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Thin-Film Optical Spectroscopic Investigations of 1-Alkyl-2-(carbomethoxy)- and 2-Acetylpyridinyl Radical Monomers and Dimers

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Abstract: A surprisingly versatile new apparatus for the investigation of the optical properties of thin films at temperatures ranging from 77 to 577 K and over the wavelength range of 200 to 6200 nm is described. The properties of 1-alkyl-2-(carbomethoxy)- and 1-alkyl-2-acetylpyridinyl radicals [**2·** and (CH$_3$CO)**2·**] in thin films as determined with the apparatus are reported, including UV, visible, and IR spectra (from 210 to 6200 nm) of both monomers (**2·**) and dimers (**2–2**), temperature effects on the formation of dimers from monomers, photodissociation of the dimers to monomers, and temperature effects on the absorption spectra of the dimers. Radical properties in thin films are analyzed. The near UV and visible absorption in the radical dimers is identified as a π–σ to π–σ^* transition. A scheme relating dimers, π-mers, singlet and triplet radical pairs, and monomers is presented for 1-alkyl-2-substituted-pyridinyl radicals, along with a more general formulation for other radicals. Other applications of thin-film spectroscopy are pointed out.

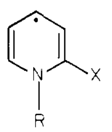
During the investigation of 1-alkyl-2-(carbomethoxy)pyridinyl radicals (**2·**), the necessity for measuring the spectroscopic properties of the blue film initially formed through distillation of the radicals became evident.[2] Since the usual methods did not seem convenient,[3] we constructed an apparatus for our specific need, that of measuring an absorption spectrum quantitatively for a film at 77 K. We then found that the apparatus was versatile and useful, not only for pyridinyl radicals but also for obtaining quantitative spectroscopic data on pyrolysis products and for studying solid-state rearrangements in which there is an observable spectroscopic change.[4]

So that others may benefit from our experience, we give a fair amount of detail on the construction and operation of the apparatus in the Experimental Section. Studies carried out with 1-alkyl-2-(carbomethoxy)pyridinyls and the 1-methyl-2-acetylpyridinyl radical in thin films are reported; the behavior of 1-alkyl-4-(carboalkoxy)pyridinyls will be described in the following article.[5] Previous studies on pyridinyl radicals have been summarized elsewhere.[6,7]

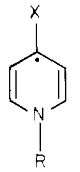
Results

Thin-Film Spectroscopy. The blue film produced by distillation of a 1-alkyl-2-(carbomethoxy)pyridinyl radical, **2·** onto a 77 K surface, disappears on warming. For measurement of the spectrum of the blue material, a technique was needed for the quantitative study of spectroscopic properties of unstable compounds. Trapping unstable materials from a gas stream on a window mounted on a copper cooling bar connected to a liquid nitrogen cooled Dewar seemed to us too awkward and inflexible. In order that (a) the condensing surface could be cooled directly (temperature could then be manipulated without delay) and (b) the amount of material deposited and the rate of deposition on the surface could be followed interferometrically, the apparatus depicted in Figure 1 was constructed. Sapphire was an optically transparent (200–6200 nm), thermally conductive substance available in the required optical form. Glueing the optical windows to their bases made them easy to replace and repair, and the glue obviated possible difficulties from differences in thermal conductivities and coefficients of expansion of the glass and the window. The sapphire window was glued to the ground surface of a hollow torus which carried the coolant, assuring good temperature control of the sample. The thickness of the films deposited on the sapphire was measured with a interferometer made from light-emitting diode and two photodiodes, using the number and shape of interference fringes and the wavelength of the light (890 nm).

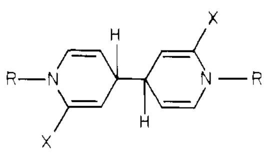
The apparatus has proven to be extremely useful for studies of thin films of viscous liquids and glassy and organized solids over a wide range of temperatures, from 77 to 577 K. With simple adaptors, the apparatus may be placed in an ultraviolet-visible spectrophotometer, a spectrofluorimeter, and an IR spectrometer. It is small enough (weight, 200–300 g) to be carried around in one hand. Additional details on its construction and operation are given in the Experimental Section.



2·



4·



2–2

X = COOCH$_3$, except where noted as (X)n·

Behavior of 1-Methyl-2-(carbomethoxy)pyridinyl Radical (2·) and Its Dimer (2-2) in Thin Films. Spectra of blue films of **2·** on the sapphire window are shown in Figure 2. The ultraviolet absorption [λ_{max}, ϵ_{max}: 294 (8400), 345 nm (3600)] is similar to that for the 1-methyl-2-carbamidopyridinyl radical in water (λ_{max} 307 and 365 nm).[8] The beautiful blue color (λ_{max} 645 nm, ϵ_{max} 2000) of the 77 K films is lost on warming the condensate from 77 K to ca. −160 °C along with some loss of the UV radical absorption bands. Further absorption decreases occur on warming (Figure 2) from −160 to −90 °C, the radical absorption being

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[1] (a) Tel-Aviv University; (b) State University of New York.

[2] Hermolin, J.; Levin, M.; Ikegami, Y.; Sawayanagi, M.; Kosower, E. M., preceding article in this issue.

[3] The infrared spectrum of 1-ethyl-4-(carbomethoxy)pyridinyl radical was measured for radical deposited on a KBr window connected through a copper bar to a 77 K Dewar. The experiment was not simple and did not yield absorption coefficients. The spectrum is reported by Kosower, E. M.; Poziomek, E. J. *J. Am. Chem. Soc.* **1964**, *86*, 5515.

[4] Kosower, E. M.; Hermolin, J.; Ben-Shoshan, M.; Faust, D., submitted for publication.

[5] Hermolin, J.; Levin, M.; Kosower, E. M., following paper in this issue.

[6] The subject of pyridinyl radicals is reviewed by Kosower, E. M. In "Free Radicals in Biology"; Pryor, W. A., Ed., Academic Press: New York, 1976; Vol. 2, Chapter 1.

[7] (a) Kosower, E. M. *ACS Symp. Ser.* **1978**, *No. 69*, 447–456; (b) Kosower, E. M.; Waits, H. P.; Teuerstein, A.; Butler, L. C., *J. Org. Chem.* **1978**, *43*, 800.

[8] Kosower, E. M.; Land, E. J.; Swallow, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 986–987.

