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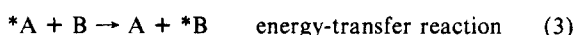
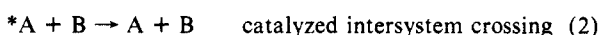
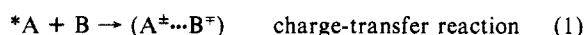
# Sensitized Photoreduction of Bis(acetylacetonato)nickel(II) by Triplet State Aromatic Ketones

Yuan L. Chow,\*<sup>1a</sup> Gonzalo E. Buono-Core,<sup>1a</sup> Carolyn W. B. Lee,<sup>1a,b</sup> and J. C. Scaiano<sup>1c</sup>

Contribution from the Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6, and Division of Chemistry, National Research Council, Ottawa, Canada K1A 0R6. Received April 14, 1986

**Abstract:** Bis(acetylacetonato)nickel(II), Ni(acac)<sub>2</sub>, quenched triplet state aromatic ketones with high efficiency but only certain aromatic ketones with high triplet energy levels successfully sensitized the photoreduction of Ni(acac)<sub>2</sub> to give the acetylacetonone radical and Ni(I) complexes. A short-lived Ni(I) species was detected by ESR and UV spectroscopy, and the acetylacetonone radical was trapped by 2-nitroso-2-methylpropane or phenyl-*tert*-butylnitrone as a stable nitroxide and by H atom donors as acetylacetonone. The transient Ni(I) complexes decayed by either first-order or second-order kinetics, depending on the concentrations, to give Ni(0) complexes or ferromagnetic colloidal nickel. The photoreduction of Ni(acac)<sub>2</sub> occurs only if the acetylacetonone radical was trapped. Various evidence suggested that the quenching mechanism was not likely to occur by energy transfer and was best interpreted to involve a partial charge transfer within an excited-state complex. The acetylacetonone radical in the complex undergoes hydrogen abstraction from solvent in competition with reverse electron transfer. The quantum efficiency of the photoreduction is attributed to the extent of charge-transfer contribution and the hydrogen atom donating ability of solvents. It is also confirmed that the ketyl radical derived from triplet state ketones is not responsible for the reduction of Ni(acac)<sub>2</sub>.

In solution, transition-metal complexes and cations quench the triplet excited states of aromatic ketones and hydrocarbons with high efficiency<sup>2-8</sup> and have been shown to be potential "ultraviolet stabilizers" of polymers in recent years.<sup>4c</sup> The mechanism of deactivation of electronically excited states has been studied extensively by kinetic flash photolysis,<sup>2-6</sup> the investigations of which have lead to a variety of proposals. In early investigations, Hammond's group<sup>3</sup> observed that transition-metal  $\beta$ -diketonates quench the triplet states of the aromatic compounds with similar rate constants in the range of  $10^9 \text{ M}^{-1} \text{ s}^{-1}$  regardless of the triplet state energy levels.<sup>3</sup> Porter's group<sup>2</sup> which pioneered the investigations in this area has found efficient quenching of triplet excited states by paramagnetic species such as oxygen, nitrogen oxides, and metal ions, and suggested a catalyzed intersystem crossing as the mechanism, the nature of which has been expanded along allowed electron spin exchange<sup>9,10</sup> (eq 1) and charge-transfer<sup>2,6,10</sup>



(eq 2) interactions in a complex. The intermediacy of CT com-

plexes in triplet quenching by transition-metal ions was first proposed in the early<sup>6</sup> 60's. Similar patterns of quenching rate constants by a variety of transition-metal complexes were interpreted by Wilkinson's group<sup>4</sup> with an energy-transfer mechanism (eq 3) in which the triplet state energy of sensitizers is assumed to transfer to a lower energy manifold of numerous excited states available in metal complexes (e.g., ligand, CT, and ligand field states, etc.). Balzani et al.<sup>5</sup> have rationalized the energy-transfer mechanism by stating that different plateaus of quenching efficiency arise from the degree of orbital overlaps which affect the transition coefficient. However, more recently, Wilkinson and Tsiamis<sup>4e</sup> have proposed that tris(hexafluoroacetylacetonato)-chromium(III) quenches triplet state aromatic compounds by a combination of energy and electron transfer.

We have discovered that the quenching of certain triplet excited state ketones by bis(acetylacetonato)copper(II), Cu(acac)<sub>2</sub>, was accompanied by various degrees of reduction of copper(II) state<sup>11</sup> and proposed a mechanism involving electron spin exchange (catalyzed intersystem crossing) with a contribution of charge-transfer character.<sup>8</sup> Similar studies of the sensitized photoreduction of bis(acetylacetonato)nickel(II), Ni(acac)<sub>2</sub>, have shown that a charge-transfer process is most likely involved. We wish to expand and elaborate the mechanism reported in an earlier communication.<sup>12</sup>

## Results

**General Reaction Pattern.** Anhydrous bis(acetylacetonato)-nickel(II) has the trimeric form<sup>13-15</sup> showing emerald green color either in the solid state or in noncoordinating solvents at ambient temperature. Its dihydrate, Ni(acac)<sub>2</sub>·2H<sub>2</sub>O, shows aqua blue color. Both forms show similar UV-vis spectra and paramagnetic properties<sup>13</sup> and are assumed to have octahedral structures.<sup>16,17</sup> In this report, the dihydrate form has been used for the experiments but will be written as Ni(acac)<sub>2</sub> for convenience.

We confirmed a previous report<sup>18</sup> that direct irradiation of Ni(acac)<sub>2</sub> in alcohols on the low-energy shoulder (at ca. 310 nm) of the 295-nm absorption band (Pyrex filter) gave no detectable

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**Table I.** Quantum Yields of Ni(acac)<sub>2</sub> Photoreduction Sensitized by Xanthone

