

# JOURNAL

## OF THE AMERICAN CHEMICAL SOCIETY

Registered in U.S. Patent Office. © Copyright, 1981, by the American Chemical Society

VOLUME 103, NUMBER 25

DECEMBER 16, 1981

### Photochemical Studies of an Oleate Oil in Water Microemulsion

S. S. Atik and J. K. Thomas\*

Contribution from the Chemistry Department, University of Notre Dame,  
Notre Dame, Indiana 46556. Received June 12, 1981

**Abstract:** Photochemical and photophysical studies are carried out in a potassium oleate, hexanol, hexadecane, water, and water in oil microemulsion. The photophysical studies, fluorescence polarization, and solvent dependent fluorescence show that the polarity and fluidity of the microemulsion water pools increase with increasing water content up to 15% water, and remain constant to 40% water. Similar fluidity changes are noted in the oil phase up to ~40% when rapid fluctuations are observed due to the formation of large rod-like micelles. Photoinduced  $e^-$  transfer studies between excited ruthenium bipyridyl (RuII)\* and  $\text{Fe}(\text{CN})_6^{3-}$ , or methyl viologen, reactions confined to the water pools show behavior which may be interpreted as an increased fluidity of the water pool up to 15% water, followed by an abrupt decrease as the layer structures are formed at 40% water. The reactants tend to distribute among the water pools according to Poisson statistics, which enable measurements of pool radii, reaction rate constants in the pool, and exit rates of reactant from the pools to be measured.

Interest in the influence of colloidal systems on photochemical reactions has increased sharply over the past few years. This is well prefaced in several conferences, now published as texts and in journals.<sup>2-5</sup> In addition the literature contains numerous reports of a great variety of systems, in particular those related to storage of solar energy. Microemulsion systems has received some attention following the original work by Mackay and co-workers.<sup>6</sup> For the most part work has been carried out in oil in water microemulsions,<sup>6-9</sup> although some photochemistry in reversed micellar AOT (disodium diisooctylsulfosuccinate)<sup>10</sup> and other oil in water systems have been reported.<sup>10-13</sup>

The oil in water microemulsion systems consist of small spheres of water ( $r$  up to 150 Å), solubilized in an oil by means of a surfactant and cosurfactant system. Many excellent descriptions of these systems are available.<sup>14-17</sup> A point of particular interest

to the photochemist lies in the varied nature of the water pool under different experimental conditions. It is usual to define a parameter  $\omega_0$ , the molar ratio of water to surfactant. In the AOT system, at small values of  $\omega_0$  the physical properties of the water pool as measured by fluorescence,<sup>18</sup> and NMR spectroscopy,<sup>19</sup> are quite unlike those of bulk water. However, the physical measurements indicate properties of bulk water at larger  $\omega_0$ . Photophysical properties of many molecules are affected by this change in  $\omega_0$ , a point of particular interest to photochemists.

This study describes photophysical measurement on the potassium oleate, hexanol, hexadecane, and water system, the parameters of which are well known. This system is convenient as the water content can be varied over a large range. In particular, attention is focussed on the size of the water pools, photophysical measurements of the nature of these pools, and the influence of size on several photolytic reactions.

#### Experimental Section

Fluorescence spectra were measured on a Perkin-Elmer MPF 44 spectrofluorimeter. Laser flash photolysis studies were carried out using a Korad K1Q frequency doubled Q switch ruby laser ( $\lambda = 3471$  Å; pulse width = 15 ns; energy = 0.1 J) as an excitation source, and a Tektronix 7912AD transient capture device to monitor the short lived species formed. Data analysis was carried out on a Tektronix 4051 computer.

Pyrene and 1-pyrenecarboxaldehyde, PCHO, were purchased from Aldrich and recrystallized from ethanol; 1-pyrenesulfonic acid, PSA, from Frinton; 1-pyrenebutyric acid, PBA, from Pfaltz and Bauer; and dimethylaniline, DMA, from Fisher Scientific. Oleic acid was obtained

(1) The authors would like to thank NSF for support of this work via Grant No. CHE78-24867.

(2) "Micellization, Solubilization, and Microemulsions", K. L. Mittal, Ed., Plenum Press, New York, 1977.