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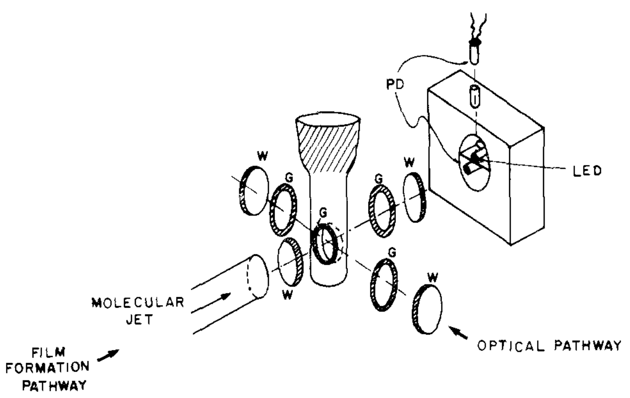

Figure 1. Exploded view of the thin-film spectroscopy apparatus, showing the relative positions of the optical cooling surface, the interferometer, the optical pathway for measurement, and the material source for the film. The labels are as follows: W, window (polished quartz or sapphire); G, ground surface onto which windows are glued; LED, light emitting diode; PD, photodiode.

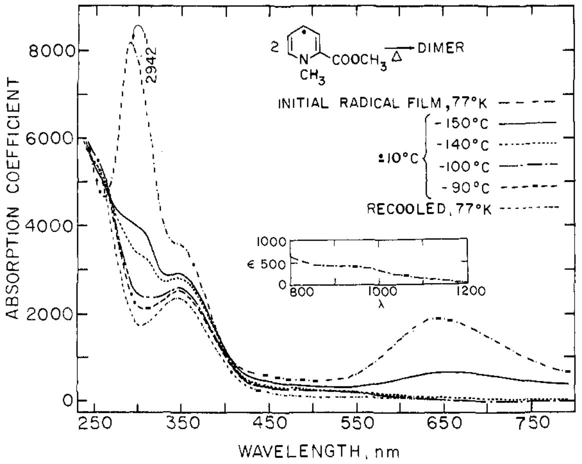

Figure 2. Annealing sequence for 1-methyl-2-(carbomethoxy)pyridinyl radical (**2**·). The spectrum of **2**· (230–1200 nm) in a thin film at 77 K is the "initial radical film". π-mer (**2**·,**2**·) (π complex) absorption at 645 nm overlies the weak monomeric radical absorption in the same wavelength region. At −150 °C, the visible absorption disappears, and both UV bands decrease in intensity. The characteristic radical bands are lost at still higher temperatures, replaced by the specrum of the radical dimer (**2**-**2**). Successive spectra for −140, −100, and −90 °C are shown, with the last repeated after cooling to 77 K.

replaced by a broad, low intensity band [λ_{max} (ϵ_{max})] 345 nm (2400) extending well past 450 nm, with a shoulder at 245 nm.

Spectra resulting from a different annealing sequence are shown in Figure 3. The 345-nm band decreases in intensity and moves toward shorter wavelengths over the range from −113 to −8 °C accompanied by an increase in the 245-nm shoulder. Further warming[9] produces only minor changes, the final spectrum having a maximum at 340 nm (1900) (ϵ_{max} 3800 for dimer) and an ϵ at 245 nm of 7000 (ϵ 14 000 for dimer) (**2**-**2** radical dimer in acetonitrile, λ_{max} 332 nm (2000), ϵ (245 nm) 10 000).[2]

Recooling the film to 77 K does not change the spectrum of the annealed film;[10] the transformation by annealing of the radical **2**· to the dimer **2**-**2** is not reversible by cooling. The blue color (i.e., absorption at 645 nm) is due to a π-mer (self-complex) or **2**· like that found for **4**·.[11]

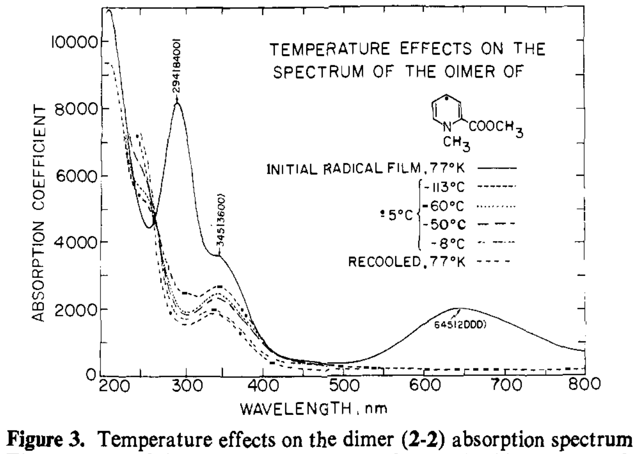

Figure 3. Temperature effects on the dimer (**2**-**2**) absorption spectrum. The spectrum of the radical **2**· from 220 to 800 nm in thin film at 77 K is given (800–1200 nm not shown). At −113 °C, almost pure dimer is present. At −60 °C, the maximum is at 345 nm. Further temperature increases (up to −8 °C) shift the maximum gradually to 340 nm and decrease the intensity, the final spectrum being taken after recooling to 77 K.

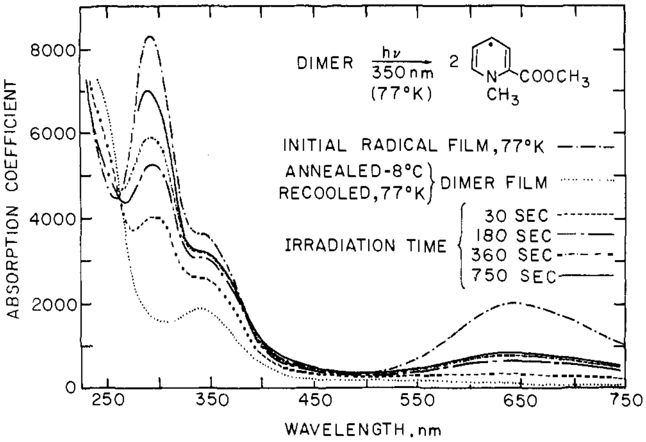

Figure 4. Photodissociation of 1-methyl-2-(carbomethoxy)pyridinyl dimer (**2**-**2**) to the monomeric radical, **2**·. After annealing a thin film of **2**· at −8 °C and then cooling to 77 K, irradiation at 350 nm for 30, 180, 360, and 750 s produces rapid formation of radical **2**· and some π-mer.

