Stable Free Radicals. 12. New Aspects of the Behavior of 1-Alkyl-4-(carboalkoxy)- and 1-Alkyl-4-carbamidopyridinyl Radicals in Solution and in Thin Films

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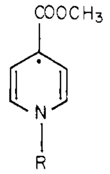
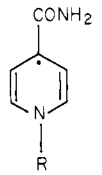
Abstract: New techniques (thin-film spectroscopy, spectroelectrochemistry) have led to (a) revised absorption coefficients and maxima for 1-alkyl-4-(carbomethoxy)pyridinyl radicals (**4**·), (b) stable solutions of 1-alkyl-4-carbamidopyridinyl radicals [(CONH$_2$)**4**·] (in the presence of LiClO$_4$), (c) variation of the visible π-mer absorption with alkyl group size for **4**· in thin films at 77 K, (d) reversible dimerization of **4**· in thin films (dimerization, >−100 °C; dissociation of dimer, >−54 °C), (e) photodissociation of covalent dimers of **4**· to monomeric radicals, and (f) ester conformations as the origin of the "splitting" in the 395-nm band observed for **4**· radicals. A novel vacuum variable-path-length UV-vis-near-IR cell ("VV-cell") is described in detail along with its application to the problem of the concentration dependence of the absorption spectra of pyridinyl radicals in solution. The results provide a paradigm for the study of stable but reactive intermediates in concentrated form (thin films) or in solution.

The stable 1-ethyl-4-(carbomethoxy)pyridinyl radical was isolated as a pure compound more than 15 years ago;[2] its preparation and distillation have been standardized[3] and closely related analogues, the 1-methyl-, 1-isopropyl- and 1-*tert*-butyl-4-(carbomethoxy)pyridinyl radicals [R,COOCH$_3$)**4**·], have been described.[4]



(R,COOCH$_3$)**4**·,
R = CH$_3$, CH$_3$CH$_2$,
(CH$_3$)$_2$CH, (CH$_3$)$_3$C



(R,CONH$_2$)**4**·,
R = CH$_3$, (CH$_3$)$_3$C

Schwarz, who discovered the stability of 1-alkyl-4-(carbomethoxy)pyridinyl radicals, noted that electrochemically generated 1-alkyl-4-carbamidopyridinyls [(R,CONH$_2$)**4**·] were fairly stable in CH$_3$CN.[5] Itoh and Nagakura,[6] however, reported that the same radicals were somewhat unstable, an apparent contradiction which has been resolved by the finding that the pyridinyl radicals are stabilized by cations such as Li$^+$.

One of the special features of the spectra of pyridinyl radicals at low temperatures, the strong visible absorption, was ascribed to complex formation (π-mers) by Itoh and Nagakura.[7] A new thin-film spectroscopic apparatus[8] has now been used to show that covalent dimers also form (reversibly) over certain temperature ranges from pure 1-alkyl-4-(carbomethoxy)pyridinyl radicals, that the dimers can be photodissociated, and that the absorption band of π-mer varies with the size of the 1-alkyl group.

Itoh[9] has suggested exciton splitting as the origin of the structure seen in the near-UV absorption band. However, we have now shown that the band structure is independent of concentration, using a vacuum variable-path-length ("VV") cell.

Table I. Absorption Maxima for 1-Alkyl-4-carboalkoxy- and 1-Alkyl-4-carbamidopyridinyl Radicals in Acetonitrile and Reduction Potentials for the Corresponding Pyridinium Ions

(1-alkyl) R	(4-subst) R'	maxima (ϵ_{max}), nm[a] λ_1 (ϵ_{max})	λ_2 (ϵ_{max})	$E_{1/2}$,[b] V
CH$_3$	COOCH$_3$	309 (12 300)	400 (6900)	−1.081
(CH$_3$)$_3$C	COOCH$_3$	308 (14 000)	398 (7800)	−1.084
CH$_3$	COOC(CH$_3$)$_3$	309 (13 200)	400 (7800)	−1.121
(CH$_3$)$_3$C	COOC(CH$_3$)$_3$	308 (13 500)	399 (7600)	−1.124
CH$_3$	CONH$_2$	307 (11 000)	404 (7100)	−1.157
(CH$_3$)$_3$C	CONH$_2$	306 (13 000)	401 (8000)	−1.161

[a] Generated electrochemically from the pyridinium ion in CH$_3$CN/(0.2M) LiClO$_4$, using the vacuum cell described by Hermolin, J.; Levin, M.; Ikegami, Y.; Sawayanagi, M.; Kosower, E. M. *J. Am. Chem. Soc.*, accompanying paper in this issue. [b] Reference electrode Ag/Ag$^+$ (0.01 M), 0.4 M LiClO$_4$/CH$_3$CN. Polarographic measurements were made with solutions of the pyridinium ion in 0.4 M LiClO$_4$/CH$_3$CN. The half-wave potentials were independent of the concentration of pyridinium ion over the range from 10^{-5} to 10^{-2} M and the drop time (0.55–8 s).

Results

The spectroelectrochemical cell[10] developed for the study of 1-alkyl-2-(carbomethoxy)pyridinyl radical dimers was used to generate 1-alkyl-4-carbamidopyridinyls [(CONH$_2$)**4**·] in CH$_3$CN. Electrochemical reduction is rapid (usually less than 1 h) and yields accurate absorption coefficients. The reduction potentials of the pyridinium ions were measured by polarographic techniques as described in the Experimental Section. Two 4-(carbomethoxy)pyridinyl and two 4-(carbo-*tert*-butoxy)pyridinyl radicals (the 1-methyl- and the 1-*tert*-butyl) were made electrochemically. The absorption maxima and reduction potentials are listed in Table I.

4-Carbamidopyridinyls. Reduction of 1-methyl-4-carbamidopyridinium iodide with 3% sodium amalgam[3] was followed spectroscopically. The product mixture contained an air-stable, fluorescent compound (absorption and excitation maximum, 360–380 nm; emission maximum, 440–500 nm) of unknown structure, perhaps due to overreduction of the poorly soluble pyridinium salt. Reduction with added LiClO$_4$ (190 mM) led to substantial amounts of the 1-methyl-4-carbamidopyridinyl radical.

