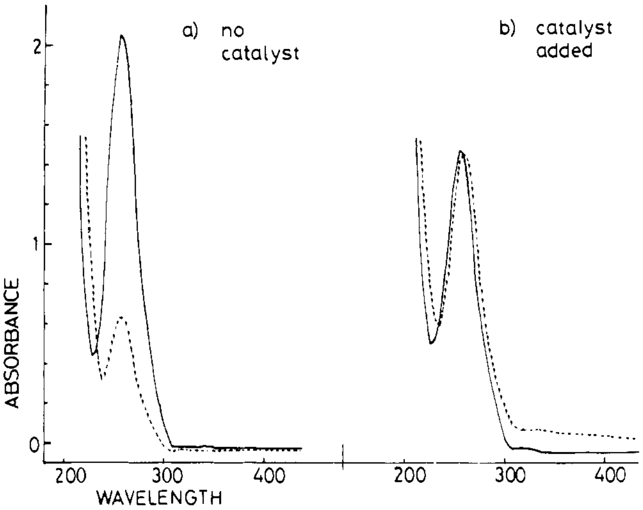


Figure 2. Continuous illumination of a benzophenone solution (3×10^{-3} M) in 2-propanol-water: solid line, prior to irradiation; dashed line, after 30 min of irradiation. The dashed line for b has been displaced to the right by several nm. Samples were deoxygenated by bubbling with Ar. Catalyst concentration: 2.5 mg/100 mL.

7 is positive ($\Delta H^\circ = 13.2$ and $\Delta G^\circ = 7.6$ kcal for the pure liquids), which makes this process light energy storing.

The mechanism derived from the laser photolysis studies is corroborated by results obtained from continuous illuminations of alcoholic benzophenone solutions. These were carried out with light of a XBO 450-W xenon lamp which was passed through water and a Corning CS 7-51 interference filter. The latter transmits in the 320-380-nm region allowing for selective excitation in the n-π^* absorption band. The irradiation vessel contained ~24 mL of solution and was equipped with a septum through which gas samples could be taken for chromatographic analysis. A Gow-Mac thermal conductivity detector with a limit of 0.1 μmol was used for hydrogen analysis. The ferrioxalate actinometry gave a value of 1×10^{18} quanta/min for the light flux.

In Figure 2 spectrophotometric data obtained prior and after irradiation of samples with and without catalyst are compared. In the case of the Pt-free solution a photolysis time of 30 min suffices to remove >70% of the benzophenone absorption at 260 nm. In striking contrast to this result, one finds practically no depletion of $Ph_2C{=}O$ under illumination if the Pt catalyst is present in solution. (The turnover number for benzophenone is ~2 after this irradiation time.) Instead, hydrogen is evolved, which is readily shown by the gas chromatographic analysis. From this, we infer that the catalyst can intervene efficiently to prevent the ketyl radical dismutation or recombination making feasible water reduction via eq 6. The quantum yield for H_2 production in this system was found to be 0.9 ± 0.1, showing that the water reduction occurs stoichiometrically.

In conclusion, we find that, in the presence of Pt catalyst, benzophenone sensitizes the dehydrogenation of 2-propanol to acetone. Although a similar catalytic system has been reported previously,[8] it was necessary in the latter case to add an electron relay, such as V^{3+} or Eu^{3+} which produced H_2 after scavenging the ketyl radicals. The importance of the findings presented here lies in the fact that the finely dispersed colloidal Pt particles can operate on the radical reaction itself to produce hydrogen selectively.

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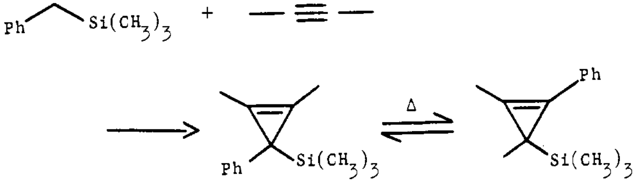
Trimethylsilyl Shifts in Cyclopropenes[1]

Sir:

Although the sigmatropic shift has been known as an important class of "no mechanism" reaction for 15 years,[2] and migrations in small rings found to be commonplace,[3] there exists but one report of such a reaction in a cyclopropene.[4,5] Moreover, in this lone example intramolecularity has not demonstrated. Although such shifts have been specifically considered in simple systems, they have not been found. 3,3-Dialkylcyclopropenes undergo thermal ring opening to vinylcarbenes without prior sigmatropic shift.[6] 3-Aryl-1,2,3-triphenylcyclopropenes rearrange apparently without formation of the 2-arylindenes which would signal a shift of phenyl in the original cyclopropene.[7] We describe here the relatively rapid rearrangement of the trimethylsilyl group in cyclopropenes.

Phenyltrimethylsilylcarbene[8] was allowed to add to 2-butyne to produce cyclopropene **1**.[9] Pyrolysis of **1** in benzene-d_6 in sealed ampules at 117-148 °C, as monitored by nuclear magnetic resonance and gas chromatography, revealed a clean equilibration with a new cyclopropene, **2**.[9] Measurements at four temperatures for at least 2 half-lives over a 30 °C range gave the following activation parameters for the forward and reverse reactions: forward (**1** → **2**), $E_a = 31.22 \pm 0.52$ kcal/mol, log $A = 12.06 \pm 0.10$; reverse (**2** → **1**), $E_a = 32.80 \pm 0.52$ kcal/mol, log $A = 12.16 \pm 0.25$. The activation energy for this new rearrangement thus falls squarely in between that for 1,3 trimethylsilyl shifts in simple allyl systems ($\Delta H^{\ddagger} = 41-46$ kcal/mol)[3] and the 1,5 trimethylsilyl shift in 5-trimethylsilylcyclopentadiene ($\Delta H^{\ddagger} = 13.0$ kcal/mol).[10]



1 **2**

For this new reaction to be considered a true sigmatropic shift of the trimethylsilyl group, it must obviously be shown that it is indeed the trimethylsilyl group that migrates and that the reaction is intramolecular. The first point is less simple than it seems. Although there is no evidence for phenyl shifts in cyclopropenes,[7] there does not appear to have been a concerted search for the reaction, and the phenyl ring is known to be a good migrating group.[3]

The distinction between **2** and the product of a phenyl shift, **3**, was made using ^{13}C and ^{29}Si NMR. In going from compound **1** to **2**, one expects a relatively large upfield shift at C_a as phenyl is replaced by methyl,[11a] and an upfield shift for C-1 of the benzene ring (C_b) in moving from the 3 position to the 1 position on the cyclopropene.[11b] This is in fact exactly what is observed: C_a shifts from 23.3 to 14.5 ppm and C_b from 150.0 to 130.6 ppm.

We predict just the opposite effects for the hypothetical compound **3**. Here we would expect small downfield shifts for both C_a and C_b. Thus both the methylene and substituted aromatic carbons in benzyltrimethylsilane[12a] appear at higher field than the corresponding positions in ethylbenzene.[12b]

Confirmation of the assignment of structure **2** was obtained by ^{29}Si NMR. The ^{29}Si resonances and **1** and **2** appeared at 1.18 and 1.84 ppm downfield from $(Me)_4Si$, respectively. Attachment of the trimethylsilyl group to a vinyl carbon as in **3** should result in a substantial upfield shift of the silicon resonance relative to **1**.[13] For instance, the ^{29}Si signal in trimethylvinylsilane appears at −6.8 ppm, 8.4 ppm upfield from that of ethyltrimethylsilane.[13]

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