Photochemical Changes. Irradiation (300–450 nm) of the cold (77 K) annealed film (a film that had been warmed until the initial spectrum had been completely lost and then recooled) regenerates somewhat broadened spectra like that of the initially "plated" film[12] (Figure 4), except that only about 50% of the 645-nm band was regained ($\epsilon_{initial}$ ~2000). The higher the annealing temperature, the lower the intensity of the regenerated visible band, no visible band being observed in the limit. A film with OD at 645 nm = 0.32 gave, after annealing at −70 °C and 42 min irradiation at 390 nm, a film with OD at 645 nm = 0.14. Another film (OD 0.21 at 645 nm) was annealed at 45 °C but gave no absorption at 645 nm after irradiation for 35 min at 350 nm.

Irradiation increased the ultraviolet absorption of **2**· somewhat before that at 645 nm. The quantum yield (irradiation between 300 and 400 nm) for photodissociation was about 0.07. Further irradiation increased absorption at both 645 and 300 nm, with 290-nm absorption appearing on annealing. The unknown 290-nm photoproduct was formed in a low quantum yield and was not further investigated.

Similar responses to irradiation were found for thin films of 1-ethyl- and 1-isopropyl-2-(carbomethoxy)pyridinyl radicals, which have, however, lower absorption coefficients at 645 nm (ϵ 1500–2000).

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(9) (a) The normally volatile radical does not vaporize rapidly from the window in the sealed off thin-film apparatus because of its own vapor pressure and the lack of an alternative condensing surface. (b) The pure radical dimer (**2**-**2**) is apparently viscous enough not to flow until temperatures as high as 45 °C, but its fluidity is increased by the presence of impurities or residual solvent and, thus, the maximum temperature which could be attained for observation varied from −20 °C to the above mentioned 45 °C.

(10) Annealing is used here in the sense of a warming process which relieves physical and/or chemical "strain".

(11) Itoh, M.; Nagakura, S. *J. Am. Chem. Soc.* **1967**, *89*, 3959–3965.

(12) "Plating" is a brief way of referring to the process of depositing a thin film on the sapphire window of the thin-film spectroscopic apparatus. A plate is defined as a smooth, flat piece of any material, thin or of uniform thickness.

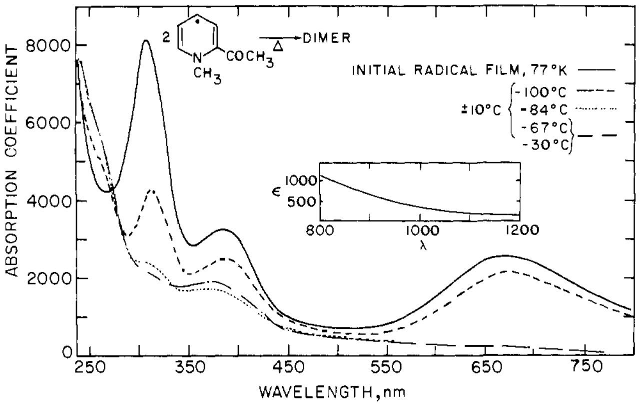
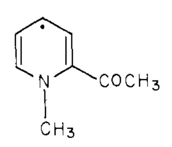


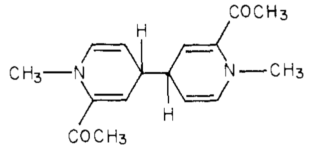
Figure 5. Annealing a thin film of 1-methyl-2-acetylpyridinyl radical [(CH_3CO)**2**·]. The radical spectrum from 240 to 1200 nm in a thin film at 77 K is shown; at ~−100 °C, there is >50% loss of ultraviolet absorption along with <25% loss in the visible. At 84 °C, the visible absorption is lost, and at −67 °C (or at −30 °C), radical absorption in the ultraviolet disappears, the spectrum now exhibiting the characteristic broad UV–vis absorption of the radical dimer, (CH_3CO)**2**-(CH_3CO)**2**.

A more subtle photochemical change was noted by careful examination of the ratio of the 300- and 350-nm absorption changes resulting from irradiation. For example, the height at the 295-nm peak should be 15.5 cm to correspond to the 2.5-cm increase noted at 350 nm, provided that the latter were due only to loss of dimer and gain of radical during a 30-s irradiation. The height increase was 14.2 cm, a discrepancy of 9%, much more than the experimental error. Thus, the increase at 350 nm includes also an increase in dimer absorption coefficient. Similar observations were made for other samples of **2**-**2** and for (CH_3CO)-**2**-(CH_3CO)**2**. Irradiation of the latter at 500 nm showed no discrepancy in absorption changes, but irradiation at shorter wavelengths produced changes suggesting an increased dimer absorption coefficient.

Behavior of 1-Methyl-2-acetylpyridinyl Radical in Thin Films. The green film formed by distillation of the 1-methyl-2-acetylpyridinyl [(CH_3CO)**2**·] radical[2] has maxima at 310 (8100), 390 (3200), and 680 nm (2600). Warming the film to −120 °C causes very little change, but at −90 °C dramatic changes are seen. At 70 °C, the spectrum of (CH_3CO)**2**· is very similar to that of an annealed film of **2**· [260 (5300) (sh), 310 (1800) (sh), λ_{max} 375 nm (1800) (broad, extends well past 600 nm)] (Figure 5). Warming to 10 °C[13] causes an increase in intensity at 260 nm (5900), the loss of the 310-nm shoulder, and a shift of the 375-nm absorption maximum to 370 nm. The spectrum of the annealed film is assigned to the radical dimer [(CH_3CO)**2**-(CH_3CO)**2**] in view of the similarity of the spectroscopic changes to those noted on the transformation of **2**· into **2**-**2**. Recooling the film to 77 K does not change the spectrum appreciably, as found for annealed films of **2**· and ascribed to the stability of **2**-**2**.



(CH_3CO)**2**·



(CH_3CO)**2**-(CH_3CO)**2**

Photochemical Changes in Thin Films of the 2-Acetylpyridinyl Dimer. Irradiation (300–500 nm) at 77 K of the dimer film formed by annealing produces films exhibiting the (CH_3CO)**2**· spectrum. Repetition of the cycle (annealing, photodissociation) could be carried out many times (in one case, 20 times over a period of 12 h). There was no sign of irreversible thermal or photochemical change under our conditions.

Irradiation at 500 nm, for example, leads only to some small changes in position (314 nm rather than 310 nm, 394 nm rather than 390 nm, 680 nm no change). Almost all (>98%) of the ultraviolet absorption can be regenerated along with over 90% of the visible absorption band. The quantum yield for the photodissociation process is almost constant at ~0.5 from 300 to 400 nm. The yields decrease at longer wavelengths as follows: 425 (~0.25), 450 (~0.05), 500 nm (~0.004).