(3) "Solution Chemistry of Surfactants"; K. L. Mittal, Ed., Plenum Press, New York, 1979.

(4) *J. Phys. Chem.* **84** (1980).

(5) *Isr. J. Chem.* **19**, No. 1 and 2 (1979).

(6) K. Letts and R. A. Mackay, *Inorg. Chem.*, **14**, 2990 and 2993 (1975); C. E. Jones and R. A. Mackay, *J. Phys. Chem.*, **82**, 63 (1978); also, K. Letts and R. A. Mackay, **2**, p 801.

(7) J. Kiwi and M. Grätzel *J. Am. Chem. Soc.*, **100**, 6314 (1978).

(8) M. Almgren, F. Grieser, and J. K. Thomas, *J. Am. Chem. Soc.*, **102**, 3188 (1980).

(9) S. Gregoritch and J. K. Thomas, *J. Phys. Chem.*, **84**, 1491 (1980).

(10) M. Wong and J. K. Thomas, ref 2, p 647.

(11) T. Nagamura, K. Takuma, Y. Tsutsui, and T. Matsuo, *Chem. Lett.*, **503** (1980).

(12) W. E. Ford, J. W. Otvos, and W. Calvin, *Nature (London)*, **274**, 507 (1978).

(13) D. J. Miller, U. Klein, and L. M. Hauser, *Z. Naturforsch.*, **329**, 1020.

(14) K. Shinoda and S. Friberg, *Adv. Colloid Interface Sci.*, **4**, 281 (1975).

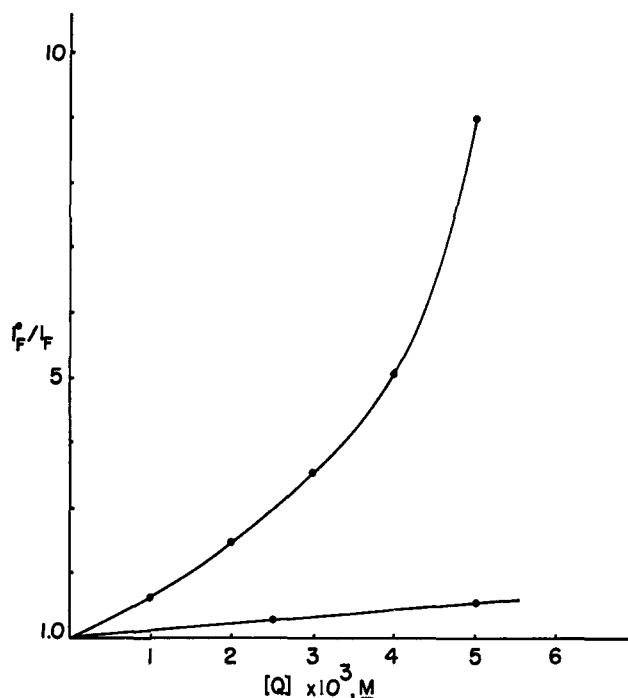
(15) L. M. Prince, *Chem. Phys. Lett.*, **1**, 45 (1977).

(16) H. F. Eiche, J. C. W. Shepherd, and A. Steinermann, *J. Colloid Interface Sci.*, **56**, 168 (1976).

(17) D. O. Shah, R. D. Walker, N. J. Stal, S. Divivedi, R. Pepensky, and D. W. Deamer, SPE. No. 5815 1976; P. O. Shah, *J. Colloid Interface Sci.*, **37**, 744 (1971).

(18) M. Wong, M. Grätzel, and J. K. Thomas, *J. Am. Chem. Soc.*, **98**, 4730 (1976).

(19) M. Wong, T. Nowak, and J. K. Thomas, *J. Am. Chem. Soc.*, **99**, 4730 (1979).



**Figure 1.** Effect of  $\text{Fe}(\text{CN})_6^{3-}$  and  $\text{MV}^{2+}$  on the luminescence efficiency of excited RuII in a potassium oleate (1 g), hexanol (2.0 mL), hexadecane, (5.0 mL), water in oil microemulsion,  $\omega_0 = [\text{H}_2\text{O}]/[\text{oleate}] = 31$ . Upper curve:  $\text{Fe}(\text{CN})_6^{3-}$ . Lower curve:  $\text{MV}^{2+}$ .

as ultra pure grade from Sigma Chemical Co.; KOH was analar grade from Matheson Co., hexanol was pure grade from the Baker Co., and water was doubly distilled.

