heterogeneous) are clusters of active sites and that the rates of alkylidene scrambling with a represenative number of olefins coordinated to a given cluster is faster than olefin escape from the cluster. Clustering in homogeneous systems involving highly unsaturated transition metals (e.g., reduced group 4b metal complexes) would not be unusual.

Frank D. Mango
Shell Development Company
Westhollow Research Center
P.O. Box 1380, Houston, Texas 88001
Received February 7, 1977

Aperiodic and Periodic Oscillations in Fluorescence Intensity from Irradiated Chlorocarbon Solutions of Anthracene and 9,10-Dimethylanthracene

Sir:

We wish to report some unusual results concerning the fluorescence of anthracene and 9,10-dimethylanthracene in chlorocarbon solutions. Our observations add to the known examples of photoinduced *chemical instabilities.*[1] The findings are important, in part, because an analytical procedure[2] for determination of certain organic materials in water involves extraction with a chlorocarbon followed by a fluorescence determination in another solvent. This work was initiated by the desire to carry out the fluorescence measurement in the extraction solvent. Under certain conditions, we find that excitation of the fluorescence of anthracene and 9,10-dimethylanthracene also results in photoinduced chemistry giving rise to aperiodic and periodic *oscillations* in emission intensity.

Both anthracene and 9,10-dimethylanthracene are well-characterized substances with respect to luminescence properties,[3] and each fluoresces in the blue with a good quantum efficiency which is independent of the excitation wavelength. We observed these typical properties in aliphatic hydrocarbons like cyclohexane, but in $CHCl_3$ solutions some unusual results were found. Excitation of a quiet $CHCl_3$ solution of $\sim 10^{-5}$ M anthracene or 9,10-dimethylanthracene at 260 nm gives fluorescence which varies in time in a periodic or aperiodic oscillating manner. The observation was first made with an Aminco-Bowman emission spectrophotometer (by R.J.B.) and was subsequently repeated in a second laboratory with a Hitachi-Perkin Elmer MPF3 emission spectrophotometer (M.S.W.).

In both cases, the oscillation in fluorescence intensity was found to occur under the conditions where 298 K fluorescence spectra are normally recorded. In all cases where oscillatory behavior was observed, the sample volume was significantly larger than the irradiated volume. Stoppered, but not degassed, ~3-cc samples in square (1.00 × 1.00 cm i.d.) fluorescence cells were typically used, and the $CHCl_3$ (and the other chlorocarbons) was either spectroquality or reagent grade and used as received. The anthracene and 9,10-dimethylanthracene were obtained from several different suppliers and used as received. The point is that the behavior to be described below is easy to observe and the essential results are independent of the sources