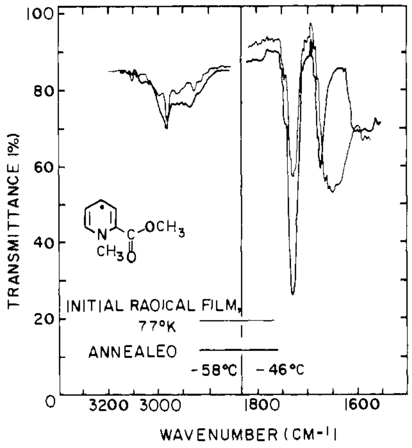


Figure 6. Infrared spectra of 1-methyl-2-(carbomethoxy)pyridinyl radical, illustrating the changes on annealing a 1.5–2.0-μm film at 77 K to between −58 and −46 °C.

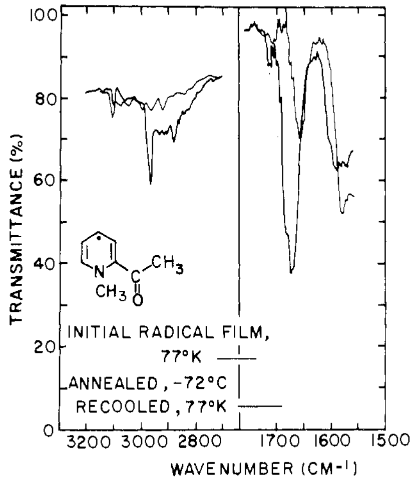


Figure 7. Infrared spectra of 1-methyl-2-acetylpyridinyl radical [(CH_3CO)**2**·] showing the changes on annealing a 1.5–2.0-μm film at 77 K at −72 °C (recooled to 77 K for spectrum).

Infrared Spectra. External sapphire windows on the thin-film apparatus permits spectra to be measured at wavelengths as long as ~6200 nm. Since IR absorption coefficients are much lower than those in the visible or ultraviolet regions, the thin films had to be about 10–15 times as thick (~1.5–2.0 μm instead of 0.1–0.2 μm) as those used for UV-vis spectra.[14]

The IR spectrum (between 3300 and 1570 cm^{-1}) of a film of 1-methyl-2-(carbomethoxy)pyridinyl radical (**2**·) plated at 77 K has maxima corresponding to C–H stretching, C=O stretching, and C=C stretching vibrations. Annealing between −60 and −40 °C changes the IR spectrum. There is a ~25% increase in intensity in the C–H stretch region, a 100% increase of intensity in the C=O region, and ~60% loss of intensity of the C=C stretch region, the latter change connected with the replacement of a broad band by a sharp band and an intermediate strength broad band (see Figure 6). The IR spectrum of a film of (CH_3CO)**2**· plated at 77 K changes markedly on annealing in the region of the C–H, C=O, and C=C stretching vibrations (Figure 7). Photolysis of the annealed films causes the spectra to revert to that observed for the initially plated film (not shown). To

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(13) Footnote 9b is applicable here over a lower temperature range.

(14) The use of a Fourier transform spectrometer would make it possible to use the same film for the measurement of spectra in the wavelength range from 200 to 6200 nm.

simplify comparison of the maxima for the initially plated radical films with those for the annealed films, the positions of the bands are listed in Table I.

Discussion

In the preceding article, we described the reason for designing the thin film spectroscopy apparatus.[2] Free radicals of sufficient stability (persistence depends upon reactivity, concentration, temperature, viscosity) can be studied in pure form in thin films. Unsuspected properties appear under these conditions, of which the most striking is the formation of unstable covalent dimers. Our thin-film spectroscopy apparatus simplifies experiments on such highly reactive species, especially those involving temperature control or irradiation. For example, photolysis of the dimers readily yields the monomers even in the concentrated form in which the molecules are found in thin films. The spectroscopic measurements can be done in a quantitative way at a specific temperature, since the quantity present in the film is known. The recovery of the material in the thin film as a solution without exposure to air is possible and represents an additional virtue of the apparatus design and a valuable check on the overall success of a particular experiment.

Components of the 2· System. The species of the **2·** radical system include the following: the monomeric radical, **2·**; the radical dimer, **2-2** (in two forms, s-cis and s-trans); the radical π-mer, **2·,2·**; a singlet pair, ^{1}**2·,2·**; and the triplet pair, ^{3}**2·,2·**. The thin-film spectrum of **2·** shows the UV expected for a pyridinyl radical and also a visible π-mer (π complex) absorption (645 nm) due to a charge-transfer transition, almost the same as the π-mer absorption of **4·** (630–640 nm) in thin films.[5] The thin-film π-mer absorption of the 2-acetylpyridinyl radical appears at 680 nm.

Electronic Transitions in Pyridinyl Radical Dimers. At first sight, the 332-nm absorption observed for the dimer (**2-2**) in solution resembled that expected for a 1,4-dihydropyridine.[15] However, the intensity, position, band shape, response to irradiation, and variability in position were unusual.

First, the intensity was extremely low in comparison with that for other 1,4-dihydropyridines (ϵ_{max} 2000 vs. 12 000 for two dihydropyridine rings). Second, its position was quite strange, since the 2-substituent is cross-conjugated and not conjugated with the π system as in the case of 3-substituted dihydropyridines. A 6,6′ structure was rejected on other grounds;[2] in addition, the absorption spectra of 6,6′ dimers should exhibit three bands, including one between 250 and 300 nm.[15a] Such absorption has not been observed for any of the dimers we have examined. Third, the absorption band at 332 nm in solution was unusually broad, with appreciable intensity well past 400 nm. In the thin film, the breadth of the absorption bands due to the dimers was even greater, extending well past 450 nm for **2-2** and past 600 nm for (CH_3CO)**2**-(CH_3CO)**2**.

Fourth, irradiation of **2·** in the absorption band produced dissociation of the dimer into the monomeric free radical, persistent in the thin film at 77 K but reverting rapidly to dimer in solution.[2,8,19] Fifth, the dimer absorption was apparently quite sensitive in intensity and position to the geometry around the single bond connecting the two pyridinyl rings, the absorption intensity being higher in the s-cis form.