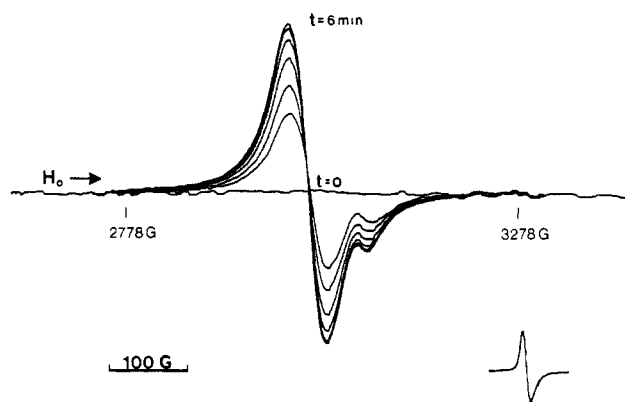
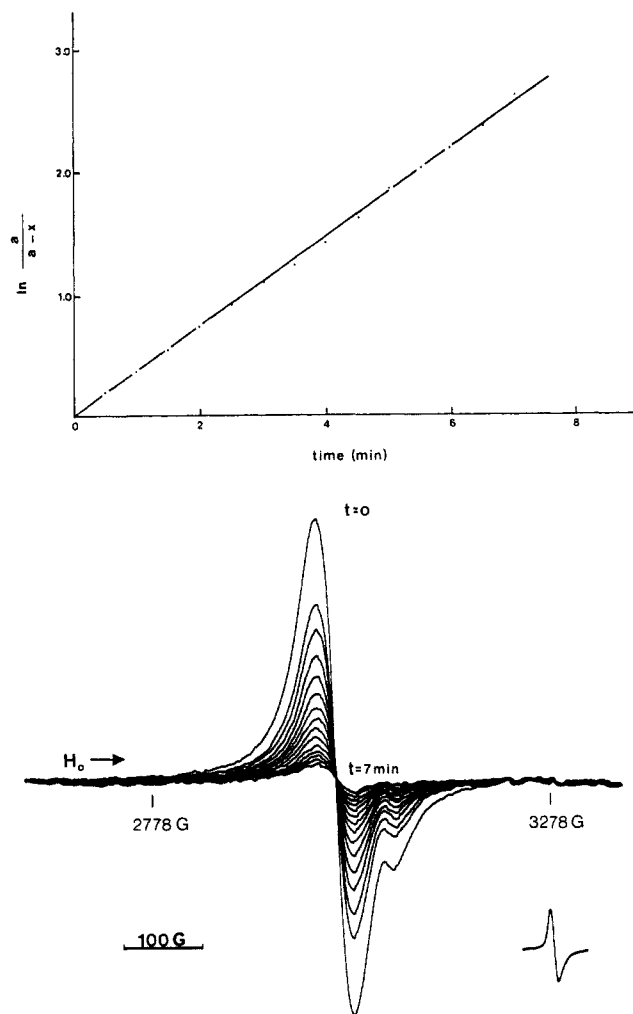
(A) In Ethanol <sup>a</sup>			
[Ni(acac) <sub>2</sub> ], mM	$\Phi_c \times 10^2$	1/[Ni(acac) <sub>2</sub> ]	1/ $\Phi_c$
4.0	13.00	250	7.69
2.0	10.15	500	9.95
1.8	10.10	556	9.90
1.6	9.52	625	10.50
1.4	9.26	714	10.80
1.2	9.22	833	10.85
1.0	8.51	1000	11.75
(B) In Other Alcohols <sup>b</sup>			
solvent	% conversn of Ni(acac) <sub>2</sub>	$\Phi_c$	
methanol	11.7	0.08	
ethanol	21.2	0.14	
2-propanol	50.8	0.32	

<sup>a</sup>Solutions (5 mL) containing xanthone ( $1.5 \times 10^{-2}$  M) were irradiated for 20 min to a 15–25% conversion. Average errors of  $\Phi_c$  were  $\pm 20\%$ . <sup>b</sup>Solutions (5 mL) of Ni(acac)<sub>2</sub> ( $4 \times 10^{-3}$  M) and xanthone ( $1.5 \times 10^{-2}$  M) were irradiated for 25 min. Average errors of  $\Phi_c$  were  $\pm 20\%$ .

photochemical reaction but that on the high energy side (254-nm irradiation) caused slow photoreduction. When a methanolic solution of Ni(acac)<sub>2</sub> and benzophenone (or xanthone) was irradiated under nitrogen through a Pyrex filter, the initial blue-green color faded leading to the deposition of metallic nickel. Exposure of the photolysate to the air caused the slow dissolution of the Ni(0) suspension and film to form blue solution and the restoration of the Ni(acac)<sub>2</sub> absorption at 634 nm. Immediate filtration of the photolysate through Celite gave a colorless solution showing the disappearance of the absorption at 634 nm. GC and HPLC analysis of the filtrate showed that benzophenone (or xanthone) was not consumed and that acetylacetonate (75%) and formaldehyde (65%) were the other products. Similar photolysis in toluene gave acetylacetonate and 1,2-diphenylethane in a 2.3:1 ratio as the products and also deposited metallic nickel. In the presence of triphenylphosphite, the photoreduction of Ni(acac)<sub>2</sub> in ethanol gave<sup>19</sup> Ni[P(OPh)<sub>3</sub>]<sub>4</sub>, confirming Ni(0) as the final state.

In ethanol, the photoreduction of Ni(acac)<sub>2</sub> was readily sensitized in the presence of benzophenone, acetophenone, or xanthone, in this order to decreasing efficiency, under comparable conditions. Other sensitizers such as fluorenone, 2-acetonaphthone, phenanthrene, and *p*-methoxyacetophenone failed to photodecompose Ni(acac)<sub>2</sub> even after prolonged irradiation. The quantum yields of Ni(acac)<sub>2</sub> disappearance ( $\Phi_c$ ) sensitized by xanthone in alcoholic solvents are as shown in Table I:  $\Phi_c$  varied with the order of H atom donating ability of alcohols. Similar sensitized photoreductions in THF also occurred, but the solutions changed to a clear yellow color first before giving Ni(0) precipitate after prolonged irradiation. No photochemical change could be observed in benzene or acetonitrile. This indicated the requirement of hydrogen atom donors to promote the sensitized photoreduction.

**ESR Studies.** Whereas the dihydrate of Ni(acac)<sub>2</sub> exhibited a magnetic moment<sup>13</sup> ( $3.15 \mu_B$  at 26 °C), its solutions in most organic solvents showed feeble ESR signals at  $-150 \text{ }^\circ\text{C} \approx 30 \text{ }^\circ\text{C}$ . Sensitized photoreduction of Ni(acac)<sub>2</sub> in toluene, methanol, or dioxane under argon afforded stable and broad ESR signals of ferromagnetic colloidal<sup>20</sup> Ni(0) ( $g$  value 2.20,  $\Delta H_{pp} \approx 500$  G). However, similar photolysis in THF exhibited rapid increases of an ESR isotropic signal at  $g$  value 2.1867 and  $\Delta H_{pp} = 46$  G (see Figure 1 in ref 12) reaching a photostationary state in a few minutes. The signal was assigned to Ni(I) complexes in analogy to the Ni(I) ESR data reported; e.g., INi(Ph<sub>3</sub>P)<sub>3</sub> in THF<sup>21c</sup> showed

**Figure 1.** ESR signals (recorded at every 1-min interval) obtained in the photolysis of Ni(acac)<sub>2</sub> ( $2 \times 10^{-2}$  M), benzophenone (0.1 M), and P(*n*-Bu)<sub>3</sub> ( $8 \times 10^{-2}$  M) in THF at 23 °C;  $g$  value 2.1867,  $\Delta H_{pp} = 47$  G.**Figure 2.** The decay of the ESR signal of Figure 3 at 29 °C; the spectra were recorded at every 30-s interval. The top is the first-order plot of the decay.

