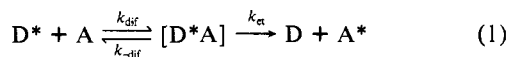


Figure 1. Arrhenius plots for the quenching by dienes of ketone triplet-triplet absorption in chlorobenzene: (□) acetophenone and dMH ( $A = 10^{11.0}$ ); (○) acetophenone and COD ( $A = 10^{10.5}$ ); (■) KPC and dMH ( $A = 10^{10.0}$ ); (●) KPC and COD ( $A = 10^{9.0}$ ).

light solvents are typically about half that for diffusion.<sup>10</sup> Cutting the observed rate constant in half represents a factor of 4 decrease in  $k_{et}$  itself. These steric effects would not be detectable at all if  $n, \pi^*$  triplets were not somewhat inefficient energy donors.<sup>6,10</sup>



We prepared ketoparacyclophane (KPC) to see how the orthogonal arrangement of carbonyl and aromatic  $\pi$ -systems would affect energy transfer. In glasses at 77 K KPC shows a 0-0 phosphorescence band at 69 kcal/mol, as Cram found.<sup>11</sup> The almost featureless nature and 20-ms lifetime of the emission suggests a  $\pi, \pi^*$  lowest triplet. This conclusion is reinforced by the  $>2$ - $\mu$ s lifetime of triplet KPC in cyclopentane, where  $n, \pi^*$  ketone triplets react in less than 0.2  $\mu$ s.<sup>12</sup> Energy-transfer rate constants in methanol and chlorobenzene are  $1/4$  and  $1/6$ , respectively, the values for acetophenone. In contrast, triplet paracyclophane and triplet phenanthrene, which have the same  $\pi, \pi^*$  excitation energy, are quenched by dimethylhexadiene at much the same rate. We judge the relatively slow energy-transfer rate constants for KPC to reflect stereoelectronic factors rather than steric hindrance. The  $n$  orbital is less shielded than in any other phenyl ketone, whereas the carbonyl  $\pi$ -orbital is relatively more shielded than usual by the ortho hydrogens. Since the lowest triplet is  $\pi, \pi^*$ , the orthogonality of the phenyl and carbonyl  $\pi$ -systems apparently inhibits proper orbital overlap. It has been suggested already that energy-transfer rate constants are affected by the ease with which the orbitals involved can develop sufficient overlap.<sup>10,13</sup>

It has been known for some time that 1,3-cyclooctadiene<sup>14</sup> and biphenyl<sup>15</sup> are sufficiently twisted to be slower quenchers than are planar dienes and aromatics. The table points out that both compounds quench nonhindered triplet ketones with rate constants  $\sim 1/3$  as large as the maximum values observed in a given solvent. Toward KPC the difference is a factor of 10 for cyclooctadiene. Figure 1 compares Arrhenius plots for diene quenching in chlorobenzene. The observed  $E_a$  values are all  $1.6 \pm 0.4$  kcal. Remarkably, the differences in rates involve mainly entropy effects, as enumerated in the figure caption. This observation means that the rate decreases accompanying twisted acceptor  $\pi$ -systems do not involve the acceptors' higher triplet energies. Rather, at van der Waals approach distances there must be fewer accessible orientations that allow the orbital overlap necessary for energy transfer. Current models for energy transfer that assume negligible

entropic effects<sup>16</sup> may require reevaluation.

The behavior of biphenyl further dramatizes this stereoelectronic effect. With xanthone ( $\pi, \pi^*$ ) and acetophenone ( $n, \pi^*$ ) as donors, energy transfer is several kilocalories per mole exothermic and  $k_q$  is relatively large, close to the maximum solution value for the former. With benzophenone and KPC as donors, energy transfer is thermoneutral,<sup>15</sup> and the combination of twisted donor and acceptor results in a 1000-fold decrease in  $k_q$ , comparable to that for acetone-acetone energy transfer.<sup>17</sup>

We feel that these results combined with scattered literature reports allow two important general conclusions. Steric effects that limit closeness of approach are relatively unimportant in triplet energy transfer, primarily because diffusion control masks small but real steric decreases in in-cage energy-transfer rates. However, large stereoelectronic effects appear when the  $\pi$ -systems of donor or acceptor are twisted such that the orbital overlap necessary for electron exchange is minimized.<sup>18</sup> In such cases, the built-in inefficiency already noted for  $n, \pi^*$  triplets<sup>10,13,17</sup> takes over.