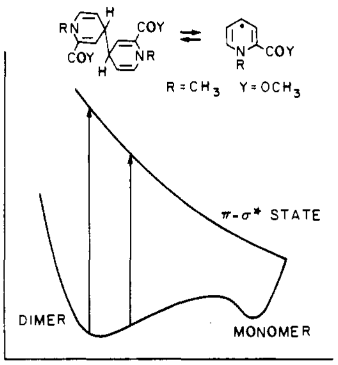

Figure 8. An energy vs. reaction coordinate diagram illustrating the relationship between the **2·** monomer, the **2-2** dimer, and the excited state resulting from the π–σ → π–σ^* electronic transition. The observed spectra vary with the particular radical and its local environment. For 1-alkyl-2-(carbomethoxy)pyridinyl radical, the dimer is the predominant form in solution and in the annealed thin film. For the 2-acetylpyridinyl radical, the monomer is predominant in solution, but the dimer is the chief component of annealed thin films.

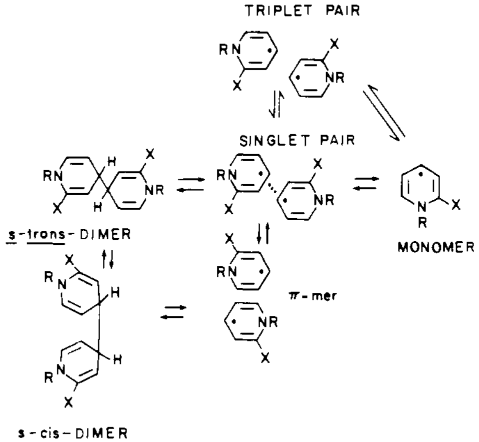

Figure 9. A scheme illustrating the species identified as components of the **2·** radical system. Two forms (s-cis and s-trans) of the pyridinyl radical dimer are proposed because photolysis of dimers annealed at low temperatures yield π-mer, and dimer annealed at high temperatures does not yield π-mer, although all dimers yield pyridinyl radical.

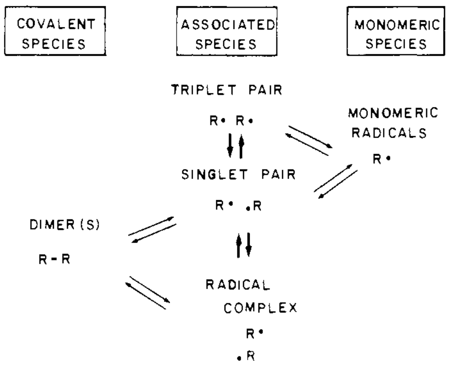

Figure 10. A generalized scheme illustrating the species that might be expected in thin films and concentrated solutions of radicals.

These points suggest an assignment of the absorption to a π–σ → π–σ^* transition. Orbital level schemes (not illustrated) for the radical dimer and a radical pair show (a) that both photodissociation and thermal dissociation are allowed and (b) that the highest bonding level in the dimer, the σ bond between the radicals, can conjugate with both π systems of the dimer. "Through-bond" interaction (i.e., conjugation between π orbitals mediated by σ bonds and first reported by Cookson et al.[20]) probably occurs in many molecules and affects both chemical (e.g., fragmentation[21]) and spectroscopic properties.[22-24] The theory of Hoffmann et

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(15) (a) Eisner, U.; Kuthan, J. *Chem. Rev.* **1972**, *72*, 1: (b) Biellmann, J.; Lapinte, C. *Tetrahedron Lett.* **1978**, 683–686; (c) Carelli, V.; Liberatore, F.; Casini, A.; Mondelli, R.; Arnone, A.; Carelli, I.; Rotilio, G.; Mavelli, I. *Bioorg.* Chem. **1980**, *9*, 342–351.

(16) Bellamy, L. J., "The Infrared Spectra of Complex Molecules", 3rd ed.; Chapman and Hall: London, 1975.

(17) 1,5-Diazabicyclo[3.3.0]octadienediones. Cf. Kosower, E. M.; Pazhenchevsky, B. *J. Am. Chem. Soc.* **1980**, *102*, 4983–4993.

(18) The density of the film was estimated as follows. Kosower and Poziomek (ref 3) measured the density of 1-ethyl-4-(carbomethoxy)pyridinyl radical directly as 0.85 at 20 °C. Judging from the density change of CH_3CN as a function of temperature, it is estimated that the density of the pyridinyl radical at 77 K on the window would be ~1.0.

(19) Hermolin, J.; Kirowa-Eisner, E.; Kosower, E. M. *J. Am. Chem. Soc.* **1981**, *103*, 1591–1593.

(20) Cookson, R. C.; Henstock, J.; Hudec, J. *J. Am. Chem. Soc.* **1966**, *88*, 1060.

(21) Grob, C. A. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 535–546.

Table I. Infrared Absorption Bands of 2-Substituted Pyridinyl Radicals and Their Dimers

maxima, cm^{-1}			
2·[a]	**2-2**[b]	(CH_3CO)**2·**[a]	(CH_3CO)2-(CH_3CO)2[b]
3100	3100	3105	3105
3080		3080	3080
	3060	3050	
		2998	
2990			2970
		2960	2932
2919		2920	2918
2879	2882	2880	2883
2850	2865	2840	2863
2830s			
1728	1730		
			1692
		1685	1685
		1680	1680
1663	1672	1665	1672
1655			
1650			
1630			
		1590	1590
			1580
			1570

[a] Thin film plated at 77 K. [b] Annealed films: **2·**, −50 to −43 °C; (CH_3CO)**2·**, −59 °C.

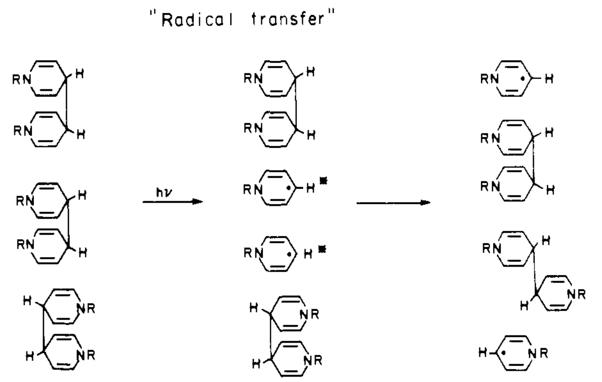


Figure 11. "Radical transfer". The photolysis of pyridinyl radical dimers formed by annealing at low temperatures produces radicals before π-mers, i.e., radicals that are not in proximity even though π-mer formation should be favored in the film at 77 K. A postulated transport process involves the reaction of the "hot" radicals (excess energy, ~30 kcal mol^{-1} monomer^{-1}) with neighboring dimers. New dimers, one moiety from the "hot" radical and the other from the reacted dimer, are produced. The radicals that remain are now separated by two dimer molecules. The mechanism is the radical analogy of the well-known Grotthus mechanism for the mobility of protons through hydrogen-bonded solvents.