### Results and Discussion

**Poisson Statistics and Quenching.** Figure 1 shows the effect of  $[\text{Fe}(\text{CN})_6^{3-}]$  and  $[\text{MV}^{2+}]$  on the luminescence efficiency of excited RuII,  $(\text{RuII})^*$ . The efficiency decreases with concentration for both solutes due to quenching of  $(\text{RuII})^*$ . The quenching efficiency of  $\text{Fe}(\text{CN})_6^{3-}$  is much greater than that of  $\text{MV}^{2+}$ , as this latter quencher is bound to the negatively charged surface of the water pool, while  $\text{Fe}(\text{CN})_6^{3-}$  is free to move in the pool itself. In the RuII/ $\text{MV}^{2+}$  system both reactants are bound to the negative surface of the water pool, a region of restricted movement. In the RuII/ $\text{Fe}(\text{CN})_6^{3-}$  system  $\text{Fe}(\text{CN})_6^{3-}$  is free to move in the water pool and hence approaches  $(\text{RuII})^*$  more readily than  $\text{MV}^{2+}$ .

Figure 2 shows the decrease in  $(\text{RuII})^*$  luminescence with time at several  $[\text{Fe}(\text{CN})_6^{3-}]$  and several  $\omega_0$ , where  $\omega_0 = [\text{H}_2\text{O}]/[\text{oleate}]$ . The kinetics in the system are envisaged as follows: (a) The system consists of water pools separated from the hydrocarbon phase by surfactant and cosurfactant (b) the ionic reactants are located at the water pools, the distribution following Poisson statistics, and (c) rapid quenching of  $(\text{RuII})^*$  takes place if the probe and a quencher, i.e.,  $\text{Fe}(\text{CN})_6^{3-}$ , are located in the same water pool. Slower quenching arises if  $(\text{RuII})^*$  is alone in a water pool, when transport of the reactants between water pools is necessary for quenching to occur. As  $[\text{Fe}(\text{CN})_6^{3-}] \gg [(\text{RuII})^*]$  then the transport in question is that of  $\text{Fe}(\text{CN})_6^{3-}$ .

It can be shown<sup>20</sup> that the  $(\text{RuII})^*$  luminescence  $I_F(t)$ , at time  $t$ , is related to the intensity at  $t = 0$ ,  $I_F(t = 0)$ , by the expression:

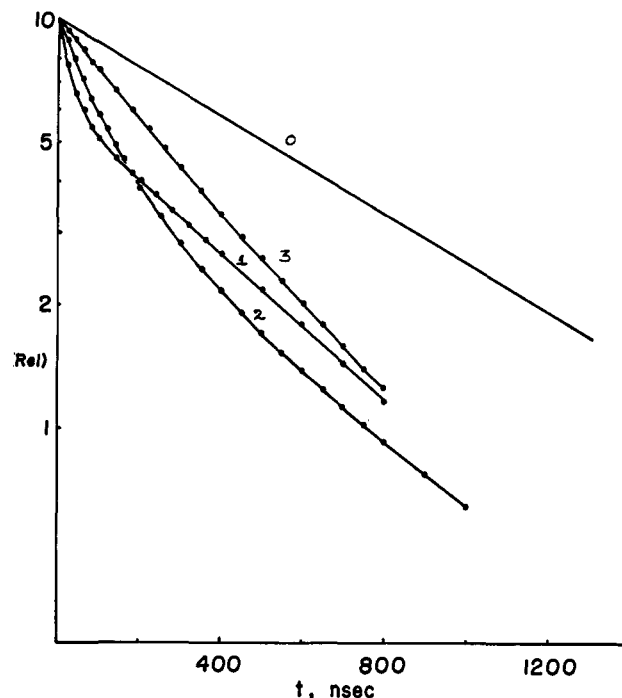
$$I_F(t) = I_F(t = 0) \exp[-\bar{n}(1 - e^{-k_q t}) + k_1 t]$$

where

$$k_1 = \frac{1}{\tau_0} + \sum_{n=1}^{\infty} n k_e (P_n [\text{WP}]_T)$$

(20) S. S. Atik, and L. A. Singer, *Chem. Phys. Lett.*, **59**, 519 (1978); **66**, 234 (1979); S. S. Atik and J. K. Thomas, *J. Am. Chem. Soc.*, **103**, 3543 (1981).