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## Photodisproportionation of (4-Acylpyridine)tungsten(0) Pentacarbonyl Complexes

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We wish to report an overlooked photoreaction of the much-studied  $W(CO)_5(\text{pyridine})$  complexes.<sup>1-8</sup> Irradiation of these complexes in the presence of CO, alcohol, or alkene causes efficient replacement of the pyridine by added ligand.<sup>3-8</sup> In the presence of excess pyridine,  $W(CO)_4(\text{pyr})_2$  formation occurs in low efficiency.<sup>2-4,6</sup> This competing reaction has been attributed to CO cleavage competing with pyridine cleavage.<sup>2-4,6</sup> We chose to do the irradiations in nonnucleophilic hydrocarbon solvents, under which conditions a clean, hitherto unreported disproportionation to  $W(CO)_6$  and  $W(CO)_4(\text{pyr})_2$  occurs.<sup>9</sup> Unexpectedly, the reaction caused by visible light involves dissociation of pyridine rather than CO and subsequent attack of  $W(CO)_5$  on ground-state reactant.

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(10) The red product is far more photostable in benzene than in methylcyclohexane, which probably explains why previous workers could not detect its formation. A dimerization caused by pyridine loss was suggested to occur.<sup>7</sup>

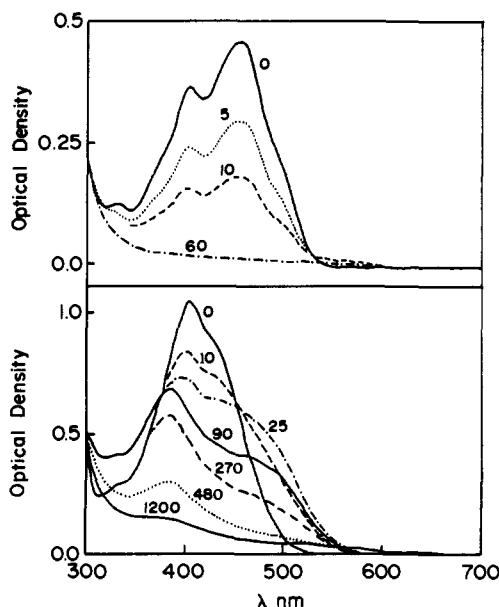
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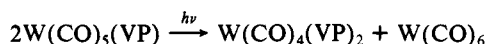
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**Figure 1.** Absorption spectra of  $1.4 \times 10^{-4}$  M  $W(CO)_5(4-CNpyr)$  in argon-saturated methylcyclohexane (top) and benzene (bottom) upon irradiation with visible light ( $\lambda > 400$  nm). Numbers next to each curve indicate total seconds of irradiation.

All the complexes studied were prepared from the tetrahydrofuran complex  $W(CO)_5(THF)$  by standard procedures.<sup>1</sup> Solutions 0.02 M in the 4-valerylpyridine complex  $W(CO)_5(VP)$  (I) were prepared in benzene or in methylcyclohexane and were extensively degassed. Low-intensity irradiation anywhere between 313 and 490 nm causes the bright yellow solutions to turn deep red. HPLC analysis at low conversions revealed only two products in equal yield, which together account for all  $W(CO)_5(VP)$  reacted. One of the products proved to be  $W(CO)_6$ . The other was isolated as deep red crystals by column chromatography on alumina and by recrystallization from hexane-ethyl acetate; it was shown to be  $W(CO)_4(VP)_2$  (II) by the correspondence between its spectroscopic properties<sup>11</sup> and those of reported tetracarbonyls<sup>2,3,12</sup> and from an appropriate elemental analysis and mass spectrum.