$g$  value 2.180,  $\Delta H_{pp} = 120$  G, which varied substantially depending on the coordinating ligands and conditions.<sup>21</sup> In the dark, the signal decayed with first-order, but not second-order kinetics, with  $k = 5.36 \times 10^{-3} \text{ s}^{-1}$  ( $R = 0.9927$ ), indicating that the Ni(I) species did not decompose by a bimolecular disproportionation (see Figure 2 in ref 12). Irradiation of a similar solution in the presence of P(*n*-Bu)<sub>3</sub> exhibited a split signal (Figures 1 and 2), most probably

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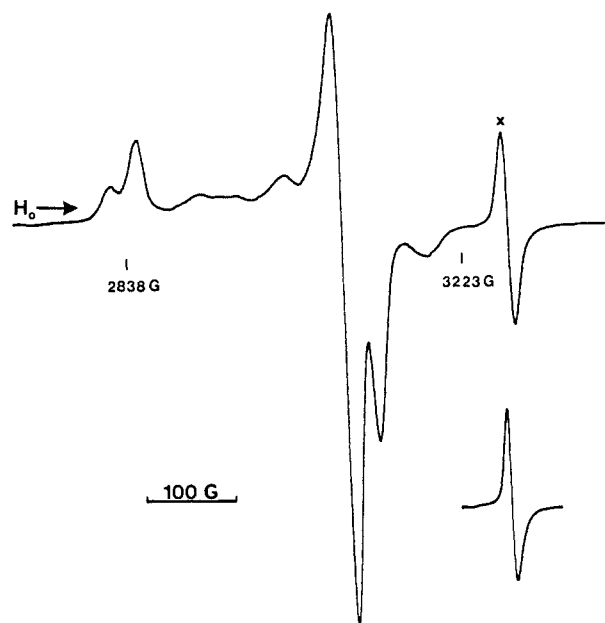
**Table II.** ESR Parameters of Ni(I) Complexes in THF Solution

sensitizers	<i>g</i> values	$\Delta H_{pp}$	<i>T</i> (°C)	ligand
benzophenone	2.1867	46 G	23	
xanthone	2.1872	48 G	22	
benzophenone	2.1945	46 G	22	PPh <sub>3</sub>
benzophenone	2.1867	47 G	23	P( <i>n</i> -Bu) <sub>3</sub>
benzophenone	2.1846	43 G	22	diphos
benzophenone	2.2941			
	2.1270		-150	
	2.0029			
xanthone	2.2936			
	2.1259		-140	
	2.0052			
acetophenone	2.2928			
	2.1259		-150	
	2.0026			
benzophenone	2.2935			
	2.1248		-150	PPh <sub>3</sub>
	2.0018			
benzophenone	2.3037 ( <i>a</i> = 30 G)			
	2.1200 ( <i>a</i> = 30, 55 G)		-140	P(Et) <sub>3</sub>
	2.0032			
benzophenone	2.3140 ( <i>a</i> = 28 G)			
	2.1231 ( <i>a</i> = 28, 54 G)		-140	P( <i>n</i> -Bu) <sub>3</sub>
	2.0064			
benzophenone	2.2926		-150	diphos
	2.1214			
	2.0021			

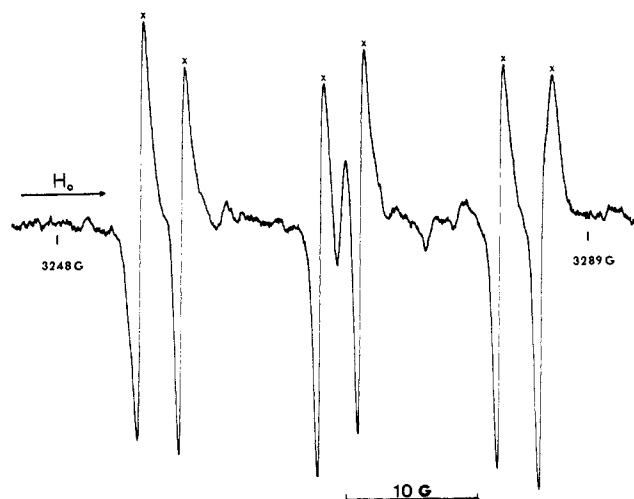
due to coupling with the phosphine ligand. Under these conditions, the Ni(I) complex decayed with  $k = 6.13 \times 10^{-3} \text{ s}^{-1}$  ( $r = 0.9994$ , Figure 2 top). In both cases, second-order plots gave significant curvature. The ESR data of the Ni(I) signal generated under various conditions are summarized in Table II.

The signals were confirmed to arise from a Ni(I) complex by low-temperature experiments. When a Ni(acac)<sub>2</sub>/benzophenone solution in THF was photolyzed at  $< -100^\circ\text{C}$  anisotropic signals at  $g = 2.1270$  and  $g = 2.2941$  became observable (see Figure 3 in ref 12). The higher field signal ( $g = 2.0029$ ) was due to the ketyl radical<sup>22</sup> generated from H abstraction of triplet state benzophenone under the viscous conditions owing to slow diffusion controlled quenching by Ni(acac)<sub>2</sub>. This signal was also obtained in the photolysis of benzophenone in THF without Ni(acac)<sub>2</sub>. At  $-100^\circ\text{C}$ , the ketyl radical signal decayed more rapidly than the other two Ni(I) signals which coalesced to one with  $g$  value 2.1747. On recooling the sample to  $-150^\circ\text{C}$ , the two anisotropic signals reappeared without the ketyl radical signal; thus it was unlikely that the ketyl radical reacted with the Ni(I) species. When xanthone or acetophenone were used as sensitizers, similar ESR patterns were observed in addition to the corresponding ketyl signals (Table II). Low-temperature irradiation in the presence of alkyl phosphines exhibited two anisotropic signals split by phosphorus atoms (Figure 3). The close agreement in  $g$  values and shapes of these two signals with published spectra<sup>21</sup> left no doubt that Ni(I) complexes were formed in the sensitized photoreduction.

The generation of acetylacetonyl radicals during photoreduction was confirmed by spin trapping experiments. In benzene or CH<sub>2</sub>Cl<sub>2</sub>, benzophenone-sensitized photoreduction in the presence of 2-nitroso-2-methylpropane (NMP) gave a doublet of triplet ESR signal ( $a_N = 13.5$ ,  $a_H = 3.13$  G,  $g$  value 2.0058) of *tert*-butyl acetylaceton-3-yl nitroxide<sup>23</sup> (**1**), in addition to other minor unknown signals (Figure 4). In the presence of phenyl-*tert*-butylnitron (PBN) as the trapping agent a different doublet of triplet ( $a_N = 14.38$ ,  $a_H = 5.63$  G) signal was obtained, although the observation only indicates that a radical was generated. In both cases, Ni(acac)<sub>2</sub> was photoreduced as shown by the disappearance

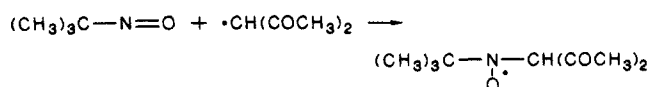


**Figure 3.** ESR spectra recorded at  $-150^\circ\text{C}$ , after irradiation at  $-110^\circ\text{C}$ , of THF solution containing Ni(acac)<sub>2</sub> ( $2 \times 10^{-2}$  M), benzophenone (0.1 M), and P(*n*-Bu)<sub>3</sub> (0.08 M). The benzophenone ketyl radical is marked with an asterisk.



