total of 8 min.) Note that we observe strong signals from the nonprotonated carbons in polysulfone. That is, in spite of reasonable fears to the contrary,[1,4] the 3-kHz magic-angle spinning does not eliminate, by motional averaging, the dipolar interactions required for transfer of magnetization from polarized nonbonded protons to nearby quaternary carbons.

This result is understandable qualitatively in view of the results of some *single* resonance experiments on solid polymers.[6] The undecoupled ^{13}C NMR spectra of the quaternary carbons of amorphous polymers such as polysulfone invariably have room-temperature dipolar line widths of 3–4 kHz, which narrow by only a factor of 2–4 under 3-kHz magic-angle spinning.[6] This narrowing is far less than that observed for combination spinning and dipolar decoupling experiments. Part of the failure of spinning to narrow more completely the undecoupled line is due to the spinning speed being somewhat less than the dipolar line width, while part is due to dipolar interactions arising from segmental motions of the polymer having correlation frequencies on the order of 10 kHz.[6] (Broadening due to the latter is not removed by spinning at 3 kHz, but is removed by resonant dipolar decoupling at 30 kHz.) In either situation, substantial spectral density associated with ^{1}H–^{13}C dipolar interactions remains at zero frequency[7,8] under magic-angle spinning at 3 kHz. This is consistent with the observation that the spin-lock T_{CH}'s for quaternary carbons in amorphous polymers (which are on the order of 300 μs at room temperature) increase by less than a factor of about 2 under spinning conditions. Of course, there is virtually no effect of spinning on protonated carbon T_{CH}'s because the 3-kHz spinning frequency is so much less than the dipolar line width.

Regardless of the details of the spin dynamics, the fact remains that for a wide variety of macromolecular systems near room temperature, efficient ^{1}H–^{13}C CP transfers do indeed occur under magic-angle spinning conditions. In the case of polysulfone, with individual lines resolved for all types of carbons, a variety of ^{13}C relaxation experiments can be performed and interpreted unambiguously in terms of the motions of the polymer in the solid state.[6] In addition, for many synthetic polymer systems, the magic-angle CP ^{13}C NMR spectra are well enough resolved not only to simplify relaxation experiments but also to begin to identify details such as rotational and configurational isomerism in the main chain.[6] In short, we are convinced that spinning will prove to be invaluable in the study of the chemistry and physics of synthetic polymers in the solid state.

Also shown in Figure 1 are the CP ^{13}C NMR spectra of a dense wood under nonspinning and spinning conditions, compared to a standard FT spectrum of a solution of glucose (with lines articificially broadened somewhat for display purposes). Wood is a complicated blend of celluloses, hemicelluloses, and lignin. We attempt no detailed analysis of the spectra here, except to note that the resolution of the magic-angle CP spectrum of wood is adequate to identify lines associated with each of the three major components. In addition, we find that the spectra are of high enough quality to distinguish, semiquantitatively, between the overall composition of different woods such as maple and pine. While the quality of the CP spectra of wood is comparable to that of the plastic, the chemical complexity of wood itself hampers realizing truly high resolution. For example, the lowest field lines in the wood spectrum (due entirely to lignin) are relatively poorly resolved and for most practical purposes must be considered as a resonance band, rather than as a collection of identifiable lines. The 50-Hz resolution presently achieved by spinning is simply not quite good enough to obtain high resolution in highly complex systems. (However, we feel that as much as a fivefold improvement in resolution may be obtained by order of magnitude increases in the decoupling power and in the accuracy of positioning of the rotor axis, together with a 50% increase in the spinning frequency, all of which should have only modest effects on CP transfer rates.)

The existing limitation on resolution is further illustrated by the third system displayed in Figure 1, ivory, the organic component of which is the protein collagen. Clearly, magic-angle spinning produces a dramatic improvement in the resolution of the CP spectrum of the solid, allowing the chemical shifts of some half-dozen or so lines to be immediately identified. If one happens to be interested in the particular residues whose resonances are fortuitously resolved, then obviously spinning is a great advantage. Unfortunately, the vast majority of resonances fall into one of two poorly resolved bands. While the kind of resolution presently obtainable may be, therefore, disappointing for use in some chemical structure studies, spinning is, nevertheless, still useful in simplifying the interpretation of T_1 or $T_{1\rho}$ experiments[6] by reducing the dispersion of relaxation times across an individual resonance line normally observed in the solid state.[1]

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Temporal Fluctuations in the Emission from Irradiated Acetone Solutions

Sir:

Systems of chemical reactions which display temporal or spatial oscillations have aroused considerable interest, although the number of homogeneous chemical systems known to display such phenomena is quite small.[1-5] We therefore consider it important to report the observation of temporal fluctuations in the photochemical formation of biacetyl from acetone in fluid solution.

