reflux. We imagine that the resulting olefin complex of **9** is unstable and readily dissociates olefin to allow the alkane access to the active site.[12]

Alternative interpretations of our results can be envisaged.[13] Trace acid, for example, might protonate **9** and the resulting carbonium ion dehydrogenate the cycloalkanes. We find, however, that the deliberate addition of trace acid to the system completely inhibits the activation, and that some **7** ($\sim$7%) is formed from cyclopentane in the absence of **9**.

Even though the reaction mixtures appear entirely homogeneous, colloidal iridium might still have been formed and be the true active species.[13] Metallic Ir, like Pt and Rh, can indeed be active for H/D exchange in alkanes[14] under mild conditions, and for cycloalkane dehydrogenation[15] above $\sim$150 °C. We have not yet been able to eliminate this possibility definitively. If true, however, this hypothesis is difficult to reconcile with our observation of activity only with **9** as hydrogen acceptor (or, in the case of cyclopentane, without a hydrogen acceptor), rather than with other olefins. We have also done photon-correlation light-scattering experiments to explore this question: our measurements showed no evidence for the presence of any colloid in the reaction mixtures.

That our system is so active in alkane dehydrogenation may be related to its unprecedented activity[2,3] for the reverse reaction, alkene hydrogenation.

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(4) The uniquely high activity of $[Ir(cod)L_2]PF_6$ and related complexes under our conditions[2,3] for the hydrogenation of olefins may arise because the majority solution species are the dihydrido–olefin complexes, **1**, which can collapse directly to give the product alkane. The substrate is not in competition with the solvent or a tertiary phosphine for the active site at the metal. It is for substrates that are poor ligands that our catalysts can show their greatest rate enhancements ($>10^4$), compared with classical hydrogenation systems (e.g., J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, **1711** (1966)).
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Laser Photolysis Study of the Exciplex between Triplet Benzil and Triethylamine

Sir:

The behavior and properties of exciplexes is a subject of current interest; they are frequently proposed as reaction intermediates in singlet- and triplet-state processes.[1,2] The former have been characterized in more detail, largely because many singlet exciplexes are strongly fluorescent,[3] although some absorption studies using laser flash photolysis have also been carried out.[2] Triplet-derived exciplexes do not usually luminesce, and as a result their direct characterization is more difficult; they have been observed directly in very few systems,[4] e.g., zinc ethioporphyrin I-hexachloroethane, where the exciplex absorption spectrum resembles that of the porphyrin triplet.[4]

One of the photochemical systems where the intermediacy of triplet-derived exciplexes is most strongly supported by indirect evidence is the quenching and/or photoreduction of triplet carbonyls by amines;[5,6] no direct evidence for the intermediacy of exciplexes has been reported in these systems.[7]

Triplet benzil has a T-T absorption spectrum quite different from that of benzil radical anion,[8] therefore allowing the independent study of triplet decay and radical-ion formation in benzil-amine systems using nanosecond laser flash photolysis techniques. Using this approach, we have examined the triethylamine (TEA)-benzil system in wet acetonitrile and observed that, under conditions of short triplet lifetime (i.e., high TEA concentration), the formation of benzil radical anion is considerably slower than the decay of the triplet state; we attribute this "delay" to the intermediacy of a relatively stable exciplex, whose properties are reported in this study.

The effect mentioned above is observed over a wide range of water-acetonitrile compositions, with the exciplex lifetime being apparently longer the higher the water content. At the same time the increase in water content seems to favor the formation of ground-state complexes (from UV spectroscopy studies). The results reported herein have been obtained in 12:88 water-acetonitrile (v/v) mixture containing 0.003 M sodium hydroxide.[9] In this mixture we do not observe any ground-state complexation;[10] at the same time, the presence of a strong base assures that the basicity of the medium will not be changed by the addition of amine. The rate of triplet quenching was monitored at 450 nm, examining the decay of the signal (due to T-T absorption) as a function of TEA concentration, and led to $k_q = 1.3 \times 10^9\ M^{-1}\ s^{-1}$.[11] That is, in the presence of 0.1 M TEA, the triplet lifetime will be $\tau_T < 8$ ns; when under these conditions we monitor transient absorptions

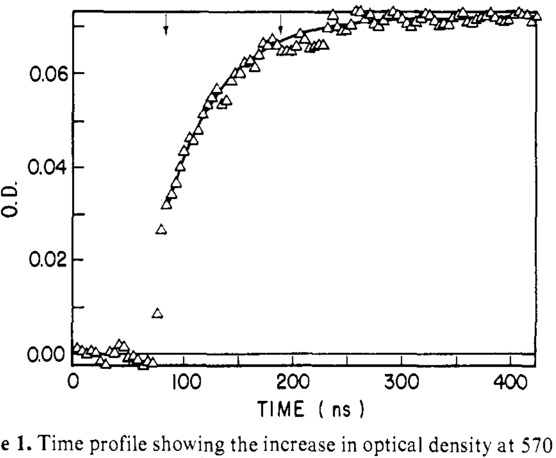

Figure 1. Time profile showing the increase in optical density at 570 nm following laser excitation of benzil in the presence of 0.1 M TEA. The arrows indicate the section of the curve used to determine the exciplex lifetime.

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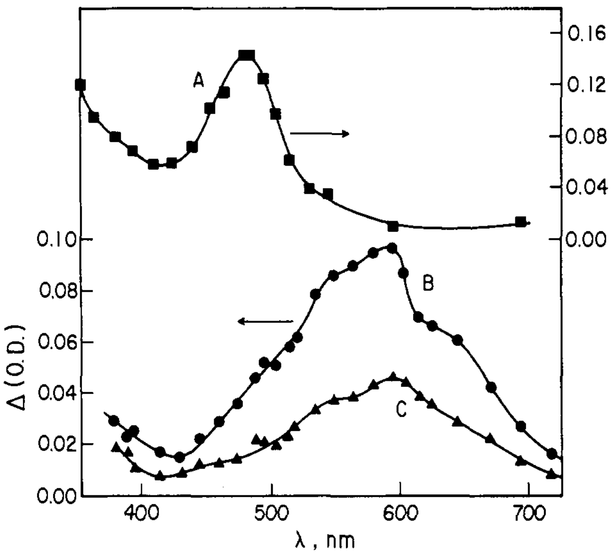

Figure 2. Transient spectra due to triplet benzil (A) in the absence of TEA; in the presence of TEA, 250 ns after the pulse (B); and 10 ns after the pulse (C), i.e., "jump" spectrum.

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]

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

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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(10) In fact ground-state complexation is not likely to have a large effect on exciplex behavior.
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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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