(21) W. G. M. Agterof, J. A. J. Van Zomeren, and A. Vrij, *Chem. Phys. Lett.*, **43**, 363 (1976).



	$\omega_0$	$[\text{Fe}(\text{CN})_6^{3-}] \times 10^3$	$\bar{n}$	$k_q, \text{s}^{-1}$
0	16	0		
1	16	3.0	0.52	$2.5 \times 10^7$
2	31	1.5	1.00	$4.5 \times 10^6$
3	53	1.5	2.05	$7.0 \times 10^5$

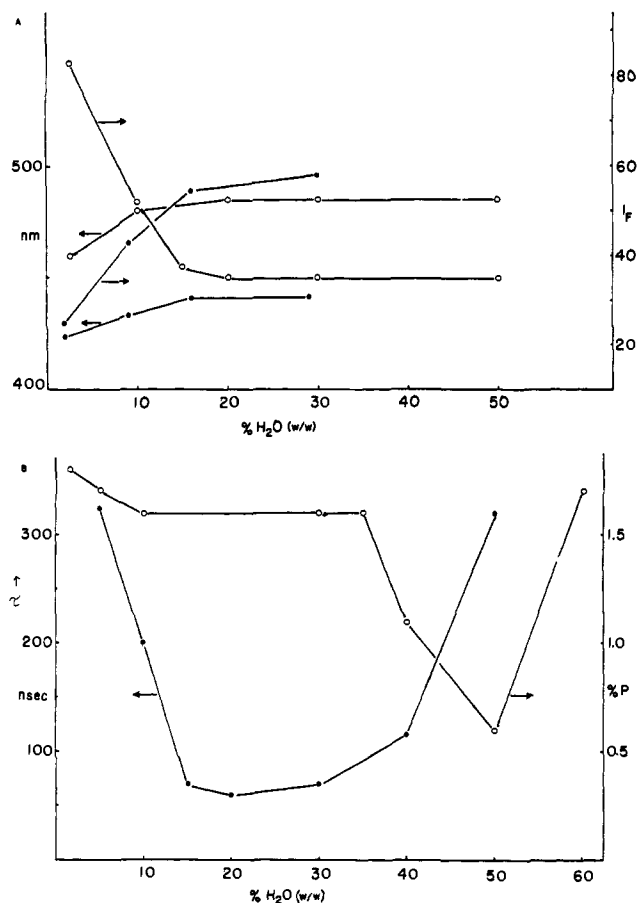
**Figure 2.** Variation in the intensity of RuII\* fluorescence with time in an oleate oil in water microemulsion.

where  $\tau_0$  is the lifetime of  $(\text{RuII})^*$  in the absence of quencher,  $k_e$  is the exit rate constant of solute from one pool to another,  $P_n$  is the Poisson distribution of solutes among water pools given by  $P_n = \bar{n}^n e^{-\bar{n}} / n!$  where  $\bar{n} = [\text{quencher}]_i / [\text{WP}]_i$  and  $[\text{WP}]_i$  is the total water pool concentration, and  $k_q$  is a first-order specific quenching rate constant effected by one quencher in a water pool. Assuming a Poisson statistical distribution of quenchers among water pools, it can readily be shown that  $k_1$  would then be given by  $k_1 = \tau_0^{-1} + k_e [\text{Q}]$ . Figure 2 gives the various types of  $(\text{RuII})^*$  luminescence decays observed in the presence of  $\text{Fe}(\text{CN})_6^{3-}$  with varying amounts of solubilized water ( $\omega_0$ ). The solid curves are the best-fit simulations obtained by varying the adjustable parameters  $k_q$ ,  $\bar{n}$ , and  $k_e$ . Table I gives the optimal values of these parameters for different  $\omega_0$ . The agreement of experimental and calculated data supports the proposed kinetics which involves a Poisson distribution of reactants among the water pools.