Complexes made with 4-cyano- and other 4-acylpyridines undergo the same photoreaction, as judged by changes in the UV-vis spectra of sample solutions (Figure 1).<sup>10</sup> No free CO product could be detected by GC-MS analysis. As expected, irradiation of I under a CO atmosphere produced primarily  $W(CO)_6$  and free VP. Visible irradiation of a 50:50 mixture of I and the 4-butyrylpyridine complex produced three product HPLC peaks in the statistical 1:2:1 ratio, the major product having a HPLC retention time intermediate between those of the products formed from irradiation of the individual reactants.

More quantitative studies were undertaken on I with visible excitation at room temperature. Quantum yields for formation of II from dilute I are much higher at 410 nm (0.03) than at 490 nm (0.003); they depend on ground-state complex concentration, doubling as [I] is increased from 0.005 to 0.05 M.<sup>13</sup> Tetracarbonyl formation and I's characteristic 625-nm emission<sup>8</sup> are both quenched with equal efficiency by added anthracene at 490-nm excitation. Linear Stern-Volmer plots yield a  $k_q\tau$  value of  $547 \pm 17$  M<sup>-1</sup> in benzene at  $10^{-3}$  M complex. Quenching of product formation gives plots dependent on excitation wavelength. With 410-nm excitation of  $10^{-2}$  M complex, the Stern-Volmer

**Table I.** Effect of Added Butyrylpyridine on  $W(CO)_4(VP)_2$  Formation with Visible Irradiation<sup>a</sup>

[4-BP], M	$[W(CO)_5(BP)]^b$		$[W(CO)_4(VP)_2]^b$		$[W(CO)_4(BP)(VP)]^b$	
	>400	>475	>400	>475	>400	>475
0	0	0	37.6	12.2	0	0
0.0008	3.3	5.1	25.6	5.2	2.5	0.2
0.0015	7.5	9.1	18.4	2.1	3.6	2.3
0.0031	15.4	15.2	11.0	0.2	4.6	2.2
0.0046	19.3	18.9	7.2	0	5.0	1.6
0.0077	27.8	23.0	3.6	0	4.4	0.6

<sup>a</sup> Argon-bubbled benzene solutions 0.020 M in  $W(CO)_5(VP)$  (VP = 4-valerylpyridine), irradiated in parallel through the appropriate cutoff filters such that yields are proportional to quantum yields; 6 h at >400 nm, 24 h at >475 nm. A 450-W Hanovia mercury arc provided  $10^{16}$ – $10^{17}$  photons L<sup>-1</sup> s<sup>-1</sup>. <sup>b</sup> Product concentrations in units of  $10^{-4}$  M.

plot curves down to a slope of only 30 M<sup>-1</sup>.

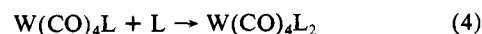
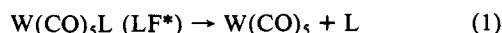
It has been established that these complexes have lowest MLCT excited states<sup>5,7,8</sup> that are relatively substitution inert. The low substitution quantum yields are characteristic of such complexes.<sup>5-8,14</sup> Identical quenching behavior has been observed for the photosubstitution of more dilute complexes by 0.05 M ethanol.<sup>8</sup> If  $k_q$  is the same in benzene as in methylcyclohexane,  $4 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>,<sup>8</sup> then our quenching indicates an excited-state lifetime of 137 ns, which compares to the 197 ns reported for the 4-acetylpyridine complex.<sup>8</sup> Earlier workers have interpreted these kinetics in terms of only the LF state undergoing ligand dissociation, with the lower energy MLCT state merely serving as a thermal reservoir for the slightly higher energy, reactive LF state.<sup>5,8</sup> More importantly, we can conclude that the same excited state processes give rise to both tetracarbonyl formation and solvent displacement of pyridine.

Prior work has suggested that excited  $W(CO)_5L$  complexes undergo competitive dissociation of L (pyridine) or CO, with the latter significant only at higher energy excitation.<sup>2-6</sup> Our results indicate that a coordinatively saturated ground-state complex can serve as a ligand source to a pentacoordinate intermediate. If  $W(CO)_4L_2$  formation were to involve minor CO cleavage, followed by coordination of  $W(CO)_4L$  with a L either on  $W(CO)_5L$  or free in a small-steady state concentration, the presence of excess L should enhance the formation of tetracarbonyl. To our surprise, irradiation (>400 nm) of I in the presence of excess valerylpyridine did not produce II, despite the fact that  $W(CO)_4L_2$  complexes are formed by UV irradiation of such mixtures.<sup>2-6</sup> However, a careful study of the effect of added pyridines on product ratios clarified the situation.