**Figure 4.** The ESR spectra of nitroxide **1** (marked with X) was generated by photolysis of Ni(acac)<sub>2</sub> (0.001 M), benzophenone (0.005 M), and NMP (0.002 M) in methylene chloride.

of the blue-green color. In contrast, in the absence of NMP or PBN, irradiation of benzophenone-Ni(acac)<sub>2</sub> in benzene or CH<sub>2</sub>Cl<sub>2</sub> caused no photoreduction; e.g., no ESR signal and no color change. In THF, sensitized photoreduction of Ni(acac)<sub>2</sub> in the presence of NMP generated the ESR signal of Ni(I) complexes as that observed above, but the doublet of triplet of nitroxide **1** superimposed with other nitroxide signals to give a complex pattern. These observations clearly indicated that acac\* was generated and trapped by NMP in the photoreduction in benzene or CH<sub>2</sub>Cl<sub>2</sub>, but acac\* was partially deactivated presumably by H abstraction from THF. A control experiment by photolysis of benzophenone, acetylacetone, and NMP in benzene showed that no nitroxide **1** but only di-*tert*-butylnitroxide was formed. Even in benzene, both ESR signals of Ni(I) complexes and nitroxide **1** could be obtained if both NMP and P(*n*-Bu)<sub>3</sub> were present.



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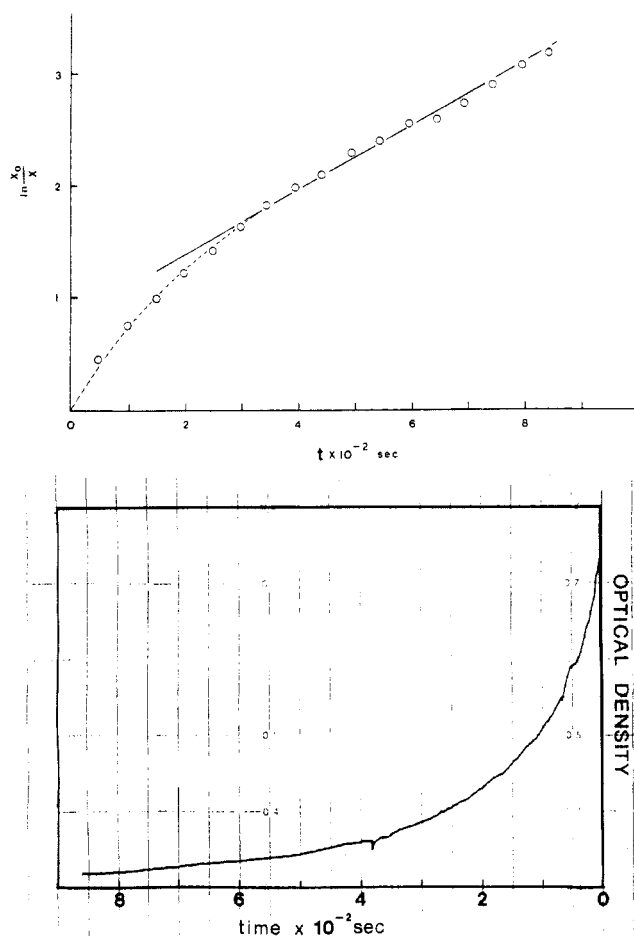


Figure 5. The UV decay trace (OD range 0.05) at 490 nm and 22 °C from the photostationary state (30-s irradiation) of a THF solution containing  $\text{Ni}(\text{acac})_2$  ( $6.85 \times 10^{-3}$  M) and xanthone ( $1.53 \times 10^{-2}$  M). The top is the first-order plot.

**UV Spectroscopic Studies.** In THF, irradiation of  $\text{Ni}(\text{acac})_2$  and xanthone either in the presence or absence of  $\text{P}(\text{OEt})_3$  immediately gave a short-lived absorption in the 450–700-nm region reaching the photostationary state rapidly in 30 s. In the dark, the spectrum rapidly reverted to nearly the original spectrum. The transient absorption obviously arose from the emergence of an intense peak in the 400–500-nm region and decayed rapidly in a few minutes as shown by a trace at 490 nm (Figure 5). The decay trace followed second-order kinetics in the initial portion and first-order kinetics with  $k = 2.68 \times 10^{-3} \text{ s}^{-1}$  at 22 °C ( $r = 0.9975$ ) in the latter portion (Figure 5, top). By analogy to the ESR studies, the transient was assigned to a Ni(I) complex which generally exhibits an intense absorption in the 500-nm region<sup>21b</sup>.

Taking advantage of the homogeneity of the photolysate in the presence of  $\text{P}(\text{OEt})_3$ , the sensitized photoreduction of  $\text{Ni}(\text{acac})_2$  in ethanol (or other alcohols) by longer irradiation intervals (15 min) was followed at 630 nm to give a zero-order decrease of the intensity with respect to irradiation time. In absence of  $\text{P}(\text{OEt})_3$ , irradiation caused Ni(0) metal deposition and frustrated quantitative determinations.

**Quantum Yields Determination.** The quantum yields of  $\text{Ni}(\text{acac})_2$  disappearance ( $\Phi_x$ ) in alcohols were determined by monitoring the  $\text{Ni}(\text{acac})_2$  absorption at 630 nm. The average errors of these determinations was large ( $\pm 20\%$ ) arising from the masking of the absorption due to the transient Ni(I) complex in the 300–400-nm range and due to small amounts of Ni(0) precipitates (see Experimental Section). However, these effects are common and compensated relatively in a series of samples irradiated under the same conditions. As shown in Table I (part A), the quantum yield of the disappearance of  $\text{Ni}(\text{acac})_2$ ,  $\Phi_x$ , in ethanol increased in the  $\text{Ni}(\text{acac})_2$  concentration range of 1.0–4.0 mM to reach a nearly limiting value of 0.13 at  $>4.0$  mM. In the

Table III. Quantum Yields of Xanthone Disappearance by  $\text{Ni}(\text{acac})_2$  Quenching in Ethanol at 23 °C<sup>a</sup>

$[\text{Ni}(\text{acac})_2]$ , mM	% conversn	$\Phi_x$	$\Phi_x^\circ/\Phi_x$
4.0	0.0	0.000	
2.0	5.4	0.011	6.53
1.0	8.6	0.017	4.12
0.8	11.7	0.023	3.01
0.6	14.1	0.028	2.49
0.4	16.8	0.033	2.09
0.2	18.4	0.037	1.92
0.0	35.3	0.070 ( $\Phi_0$ )	1.00

<sup>a</sup> The concentration of xanthone was  $1.53 \times 10^{-2}$  M, and the solutions were irradiated for 90 min. Average errors  $\Phi_x$  were  $\pm 15\%$ .

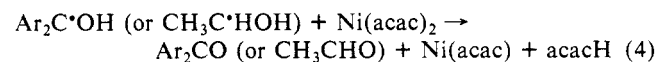
presence of low concentrations of  $\text{Ni}(\text{acac})_2$ , the quantum yields of xanthone disappearance,  $\Phi_x$ , decreased as  $[\text{Ni}(\text{acac})_2]$  increased reaching  $\Phi_x = 0$  at the  $\text{Ni}(\text{acac})_2$  concentration above 4 mM (Table III). This indicated that total quenching of the triplet state by  $\text{Ni}(\text{acac})_2$  at this concentration coincided with  $\Phi_c$  reaching the limiting value of 0.13.