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

[2] Kosower, E. M.; Poziomek, E. J. *J. Am. Chem. Soc.* **1964**, *86*, 5528-5523.

[3] Kosower, E. M.; Waits, H. P. *Org. Prep. Proced. Int.* **1971**, *3*, 261-267.

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[5] Schwarz, W. M., Jr., Ph.D. Thesis, University of Wiconsin, 1961.

[6] Itoh, M.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 369.

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[8] Hermolin, J.; Levin, M.; Kosower, E. M., preceding paper in this issue. The temperature of the thin film can be raised to temperatures as high as 577 K, insofar as the physical limitations imposed by the construction and operation of the thin-film apparatus are concerned. However, the volatility of simple pyridinyl radicals and/or their tendency to collect into droplets above certain temperatures have limited the current study of these radicals to temperatures below 45 °C.

[9] Itoh, M. *Chem. Phys. Lett.* **1968**, *2*, 371.

[10] Hermolin, J.; Levin, M.; Ikegami, Y.; Sawayanagi, M.; Kosower, E. M., accompanying paper on 1-alkyl-2-(carbomethoxy)pyridinyls in this issue.

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Table II. Absorption Maxima for 1-Alkyl-4-(carbomethoxy)pyridinyl Radicals in Thin Films on a Sapphire Window at 77 K

R(alkyl)	λ_{max} (ϵ_{max})				
CH_3	630–640[a] (2800)	400 sh (3500)[b]	378 (7200)	288 (13 000)[c]	244 (6850)
CH_3CH_2	640–650[a] (2550)	400 sh (5100)[b]	380 (6750)	293 (13 000)[c]	234 (6050)
$(CH_3)_2CH$	655–665[a] (1750)	396 sh (5450)[b]	381 (6050)	295 (13 000)[c]	232 (4550)
$(CH_3)_3C$	660–670[a] (1400)	400 (5900)[b]	382 (6250)	297 (13 000)[c]	231 (5200)

[a] Very broad absorption band. [b] Shoulder of modest size: ϵ approximate. [c] Measured absorption coefficients, using two techniques: film thickness and comparison with spectrum after dissolution of film. Numbers varied from 9000 to 13 000. All coefficients for the absorption bands of alkylpyridinyls have been normalized to 13 000 for the ~300-nm band in order to simplify comparisons between the radicals and on the basis of its approximate invariance in absorption spectra of dilute solutions of the radicals.

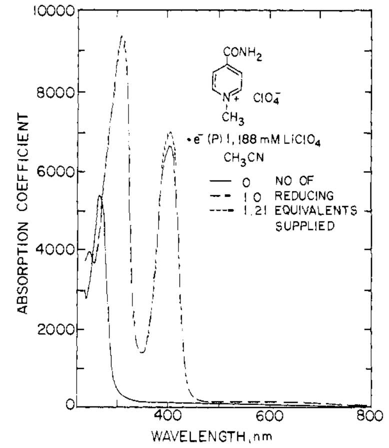

Figure 1. Absorption spectra of 1-methyl-4-carbamidopyridinium perchlorate in $CH_3CN/(0.19\ M)\ LiClO_4$ during electrochemical reduction to 1-methyl-4-carbamidopyridinyl radical, using a spectroelectrochemical cell (Hermolin, J.; Levin, M.; Ikegami, Y.; Sawayanagi, M.; Kosower, E. M., submitted for publication). Three spectra are shown: before reduction, after passage of 1.0 reducing equivalent/mole of cation, and after passage of 1.21 reducing equivalents. The third spectrum is that of a 1-alkyl-4-substituted-pyridinyl radical; the solution is stable in the absence of oxygen for long periods of time, demonstrating that a 1-alkyl-4-carbamidopyridinyl radical may be prepared and retained for use in other studies.

Electrochemical reduction of 1-methyl-4-carbamidopyridinium perchlorate with $LiClO_4$ (188 mM) gave a typical pyridinyl radical, with maxima at 305 (11 000), 404 (7100), and 620 nm (80) (Figure 1). Electrochemical reduction of $(CH_3,CONH_2)4^+$ in the presence of $Bu_4N^+ClO_4^-$ gave radical with maxima at 302 (9700), 394 (6000), and 620 nm (80).

Reduction of $(t\text{-}Bu,CONH_2)4^+I^-$ with sodium amalgam in CH_3CN yields the pyridinyl radical, with maxima at 300 (14000) and 391 nm (7000), if reaction is interrupted at the point a which the radical absorption begins to decrease. The 1-*tert*-butylpyridinium salt is more soluble than the 1-methyl salt.

Thin-Film Spectroscopy of 4-(Carboalkoxy)pyridinyl Radicals. 1-Alkyl-4-(carbomethoxy)pyridinyl radicals (4·) [1-alkyl = CH_3, CH_3CH_2, $(CH_3)_2CH$, $(CH_3)_3C$], prepared by Na(Hg) reduction and extraction, are "plated" onto the sapphire window of the thin-film spectroscopy apparatus,[11] film thickness being monitored by 890-nm interferometry. Spectra are shown in Figure 2. The visible (pimer) band decreases in intensity and shifts to longer wavelengths with increasing 1-alkyl group size. The ratio of two overlapping bands in the 400-nm region changes markedly with 1-alkyl group change, but much smaller shifts occur in the 300- and 240-nm bands (Table II).