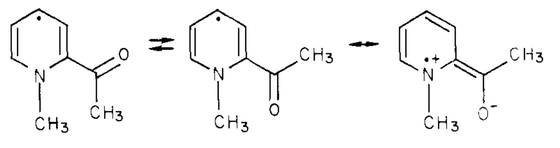
al.[25] for the interaction has been extended by Gleiter.[26]

The pyridinyl radical absorptions represent excellent examples of the interaction; the photodissociation of the dimers to radicals is an example of a photochemical consequence of the "through-bond" interaction. An analysis of the spectrum of dimers of **3·** (e.g., 1-methyl-3-(carbomethoxy)pyridinyl) led to experiments in which a photodissociation spectrum for **3-3** was matched to the dimer absorption band.[19] An energy vs. reaction coordinate diagram for dimer and monomer (Figure 8) implies that π–$\sigma \rightarrow \pi$–σ^* transitions should be broad and temperature sensitive.

A general scheme for pyridinyl radicals is shown in Figure 9 and includes the following species: s-cis and s-trans dimers, singlet pairs, π-mers, triplet pairs, and monomers. An unusual, long wavelength absorption and facile photodissociation will characterize the dimers. The monomeric radicals will form complexes and pairs of various kinds. The singlet complexes (π-mers) will exhibit a charge-transfer absorption band. Under some conditions, singlet pairs and triplet pairs may be present. A general radical scheme is given in Figure 10.

Infrared Spectra. The infrared spectra of the pyridinyl radicals **2·** and (CH_3CO)**2·** in thin films change on warming. The ester methyl group should be relatively unaffected by dimerization; a pair of bands is present for both monomer and dimer. (Methyl groups are characterized by a pair of bands, corresponding to the asymmetrical and symmetrical stretching motions.[16]) However, a weak absorption, the *N*-methyl group stretch, which occurs at slightly shorter wavelengths (2990 cm^{-1}) than the ester methyl band, becomes a strong shoulder in the dimer spectrum. The methyl group bands of the 2-acetylpyridinyl radical are a little more complex, possibly due to two equivalent conformations of the 2-acetyl group. Only one of the three pairs of methyl group bands, that due to the *N*-methyl group, increases strongly in intensity on dimerization.

The intensity increase of the *N*-methyl stretch can be related to the observation that such absorptions are often weaker in methyl groups attached to electronegative atoms.[16] Spin density on the nitrogen in the pyridinyl radical reflects a positive charge; dimerization of the radical would diminish the transfer of charge into another group, as shown with resonance forms.



(CH_3CO)2· forms

IR absorptions due to double-bond stretching motions (1663 and 1655 cm^{-1}) change on dimerization. In the dimer, an absorption for an isolated double bond appears on dimerization and that assigned to a conjugated double bond (see the formula for **2-2**) moves to longer wavelengths and becomes unobservable (sapphire optics). The carbonyl and double-bond stretching bands in the IR spectrum of the 2-acetyl radical overlap and have not been analyzed.

Nature of Dimers in Thin Films. The weaker the pyridinyl-pyridinyl bond, the longer the wavelength and the broader the shape that should be found for the dimer absorption (see Figure 8). Dimer absorption is influenced by the environment of the molecule, probably an effect on the geometry of the dimer. Since the π-mer reappears on irradiation of dimers annealed at low temperatures and not from those annealed at high temperatures, the first dimer formed may be face-to-face (i.e., s-cis). At higher temperatures, the medium (the radical itself) becomes less viscous, and the dimers can rotate more freely. The dimer produced at high temperatures is s-trans and, if irradiated in a viscous medium (the dimer thin film at 77 K), does not form the π-mer. Since the dimer absorption maximum shifts to shorter wavelengths at higher temperatures for thin films, we infer an s-trans structure for the dimer in solution.

On irradiation of the dimer, radical absorption reappears somewhat before that of the π-mer. Photodissociation of an s-cis dimer produces two energetic monomeric radicals (excess energy ~30 kcal mol^{-1} monomer^{-1} at 400 nm). Collision with neighboring dimers produces two new dimers, one from each "hot" radical and two new monomeric pyridinyl radicals, separated by two dimer molecules. As the extent of dissociation of the dimer increases, the chance of the "radical transfer" process decreases, and, eventually, π-mers will form directly with neighboring radical molecules. The "radical transfer" process (Figure 11) is related to the classical Grotthus proton transfer mechanism in water and several other strong acids.

The quantum yield of photolysis does not vary from 300 to 400 nm, where both dimer and radical absorb. The excess of energy

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over that required for dissociation is dissipated in the radical-transfer process described above. Even though dimer is replaced by monomer during irradiation, the rate of radical formation not fall off. Although overlap of the dimer and monomer absorption prevents analysis, it appears that dimer dissociation is produced through light absorption by the radical.

Formation of π-mer. The striking blue or green color of new thin films (77 K) of 1-methyl-2-(carbomethoxy)- and 2-acetylpyridinyl radicals is due to π-mers, involving most of the pyridinyl radicals. Extrapolating from the rate constants[2] for dimer dissociation (1 s^{-1}) and radical dimerization (10^5–10^6 M^{-1} s^{-1}) at 20 °C, interconversion of dimer and monomer at low temperatures in thin films would be relatively slow. π-mer formation should be faster since much less bond rearrangement and bond stretching is required. Thermal equilibration of the molecules impinging on the cold surface is evidently faster than dimerization but slower than π-merization.

Photolysis of the dimer of the 2-acetylpyridinyl radical leads to the same proportion of π-mer as obtained in the initial plating process, whereas photolysis of the 2-(carbomethoxy)pyridinyl radical may, after appropriate annealing, give no π-mer. The ester radical is probably more dense and therefore more viscous than the acetylpyridinyl radical, thus inhibiting the motions that would allow formation of the π-mer. A local viscosity difference between the 2-acetylpyridinyl and 2-(carbomethoxy)pyridinyl radicals was used to explain the broader triplet spectrum of the former.[2]

The dimer absorption coefficient appears to increase during the initial stages of photolysis. The initially formed dimer ("high" absorption coefficient) reverts to π-mer more readily on irradiation than the dimer ("low" absorption coefficient) formed after high-temperature annealing. The s-cis dimer thus has a higher absorption coefficient than the s-trans dimer. The radical transfer mechanism could account for the absorption coefficient increase if the s-cis dimer were formed at the expense of the s-trans dimer by the reaction of monomeric radical with a mixture of isomeric dimers.