Table I lists the products observed from I in the presence of added butyrylpyridine (BP). The lowest concentrations give both II and  $W(CO)_4(VP)(BP)$ ; at higher concentrations formation of both  $W(CO)_4(pyr)_2$  complexes is quenched and exchange is the dominant reaction. Stern-Volmer plots for quenching of I by added VP revealed  $k_q\tau$  values of only 2 M<sup>-1</sup> for 625-nm emission quenching but 280 M<sup>-1</sup> for product quenching (>400 nm excitation). VP obviously quenches formation of II via a degenerate exchange reaction which involves trapping of an intermediate rather than quenching of excited complex.

Scheme I presents what appears to be the simplest mechanism

#### Scheme I



consistent with our findings.<sup>15</sup> The only significant excited-state

(11) The product does not melt but sublimes at ca. 260 °C; IR (KBr) 1990, 1880, 1855, 1810, 1695, 1410 cm<sup>-1</sup>; UV (MCH)  $\lambda_{max}$  520, 610 (sh) nm, (benzene) 490 nm; <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  198, 204.5, 213.

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(15) The concentration dependence of quantum yields and the apparent wavelength dependence of quenching by added pyridine suggest that more complicated processes may compete with Scheme I, as is already implicit in earlier results.<sup>8</sup>

cleavage at long wavelengths produces  $W(CO)_5$  and pyridine. The former is known to react very efficiently with any ligands present in solution; when extra pyridine is present, exchange results. In pure hydrocarbon solvent, ground-state complex is the only ligand source available. The resulting  $W(CO)_4L$  eventually finds a free pyridine to produce  $W(CO)_4L_2$ . The Stern–Volmer study at 0.02 M I indicates a 5:1 value for  $k_2/k_3$ , which explains why II formation occurs even with dilute I.

Yields of  $W(CO)_4L_2$  previously have been assumed to represent how well CO cleavage competes with L cleavage in excited  $W(CO)_5L$  complexes.<sup>2–6</sup> Our results indicate that, at least for irradiation at wavelengths greater than 400 nm, most of this product arises from L cleavage followed by CO exchange. Of broader interest is the question of how general such CO exchange is.

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### Ultrahigh Resolution NMR. 1. General Considerations and Preliminary Results for Carbon-13 NMR

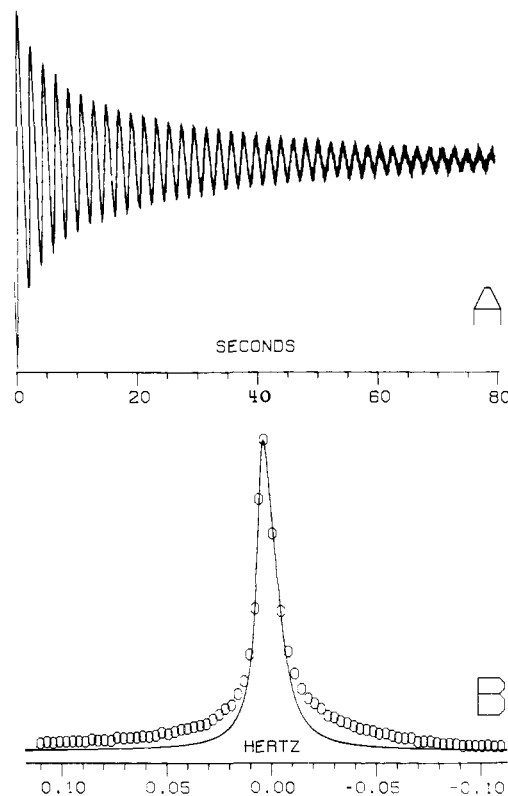
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The efforts to reach higher and higher magnetic fields are justified by the resulting improvements in resolution and sensitivity. Unfortunately, in the last quarter of a century the highest commercially available high-resolution magnetic field has only about doubled. While we wait another quarter of a century to get another factor of 2, we can ask if there are some interim measures that may yield much greater resolution *today*. We describe in this paper the simple instrument modifications that have yielded what we call "ultrahigh resolution" NMR, which we arbitrarily define as having been achieved when there is less than 20-mHz instrumental contribution to the line width (in  $^{13}C$  NMR). The experiments were done on a slightly modified Nicolet NT-200 NMR spectrometer at a  $^{13}C$  resonance frequency of 50.3 MHz, with a standard 12-mm probe and a sample volume of 4.2 mL. Standard single-pulse  $^{13}C$  excitation was used.