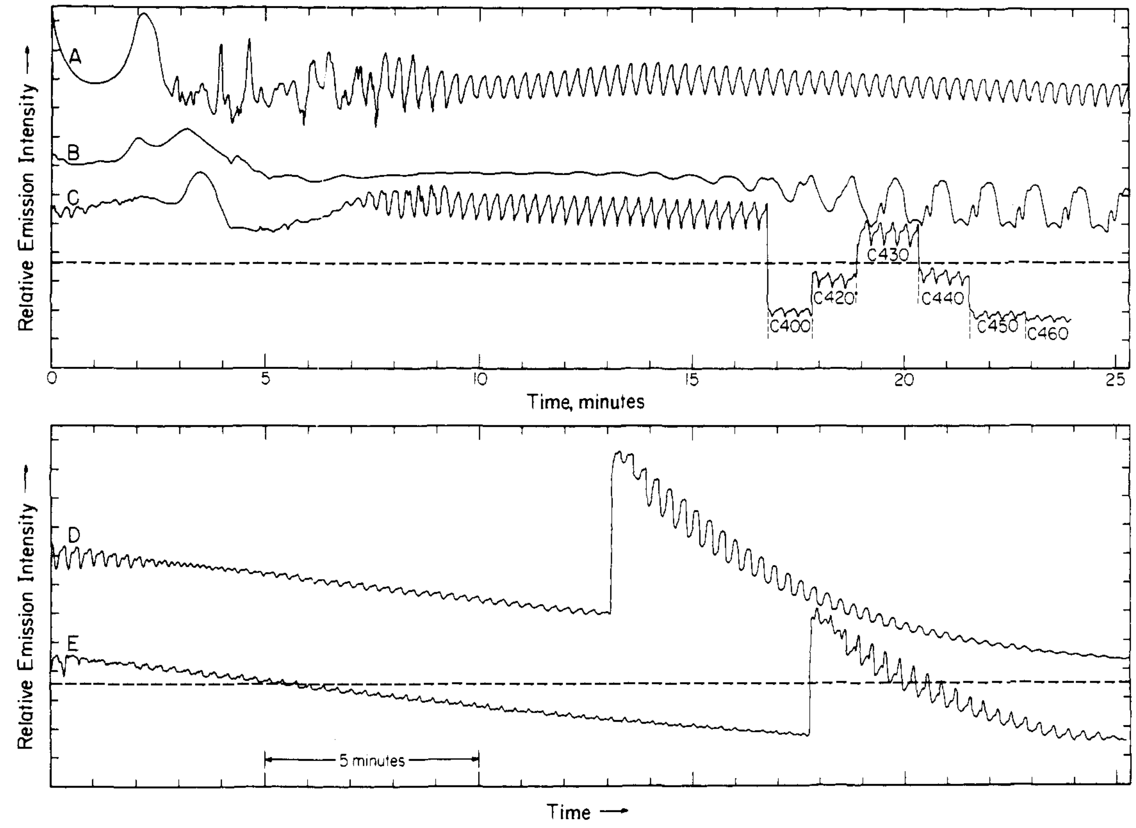

Figure 1. Plots of 9,10-dimethylanthracene (DMA) fluorescence intensity against time in ~3 cc of $CHCl_3$ solution at 298 K. All plots were obtained using a Perkin-Elmer MPF3 emission spectrophotometer and the sample was in a square (1.0 × 1.0 cm i.d.) fluorescence cell. All curves are for an excitation wavelength of 260 nm (slit 16 nm) and a monitoring wavelength of 410 nm (slit 6 nm) unless specified otherwise. Curve A: the baseline is the dashed horizontal line in the upper half of the figure; $[DMA] = 2.0 \times 10^{-5}$ M. Curve B: the baseline is at the solid horizontal line of the upper half of the figure; $[DMA] = 4.0 \times 10^{-5}$ M. Curve C: the baseline is as in curve B, and the sample is just a fresh solution of that used in curve A; the excitation and emission slits are the same, but the monitoring wavelength is 410 nm only up to *T* 16.7 min (during the intervals marked C400, C420, C430, C440, C450, and C460 the monitoring wavelength was 400, 420, 430, 440, 450, and 460 nm, respectively). Curve D: the baseline is the dashed horizontal line of the lower half of the figure; $[DMA] = 1.0 \times 10^{-5}$ M; the ~25-min time interval shown is 15 min after the start of the irradiation (the sharp increase in intensity corresponds to the point where the excitation slit was opened from 16 nm to 40 nm to increase the light intensity by a factor of ~3.3). Curve E: repeat of curve D except the baseline is the solid line at the bottom of the lower half of the figure.

of the materials and of the instrumentation.

Figure 1 shows typical plots of time against 9,10-dimethylanthracene fluorescence intensity at 410 nm excited at 260 nm in $CHCl_3$ solvent at 298 K. During the first several minutes the intensity varies (often wildly with excursions of the order of 75%), and then the variation in intensity becomes periodic. Oscillations have been observed for a duration of the order of 1 h. With time, the overall luminescence intensity gradually declines consistent with the measured irreversible consumption of the 9,10-dimethylanthracene. The period and the pattern of the oscillation and the induction time for the entrainment are not always the same. However, the aperiodic variations can always be induced immediately, and the prolonged periodic oscillations generally begins several minutes subsequent to the start of the experiment.