Other Applications of Thin-Film Spectroscopy. A wide variety of materials can be plated on the sapphire window. Structural rearrangements[4] in bimane[17] crystals, collection of sulfone pyrolysis products for spectroscopic examination without transfer, high-temperature effects (577 K) on UV–vis absorption spectra, and fluorescence spectra of solids are among the experiments that have been carried out with the thin-film spectroscopic apparatus.

Conclusion

Readily dimerizable pyridinyl radicals can be investigated in pure form in low-temperature thin films by using a specially designed spectroscopic apparatus.

Experimental Section

Vacuum line techniques, materials, and solvents have already been described.[2] Pressure was 10^{-6} torr or less, and the system was normally pumped for up to 12 h to ensure degassed surfaces, which were flamed where practical.

Instrumentation. UV–vis spectra were recorded on a Cary Model 17 spectrophotometer, IR spectra were recorded on a Perkin Elmer Model 297, irradiations were carried out with monochromatic light of the exciting beam of the MPF-4 Hitachi-Perkin-Elmer spectrofluorimeter.

Thin-Film Spectroscopic Apparatus. The apparatus consists of these basic elements: (1) an optically suitable condensing surface for which the temperature can be controlled, (2) a simple interferometer for measurement of the thickness of the film deposited or "plated" on the optical surface, and (3) a system that can deposit pure materials on the condensing surface such that the rate of deposition does not exceed the thermal equilibration capacity of the condensing surface (in practice, slow distillation under high vacuum is the easiest way to accomplish this).

An overall view of the apparatus is presented in Figure 1. The details of the construction are given by the schematics in Figure 12 (condensing surface) and Figure 13 (circuits for signal analysis). The condensing surface is an optically polished sapphire window (1.6–2.0-cm diameter) cemented to a surface ground into a hollow glass torus. The planarity of the ground surface is important in maximizing the contact and therefore the heat transfer from the window to the coolant within the torus. RTV-108 silicone glue (General Electric) is flexible enough to maintain the bond to the window at 77 K and thermally stable enough to be used at 600 K. The glue is also thermally conductive enough to allow the required heat transfer between the window and the coolant during plating. The external windows of the apparatus are glued ("Araldite" epoxy, Ciba-Geigy) to ground surfaces in the outside shell. This technique for attaching windows is extremely simple and very rapid and makes optical alignment easy. Furthermore, glueing the windows to the apparatus makes it possible to use various sorts of optical materials (we have used quartz and sapphire). The glue remains sealed over all the temperature ranges we have used. In addition, the problem of matching the temperature coefficients of the window and the window holder disappears. A further advantage of the glue is ease of removal: the RTV-108 is cut with a razor, the sapphire window removed and cleaned thoroughly with lens tissue, detergent, water, and organic solvents (CH_3CN, CH_3OH, etc.), and then fired in an oven to remove residual organic material, and the epoxy glue is burned away by heating the apparatus in an oven at 560 °C, after which the windows may be remounted and the apparatus used again.

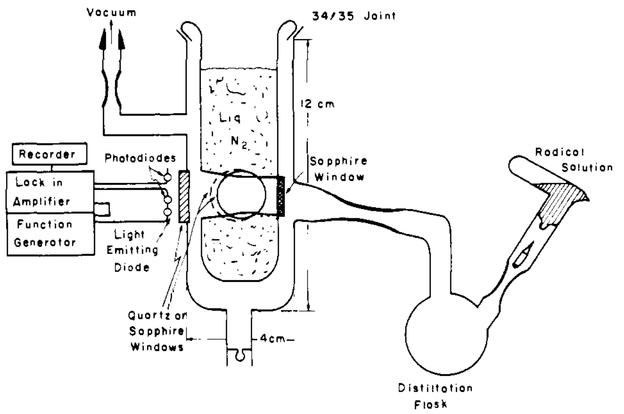

Figure 12. The thin-film spectroscopic apparatus. Condenser dimensions are indicated. Pyridinyl radicals or pyridinyl radical dimers are introduced into the distilling flask via a breakseal, solvent is distilled into a trap on the vacuum line, and the radical or dimer is transferred to the upper surface of the distilling flask with hot air to facilitate removal of residual volatiles. Liquid nitrogen is added and the distilling flask gently warmed, the interferometer being used to monitor the amount of material deposited on the window. After the desired thickness has been obtained, the distillation is halted, the interferometer detached, and the sample section sealed off from the distilling flask and then from the line. The thin-film sample may now be examined by a variety of spectroscopic techniques. The material can also be recovered from the window without exposure to oxygen by attaching the apparatus back to the line, adding liquid nitrogen, distilling in a suitable solvent, warming, and collecting the resulting solution for analysis by chemical or spectroscopic methods.

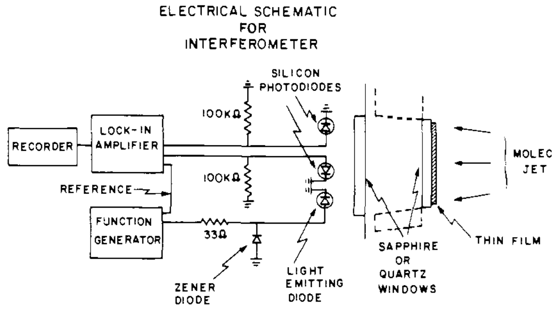

Figure 13. Electrical schematic for the interferometer used with the thin-film spectroscopic apparatus. The windows are included in the diagram to indicate the general location of the LED and photodiodes with respect to the thin films (see Figures 1 and 12).

The high thermal conductivity of sapphire, especially at low temperature, allows films of unstable materials to be deposited without further chemical reaction on the surface. The torus-cooled sapphire window section makes temperature control very simple. Liquid N_2 is normally used for the initial deposition, but for higher temperatures, the N_2 may be poured out and another liquid poured in (acetone and liquid nitrogen for −94 °C; isopentane and liquid nitrogen for −160 °C; etc.). More elaborate and refined temperature controls would also be possible but have not been necessary in the work we have done thus far.