**Spectroscopic Investigation of the System.** Fluorescent probes have been successfully used to investigate the nature of the disodium diisooctylsulfosuccinate/heptane/water reversed micellar, or microemulsion system.<sup>18,19</sup> Similar studies were carried out in the CTAB system under study. Figure 3, A and B, shows the variation in the spectroscopic properties of anilino-naphthalene-sulfonate (ANS), pyrene carboxaldehyde (PCHO), and diphenyl hexatriene (DPH), at various water contents. The variation in the lifetime of  $(\text{RuII})^*$  in an undegassed system containing  $10^{-4}$  M RuII and  $5.0 \times 10^{-3}$  M  $\text{Fe}(\text{CN})_6^{3-}$  is also shown in this figure. Under these conditions where  $\bar{n} > 1$  and  $k_q < \tau_0^{-1}$  the luminescence decay of  $(\text{RuII})^*$  is nearly exponential.

Increasing the water content of the system leads to a decrease in the ANS fluorescence intensity and an increase in the PCHO fluorescence intensity, together with a concomitant increase in  $\lambda_{\text{max}}$  for this probe. The effects appear to level out above 15% water. The trends in the spectroscopic data show that the environments of the probes show increasing polarity with increasing water, approaching that of bulk water at 15% water.

The RuII/ $\text{Fe}(\text{CN})_6^{3-}$  lifetime data and the DPH fluorescence polarization both monitor the rigidity of the environments of these



**Figure 3.** (a) Variation in the spectroscopic properties  $\lambda_{\max}$  and fluorescence intensity of pyrene carboxaldehyde (●) and anilino naphthalene sulfonate (○) with percentage water. (b) Variation with percentage water of (●) the lifetime of RuII\* fluorescence with  $5.0 \times 10^{-3}$  M  $(\text{Fe}(\text{CN})_6)^{2-}$  and (○) the degree of fluorescence polarization, % P, of diphenyl hexatriene.

systems, the RuII/ $\text{Fe}(\text{CN})_6^{3-}$  system, the water pool, and the DPH hydrocarbon. The lifetime of  $(\text{RuII})^*$ ,  $\tau$ , decreases with water content up to 15% indicating that the efficiency of the  $(\text{RuII})^* + \text{Fe}(\text{CN})_6^{3-}$  quenching reaction increases as the reactants become more mobile. However, the  $\tau$  increases again, i.e., lower mobility of reactants, above 40% water. The DPH fluorescence polarization decreases slightly up to 15% water, but shows a much larger decrease above 38% water with an increase above 50% water. The fluorescence polarization of this probe varies with the degree of rigidity of the probe environment, i.e., the hydrocarbon.

It is important to note that the lifetime of  $(\text{RuII})^*$  is almost independent of  $\omega_0$  (being 780 ns at  $\omega_0 = 16$  and 750 ns for  $\omega_0 = 53$ ) but longer than that observed in water ( $\tau_0 = 650$  ns). Moreover the wavelength of maximum emission of  $(\text{RuII})^*$  is found also to be invariant with respect to change in  $\omega_0$  (630 nm) which is  $\sim 20$  nm red-shifted from that observed in pure water. These results could probably be interpreted to mean that RuII stays electrostatically bound to the anionic surface of the water pool during its excited state lifetime.

**Photochemical Reactions.** Table II lists the rate constants for several photochemical reactions induced in the microemulsion system. In each case the pyrene chromophore is excited and the quenching of the fluorescence by  $\text{Ti}^+$ , DMA,  $\text{O}_2$ , and  $\text{I}^-$  is monitored. Pyrene is located in the hydrocarbon phase while PBA and PSA are located at the water bubble/hydrocarbon interface.  $\text{Ti}^+$  and  $\text{I}^-$  are confined to the water pools,  $\text{Ti}^+$  being bound to the negatively charged surface, while  $\text{I}^-$  is in the pool itself. Both DMA and  $\text{O}_2$  move in both hydrocarbon and water phase. Pyrene is poorly quenched by  $\text{Ti}^+$  as  $\text{P}^*$  has to approach the aqueous phase for reaction to occur. The  $\text{I}^-$  quenching is almost nonexistent as here  $\text{P}^*$  has to enter the pool for reaction to occur.  $\text{Ti}^+$  readily quenches both PSA and PBA as all reactants are located at the interface; again  $\text{I}^-$  quenching is lower as it is repelled from the