While we do not yet have a detailed interpretation of the results, we can state a number of additional facts that point toward a working hypothesis: (1) oscillations in fluorescence intensity are not observed for excitation wavelengths longer than ~300 nm in $CHCl_3$, and it appears that excitation of the chlorocarbon is necessary; (2) the oscillations in the emission are essentially independent of the monitoring wavelength (i.e., the entire fluorescence spectrum of the anthracene or 9,10-dimethylanthracene seems to oscillate with the same period and amplitude; (3) oscillations in a sample open to the air cease upon stirring and commence again when the solution is quiet, and when the solution is stirred we observe only a gradual, steady, decline in emission intensity; (4) a sample oscillating at a given amplitude at a given excitation intensity can be induced to oscillate at a larger amplitude by increasing the light intensity; (5) a sample stimulated to oscillate by 260-nm light will continue to oscillate if the excitation wavelength is then changed by a small amount, e.g., to 250 or to 275 nm, although the amplitude of the oscillation can change; (6) concentrations of the luminescent substances higher than those typically employed here seem to obscure the effect. All of these facts are admittedly qualitative in nature, but we feel that they at least lead us to the experiments necessary to understand and fully characterize these systems. We conclude that the excitation beam is both the stimulus for, and the probe of, variations in the anthracene or 9,10-dimethylanthracene concentration (approximately proportional to fluorescence intensity). One primary photochemical reaction is likely the generation of $CHCl_2$ radicals and Cl atoms which may attack ground-state anthracene.[4] Subsequent steps lead to final stable photoproduct(s) which are likely chlorination products.[4] The apparent need for an irradiation volume less than the total volume of the sample and the instant cessation of oscillations in fluorescence upon stirring a quiet solution both point to the importance of diffusion in and out of the irradiation zone. Oscillations have been observed in CCl_4 and CH_2Cl_2 solvents as well, and it is known that carbon-halogen bond cleavage is the general result of electronic excitation of alkyl halides.[5] We believe that a detailed analysis of the many features of the oscillations (amplitude, pattern, period) will provide important clues for a reaction mechanism.[6]

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Robert J. Bose
Fisheries and Marine Service
Department of the Environment, Vancouver Laboratory
Vancouver, British Columbia, Canada

John Ross, Mark S. Wrighton*[7]
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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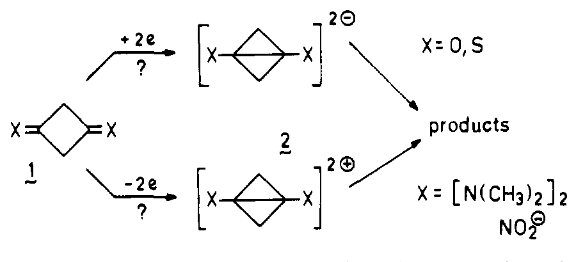
Bicyclo[1.1.0]butanes. A New Synthetic Route and Valence Isomerizations

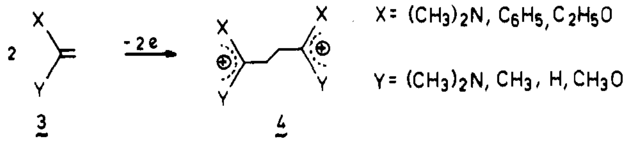
Sir:

In spite of their extremely high strain energy (67 kcal/mol[1]), bicyclobutanes are formed in reasonable yields by a variety of different reactions.[2] Ring closure of 1,3-disubstituted cyclobutanes by 1,3 elimination,[2,3] reduction,[4] or oxidation[5] are of special interest in comparison with our new approach. Conversion of 1,3-bismethylenecyclobutanes or their bishetero-analogues **1** to the corresponding bicyclobutanes by removal or addition of two electrons has been unsuccessful to date.[6-8]



However, in some cases, the isolated products may have been formed via intermediate bicyclobutanes **2**.[6a] We now describe the first example of *reversible formation of bicyclobutanes* from a special type of **1** merely *by electron transfer*.

Formation of the bridging bond of bicyclo[1.1.0]butanes is based upon the well-documented reaction **3** → **4**,[9] except that



in our systems the resonance stabilization of the end groups of **4** is enhanced by the presence of an aromatic nucleus.

Cyclobutanes **5** and **6** were obtained by photodimerization of the corresponding styrylpyridines in dilute hydrochloric acid,[10,11] followed by treatment with base. In contrast to literature reports,[11] **5** and **6** may also be synthesized in high yields (**5**, 90%; **6**, 70%) by irradiation of the styrylpyridine hydro-