Solutions of Fisher Certified acetone or Matheson Coleman and Bell spectroquality acetone were made up in Matheson Coleman and Bell spectroquality acetonitrile. The concentrations of acetone ranged from 0.07 to 0.27 M. The solutions, in quartz tubes, were degassed by six freeze–thaw cycles on a vacuum line. Uncorrected emission spectra were obtained on a Hitachi Perkin-Elmer MPF-2A fluorescence spectrophotometer, using 310-nm excitation and 10 nm wide excitation slits. Solutions were studied in the temperature range from 20 to 40 °C. The incident photon flux was approximately 6×10^{13} photons/s as determined by potassium ferrioxalate actinometry. At this photon flux no significant temperature gradient should develop around the irradiated portion of a solution.

Nondegassed solutions of acetone gave unstructured emission spectra, as shown in Figure 1, curve a, with peak maxima at roughly 395 nm. Degassed solutions yielded enhanced emission with peak maxima at roughly 410 nm.

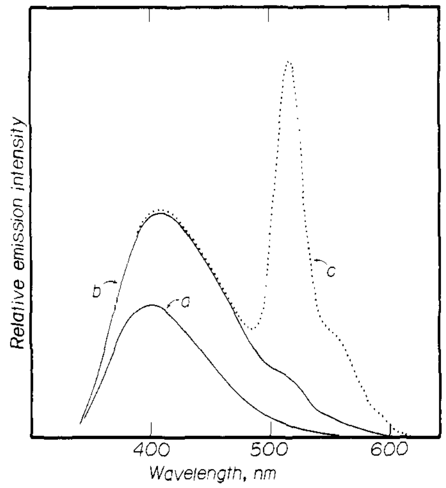

Figure 1. Emission spectra at room temperature of 0.14 M acetone in acetonitrile: curve a, nondegassed solution; curve b, first spectrum obtained from a degassed solution; curve c, spectrum of the degassed solution after 50 min of irradiation in the spectrophotometer.

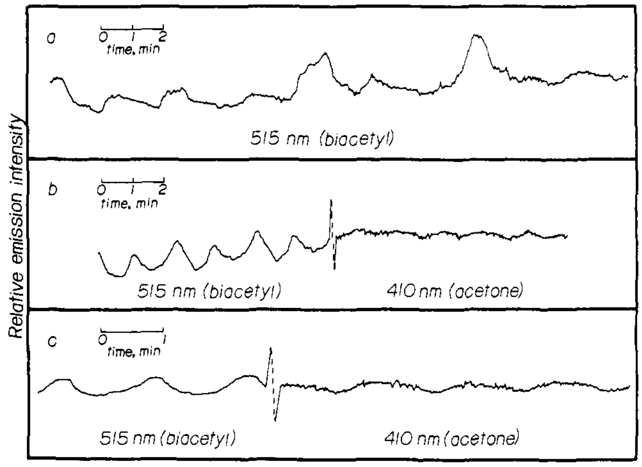

Figure 2. Emission intensities as a function of time for solutions of acetone in acetonitrile at room temperature. The emission was viewed, at the indicated wavelengths, using a 10-nm band-pass on the emission monochromator. In curves b and c the emission wavelength was changed, with the recorder on, at the dashed discontinuity.

These results are in qualitative agreement with those of Turro et al.,[6] who attributed the emission from nondegassed solutions to acetone fluorescence and the emission from degassed solutions to a mixture of acetone fluorescence and phosphorescence.

It was found that the irradiation needed in order to measure the emission spectrum of a degassed solution caused a photochemical reaction to occur. Curve b of Figure 1 shows the first emission spectrum obtained from a degassed solution of 0.14 M acetone in acetonitrile. The emission intensity is enhanced as compared to that of the nondegassed solution, curve a, and a shoulder is present between 500 and 520 nm. After the degassed sample had been irradiated for 50 min in the spectrophotometer, the spectrum shown in curve c was obtained. The shoulder seen in curve b has grown into a well-resolved peak with its maximum at 515 nm. This new emission peak has the same shape as the phosphorescence spectrum of biacetyl,[7] which is a photoproduct obtained when acetone is irradiated in inert solvents.[8,9] The excitation spectrum of the 515-nm biacetyl peak was the same as that of the 410-nm acetone peak, which is consistent with sensitized phosphorescence of biacetyl caused by triplet-triplet energy transfer[10] from acetone to biacetyl. To confirm the presence of biacetyl, a degassed tube of acetone in acetonitrile was irradiated for 7 h using a low-pressure mercury lamp. Vapor phase chromatography of the resulting yellowish solution yielded several peaks, one of which had the same retention time as did a sample of biacetyl.

