

proposed by Schulman and Sturgeon [7]. The mechanism was based on the observation that the fluorescence decay times  $T_0$  of the cations were unchanged at various concentrations of protons as the apparent quantum yield of fluorescence increased with increasing  $[H^+]$  ( $\alpha$ -NA,  $T_0 = 4.1$  ns;  $\beta$ -NA,  $T_0 = 5.0$  ns) [7]. However, the constant lifetimes such as  $T_0$  were never observed in our repeated experiments of naphthylamines [5] and also in the present work. The apparent lifetimes  $\tau_{AH}$  increased with increasing  $[H^+]$  to give a maximum value of  $\tau_{AH}$  at higher acid concentrations. Therefore, the static quenching mechanism is not acceptable for the present work.

From  $k_1$  and  $k_2$  values the correct  $pK_a^*$  values were determined, which were different from those obtained from the Förster cycle and also the fluorescence titration curve. These data are summarized in Table 1.

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## THE PRIMARY PROCESSES IN THE $Cd(^3P_1)-C_2H_6$ REACTION AT 265 °C

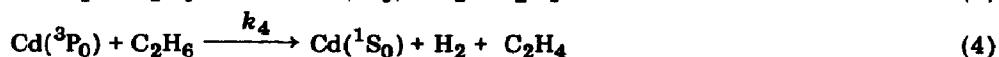
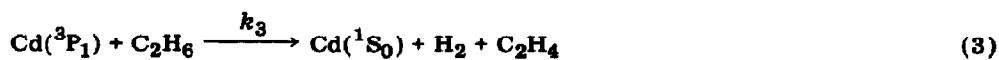
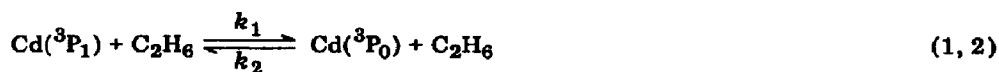
R. S. KONAR

*Regional Engineering College, Durgapur 713209, West Bengal (India)*

B. de B. DARWENT\*

*Chemistry Department, The Catholic University of America, Washington D.C. 20017 (U.S.A.)*

A detailed analytical investigation of the  $Cd(^3P_1)-C_2H_6$  reaction at 265 °C in the gas phase has been made with a gas chromatograph (GC) and a mass spectrometer. The reaction has a well-defined induction period, the length of which decreases with an increase of the incident light intensity, cadmium concentration in the cell or of the reactant pressure. During the induction period no products could be detected (the lower detectability limit of the GC is  $5 \times 10^{-9}$  mol l<sup>-1</sup> of hydrocarbons in the reaction cell). The major products detected are  $H_2$ ,  $n-C_4H_{10}$  and  $C_2H_4$ , while the minor products are  $CH_4$ ,  $C_3H_8$ ,  $C_3H_6$ ,  $C_4H_8-1$ ,  $C_5H_{10}-1$  and  $n-C_6H_{14}$ . The major products and methane were estimated and they were found to form at accelerated rates with conversion after the induction period. It was noted that the hydrogen and ethylene were formed by the primary and secondary processes, while  $n$ -butane and methane were formed entirely by the secondary processes. The initial rates of hydrogen and of ethylene were found to be approximately equal at a given reactant pressure. It has been suggested that the primary processes are



$[Cd(^3P_0)]/[Cd(^3P_1)] = K = k_1/k_2 = 1.35$  at 265 °C at equilibrium by Boltzmann statistics. The measured value of  $k_3$  is  $1.95 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$  if the radiative lifetime of  $Cd(^3P_1)$  is  $2.0 \times 10^{-6} \text{ s}$  and the quenching cross section ( $\sigma_3^2$ ) is  $0.015 \text{ \AA}^2$  per ethane molecule. The estimated value of  $k_3/k_4$  at 265 °C is 4, if  $E_4 = E_3 + 1.50 \text{ kcal}$  and  $A_4 = A_3$ ;  $\sigma_4^2$  is about  $0.004 \text{ \AA}^2$ . It has been shown that the auto-acceleration is due to the  $Cd(^3P_1)\text{-H}_2$  reaction, while ethylene inhibits the  $Cd(^3H_1)\text{-C}_2\text{H}_6$  reaction. The quenching rate constant of the reaction  $Cd(^3P_{1,0}) + \text{H}_2 \rightarrow CdH + H$  was found to be  $2.09 \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$ , which gives  $4.60 \text{ \AA}^2$  for the quenching cross section.

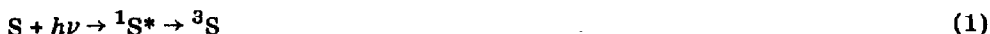
\*Present address: Post Box No. 84, Kingston, Md. 21834, U.S.A.

## ON THE REACTIVITY OF SINGLET OXYGEN IN AQUEOUS MICELLAR SYSTEMS

N. BARBOY and I. KRALJIC

*Laboratoire de Physico-Chimie des Rayonnements (associé au CNRS), Université de Paris-Sud, 91405 Orsay (France)*

Singlet oxygen ( $^1O_2$ ) in aerated aqueous solutions can be conveniently produced by a process of energy transfer between certain sensitizers (S) in their triplet state ( $^3S$ ) and molecular oxygen ( $^3O_2$  or simply  $O_2$ ):



Many fluorescent dyes can be used as sensitizers in photooxidation of different substrates (A, acceptor) in which besides the singlet oxygen mechanism, reaction (3), the so-called free radical mechanism may also play an important role, reactions (4) and (5):



The transient formation of  $^1O_2$  in aqueous systems is usually checked by some tests based on interception or quenching of  $^1O_2$  by a more or less selective reagent. Recently, a general method for identification of the mechanism of dye sensitized photooxidations has been developed [1]. Using this method one can "calculate" the mechanism of any chemical change observed in sensitized photooxidation provided that the corresponding rate constants for  $^3S$  and  $^1O_2$  reactions are known. Since in many sensitized photooxidations the free radical mechanism may take place, the determination of  $^1O_2$  rate constants in aqueous solutions can be a rather difficult problem. Accordingly, only a limited number of its rate constants have been determined thus far. Owing to a lack of specific  $^1O_2$  reagents, its reactivity can be studied in systems with no or negligible participation of free radical mechanism. The use of sensitizers showing a rather low reactivity in their triplet state is one possibility, at least for some substrates [2, 3]. Prevention of reactions between a  $^1O_2$  producing triplet sensitizer and a substrate by their "separation" would be another possibility. Such a rather "clean" system for the study of singlet oxygen reactions can be constructed in micellar systems since  $^1O_2$  can diffuse through thin membranes. Thus, by the choice of a water insoluble sensitizer, which would be dissolved inside the micelle with a substrate outside it, only the  $^1O_2$  mechanism would lead to the