**Flash Photolysis.** The quenching of the triplet states of several sensitizers by  $\text{Ni}(\text{acac})_2$  in methanol was examined under oxygen free conditions by flash photolysis by using a pulsed nitrogen laser (337.1 nm, 8 ns,  $<10$  mJ/pulse) for excitation. The details of the instrument have been published,<sup>24</sup> and the procedures and calculations of bimolecular quenching rate constants  $k_q$  follow well-established methods.<sup>8,24</sup>

The results together with the relevant triplet state energies<sup>25</sup> and reduction potentials<sup>8</sup> ( $E_{A/A^-}$ ) are summarized in Table IV. When  $\log k_q$  was plotted against  $E_T$  a poor linear correlation with  $r = 0.94$  was observed. A better correlation was obtained between  $\log k_q$  and  $-(E_T + E_{A/A^-})$  with  $r = 0.9905$ . The quantity  $-(E_T + E_{A/A^-})$  is defined as the free energy available for sensitizers to accept one electron according to Weller's empirical relation<sup>26</sup> for electron transfer. If only aromatic ketones were examined as a homogeneous family of sensitizers, the spread of  $E_T$  is merely 5 kcal/mol but that of  $-(E_T + E_{A/A^-})$  is 14 kcal/mol. As the  $k_q$  for aromatic ketone sensitizers changed only by a factor of about 2.5, the correlation is not unambiguous but still suggests electron transfer rather than energy transfer (vide infra) as a reaction mechanism.

## Discussion

The results indicate, first, that the triplet excited state ketones sensitized photoreduction of  $\text{Ni}(\text{acac})_2$  generate  $\text{Ni}(\text{acac})$  complexes which either disproportionate bimolecularly to Ni(0) and  $\text{Ni}(\text{acac})_2$  or dissociate by an unimolecular (or pseudounimolecular with ligands) reaction to give Ni(0) and  $\text{acac}^\bullet$ . Second,  $\text{acac}^\bullet$  is generated on irradiation and trapped by H atom donors as acetylacetone or by NMP as nitroxide 1. Third, the sensitized photoreduction of  $\text{Ni}(\text{acac})_2$  can occur as long as  $\text{acac}^\bullet$  is trapped by H atom donors or radical trappers (NMP or PBN). Fourth, the interaction of triplet excited ketones with  $\text{Ni}(\text{acac})_2$  is very fast and unlikely to involve energy transfer but may involve a degree of electron transfer. Finally, a mechanism utilizing a ketyl radical as a reducing agent of  $\text{Ni}(\text{acac})_2$  (eq 4) can be definitely



excluded by the observation that the sensitized photoreduction of  $\text{Ni}(\text{acac})_2$  occurs in benzene as long as NMP or PBN is present. The last conclusion is supported by kinetic analysis of the quenching of triplet xanthone by  $\text{Ni}(\text{acac})_2$  in which the bimolecular rate constant is shown to be nearly diffusion controlled

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**Table IV.** Rate Constants for Quenching ( $k_q$ ) of Triplet Sensitizers by Ni(acac)<sub>2</sub> in Methanol (at 23 °C) as Determined by Flash Photolysis

sensitizer (nm) <sup>a</sup>	$E_T^b$	$E_{A/A^-}^c$	$-(E_T + E_{A/A^-})$	$k_q \times 10^{-9} \text{ M}^{-1} \text{ s}^{-1}$
xanthone (610)	74.2	-26.9	-47.3	6.42
benzophenone (535)	69.1	-31.3	-37.8	2.90
propiophenone (365)	74.6	-35.9	-38.7	4.85
<i>p</i> -methoxyacetophenone (390)	71.7	-39.1	-32.6	2.48
phenanthrene (483)	62.2	-56.1	-6.1	0.20
fluorenone	53.3	-18.2	-35.1	<i>d</i>
anthracene (435)	42.0	-44.2	+2.2	<0.001

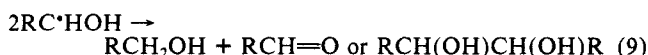
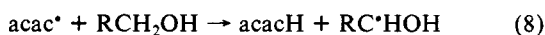
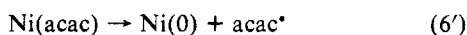
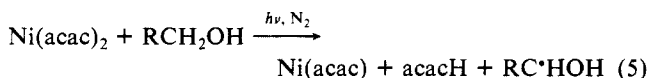
<sup>a</sup>The wavelength (nm) at which the triplet decay was monitored. <sup>b</sup>The lowest triplet state energy quoted from ref 25 (in kcal/mol). <sup>c</sup>The half-wave reduction potential of sensitizers as determined by cyclic voltammetry in kcal/mol (see ref 8). <sup>d</sup>The triplet state signal was weak and quenched very feebly.

one and several orders of magnitude higher than that of H abstraction from solvent (vide infra). Such a mechanism is expected to generate acacH but not acac<sup>•</sup>, as shown in eq 4. It is also known<sup>22</sup> and confirmed by us that triplet excited benzophenone does not undergo photoreduction in benzene (and, therefore, no ketyl radical formation), either in the presence or absence of NMP.

**Sensitized Reduction of Ni(acac)<sub>2</sub>.** The observations of the ESR signal of Ni(I) complexes in THF as opposed to that of ferromagnetic colloidal Ni(0) in toluene, alcohols, and dioxane may reflect sufficient stabilization of Ni(acac) by coordination with THF to enable the transient species to be detected by ESR and UV spectroscopy as shown in Figures 1–5. The lack of coordinating ligands in the latter solvents may permit Ni(acac) to rapidly form colloidal Ni(0), as in eq 6'. Indeed, even in benzene the ESR signal of the Ni(I) complex could be detected if P(*n*-Bu)<sub>3</sub> and NMP are present. While the latter traps the acac<sup>•</sup> radical, the former stabilizes the Ni(acac) species. The ESR anisotropic signals at low temperature are typical for Ni(I) complexes<sup>21</sup> in which  $\Delta g_{\perp} < \Delta g_{\parallel}$ . This is a clear indication that the signals do not arise from Ni(III) species<sup>27</sup> which should have negative  $\Delta g_{\parallel}$ .

In the UV and ESR monitors, the first-order decay rate constants of Ni(I) complex arising from primary photoreduction (Figures 2 and 5) are comparable considering the temperature differences. In ESR monitors, detectable concentrations of Ni(I) transient are typically in the range of 10<sup>-6</sup>–10<sup>-8</sup> M. Because of this low Ni(I) concentration range, Ni(I) complexes preferentially undergo an unimolecular reaction (eq 6') or with the participation of solvent (eq 6). When the reaction is monitored by UV detection, the Ni(I) concentration will be higher, typically in the 10<sup>-3</sup>–10<sup>-4</sup> M range; the initial stage of the decay is dominated by bimolecular kinetics (eq 7). Considering the light intensity of preparative and quantum yield runs and the slow unimolecular decay rate constant, it is expected that Ni(I) complex concentrations are high enough at a photostationary state to follow the bimolecular path, as in eq 7.