The rate of change of emission intensity with time was examined by placing a sample in the spectrophotometer, setting the emission monochromator to the desired wavelength, and monitoring the emission under steady-state illumination. It was found that in general the emission intensity at 515 nm exhibited fluctuations as it increased. In one case these fluctuations were as large as ±25% of the average emission intensity, although in general the fluctuations were on the order of ±5%. In some cases these fluctuations displayed enough regularity to be termed oscillations, although typical behavior was irregular, as shown in curve a of Figure 2. It was found that, as the irradiation continued, the rate of growth of biacetyl emission decreased, as did the relative size of the fluctuations.

Fluctuations were sometimes observed in the acetone emission, at 410 nm, although these fluctuations were much smaller than those of biacetyl. On those occasions when regular fluctuations were observed, it was found that the emission fluctuations of acetone were 180° out of phase with those of biacetyl. This is evident in curves b and c of Figure 2, which show traces obtained on a chart recorder for samples, excited at 310 nm, with the emission monochromator set first on the biacetyl emission and then on the acetone emission. The recorder was left running while the emission wavelength was being changed. The discontinuities result from changing the monochromator setting and the instrumental sensitivity. The fact that the emission of the two species is out of phase suggests that the fluctuations in the acetone emission are due to fluctuations in the concentration of biacetyl rather than to variations in the concentration of some other quenching species.

During the above measurements, the stability of the spectrophotometer was checked periodically using a nondegassed solution of 1,1′-binaphthyl. No fluctuations were observed in the emission from this solution. In addition, it was found that for acetone solutions which displayed regular fluctuations, the period of the fluctuations decreased on warming the solutions, and increased on cooling. These experiments indicate that the oscillatory phenomena are real rather than being instrumental artifacts.

The design of the fluorescence spectrophotometer is such that only a small portion of a solution is illuminated. A cell was designed with a bulbous bottom containing a Teflon coated magnetic stirring bar. When degassed acetone solutions were illuminated in this cell, fluctuations were observed, at 515 nm as long as the solution was not stirred. When stirring was begun the emission intensity at 515 nm decreased and the fluctuations ceased. This may indicate that the fluctuations are dependent on high local concentrations rather than on overall bulk concentrations.[11]

Ross and co-workers[12,13] have examined the possibility of oscillations in illuminated systems. It is not known at this point whether Ross's model systems are comparable to the acetone-biacetyl system. Reaction mechanisms that give oscillatory behavior require that the system be "open" in that reactants are taken from a large reservoir, that the system be far from equilibrium, and that the mechanism contains either a feedback step or an autocatalytic step.[1] A rough calculation using the Stern-Volmer equation[10] shows that these acetone solutions do constitute an open system. That is, if one assumes that the phosphorescence lifetime of acetone in solution, in the absence of biacetyl, is of the order of microseconds,[6,9] and that biacetyl quenches acetone phosphorescence at a diffusion controlled rate,[10] then in order to quench 10% of the acetone phosphorescence the biacetyl concentration need be only of the order of 10^{-5} M. Since the average emission intensity at 410 nm does not decrease during the period that biacetyl fluctuations are being observed, the acetone can be thought of as a reservoir for the production of biacetyl.[14]

The feedback or autocatalytic step, necessary for oscillations, is not known, although the quenching of acetone by biacetyl might be thought of as feedback. The possible reactions involve both free radicals and hydrogen abstraction from acetone and biacetyl. The acetonitrile probably does not enter into the reaction mechanism, since Porter et al. did not observe any incorporation of deuterium into acetone when acetone was irradiated in CD_3CN.[9]

Data for photolyzed acetone and for photolyzed biacetyl are available both in the gas phase[15,16] and in solution,[8,17-20] but before a mechanism can be proposed with any confidence work must be done to identify the photoproducts, in acetonitrile, after only a small amount of photoreaction.