**Table I.** Physical Parameters in Oleate Microemulsions

$\omega_0$	$[\text{K}_3\text{Fe}(\text{CN})_6] \times 10^3$	$\bar{n}$	$k_g, 10^6 \text{ s}^{-1}$	$k_1, 10^6 \text{ s}^{-1}$	$k_e, 10^8 \text{ L M}^{-1} \text{ s}^{-1}$
5.0 × 10 <sup>-5</sup> M RuII/Potassium Oleate Microemulsion (Hexanol): System—1.0 g of Potassium Oleate, 2.0 mL of Hexanol, 5.0 mL of Hexadecane, in N <sub>2</sub>					
16	3.0	0.52	2.5	2.00	2.2
31	1.5	1.00	0.45	1.75	2.8
53	1.5	2.05	0.070	1.50	1.1
$\omega_0$	$R_w, \text{ \AA}$	$k_g, \text{ s}^{-1}$	$k_e, \text{ L M}^{-1} \text{ s}^{-1}$		
System—1.0 g of Potassium Oleate, 2.0 mL of Hexanol, 5.0 mL of Benzene, in N <sub>2</sub>					
23.5	26 (29) <sup>21</sup>	$1.0 \times 10^7$	$2.8 \times 10^7$		
49.5	50 (51) <sup>21</sup>	$7.5 \times 10^5$	$2.5 \times 10^7$		

**Table II.** Results of Fluorescence Quenching Studies in 30% (w/w) Water ( $\omega_0$ ) Oleate Microemulsions<sup>a</sup>

	$k_q \times 10^{10} \text{ L M}^{-1} \text{ s}^{-1}$			
	$\text{Ti}^+$	DMA	$[\text{O}_2]^* \times 10^3$	$\text{I}^-$
pyrene	0.4	4.0	2.0	<0.005
PSA	3.3	3.0	0.41	0.14
PBA	2.1	1.3	1.0	0.05

<sup>a</sup> Solutions of  $1.0 \times 10^{-5}$  M probe were outgassed by bubbling N<sub>2</sub>. Calculated from the relationship  $1/\tau = (1/\tau_0) + [\text{O}_2]k_q$  where  $k_q$  is taken as  $10^{10} \text{ L M}^{-1} \text{ s}^{-1}$  for air equilibrated samples.

interface where PSA and PBA reside. DMA efficiently quenches all these molecules indicating no significant barrier to its movement throughout the system. The same applies to  $\text{O}_2$  although PSA and PBA, the more polar derivatives of pyrene, are slightly lower in reactivity than P. This is most probably due to the lower ( $\text{O}_2$ ) in the water bubble compared to the bulk hydrocarbon phase.

## Discussion

The photochemical kinetic data illustrated in Figures 1 and 2 show that solutes distribute themselves among water pools according to a Poisson distribution. The distribution initially affects the time resolution of subsequent kinetics ensuing following photoexcitation. This type of behavior is typical of most micellar systems. Analysis of the kinetic data produces values for the radii of water pools which are in agreement with literature value, which again supports the overall kinetic picture suggested. Another feature of these studies is the evaluation of the rate of exit of an ion from a water pool, indicated as a rate constant  $k_e$ . These values are fairly constant in the oleate-hexanol-hexadecane system at  $10^8 \text{ L M}^{-1} \text{ s}^{-1}$ . It has been shown previously in the AOT/heptane/water system that ion exchange is via water pool collision and occurs once in every 100 to 1000 collisions. These data are similar indicating ion exchange in every 50 to 100 collisions. The introduction of benzene into the system significantly decreases the effectiveness of transfer as found in the AOT system. This is interpreted as being due to a more compact head-group region which incorporates benzene.

Although changing the percentage of water or pool radius has little effect on the effectiveness of ion exchange between the pools, nevertheless, other studies show that other physical properties of the water pools do change. Figure 3 shows that the polarity of the water pools, as monitored by the fluorescence probes ANS and PCHO, increases with increasing  $\omega_0$ . Similar data have been observed for AOT/heptane systems. The properties reminiscent of bulk water are approached beyond 15% water.