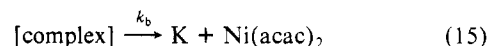
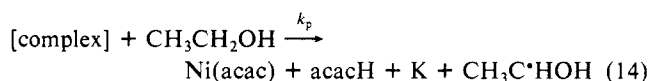
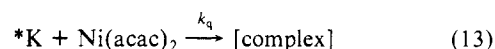
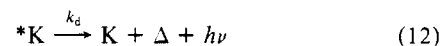
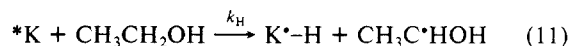
The general reaction pattern could be summarized as shown in eq 5–9, where Ni(acac) represents the transient Ni(I) complex without knowing the state of association with other ligands.



While both benzophenone and xanthone are efficient sensitizers, xanthone has an advantage in possessing a higher extinction coefficient in the 300–350-nm region and a disadvantage in having a high and solvent-dependent self-quenching rate constant of its triplet.<sup>28–30</sup> However, for concentration in 10<sup>-2</sup> M region, the

overall rate of quenching by Ni(acac)<sub>2</sub> is much faster (vide infra) than that of the self-quenching; also, the contribution from the self-quenching is largely compensated since the similar experimental conditions are used in the quantum yield determinations.

**Mechanisms of Quenching.** For the purpose of kinetic analysis a simplified mechanism shown in eq 10–15 is proposed for the sensitized photoreduction of Ni(acac)<sub>2</sub> shown in eq 5. The scheme is a minimum requirement to express events of the quenching where \*K is a triplet excited state ketone; [complex], a charge-transfer complex between \*K and Ni(acac)<sub>2</sub>, is assumed for the kinetic analysis and will be elaborated later.



The steady-state treatment of the reaction scheme affords Stern–Volmer type eq 16 and 17, where  $\tau_0 = (k_d + k_H[\text{EtOH}])^{-1}$

$$1/\Phi_c = 1/\beta + 1/(\beta k_q \tau_0 [\text{Ni(acac)}_2]) \quad (16)$$

$$\beta = k_p/(k_p + k_b)$$

$$\Phi_x^0/\Phi_x = 1 + k_q \tau_0 [\text{Ni(acac)}_2] \quad (17)$$

is the lifetime of a triplet state ketone in ethanol, and the probability of the intersystem crossing from the singlet state <sup>1</sup>K to the triplet state <sup>3</sup>K is taken as unity.<sup>28</sup> The rate constants  $k_p$  and  $k_b$  represent the reaction of the complex with the solvent leading to products (eq 14) and the reverse electron-transfer reaction leading to starting materials (eq 15), respectively; the two reactions compete to dissipate the complex.

As shown in Tables I and III, above Ni(acac)<sub>2</sub> concentration of 4 mM the rate of complex formation in eq 13 dominates the deactivation of triplet state xanthone, and the hydrogen abstraction in eq 11 becomes unimportant; below this concentration, both eq 11 and 13 compete for triplet xanthone to give quantum yields of the disappearance of xanthone and Ni(acac)<sub>2</sub>,  $\Phi_x$  and  $\Phi_c$ , respectively. The plots of  $1/\Phi_c$  vs.  $1/[\text{Ni(acac)}_2]$  according to eq 16 and  $\Phi_x^0/\Phi_x$  vs.  $[\text{Ni(acac)}_2]$  according to eq 17 give straight lines as shown in Figures 6 ( $r = 0.9680$ ) and 7 ( $r = 0.9923$ ) and yield  $k_q \tau_0$  of 2280 and 2730 M<sup>-1</sup>, respectively. The agreement of these two  $k_q \tau_0$  values is good in view of the fact that two independent measurements,  $\Phi_c$  and  $\Phi_x$ , are determined for kinetic analysis. This supports the basic mechanism outlined in eq 10–15

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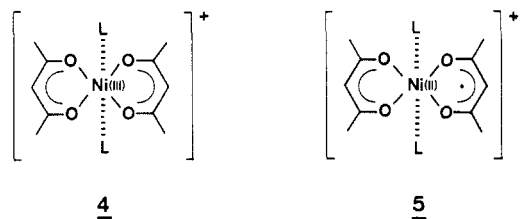
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(acac)<sub>2</sub> was studied in acetonitrile by using cyclic voltammetry.<sup>8</sup> Two irreversible oxidation waves were observed (Figure 8) with half-wave potentials ( $E_{1/2}$ ) of +1.10 and +1.50 V. Assuming that the first half-wave potential corresponds to the oxidation of Ni(acac)<sub>2</sub> → Ni(acac)<sub>2</sub><sup>•+</sup>, these triplet state aromatic ketones should have enough reduction potential,  $-(E_T + E_{A/A^{\bullet-}})$ , to drive one-electron transfer. Therefore, the formation of the CT complex 2 or 3 is certainly feasible.

It is speculated that the transient Ni(acac)<sub>2</sub><sup>•+</sup> or Ni(acac)<sup>•+</sup>·acac species may have the Ni(III) state 4 or Ni(II)-ligand radical structures 5. Structure 5 has the unpaired electron



associated within the acetylacetonate ligand and probably delocalized in the  $\pi$ -orbital. The highest occupied orbital in Ni(acac)<sub>2</sub> is probably the 3d orbital of nickel. If the overlap of the interacting orbitals in the quencher and sensitizer is favorable, and one of these electrons is transferred out, structure 4 can be obtained as the primary species. This may lead to 5 by intramolecular redox reactions depending on their energy levels. The hydrogen abstraction reaction may occur from an alkoxy or carbon radical center of acetylacetonate moiety.

## Experimental Section

**General Conditions and Materials.** Melting points were determined on a Fisher-Johns apparatus and were uncorrected. Infrared spectra were obtained with a Perkin-Elmer 599-B spectrophotometer and UV spectra with a Cary 210 spectrophotometer. Gas chromatography was performed on a Varian 1400 (FID) with a SE-30 capillary column (J&W, 15 m × 0.28 mm) or a Hewlett-Packard 5792-A with an OV-1 capillary column (HP, 12.5 m × 0.20 mm). HPLC analyses were performed on a Waters Associates HPLC system equipped with a  $\mu$ -Porasil analytical column (Waters) by using 1% isopropanol in hexane as the solvent. Anisole was used as internal standard for quantitative analysis by using a Hewlett-Packard HP-3390 integrator for area calculations. ESR spectroscopy was carried out with a Varian E-4 EPR spectrometer (X-band, 9 GHz) equipped with a Varian E-257/WL-257 variable temperature accessory. A Varian Strong Pitch sample ( $g = 2.0026$ ) was used as the external marker.

Ni(acac)<sub>2</sub> was prepared by the known method<sup>31</sup> and recrystallized twice from methanol before using. Commercially available sensitizers as well as phosphines and phosphites were purified by distillation or recrystallization. Nitrogen gas (Union Carbide) was purified by scrubbing through a Fieser solution followed by concentrated sulfuric acid and KOH pellets.