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Gas Phase Dioxetane Chemistry. Formaldehyde (A → X) Chemiluminescence from the Reaction of $O_2(^1\Delta_g)$ with Ethylene

Sir:

The reactions of $O_2(^1\Delta_g)$ with olefins have been studied extensively in recent years.[1,2] Various substituted monoolefins which are incapable of undergoing the "ene" reaction (yielding an allylic hydroperoxide) have been shown to produce 1,2-dioxetanes or their expected fragmentation products, upon reaction with $O_2(^1\Delta_g)$.[1e-g,2] It has recently been noted that,[3] "the reaction of singlet oxygen with ethylene, although not yet experimentally observed, is of special interest because it provides the simplest example of a 1,2-cycloaddition of oxygen with no competing side reactions." We report the observation of formaldehyde (A $^1A_2 \rightarrow$ X $^1A_1$) chemiluminescence from the gas phase reaction of ethylene with $O_2(^1\Delta)$. No other product emissions were observed, and the formaldehyde emission intensity was found to have a first-order dependence on the concentrations of both $O_2(^1\Delta)$ and ethylene.

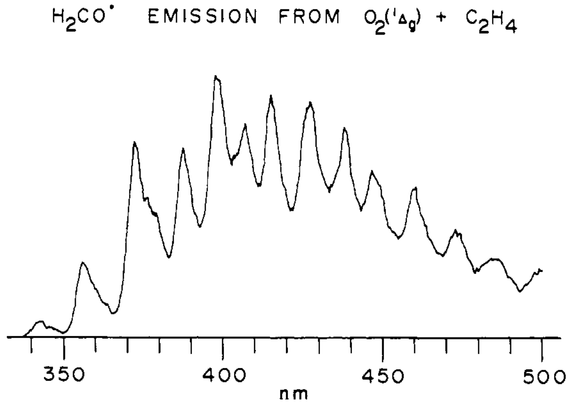

Figure 1. Formaldehyde (A–X) emission spectrum from the reaction of $O_2(^1\Delta_g)$ with ethylene. Experimental conditions: P_{total} = 4 Torr, T = 650 K, $[C_2H_4] \approx [O_2(^1\Delta_g)] \approx 2 \times 10^{15}$ molecules/cm^3; spectrometer conditions: spectral slit width = 2 nm, grating of 2360 lines/mm and blazed at 300 nm, peak intensity ≈500 counts/s, scan speed = 12.5 nm/min, time constant = 3 s.

We have previously observed formaldehyde chemiluminescence from the gas phase reactions of $O_2(^1\Delta)$ with methyl, ethyl, and *n*-butyl vinyl ethers.[4,5] Both previous and present experiments were performed at pressures of 1–10 Torr and reactor residence times of <0.5 s, conditions which minimize the effects of quenching and energy transfer processes hence allowing the observation of chemiluminescence from the primary excited products.

The experimental techniques and apparatus used for this work were the same as previously described,[4] with the following minor changes. Radiation emitted from a heated Pyrex flow reactor of 30 cm path length (viewed axially) was focused through a quartz window into a ¼ m f/3.5 grating spectrometer. The detector was an S-5 photomultiplier operated at −78 °C, and single photon counting was used, as before.

The chemiluminescence spectrum shown in Figure 1 consists solely of formaldehyde (A $^1A_2 \rightarrow$ X $^1A_1$) emission, and is very similar to formaldehyde emission spectra previously observed in this laboratory.[4-6] The small hot band peaking at 343 nm is relatively ca. three times more intense than previously observed for the vinyl ether reactions. The most satisfactory assignment for this band is the vibrational transition 4_0^3 within the electronic ($^1A_2 \rightarrow {}^1A_1$) transition[7,8] ($\nu_4$ is the out-of-plane bending vibration). Excitation in ν_4' which has B_1 symmetry, allows the electronically forbidden ($^1A_2 \rightarrow {}^1A_1$) transition to become vibronically allowed and to borrow intensity from the electronically allowed (B $^1B_2 \rightarrow$ X $^1A_1$) Rydberg transition.[8] Furthermore, it is to be expected that the initially formed excited product arising from dioxetane fragmentation will have excitation in ν_4'. This is because a rapid fragmentation (see discussion below) will be governed by essentially Franck–Condon considerations[9] and the principal difference between the geometry of the free H_2CO^* ($^1A_2$) and the H_2CO group in dioxetane is in the out-of-plane bending angle.[8,12]

While the observation of formaldehyde emission in the reaction of ethylene with $O_2(^1\Delta)$ is convincing evidence for the presence of the unobserved (directly) dioxetane adduct,[15] further support for our mechanism comes from the first-order test plots shown in Figure 2. The data for Figure 2 were obtained by monitoring the oxygen dimol emission at