Interferometer. To follow the progress of film deposition, a simple interferometer is used. The device utilizes a light emitting diode (LED)

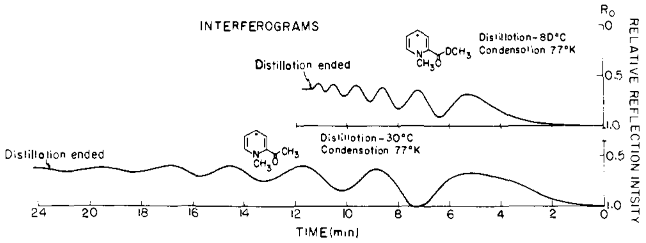

Figure 14. Interferograms for the plating of 1-methyl-2-(carbomethoxy)pyridinyl and 1-methyl-2-acetylpyridinyl radicals before the measurement of IR spectra.

(Fairchild FPE 104), $\lambda_{\max}$ 890 nm and two silicon pin photodiodes (Monsanto, MD-1), one to provide a reference signal directly from the LED and one to detect the light reflected from the surfaces of the optical system. As the optical thickness reaches $0.25\lambda/n$ (λ 890 nm), the destructive interference of the reflected light causes the signal reaching the photodiode to decrease to a minimum followed by an increase in light signal as the film thickens. The foregoing is true if the film material has a refractive index less than that of the substrate sapphire (i.e., <1.758 at 890 nm); in cases in which the film material has $n > 1.758$, the first deflection point should be a maximum. Interferograms of materials such as CH_2I_2 (n_D 1.7559 at 10 °C) showed the expected maximum if the distillation were carried out with great care to avoid microcrystal formation (light dispersion) and multilayer formation (volatile impurities can lead to multilayers with a range of refractive indices). Pyridinyl radicals do not have such high refractive indices, but the point should be kept in mind for other work, especially that involving compounds with heavy atoms.

Film uniformity can be improved by blocking the molecular jet with a shutter (held by a magnet), which is then removed quickly at the time that the distillation appears to be proceeding at the desired uniform rate. During the distillation, the number of maxima and minima are counted to obtain the film thickness according to eq 1, where d = film thickness

$$d = 10^{-7}(m/n)(\lambda/4) \qquad (1)$$

in centimeters; m = the number of maxima and minima detected by the interferometer; λ = the wavelength of the light emitted by the LED (in nanometers); n = the refractive index of the film. Phase-sensitive detection using a lock-in amplifier (Princeton Applied Research) and a function generator operating at 70 Hz was used to extract the weak signal (200 μV) from the noise. The distillation is stopped by removing the heater from the substrate source.

Interferograms, the signals recorded during the plating of 1-methyl-2-(carbomethoxy)pyridinyl radical (**2·**) and 1-methyl-2-acetylpyridinyl radical [(CH_3CO)**2·**] for IR spectra, are given in Figure 14. The decreasing signal amplitude with increasing film thickness is due mainly to absorption of the 890-nm light by the film.

The absorption coefficient of the species in the film can be obtained from eq 2, where ϵ_λ = absorption coefficient at a particular wavelength

$$\epsilon_\lambda = \mathrm{OD}(M_w/1000dD) \qquad (2)$$

λ; OD = optical density measured at λ; d = film thickness (in centimeters); D = estimated density of film[18] (grams/cubic centimeter).

The refractive index of the thin film may be estimated from the amplitude of the interferometric signal with the aid of eq 3, starting from

$$A/R_0 = 4VW[(1 - X^2)/(2X^2 - X^4)] \qquad (3)$$

the first maximum and provided that neither absorption nor dispersion affect the signal intensity too greatly [where $V = (n_s - n)/(n_s + n)$; $W = (n - 1)/(n + 1)$; $X = (n_s - 1)/n_s + 1)$; n = refractive index of film; n_s = refractive index of sapphire (1.758 at 890 nm); A = amplitude of the signal measured by the interferometer, a quantity proportional to the initial intensity of light reaching the sapphire window, and measured by a photodiode looking directly at the LED; R_0 = a signal proportional to the intensity of light reflected from the clean sapphire window before any sample has been plated on it].

Operation of the Thin-Film Apparatus. The solvent from a sample in a suitable distilling bulb (oxygen-free transfer through a breakseal required for pyridinyl radicals) is removed by distillation to a trap on the vacuum line. Warming the distilling bulb just enough to distill the material from the bottom to the sides before liquid N_2 is introduced allows the removal of the last traces of solvent and increases the purity of the thin film. After the bulb has cooled, liquid N_2 is added to the torus and distillation of the sample effected at a rate below 0.02 μm/min. Distillation of a ultraviolet–visible spectroscopic sample should take 10 min or less, with 10–25 min needed for an IR spectroscopic sample. These low rates ensure that overheating of the thin film does not occur. The interferometer provides information on the rate of distillation and on the amount which has been accumulated on the window. After the thin film has reached the desired thickness, the source of heat is removed from the distilling bulb, the bulb sealed off, and the apparatus sealed off from the vacuum line.

The apparatus, with an adaptor on the bottom, may then be carried in one hand to a UV–vis spectrophotometer (Cary Model 17) or a spectrofluorimeter (Perkin-Elmer Hitachi MPF-4) or an IR spectrometer (Perkin-Elmer 297). Ripples are observed in many of the visible absorption spectra because of interference effects like those used to evaluate the film thickness. These are smoothed out in the figures to avoid confusion. The thin film is rotated 90° into the light path of the external windows. Spectra are recorded under various conditions of time, temperature, and irradiation. The thin film is kept at an angle of 45 or 90° to the exciting beam for fluorescence spectra.

Temperature Control and Measurement. The initial temperature of the cooling torus is 77 K (liquid N_2). Pouring off the liquid N_2, adding an appropriate solvent (i.e., isopentane, −160 °C; acetone, −94 °C) together with liquid N_2 allows the temperature to be changed easily and/or raised fairly slowly. The compartment outside the TFS apparatus is purged with dry N_2 to avoid water or ice condensation on the cell windows. A convenient probe containing a platinum resistance thermometer (Hewlett-Packard Model 2802A) was used to measure the temperature. For pyridinyl radicals, the highest temperature used was 45 °C, a temperature easily reached with warm water. In other experiments, boiling water or silicone oil heated with a heating coil was used, with temperatures as high as 577 K reached and measured with the apparatus as described. It is both useful and convenient to be able to vary the temperature so widely for a single spectroscopic sample.

In addition, the material in the thin film can be used in other experiments (measurements, irradiations, etc.) after transfer through the breakseal at the bottom of the outside shell. This particular aspect of the apparatus design allows a check of absorption coefficients (through titrations independent of the spectroscopic measurements), demonstrations that chemical change had not occurred in the thin film (or, perhaps, that there had been changes), and confirmation that the vacuum system had operated in a satisfactory way during the manipulations.

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