**Apparatus.** For large scale preparative photolysis, an immersion-type photocell<sup>8</sup> was used. Quantum yield determinations were carried out in small phototubes in a "merry-go-round" apparatus, equipped with a quartz cooling jacket. The Pyrex phototubes of ca. 5 mL capacity (1.2 cm diameter × 10 cm length) were equipped with a gas inlet and outlet with a mercury seal for degassing. The light sources were a Hanovia 450-W (679A36) or a 200-W (654A36) medium pressure Hg lamps. Laser flash photolysis and the treatment of data followed the published method.<sup>8,24</sup> For cyclic voltammetry, the machine and conditions were the same as described previously.<sup>8</sup>

**Xanthone Sensitization.** (a) **In Methanol under Nitrogen.** A solution of Ni(acac)<sub>2</sub> (0.7 g, 2.4 mmol) and xanthone (0.9 g, 4.6 mmol) in methanol (150 mL) under nitrogen was irradiated with a 450-W lamp for 2 h to give a dark solution. After 4 h of irradiation, a metallic suspension was obtained. A sample of the photolysate was immediately filtered through Celite to give a colorless solution which showed no absorption of Ni(acac)<sub>2</sub> at 634 nm. The solution was analyzed by HPLC to show two peaks corresponding to acetylacetonate (75% based on the amount of Ni(acac)<sub>2</sub> used) and xanthone (97%). During photolysis, a trap containing a 2,4-DNPH solution was placed at the outlet of the nitrogen gas. After photolysis a yellow precipitate was collected and identified as the 2,4-DNPH of formaldehyde (0.325 g, 65% based on

Ni(acac)<sub>2</sub> used) by its IR spectrum. The solid was recrystallized from aqueous methanol: mp 166–167 °C (lit. mp 166 °C).<sup>32</sup>

(b) **In Toluene under Nitrogen.** A solution of Ni(acac)<sub>2</sub> (0.72 g, 2.4 mmol) and xanthone (0.5 g, 2.55 mmol) in toluene (100 mL) under nitrogen was irradiated for 1½ h to give a dark solution. After 2 hours of irradiation, the photolysate was filtered through a small column of silica gel by using a small amount of toluene as eluent to give a colorless solution. GCMS analysis of this solution (OV-1, 15 m × 0.2 mm, 60° to 230° at 10° per minute) showed three peaks as follows: at 1.83 min for acetylacetonate,  $m/e$  100 ( $M^+$ , 23), 85 (64), 43 (100); 8.01 min for 1,2-diphenylethane,  $m/e$  182 ( $M^+$ , 90), 91 (100), 65 (53); 11.80 min for xanthone,  $m/e$  196 ( $M^+$ , 100), 168 (37), 189 (30). By using anisole as internal standard, the yield of 1,2-diphenylethane and acetylacetonate were determined to be 0.83 and 1.95 mmol, respectively.

**ESR Studies.** A solution of Ni(acac)<sub>2</sub> ( $2 \times 10^{-2}$  M) and a sensitizer ( $10^{-1}$ – $10^{-2}$  M) in tetrahydrofuran (distilled over LiAlH<sub>4</sub> and stored under nitrogen and Na wires) was deaerated with argon in a quartz ESR cell (4 mm) fitted with a septum. The cell was placed in the cavity and irradiated with a 200-W PEK-202 mercury lamp through a filter solution (CoSO<sub>4</sub>·7H<sub>2</sub>O, 24 g/L) placed in a Pyrex cylinder. The distance between the cell and the lamp source was ca. 30 cm.

**UV Spectroscopic Studies.** A THF solution of Ni(acac)<sub>2</sub> (0.02 M) and xanthone (0.02 M) was irradiated in a 1-cm UV cell with the same setup described above at 22 °C. The distance of the light source and the cell is 5 cm. At every 30 s, the absorption at 400–800 nm was scanned to show intensity increased to a constant spectrum within 1 min; after 1 min, the spectrum did not change on further irradiation. In the dark, the enhanced spectrum decayed rapidly (Figure 5) in several minutes to the shape of the original spectrum with diminished intensities. Prolonged irradiation showed slow decreases of the 630-nm band.

**Quantum Yield Determinations.** Solutions (5 mL) containing xanthone ( $1.5 \times 10^{-2}$  M) and Ni(acac)<sub>2</sub> ( $10^{-3}$ – $10^{-4}$  M) were placed in Pyrex tubes and purged with purified nitrogen for 10 min. The tubes were placed in a merry-go-round apparatus and irradiated with a 450-W lamp placed in a quartz jacket for a prescribed time. For determinations of Ni(acac)<sub>2</sub> concentrations, the photolysates were centrifuged for 10 min and filtered through a pipet packed with Celite (100 mg) before being analyzed by UV spectroscopy. For HPLC determinations of xanthone concentrations, the photolysates were injected directly into the HPLC column ( $\mu$ -Porasil, 30 cm × 3.9 mm); 0.5% *i*-PrOH/hexane was the eluent, and the flow rate was 1 mL/min at 350 psi. Anisole was used as the internal standard, and readings from 2–3 injections were averaged to give the data. In each series of experiments, benzophenone (0.05 M)/benzhydrol (0.1 M) in benzene was used as the secondary actinometer.<sup>33</sup> At the concentration range ( $\sim 5 \times 10^{-2}$  M) of xanthone and benzophenone, light energy <380 is totally absorbed in both cases. The incident light absorbed by the sensitizer was calculated by the proportionality of optical density at 330 nm and was shown to range 96.0–99.7% in  $\Phi_x$  determinations and 96.9–98.4% in  $\Phi_c$  determinations.

**Photolysis of Ni(acac)<sub>2</sub> in the Presence of Various Sensitizers in EtOH.** In Pyrex tubes, 5 mL of ethanol solution containing Ni(acac)<sub>2</sub> (2 mg/mL) tetraglyme (75  $\mu$ L) and appropriate amounts of sensitizers were degassed by nitrogen purging. These tubes were irradiated with a 200-W mercury lamp placed in a quartz jacket for 5 h. Except for acetone sensitization, nickel metal precipitates began to form in less than 1 h of irradiation. When the nickel metal precipitate appeared, the tube was removed, and the solutions were filtered through small columns of Celite and were analyzed by UV spectroscopy at 630 nm and GC against the internal standard. The decreases at 630 nm and the formations of acetylacetonate for these tubes were about the same percentages in each case. The times required for the nickel metal formation were in the increasing order of benzophenone (6 mg/mL) > acetophenone (60 mg/mL) > xanthone (3 mg/mL) >> acetone (80% in EtOH).

No UV absorption change could be observed for the tubes containing fluorenone (5 mg/mL), acetophenone (5 mg/mL), phenanthrene (6 mg/mL), and *p*-methoxyacetophenone (10 mg/mL) as sensitizers after 7 h of irradiation.

**Xanthone-Sensitized Photoreduction of Ni(acac)<sub>2</sub> in the Presence of Triphenyl Phosphite.** A solution of Ni(acac)<sub>2</sub> (0.25 g, 0.86 mmol), xanthone (0.35 g, 1.75 mmol), and P(OPh)<sub>3</sub> (1.06 g, 3.42 mmol) in 95% ethanol (150 mL) was irradiated with a 200-W lamp under nitrogen to give a white solid which increased considerably after 6 hours of irradiation. The solid was collected and recrystallized from benzene/methanol to give tetrakis(triphenylphosphito)nickel(0) (49%) as white microcrystals: mp 151–153 °C (lit. mp 151–152 °C);<sup>19</sup> IR (nujol) 1853 (s), 1485

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(s), 1218 (s), 1200 (s), 1180 (s), 1158 (s), 890 (s), 750 (m), 710 (m), 690 (m), 610 (m), and 590 (s)  $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  6.83 (m, b) ppm.

**Acknowledgment.** We thank the Natural Sciences and Engineering Research Council of Canada, Ottawa, for generous financial support and Dr. A. McAuley for valuable suggestions.

**Registry No.** acac, 17272-66-1;  $\text{Ni}(\text{acac})_2$ , 3264-82-2;  $\text{Ni}^+$ , 14903-34-5;  $\text{Ni}$ , 7440-02-0; xanthone, 90-47-1; benzophenone, 119-61-9; acetophenone, 98-86-2; propiophenone, 93-55-0; *p*-methoxyacetophenone, 100-06-1; phenanthrene, 85-01-8; fluorenone, 486-25-9; anthracene, 120-12-7; methanol, 67-56-1; ethanol, 64-17-5; 2-propanol, 67-63-0; 2-nitroso-2-methylpropane, 917-95-3; phenyl-*tert*-butylnitron, 3376-24-7.

## NMR of $^{31}\text{P}$ Heteroatoms in Paramagnetic One-Electron Heteropoly Blues. Rates of Intra- and Intercomplex Electron Transfers. Factors Affecting Line Widths

Mariusz Kozik, Charles F. Hammer, and Louis C. W. Baker\*

Contribution from the Department of Chemistry, Georgetown University, Washington, D.C. 20057. Received May 5, 1986

**Abstract:** Heteropoly complexes are increasingly used as catalysts and specialized redox reagents, making knowledge of electron-exchange characteristics important. Relatively sharp  $^{31}\text{P}$  NMR signals ( $\nu_{1/2} = 1\text{--}15\text{ Hz}$ ) are observed at room temperature from the heteroatoms in paramagnetic one-electron heteropoly blue reduction products of  $\alpha\text{-}[\text{PW}_{12}\text{O}_{40}]^{3-}$  and  $\alpha\text{-}[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$  in aqueous solution. Line broadenings for equimolar mixtures of the reduction products and their isostructural oxidized parent heteropoly complexes enable calculation of rates of exchange of the delocalized electrons between each reduced complex and its oxidized isomorph. These exchange rates correspond exactly to diffusion-controlled rates for the  $\alpha$ -18-tungstodiphosphates and for the  $\alpha$ -12-tungstophosphates, although the rate for the former, larger complex is 3 orders of magnitude slower than for the latter. The similarly evaluated electron-exchange rate between  $\alpha\text{-}[\text{P}_2\text{Mo}_3\text{W}_{15}\text{O}_{62}]^{6-}$  and its one-electron reduction product, wherein the added electron is delocalized over the three Mo atoms in one end of the ellipsoidal complex, is an order of magnitude slower than that calculated for diffusion control, probably owing to necessity for contact between the  $\text{Mo}_3\text{O}_{13}$  caps of the exchanging complexes. Extents of broadenings of the two  $^{31}\text{P}$  NMR lines of 1 $\epsilon$  blue  $\alpha_1\text{-}[\text{P}_2\text{MoW}_{17}\text{O}_{62}]^{7-}$  and its  $\alpha_2$  isomer show that the  $^{31}\text{P}$  atoms' relaxation mechanism is essentially purely dipolar. Thus, intracomplex exchange rates can be calculated from line widths for electrons hopping among the 12 belt W atoms in  $\alpha\text{-}[\text{P}_2\text{W}_{18}\text{O}_{62}]^{7-}$  and among the 3 cap Mo atoms in  $\alpha\text{-}[\text{P}_2\text{Mo}_3\text{W}_{15}\text{O}_{62}]^{7-}$ . Electron hopping in the latter isomorph is  $\sim 25$  times slower than in the former.

Many heteropoly anions<sup>1-4</sup> yield, upon reduction by addition of various numbers of electrons, products which typically retain the general structures of their oxidized parents<sup>5</sup> and are frequently deep blue in color. These are generally known as "heteropoly blues". The added ("blue") electrons are usually delocalized, according to various time scales, by means of very rapid hopping between certain "addenda" atoms (i.e., W, Mo, V, etc.) in certain regions of the structures. Heteropoly complexes are finding increasing use as catalysts and specialized redox reagents,<sup>6</sup> making knowledge of electron-exchange characteristics important. Factors involved in NMR study of these complexes attract attention.<sup>7-13</sup>

This paper reports that unexpected relatively sharp  $^{31}\text{P}$  NMR lines ( $\Delta\nu_{1/2} = 1\text{--}15\text{ Hz}$ ) are observed at room temperature for the central heteroatoms in the one-electron heteropoly blue reduction products of  $\alpha\text{-}[\text{PW}_{12}\text{O}_{40}]^{3-}$  (Keggin structure) and  $\alpha\text{-}[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$  (Wells-Dawson structure). See Figure 1. This is the first report of any NMR spectra for paramagnetic heteropoly blue species (i.e., those containing odd numbers of delocalized blue electrons). Also reported and discussed below are the  $^{31}\text{P}$  NMR spectra of one-electron reduction products of  $\alpha\text{-}[\text{P}_2\text{Mo}_3\text{W}_{15}\text{O}_{62}]^{6-}$ , of  $\alpha_1\text{-}[\text{P}_2\text{MoW}_{17}\text{O}_{62}]^{6-}$ , and of  $\alpha_2\text{-}[\text{P}_2\text{MoW}_{17}\text{O}_{62}]^{6-}$  (Figure 1).

The absence of a  $^1\text{H}$  NMR spectrum for the central protons in the paramagnetic 1 $\epsilon$  blue reduction product of Keggin structure metatungstate,<sup>2,14</sup>  $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{7-}$ , and the reappearance of a slightly shifted proton signal upon further reduction to the diamagnetic 2 $\epsilon$  blue,  $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{8-}$ , had made observation of NMR signals from heteroatoms in paramagnetic blue complexes seem improbable.

For solutions of the 12-tungsto-, 18-tungsto-, and 15-tungstophosphates cited, the line widths of the  $^{31}\text{P}$  NMR signals make it possible to evaluate the rates of electron exchanges between the paramagnetic one-electron reduced species and their fully oxidized diamagnetic isomorphs. Use of ESR data to estimate such exchange rates has been precluded for these unsubstituted Keggin or Wells-Dawson complexes by very large line widths. It is also possible to use the NMR data to estimate the rates of intracomplex electron hopping from  $\text{W}^{5+}$  to  $\text{W}^{6+}$  and, in  $\alpha\text{-}[\text{P}_2\text{Mo}_3\text{W}_{15}\text{O}_{62}]^{7-}$ , among the Mo atoms.

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