Figure 1 shows that the lifetime of  $(\text{RuII})^*$  in the presence of  $\text{Fe}(\text{CN})_6^{3-}$  decreases, i.e., the reaction rate increases with addition of water up to 15% water in a similar fashion to the fluorescence probe data of Figure 2. Increasing the radius of the water pool tends to decrease the rigidity of this region of the system and leads to more rapid reaction. Further increase in water content, after 40%, leads to a sudden increase in the  $(\text{RuII})^*$  lifetime, or decrease in reaction rate. This is due to a change in the system from spherical water pools or reversed micelles to rod-like structures, as noted previously in other laboratories.<sup>14,17</sup> The  $(\text{RuII})^*$  and

$\text{Fe}(\text{CN})_6^{3-}$  are no longer confined to a small part of the system which encourages rapid reaction, but are now spread throughout larger structures. The reaction rate drops and the lifetimes of  $(\text{RuII})^*$  increases.

It is noteworthy that the polarization of diphenylhexatriene decreases abruptly at 40% water when the large structures start to be formed. This probe is located in the oil part of the system and indicates a disruption of the oil as the larger structures are formed leading to a higher mobility of the probe. At larger water contents the polarization increases again as the system forms a more organized assembly.

Reaction rate constants given in Table II for several pyrene chromophores and quenchers indicate the compartmentalized nature of the system. The probes PBA and PSA and quenchers  $\text{TI}^+$  and  $\text{I}^-$  are located in the water pools.  $\text{TI}^+$  is probably in the vicinity of the head-group region near the carboxylate groups, while  $\text{I}^-$  is repelled into the pool. Pyrene is located only in the alkane, but may approach the pool, while DMA and  $\text{O}_2$  move fairly freely through the system. The quenching rate constants of DMA and  $\text{O}_2$  with pyrene, PSA, and PBA are similar in keeping with the model given above. Iodide ion quenches both PSA and PBA, but

not pyrene as this probe cannot enter the water pool interior. Thallous ion quenches all three probes but pyrene least efficiently, although this is more efficient than the case of  $\text{I}^-$ . This is in keeping with  $\text{TI}^+$  being located at the interface and an inefficient approach of pyrene to this region of the system.

If a  $k$  of  $10^{10} \text{ L M}^{-1} \text{ s}^{-1}$  is assumed for  $\text{O}_2$  reacting with the probes, then the  $[\text{O}_2]$  can be calculated in the bulk hydrocarbon, and in the water pool. The  $[\text{O}_2]$  is larger in the hydrocarbon than in the water, again in keeping with the established solubilities of  $\text{O}_2$  in the bulk liquids.

These studies establish the kinetic patterns that take place with photoinduced reactions in oleate microemulsions. The kinetics follow structural changes in the system, which are also monitored by other physical measurements. These data are useful in designing micellar systems that act as models for biological membranes, and for solar energy research. In particular the compartmentalized nature of the systems leads to rapid reaction of excited species. The subsequent fate of the products, which are often ionic, depends on the exit rate one pool to another, and on the nature of the assembly produced under the existing matrix composition.

## Electronic Structure of the Phosphenium Ions $\text{PH}_2^+$ , $\text{HPF}^+$ , and $\text{PF}_2^+$ §

James F. Harrison<sup>1</sup>

Contribution from the Theoretical Chemistry Group, Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439. Received March 20, 1981

**Abstract:** The geometry, total energy, and charge distribution of the three lowest states of the divalent phosphorus cations  $\text{PH}_2^+$ ,  $\text{HPF}^+$ , and  $\text{PF}_2^+$  are reported using ab initio generalized valence bond (GVB) wave functions and for  $\text{PH}_2^+$  configuration interaction wave functions. The character of the valence orbitals is analyzed and related to the nature of the PH and PF bonds in the  $^2\pi$  and  $^4\Sigma^-$  states of  $\text{PH}^+$  and  $\text{PF}^+$ . GVB calculations predict that each molecule has a singlet ground state with the next electronic state being a triplet, some 20.4, 42.6, and 84.0 kcal/mol higher for  $\text{PH}_2^+$ ,  $\text{HPF}^+$ , and  $\text{PF}_2^+$ , respectively. CI calculations on  $\text{PH}_2^+$  reduce this singlet-triplet separation to 16.4 kcal/mol.