Figure 1A shows the free-induction decay (FID) of the non-protonated carbon of toluene (C-1), after four accumulations. After Fourier transformation, Figure 1A yielded an experimental best-fit Lorentzian width at half-height ( $W_{ex}$ ) of 12.6 mHz. In order to determine the instrumental contribution to  $W_{ex}$  we indirectly determined the *lower limit* to the natural line width ( $W_0$ ) from the spin–lattice relaxation time ( $T_1$ ), measured by the inversion-recovery method<sup>1</sup> with composite  $180^\circ$  pulses,<sup>2</sup>  $180^\circ$  phase alternation,<sup>3</sup> intervals between the  $180^\circ$  and  $90^\circ$  pulses in the range 5–120 s (13 values), and 400-s waiting interval between successive  $180^\circ$  pulses. The resulting best-fit least-squares  $T_1$  value was  $72.23 \pm 0.37$  s, which yielded  $1/\pi T_1 = 4.4$  mHz, a good estimate of the *lower limit* to  $W_0$ .<sup>4</sup> Therefore, the *upper limit* to the instrumental broadening ( $W_{in}$ ) of Figure 1A is 8.2 mHz. Figure 1B shows the best single-scan performance to date, with an observed line width of 11.0 mHz, which implies an upper limit to



**Figure 1.** Proton-decoupled C-1 resonance of air-free toluene (with 20% v/v  $CD_3OD$ ) under argon at 22 °C and 50.3 MHz, an acquisition time of 163.84 s, a spectral width of  $\pm 50$  Hz (quadrature detection), and 32K total data points. (A) The initial 80 s of a free induction decay obtained after four scans with a recycle time of 163.94 s. The carrier frequency was set 0.4844 Hz from the C-1 resonance frequency. (B) Fourier-transformed signal of a free induction decay obtained after one scan. Fourier transformation was done with an additional 32K of "zero fill" data points, resulting in a simulated acquisition time of 327.68 s, which yielded a digital resolution of 3.052 mHz. The hexagons are experimental points, and the curve is the best-fit Lorentzian to the top five points, which encompass the peak to just below half-height. Zero frequency has been set at the maximum of the peak.

$W_{in}$  of only 6.6 mHz. This is more than an order of magnitude better than the 200-mHz value normally quoted for high-resolution  $^{13}C$  NMR in a 10- or 12-mm tube. Furthermore, limited digital resolution and inefficiencies of  $^1H$  decoupling have normally conspired to yield  $W_{in}$  values of 500 mHz and more.

Our studies suggest that the resolution performance of typical commercially available high-resolution superconducting magnets is much better than is generally believed and that the available resolution has been masked by broadening from chemical shift gradients caused by *temperature gradients in the sample*.<sup>5</sup> This phenomenon is not surprising if one examines available reports of the temperature dependence of chemical shifts (Table I). We eliminated temperature gradients in our probe, with (i) an increase in the flow of cooling air into the probe from about 10 L/min to about 20 L/min,<sup>6</sup> (ii) a decrease in proton decoupling power from 5 to 1.5 W and less, made possible by the efficiency of WALTZ-16 decoupling,<sup>7</sup> and (iii) improved temperature stability of the cooling air. After these modifications were made an instrumental broadening of 15 mHz and less became routinely available. Magnet shimming time and effort did not increase relative to

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