Annealing Thin Films of 4· Radicals. The changes on warming thin films of 1-alkyl-4-(carbomethoxy)pyridinyl radicals to −60 and −25 °C vary with the nature of the 1-alkyl group. Visible absorption disappears at a low temperature, more easily for the 1-*tert*-butylpyridinyl radical than for the 1-methylpyridinyl radical. A striking change in the UV absorption of the 1-methylpyridinyl radical is the disappearance of the pyridinyl radical absorption, being replaced by a broad band near 400 nm, accompanied by shoulders at 270 and 220 nm. After recooling to 77 K after annealing and irradiation, the pyridinyl radical spectrum is regenerated with some differences. The 400-nm band has a different ratio of the two overlapping maxima than the initial pyridinyl

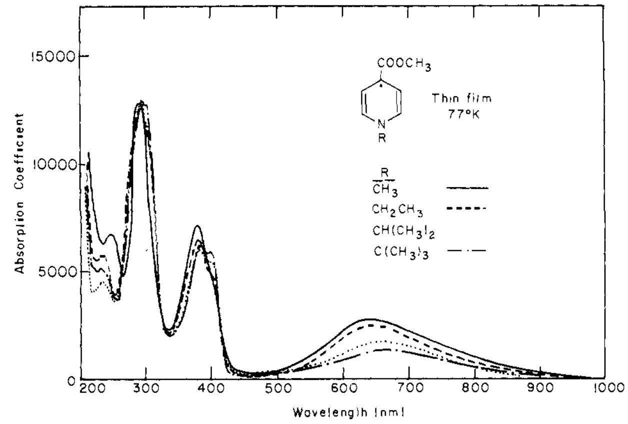

Figure 2. Absorption spectra of four 1-alkyl-4-(carbomethoxy)pyridinyl radicals in thin films at 77 K. The radicals were deposited as films on the sapphire window of a thin-film spectroscopy apparatus (TFS apparatus), using 890-nm interferometry to measure film thickness and, thus, concentration (for a fuller description of the technique, see the preceeding article in this issue). The three main bands are at 650, 400, and 300 nm. The 650-nm band (charge-transfer absorption of π-mer) shifts from 623 nm for 1-CH_3 to 675 nm for 1-$(CH_3)_3C$, along with a twofold intensity decrease. The 400-nm band is complex, with at least three contributions (pyridinyl radical absorption of the π-mer, two due to the two conformational isomers of the pyridinyl radical monomer) (see text). The 300-nm band exhibits small variations, a result of the different relative contributions of the pyridinyl radical absorption in the π-mer and the monomer.

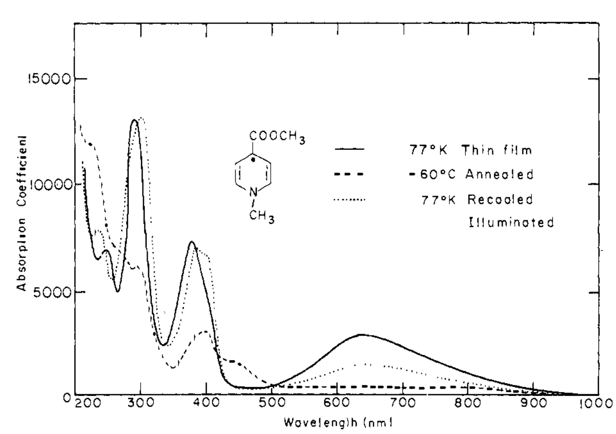

Figure 3. Changes on annealing 1-methyl-4-(carbomethoxy)pyridinyl in a thin film, using the TFS apparatus (see caption for Figure 2). At −60 °C, almost all of the characteristic radical absorption disappears and is replaced by a very broad band in the 400-nm region along with absorptions near 270 and 230 nm. Recooling to 77 K and irradiation (350–500 nm) regenerates the radical absorption spectrum in the 300- and 400-nm regions, with about 50% return of the visible band.

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[11] The thin-film spectroscopy apparatus and the techniques utilized to study radicals on the sapphire window of the apparatus have been thoroughly described in ref 8.

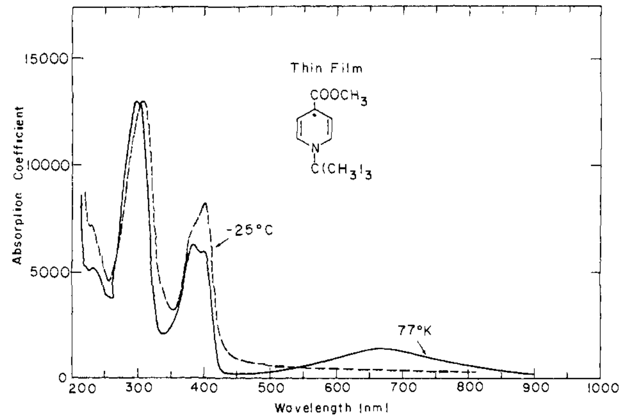


Figure 4. Changes on annealing 1-*tert*-butyl-4-(carbomethoxy)pyridinyl radical in a thin film, using the TFS apparatus (see caption for Figure 2) At −25 °C, the visible absorption is lost, with a corresponding loss in the π-mer absorption near 380 nm. Irradiation after cooling to 77 K does not change the spectrum appreciably, and the π-mer absorption is not recovered.

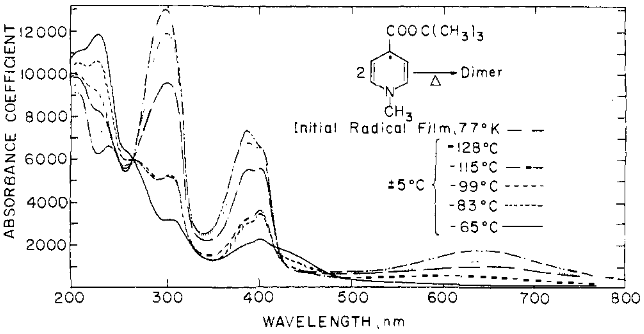


Figure 5. Changes on annealing 1-methyl-4-(carbo-*tert*-butoxy)pyridinyl radical in a thin film, using the TFS apparatus (see caption for Figure 2). Visible absorption is lost completely before the loss of all of the absorption in the 400-nm region and parallels the decrease in the 380-nm absorption. The final spectrum, at −65 °C, shows that very little pyridinyl radical is present. The long wavelength absorption extends from 350 nm past 500 nm and is assigned to a π–σ → π–σ* transition in a covalently linked dimer.

radical spectrum, and only 50% of the visible band is regained (Figure 3).

On annealing thin films of 1-*tert*-butyl-4-(carbomethoxy)-pyridinyl radical at −25 °C, the visible absorption is lost but regenerated on recooling and irradiation. Rather than loss of the 400-nm band, only changes in the ratio of the two overlapping bands, accompanied by a broad absorption in the 400-nm region extending past 500 nm, are observed (Figure 4).

In annealing thin films of 1-methyl-4-(carbo-*tert*-butoxy)-pyridinyl radical (Figure 5) to −65 °C, a change in the ratio of the 400-nm overlapping bands was observed, followed by disappearance of most of the radical absorption. Visible absorption is lost faster at first. Between −54 and −8 °C, some return (~10%) of the pyridinyl radical absorption at 400 and 300 nm implies dissociation of the covalent dimer, and these changes are reversed on cooling carefully back to −54 °C (not illustrated). Cooling the film to 77 K from −58 °C causes no further change, but irradiation at 430 nm rapidly dissociates the dimer to the pyridinyl radical (Figure 6).

Thin films of 1-*tert*-butyl-4-(carbo-*tert*-butoxy)pyridinyl radical exhibit a broad weak visible band at 625 nm (100) and maxima at 305 (14 500) and 394 nm (7500). Annealing at −20 °C produced some loss in visible absorption and a shift in the ratio of the 400-nm overlapping bands. Covalent dimers were not formed (Figure 7).

Infrared Spectra of 4· in Thin Films. The interferogram for the IR sample of 1-*tert*-butyl-4-(carbomethoxy)pyridinyl radical is shown in Figure 8, along with a comparison of the IR spectra of 1-*tert*-butyl-4-(carbomethoxy)pyridinyl and 1-methyl-4-(carbo-*tert*-butoxy)pyridinyl radical. The IR spectrum of 1-methylpyridinyl radical changes on annealing at −50 °C, increasing at 1715 cm^{-1} and decreasing at 1685 cm^{-1}, in parallel with changes in the UV–vis region. Irradiation regenerates the radical from the dimer. The IR spectrum of 1-*tert*-butylpyridinyl radical does not change on annealing, except for some irreversible broadening.

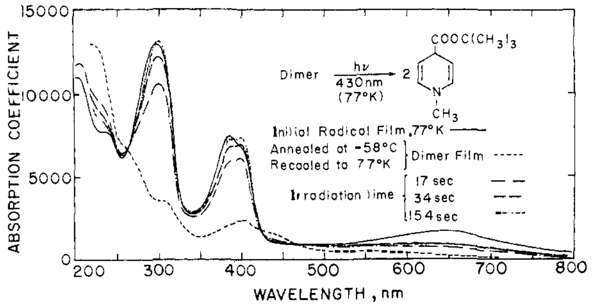


Figure 6. A film of the dimer of 1-methyl-4-(carbo-*tert*-butoxy)pyridinyl at 77 K, formed by annealing the pyridinyl radical at −58 °C and then recooling, is irradiated at 430 nm for up to 154 s, regenerating all of the pyridinyl radical and less than 50% of the visible absorption. Only part of the pyridinyl absorption of the π-mer at 380 nm was reformed.

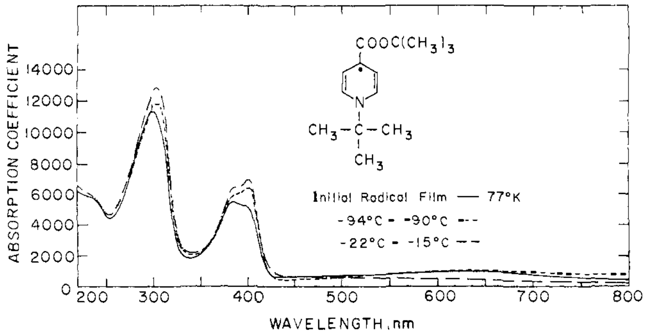


Figure 7. Changes on annealing 1-*tert*-butyl-4-(carbo-*tert*-butoxy)-pyridinyl radical in thin films, using the TFS apparatus (see caption for Figure 2) at about -90 or -20 °C. The visible absorption band due to π-mer is relatively weak but is accompanied by a band near 380 nm; on annealing, the visible band is lost and the shape of the 400-nm absorption band changes in a way that suggests the loss of the 380-nm absorption. No dimer is formed from this radical.

Concentration Independence of 1-*t*-Bu-4-COOCH$_3$Py· Absorption. The variability in the ratio of the 400-nm overlapping bands with radical structure and environment led us to examine the influence of concentration. A variable-path-length vacuum cell ("VV-cell") was designed and constructed (see Experimental Section); such cells might be useful for the study of absorption bands of very different absorption coefficients. 1-*tert*-Butyl-4-(carbomethoxy)pyridinyl was examined because covalent dimers were not formed even in thin films. The 395-nm absorption was composed of two overlapping bands and was shifted slightly in the thin film spectrum at 77 K due to the pyridinyl radical absorption of π-mers. π-Mers are not formed from this radical in solution. In CH$_3$CN, the overlapping bands at 392 nm are of equal intensity; the band is narrower than that seen in the thin film and is not "split". The concentration of the radical was varied from 10^{-4} to 10^{-1} M in both CH$_3$CN and 2-methyltetrahydrofuran. Over this 1000-fold range of concentration change in both solvents, the shape and width of the 395-nm absorption band remained the same.

Discussion

1-Alkyl-4-carbamidopyridinyl radicals in CH$_3$CN were reexamined because of contradictory evidence concerning stability, the ease of generation and examination with a spectroelectrochemical cell,[10] and the possibility that such radicals might be somewhat stronger reducing agents than the 4-(carbomethoxy)-pyridinyl radical. The report of Itoh and Nagakura[6] that a number of 1-alkyl-4-carbamidopyridinyl radicals disappeared after some hours or days is in agreement with our present finding that

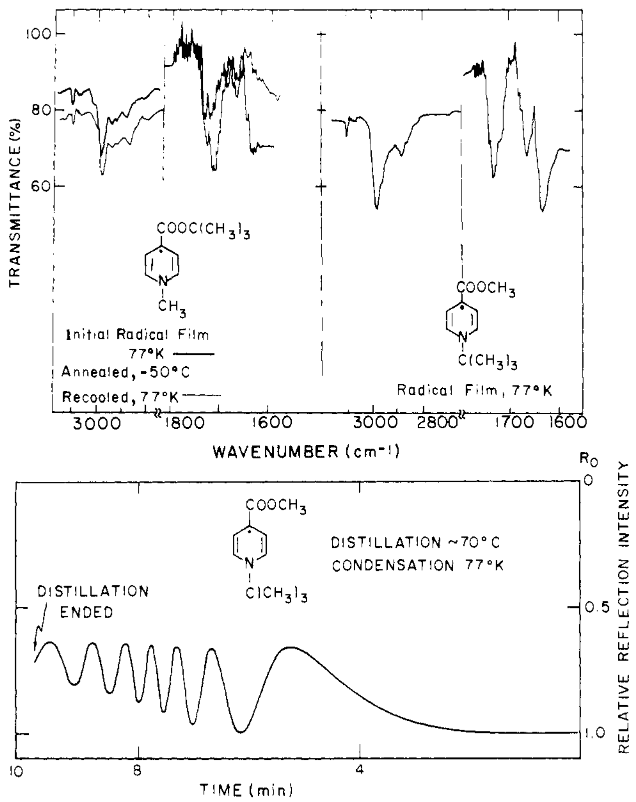
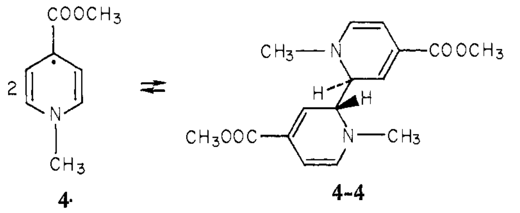


Figure 8. An interferogram for the deposition of 1-*tert*-butyl-4-(carbomethoxy)pyridinyl radical on the sapphire window of the TFS apparatus (see caption for Figure 2) is shown. The radical was distilled at 70 °C; the film thickness was about (13 × 0.89)/(4 × 1.50) = 1.9 μm. An infrared spectrum (upper right) shows no change on annealing; thus, the loss of the visible absoprtion shown in Figure 4 for the same radical does not have easily detectable consequences in the infrared region (to about 6200 nm). Infrared spectra (upper left) of 1-methyl-4-(carbo-*tert*-butoxy)pyridinyl radical in a thin film. Small changes in the C–H stretching region of the IR spectrum accompany substantial changes in the C=O and C=C stretching regions after annealing at -50 °C and then recooling to 77 K. Irradiation returned the film to its original state, indistinguishable from the initial film in IR spectrum.

$(CONH_2)$**4·** are difficult to generate by Na(Hg) reduction. Since **2·** radicals are unstable (disproportionation is likely) at high concentration, the low solubility of the 4-carbamidopyridinyls may be responsible for the formation of high local concentrations of the radicals which then disproportionate. However, 4-carbamidopyridinyl radicals may be produced and retained in the presence of Li^+, which increases the electronegativity of the carbamido group and the solubility of the pyridinyl radical by complexation. The spectroelectrochemical cell is convenient for the preparation and examination of such radicals.

Perhaps the most surprising result in the present study is that the stable 1-alkyl-4-(carbomethoxy)pyridinyl radicals can dimerize under certain conditions. The dimers are dissociated to monomers by irradiation at low temperatures, warming, and on solution. A 1-*tert*-butyl group prevents dimerization of pyridinyls.

Dimerization. Major changes in the spectrum of pyridinyl radicals occur on annealing to −90 and −60 °C and must be due to formation of dimer with a broad band near 400 nm and shoulders at 270 and 220 nm. No loss of reducing power is involved (titration) through dimerization, and irradiation at 77 K regenerates the radical. The dimer has now been detected because the thin-film spectroscopy apparatus allows the study of high concentrations (pure radicals) at the specific temperatures required. The dimer bond is probably at the 2 position, leading to a 2,2′ dimer, since a bulky 1-alkyl group prevents covalent dimerization, but a bulky ester group (e.g., 4-(carbo-*tert*-butoxy)pyridinyl) does not. Dimerization is illustrated in eq 1. The electronic transition responsible for the unusually broad and long wavelength absorption [400 nm for the 1-alkyl-4-(carboalkoxy)pyridinyl radical dimers (**4–4**)] is a π–σ → π–σ* transition, for which a detailed explanation has already been given.[10]



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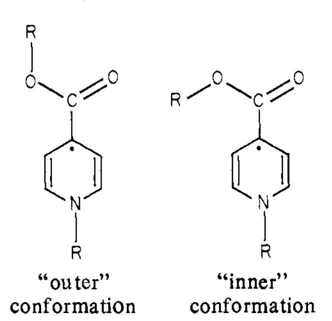
Split Band in the 395-nm Absorption Spectrum. Itoh and Nagakura[6] reported two overlapping 395-nm bands for 1-methyl-, 1-ethyl-, and 1-isopropyl-4-(carbomethoxy)pyridinyl radicals in isopentane solution and 77 K matrices. Ikegami and Seto[12] have noted such spectra for these radicals in methyltetrahydrofuran (MTHF) solution. We have also observed the "split" bands for the radicals in thin films (see Figures 2–7) and in MTHF solutions.

Itoh[9] has suggested that the 395-nm band splitting for 1-alkyl-4-(carbomethoxy)pyridinyl radicals in an isopentane matrix at 77 K, especially for the 1-isopropyl radical, is due to exciton splitting in the pimer. Our experiments imply a different interpretation. Spectra of thin films of 1-methyl-4-(carbo-*tert*-butoxy)pyridinyl radical [annealed (→ dimer), irradiated (→ monomer + π-mer), etc.] indicates that a 380-nm band represents the UV absorption of the π-mer, since 380-nm absorption decreases through these procedures without loss in radical, and the 395-nm band shape now resembles that observed for a MTHF solution. Thus, at least three bands (one for π-mer, two for monomer) occur in the 395-nm region. The 380-nm band shape for 1-methyl-4-(carbomethoxy)pyridinyl radical π-mer (Figure 2), suggests a single band. There were no changes in the 400-nm region parallel to those noted for the 380-nm region.

If the 395-nm band splitting were due to π-mers (i.e., a complex of two pyridinyl radicals), concentration effects on the splitting would be expected. Using a special cell (a "VV-cell", see Experimental Section), we have found absolutely no concentration dependence of the 395-nm band shape for 1-methyl-4-(carbo-*tert*-butoxy)pyridinyl radical over the range from 10^{-4} to 10^{-1} M.

The splitting thus has an intramolecular origin, possibly two ground-state isomers, which differ in the conformational arrangements of the ester group and which interconvert on a time scale longer than required for electronic excitation. The two conformers differ in the relationship of the alkoxy group to the pyridinyl radical ring, one conformer being "inner" (alkyl group directed toward the ring) and the second, "outer" (alkyl group directed away from the ring). The conformers would have different ground-state energies and somewhat different absorption spectra and would give rise to overlapping, or "split", absorption bands. Two different ground-state conformational isomers are now quite well established as the origin of the two different emitting states of methyl salicylate.[14-16] A pyridinyl radical π-mer might consist of three isomers, o,o (outer–outer), i,i (inner–inner),



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and o,i (outer–inner), and would exhibit broadened absorption bands; further effects from exciton splitting are not excluded.

Alkyl Group Influence on π-Merization. The strength and position of the visible pimer absorption are affected by the size of the 1-alkyl group on the pyridinyl ring, the absorption coefficient decreasing, and the absorption maximum increasing in wavelength with increasing size of the 1-alkyl group [from 635 (1-Me) to 665 nm (1-*t*-Bu)] (Figure 2). The π-mer is a face-to-face complex of two pyridinyl radicals. That the 1-*tert*-butyl radical yields as much as half of the amount of π-mer formed by the 1-methyl radical suggests that the two pyridinyl rings are antiparallel in the π-mer (i.e., the ester groups are pointed in opposite directions). Parallel alignment in the π-mer occurs for trimethylene bis(pyridinyl) metal ion complexes,[13] and we can now include another example, the magnesium complex of 1-isopropyl-4-(carbo-*tert*-butoxy)pyridinyl radical, observed after reduction of 1-isopropyl-4-(carbo-*tert*-butoxy)pyridinium ion with Mg in CH_3CN. Spectroscopic indications of π-mer formation are seen during Mg reduction of 1-methyl- and 1-ethyl-4-(carbo-*tert*-butoxy)pyridinium iodides in CH_3CN, but further reduction (faster for the non-π-merized form?) interferes, and limits the quantity of π-mer formed from the 1-isopropyl salt. π-mer formation might depend on the solvation required for the Mg^{2+} associated with the carbonyl oxygens of the COO-*t*-Bu groups in a pair of esters, the CH_3CN analouge of "hydrophobic bonding" driving the Mg^{2+} complex into the π-mer form.

Overall View of 1-Alkyl-4-(carboalkoxy)pyridinyl Radicals. The components of the $\langle \mathbf{4}\cdot \rangle$ system[13] may be summarized as follows: the free **4**· radical, the **4**·,**4**· π-mer, and the covalent s-cis and s-trans dimers of **4**· (**4-4**, linked via the 2 and 2′ positions). The π-mer is probably an intermediate in the formation of the s-cis dimer, as suggested for the **2**· π-mer formed by irradiation of the **2-2** dimer. The system is shown in eq 2.

$$\mathbf{4}\cdot = \mathbf{4}\cdot,\mathbf{4}\cdot\ \pi\text{-mer} = s\text{-}cis\text{-}\mathbf{4\text{-}4} = s\text{-}trans\text{-}\mathbf{4\text{-}4} \qquad (2)$$

Hanson[17] has pointed out that a nomenclatural problem has been created (without our knowledge) in the field of pyridinyl radicals because Chemical Abstracts and others have ignored the simple and straightforward suggestion that we made when we discovered pyridinyl radicals.[18,19] Addition of an electron to a pyridin*ium* ion produces a pyridin*yl* radical; all numbering problems are then resolved at the level of the pyridinium ion. Why add a hydride ion and subtract a hydrogen atom in order to create a radical? 1-Hydropyridinyl radical means a pyridinium with a hydrogen on the nitrogen (i.e., protonated pyridine) plus one electron. There are other research groups throughout the world who seem satisfied that our approach is clear and useful.

Conclusions

The techniques we have developed in the present and preceding articles are suitable for many stable but reactive intermediates, either as pure thin films or in concentrated solutions. The pyridinyl radicals provide useful paradigms for the study of intermediates.

Experimental Section

Vacuum line techniques used for the preparation and analysis of pyridinyl radicals have been described in the accompanying papers.[8,10,13] Titrations of radical concentration were made with 1,1′-dimethyl-4,4′-bipyridylium dichloride ($PQ^{2+}2Cl^-$).[20]

Pyridinium Ion Reduction. 1-Methyl-4-(carbo-*tert*-butoxy)pyridinium iodide [0.85 mM; $\epsilon(Py^+)_{272nm}$ 4700; OD, 0.4 (l = 0.1 cm)] in degassed CH_3CN (5 mL) is stirred with excess 3% Na(Hg) at 0 C, with spectra taken periodically after filtration of the solution through two glass sinters. After 85–90% reaction, the filtered solution is titrated with $PQ^{2+}2Cl^-$ as described in the accompanying article,[10] yielding absorption maxima for the radical of 305 (11 700) and 394 nm (6250). Similarly, 1-*tert*-butyl-4-(carbo-*tert*-butoxy)pyridinyl radical showed maxima at 305 (14 500), 394 (7300), and 620 nm (80). The manipulations and transfers involved in these experiments take from 3 to 10 h to complete.

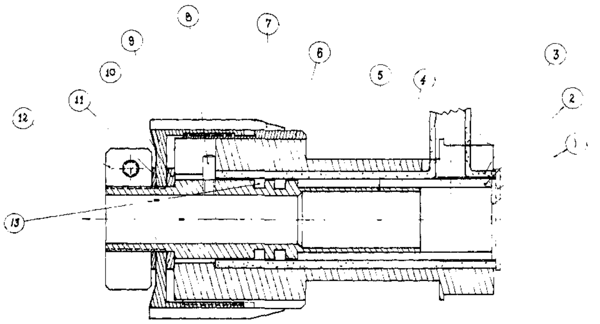

Figure 9. A detailed drawing of the VV-cell (vacuum variable-path-length cell). The cell mount may be attached to adaptors for the Cary Model 17 or an infrared spectrophotometer. The optical path goes through the center of the cell, passing through two sapphire windows and an annular opening in the calibrated handle used to turn the micrometer in order to vary the path length. The labeled parts are as follows: (1) sapphire windows, inner outside diameter, 2.0 cm; outer outside diamter, 2.5 cm; (2 and 3) precision ground Pyrex syringe tubes, inner diameter 2.0, cm; outer diamter, 2.5 cm; (4) aluminum structural support; (5) stainless steel support for inner tube and connection to micrometer drive; (6) stainless steel threaded sleeve, fixed to aluminum support; (7) calibrated micrometer drum; (8) stainless steel pin stop; (9) bronze nut; (10) stainles steel washer; (11) Delrin washer; (12) aluminum nut; (13) Viton O-rings (Parker 2-017). The overall length of the cell is 10 cm; the height of cell, not including the glass tube which is connected to the vacuum line or to a manifold carrying solvent and/or solution, is 5 cm. The glass tube protrudes at least 4 cm above the cell and should extend far enough to permit the necessary glassblowing. The weight of the cell is about 300 g, requiring that the cell be supported for glassblowing operations. The cell is connected to a manifold, which includes a breakseal tube containing freshly prepared pyridinyl radical in the desired solvent (ref 10), another breakseal tube containing additional degassed solvent, a 10-cm quartz cell for measurements of spectra using pyridinyl radical concentration below those for which the VV-cell is suitable, a calibrated, graduated cylinder (pipet) for measurement of solvent volumes, and a breakseal tube containing a titrant such as $PQ^{2+}2Cl^-$. The solution of radical is introduced into the VV-cell, the spectrum measured, and the solvent carefully distilled into the graduated cylinder, using liquid N_2-cooled cotton or ice–water to promote the distillation. The path length of the VV-cell is decreased after each solvent transfer out of the cell in order to obtain an optimum optical density (~0.9) which is matched from spectrum to spectrum. The concentration of the radical in the cell is calculated from the known total volume and the volume of solvent in the graduated cylinder. The band shapes and absorption coefficients as a function of concentration are thus easily obtained.

Magnesium Reductions. 1-Alkyl-4-(carbo-*tert*-butoxy)pyridinium ions can be reduced slowly (>48 h in some cases) with Mg turnings in CH_3CN to solutions having pyridinyl radical absorption spectra. Reduction can proceed beyond the radical stage. For 1-isopropyl-4-(carbo-*tert*-butoxy)pyridinium ion, reduction with Mg/CH_3CN gave rise to a green blue solution with maxima at 376 (4100) and 675 nm (1600), which has been stored without apparent change for 2 years. The absorption coefficients are lower than those for the 1,1′-trimethylenebis-(4-(carbomethoxy)pyridinyl) diradical Mg^{2+} complex (visible absorption coefficient ~10 000) and might signify a low complex concentration or a low complex absorption coefficient. 1-*tert*-Butyl-4-(carbo-*tert*-butoxy)pyridinium iodide is reduced with Mg/CH_3CN to the pyridinyl radical with no apparent sign of a Mg^{2+} complex.

VV-Cell. For measurement of absorptions of very different intensities with a single solution or the concentration dependence of the absorption of an oxygen-sensitive compound, a variable-path-length cell with some unusual features was designed and constructed. A detailed drawing is given in Figure 9.

The basic elements of the VV-cell (vacuum variable-path-length cell) are as follows. (A) Solution carrier: (1) inner and outer cylinders made from a precision Pyrex syringe and (2) sapphire windows affixed to the outer end of the outer cylinder and to the end of the inner cylinder. (B) Sealing elements: (1) two Viton O-rings between the outer and inner cylinders and (2) epoxy glue between the sapphire windows and the cut and ground cylinder ends, the glue being fixed under negative pressure

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[19] Kosower, E. M.; Poziomek, E. J. *J. Am. Chem. Soc.* **1964**, *86*, 5515–5523.

[20] The previously reported absorption coefficient for the visible band of the cation radical ($PQ^{+}\cdot$) derived by one-electron reduction of paraquat dication (PQ^{2+}) has been revised to λ_{max} 605 nm (ϵ 13 000) by Hermolin et al., ref 10.

J. Am. Chem. Soc. **1981**, *103*, 4813-4816

from the side away from the solution carrier, so that the organic solvent solutions used (especially those containing oxidant-sensitive pyridinyl radicals) have an absolute miniumum of contact with the glue. (C) Carriage mechanism: (1) threaded sleeve and (2) micrometer drum fixed to the inner cylinder by a stainless steel insert. (D) Structural support: (1) aluminum barrel around the outer cylinder and (2) stainless steel pin to halt motion of inner barrel. (E) External connection: a side arm is sealed to the outer cylinder and connects the cell to the vacuum line or another tube carrying an oxygen-free solution.

The dimensions of the cell are indicated in the caption to Figure 9. Mounted on an appropriate base, the cell may be placed in the Cary Model 17 spectrophotometer cell compartment. The sapphire windows permit IR spectra to be measured to wavelengths as long as 6200 nm.

The path length in the VV-cell may be varied from 0.001 to 0.8 cm (paths as long as 5-10 cm might be considered). Cell solution volume, including the external tube, may be 1-30 mL. A calibrated pipet is used as a second arm. Dilutions can be carried out by placing a solution of known concentration in the cell and distilling solvent from the calibrated pipet until the volume in the pipet has fallen to the desired level. More conveniently, a dilute solution in the cell is concentrated by distilling solvent from the cell and measuring the volume increase in the pipet. Temperature equilibration of the apparatus is necessary for accurate volume measurement. The temperature coefficient of expansion for CH_3CN is particularly high. Mixing after the removal or addition of solvent is carried out by pouring the solution back and forth at right angles to the direction in which the cell is connected to the calibrated pipet.

Spectra can be measured over a concentration range of about 1000 with the apparatus, as we showed with a study of the concentration variation of the 395-nm absorption band shape of 1-*tert*-butyl-4-(carbomethoxy)pyridinyl radical. In order to simplify the comparison of the spectra, the absorption maxima were matched in height for all concentrations, a task that would have been quite difficult without the VV-cell.

Polarographic Measurements. Reduction potentials were obtained with a two-electrode system, measuring and controlling potentials with a linear scan generator (Model S6-5, Specific Electronic, Ltd.), using a current-to-voltage converter for current measurement[21] and an X-Y recorder. The counter electrode served as reference electrode ($Ag/AgNO_3$ (0.01 M), $LiClO_4$ (0.4 M)/CH_3CN). Anolyte was separated from catholyte ($LiClO_4$, 0.4 M; depolarizer, 10^{-4}-10^{-3} M) by a porous glass tube (Corning 7930 glass) and was changed every day. Measurement of a Radiometer K-401 SCE electrode in the system yielded a value of about 0.22 V, a number which may be added to obtain the potentials vs. the SCE reference electrode.

The reduction potentials were verified with 1-methyl-4-carbamidopyridinium ion, which gave a potential of −1.156 V for the two-electrode system used here and −1.154 v for a three-electrode system measurement.[22]

Preparation of Pyridinium Salts. The 1-*tert*-Butylpyridinium salts were prepared from the 1-(2,4-dinitrophenylpyridinium) derivative and *tert*-butylamine.[23] The 1-isopropyl-4-(carbo-*tert*-butoxy)pyridinium salts were prepared by the same route, using isopropylamine. Details have been given elsewhere.[4] The 1-alkyl-4-carbamidopyridinium iodides were prepared from the corresponding 4-(carbomethoxy)pyridinium derivatives by treatment with NH_3/CH_3OH, the iodide salts being precipitated by the addition of ether followed by recrystallization from methanol/ether. The properties of the salts are as follows. 1-*tert*-Butyl-4-(carbo-*tert*-butoxy)pyridinium iodide: mp 200-202 °C, *p*-toluenesulfonate, mp 159-160 °C; ^1H NMR (D_2O) 1.84 (s, 9 H), 2.07 (s, 9 H), 8.79 (br, 2 H), 9.54 (br, 2 H) ppm; UV (CH_3CN) [λ_{max} (ϵ_{max})] 273 nm (4700), I^- peak at 246 nm.[24] 1-*tert*-Butyl-4-carbamidopyridinium iodide: mp 222-223 °C; 1H NMR (D_2O) 1.81 (s, 9 H), 8.34 (d, $J = 11$ Hz, 2 H), 9.00 (d, $J = 11$ Hz, 2 H) ppm. 1-Isopropyl-4-(carbo-*tert*-butoxy)pyridinium iodide: 220-230 °C dec, *p*-toluenesulfonate, mp 133-134 °C. All other pyridinium salts have been described in previous papers.[2,4]

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Stable Free Radicals. 13. A Reinvestigation of the Pyridinyl Diradical, 1,1'-Trimethylenebis(4-(carbomethoxy)pyridinyl)[1]

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Abstract: The absorption spectrum attributed to 1,1-trimethylenebis(4-(carbomethoxy)pyridinyl) ($\mathbf{3}\cdot\cdot$) includes major contributions from intramolecularly cyclized forms, "cyclomers": *cis*-A-**3** and *trans*-**3**. The broad, temperature-sensitive, and medium-sensitive absorption bands of the cis A and trans cyclomers arise from π-$\sigma \rightarrow \pi$-σ^* transitions. The **3** cyclomers are transformed into diradical metal ion complexes, $\mathbf{3}\cdot\cdot M^{n+}$, by $MClO_4$, and the cyclomers are reformed by removal of the metal ion with donors. Diradical oxidation level species belong to the $\langle\mathbf{3}\rangle$ system. The components are in equilibrium with one another and can be converted into the $\langle\mathbf{3}\rangle M^{n+}$ complexes. Reduction of the bispyridinium ion $\mathbf{3}^{2+}$ with Na(Hg) leads mainly to the trans cyclomer; electrochemical reduction in the presence of $LiClO_4$ or $Mg(ClO_4)_2$ yields the diradical complexes, $\mathbf{3}\cdot\cdot M^{n+}$, but with n-Bu_4NClO_4 it yields the trans cyclomer. An initial preponderance of another cyclomer, *cis*-B-**3**, is replaced by *trans*-**3** ($t_{1/2}$, 1 s). Isopentane extraction of *trans*-**3** yields a variable (usually 1:2) mixture of *cis*-A-**3** and *trans*-**3**. The spectrum of a thin film of distilled $\langle\mathbf{3}\rangle$ resembles that of the isopentane extract. Partial reduction of 3^{2+}, either with 1-methyl-4-(carbomethoxy)pyridinyl ($\mathbf{4}\cdot$) or electrochemically, gives the radical cation $\mathbf{3}^{+}\cdot$, which exhibits an intervalence transition at 1360 nm. The disproportionation constant, $K = [\mathbf{3}^{+}\cdot]^2/[\mathbf{3}^{2+}][\mathbf{3}\cdot\cdot] = \sim 0$-$18$, depends on medium, with low values found when $\mathbf{3}\cdot\cdot Mg^{2+}$ is present. The previously reported spectrum of $\mathbf{3}^{+}\cdot$ must include a contribution from *trans*-**3**. A complete scheme is given which includes $\mathbf{3}^{2+}$, $\mathbf{3}^{+}\cdot$, and various $\langle\mathbf{3}\rangle$ species: cyclomers, open diradicals, and diradical metal ion complexes.

The discovery of stable pyridinyl radicals ($\mathbf{4}\cdot$)[1,3] was soon followed by the report of diradicals in which two to five methylene groups separated the 4-(carbomethoxy)pyridinyl moieties.[4,5] Later studies revealed that pyridinyl diradical metal ion complexes had

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