In the past few years reactions of Lewis acids with various amino halophosphines have resulted in solutions,<sup>2</sup> transition-metal complexes,<sup>3</sup> and most recently isolable phosphenium salts.<sup>4,5</sup> These latter substances (such as the bis(dialkylamino)phosphenium ion  $[(\text{CH}_3)_2\text{NPN}(\text{CH}_3)_2]^+$ ) have well defined NMR spectra and are presumed to be electronically ground state singlets. Phosphenium ions are also present in the mass spectra<sup>6</sup> of numerous phosphorus compounds but are not at all structurally well defined. That the multiplicity should be in question at all is easily seen by noting that the phosphenium ions are isovalent with nitrenium ions, carbenes, and silylenes, all of which count singlets and triplets among their members. As a first step in understanding the structure of these molecules we have studied the parent ion  $\text{PH}_2^+$  as well as the mono- and difluoro compounds  $\text{PHF}^+$  and  $\text{PF}_2^+$ . Specifically we have determined, for each molecule, the singlet-triplet separation, the lowest singlet-singlet separation, and to the extent presently possible, the charge distribution. In addition to providing insight into the structure of an increasingly important class of molecules these results will improve our understanding of substituent effects in the isovalent carbenes, nitrenium ions, and silylenes.<sup>7</sup>

### Technical Details

**A. Basis Sets.** The basis functions are characterized in Table I. The primitive sets are from Huzinaga<sup>8</sup> and have been contracted as recommended by Raffanetti.<sup>9</sup> The exponents of the hydrogen s functions were scaled by 1.2 and each atom was endowed with a set of single component polarization functions. The phosphorus d and hydrogen p exponents were optimized in the lowest singlet state of  $\text{PH}_2^+$  while the fluorine d exponent was

Table I. Basis Set

atom	primitive basis	contraction	polarization function	total contracted
P	11s,7p	4s,3p	1d ( $\alpha = 0.5$ )	19(4s,3p,1d)
F	9s,5p	3s,2p	1d ( $\alpha = 0.9$ )	15(3s,2p,1d)
H	4s	2s	1p ( $\alpha = 0.6$ )	5(2s,1p)

taken as recommended by Dunning and Hay.<sup>10</sup> The number of contracted functions used for each molecule is 29 ( $\text{PH}_2^+$ ), 39 ( $\text{PHF}^+$ ), and 49 ( $\text{PF}_2^+$ ).

(1) Scientist in Residence, Argonne National Laboratory 1980/81. Address correspondence to the following address: Department of Chemistry, Michigan State University, East Lansing, MI 48824.

(2) S. Fleming, M. K. Lupton, and K. Jekot, *Inorg. Chem.*, **11**, 2534 (1972).

(3) (a) R. W. Light and R. T. Paine, *J. Am. Chem. Soc.*, **100**, 2230 (1978).

(b) R. G. Montemayor, D. T. Sauer, S. Fleming, D. W. Bennelet, M. G. Thomas, and R. W. Parry, *ibid.*, 2231 (1978).

(4) A. H. Cowley, M. C. Cushmer, and J. S. Szobota, *J. Am. Chem. Soc.*, **100**, 7784 (1978).

(5) L. D. Hutchins, R. T. Paine, and C. F. Compana, *J. Am. Chem. Soc.*, **102**, 4521 (1980).

(6) M. Halmann, *J. Chem. Soc.*, 3270 (1962). Also, see the review by I. Granth in "Topics in Phosphorous Chemistry", Vol. 8, E. J. Griffith and M. Grayson, Eds., Wiley, New York, 1976.

(7) J. F. Harrison, R. C. Liedtke, and J. F. Liebman, *J. Am. Chem. Soc.*, **101**, 7162 (1979), and references contained within.

(8) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965); Approximate Atomic Wave Functions, I & II, Technical Report from the Theoretical Chemistry Division, University of Alberta, Edmonton, Alberta 1971.

(9) R. C. Raffanetti, *J. Chem. Phys.*, **58**, 4452 (1973).

(10) T. H. Dunning, Jr., and P. J. Hay, "Modern Theoretical Chemistry", Vol. 2, H. F. Schaefer III, Ed., Plenum, New York, 1976.

§ Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy.