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

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Aromatic ketones with high triplet state energy sensitized the photoreduction of bis(acetylacetonato)nickel(II), Ni(acac)$_2$, to give transient Ni^I complexes which decomposed to Ni^0 complexes in the dark.

Triplet state aromatic ketones and hydrocarbons are known to be efficiently quenched by a variety of metal complexes, as shown by flash excitation studies.[1—5] We have found that only certain high triplet energy ketones, *e.g.*, xanthen-9-one, benzophenone, or acetophenone, can sensitize the photoreduction of bis(acetylacetonato)nickel(II), Ni(acac)$_2$, to Ni^I complexes in H-atom donating solvents such as alcohols, tetrahydrofuran, and toluene. Fluoren-9-one, 2-acetonaphthone, *p*-methoxyacetophenone, and phenanthrene, while their triplet signals were efficiently quenched, failed to sensitize the photoreduction.

The dihydrate of Ni(acac)$_2$ utilized in this investigation has a

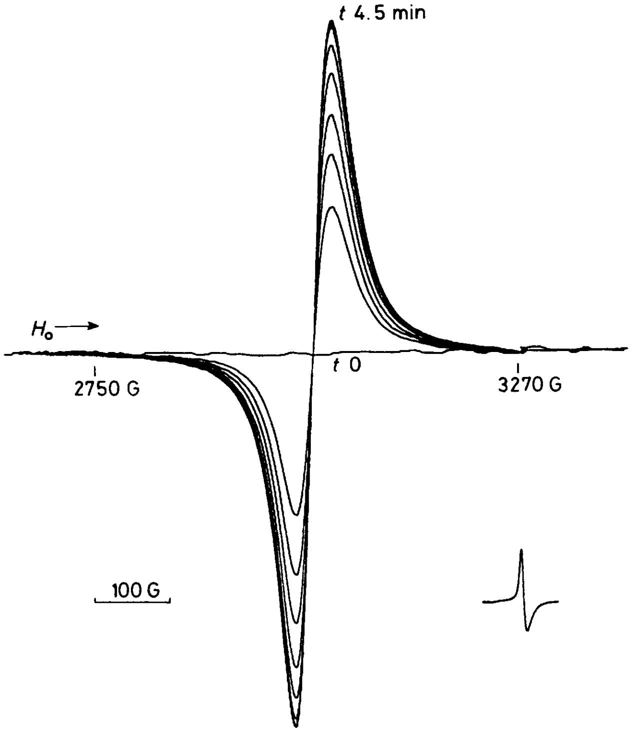

Figure 1. The e.s.r. signals recorded every 30 s following irradiation of $Ni(acac)_2$ (2×10^{-2} M) and benzophenone (10^{-1} M) in tetrahydrofuran at 22 °C; *g*-value 2.186, ΔH_{pp} = 46 G (1G = 10^{-4} T).

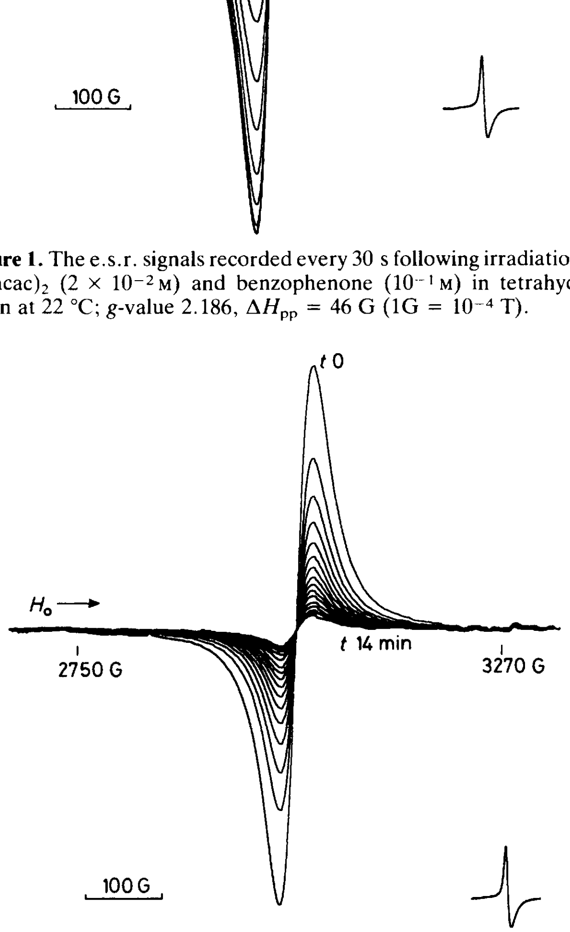

Figure 2. The decay of the e.s.r. signal of Figure 1, recorded at 29 °C at 1 min intervals.

high-spin octahedral configuration and exhibits λ_{max} 295—300 nm with shoulders at 255 and 312 nm.[6] Benzophenone (or xanthen-9-one) sensitized photolysis of $Ni(acac)_2$ in methanol under nitrogen (Pyrex filter, $h\nu > 300$ nm) gave metallic nickel, acetylacetone (75%), and formaldehyde (65%) efficiently; sensitizers were not consumed. Acetaldehyde, acetone, and 1,2-diphenylethane were the oxidation products when ethanol, propan-2-ol, and toluene were used as solvents, respectively; in benzene and acetonitrile, no photoreduction occurred although triplet state ketones were totally quenched.

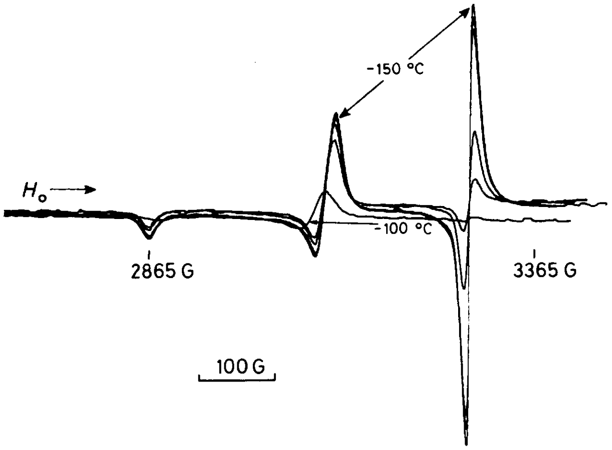

Figure 3. The e.s.r. signals recorded at −150 °C under similar irradiation conditions as in Figure 1; the spectra were taken at 10 °C increments up to −100 °C.

Direct irradiation of $Ni(acac)_2$ through a Corex or Pyrex filter caused no photoreduction.[7] The photoreduction to the Ni^0 state was confirmed by the isolation of $Ni[P(OPh)_3]_4$, Ni[1,2-bis(diphenylphosphino)ethane]$_2$, and $Ni(Ph_3P)_4$[8] from photolyses in the presence of appropriate ligands. A similar photoreduction of $Ni(acac)_2$ under carbon monoxide purging apparently gave $Ni(CO)_4$, which could be trapped with phosphines as $Ni(CO)_2(Ph_3P)_2$ or $Ni(CO)_2[P(Bu^n)_3]_2$.[9]

E.s.r. monitoring of the sensitized photoreduction exhibited an isotropic signal due to the transient Ni^I complex with a *g*-value of 2.186 (ΔH_{pp} = 46 G) which built up to reach a photostationary state (Figure 1). The decay of the transient signal in the dark at 29 °C (Figure 2) followed first-order kinetics with $k_3 = 5.36 \times 10^{-3}$ s^{-1}, indicating that the Ni^I complex most likely decomposed unimolecularly† [equation (3)]. Similar irradiation at −100 to −150 °C led to anisotropic signals with *g* 2.294 and 2.127, in addition to the benzophenone ketyl radical signal at *g* 2.0029 (Figure 3) which was also obtained by photolysis of benzophenone. The shape as well as *g*-values of both isotropic and anisotropic spectra agree well with published data[10] for Ni^I, but not Ni^{III} [11] species. The reaction pattern is represented by equations (1)—(4) where $^{*}Ar_2C{=}O$ is a triplet state ketone and L a co-ordinating ligand, and RCH_2OH serves as the substrate and solvent as well as solvate molecules.

$$^{*}Ar_2C{=}O + Ni(acac)_2(RCH_2OH)_2 \xrightarrow{k_1} Ni(acac)(RCH_2OH)_n + acac^{\bullet} + Ar_2C{=}O \qquad (1)$$

$$^{*}Ar_2C{=}O + RCH_2OH \xrightarrow{k_2} Ar_2\dot{C}OH + R\dot{C}HOH \qquad (2)$$

$$Ni(acac)(RCH_2OH)_n + 4L \rightarrow Ni^0 \text{ or } NiL_4 + acac^{\bullet} \qquad (3)$$

$$acac^{\bullet} + RCH_2OH \rightarrow acacH + R\dot{C}HOH \qquad (4)$$

The quantum yield of the xanthen-9-one sensitized photoreduction, Φ_{Ni}, in ethanol increased in the $[Ni(acac)_2]$ 0—4 mM region reaching a constant value of 0.14 at $[Ni(acac)_2] > 4$ mM. In this concentration range, the quantum yield of xanthen-9-one photoreduction, Φ_X, decreased from 0.7 to 0.0 indicating that reactions (1) and (2) are unrelated. The rate constant of the former (k_1) was calculated from the

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† E.s.r. traces by other sensitizers in the presence of phosphite or phosphine ligands gave similar features and first-order rate constants, and similar anisotropic spectra at low temperatures.

Stern–Volmer plots of $1/\Phi_{Ni}$ *vs.* $1/[Ni(acac)_2]$ and Φ°_X/Φ_X *vs.* $[Ni(acac)_2]$ to be $(7.1 \pm 1.6) \times 10^9$ and $(9.1 \pm 1.1) \times 10^9$ $dm^3\ mol^{-1}\ s^{-1}$, respectively, assuming the lifetime τ of triplet xanthen-9-one under these conditions to be 0.3 μs.[12] ‡ At $[Ni(acac)_2] > 4$ mM, the rate of equation (1) is calculated to be > 30 faster than that of equation (2) taking[12] $k_2 = 4 \times 10^4$ $dm^3\ mol^{-1}\ s^{-1}$. This means that $Ar_2\dot{C}OH$ is not the reducing species for the photoreduction.

The quenching reaction, such as that shown in equation (1), has been proposed to occur by a combination of charge transfer–spin exchange[4] and energy transfer[1] but is now evidently more complex. First, the failure of *p*-methoxyacetophenone to sensitize the photoreduction in comparison with the high efficiency of acetophenone does not agree with an energy transfer mechanism: both sensitizers possess more than enough energy to promote the ligand $\pi \rightarrow {}^3\pi^*$ or d–d transitions. Secondly, the photoreduction shows profound solvent dependency giving limiting Φ_{Ni} values of 0.08, 0.14, and 0.32 in methanol, ethanol, and propan-2-ol, respectively. These observations must be related to the sensitization process and will be discussed in a full paper together with current experiments.

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‡ The lifetime of triplet xanthen-9-one was estimated from $k_2 = 4 \times 10^4$ $dm^3\ mol^{-1}\ s^{-1}$ in ethanol and the self-quenching of triplet xanthen-9-one (ref. 12). Φ_{Ni} was determined by following decreases of the $Ni(acac)_2$ absorption at 630 nm and Φ_X by h.p.l.c. analysis.

References

1 F. Wilkinson and A. Farmilo, *J. Chem. Soc., Faraday Trans. 2*, 1976, **72**, 604; A. Adamczyk and F. Wilkinson, *J. Chem. Soc., Faraday Trans. 2*, 1972, **68**, 2031; F. Wilkinson and C. Tsiamis, *J. Am. Chem. Soc.*, 1983, **105**, 767.

2 W. H. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, 1960, **82**, 2789; A. J. Fry, R. S. H. Liu, and G. S. Hammond, *J. Am. Chem. Soc.*, 1966, **88**, 4781.

3 C. Steel and H. Linschitz, *J. Phys. Chem.*, 1964, **68**, 2577.

4 G. Porter and M. R. Wright, *Discuss. Faraday Soc.*, 1959, **27**, 18.

5 Y. L. Chow and G. E. Buono-Core, *J. Am. Chem. Soc.*, 1982, **104**, 3770; G. E. Buono-Core, K. Iwai, Y. L. Chow, T. Koyanagi, A. Kaji, and J. Hayami, *Can. J. Chem.*, 1979, **57**, 8; Y. L. Chow, G. E. Buono-Core, B. Marciniak, and C. Beddard, *ibid.*, 1983, **61**, 801.

6 D. P. Graddon, *Coord. Chem. Rev.* 1969, **4**, 1; A. W. Adamson and P. D. Fleischauer, 'Concepts of Inorganic Photochemistry,' Wiley, New York, 1975, pp. 299—332.

7 H. D. Gafney and R. L. Lintvedt, *J. Am. Chem. Soc.*, 1970, **92**, 6996. These authors reported the photoreduction of $Ni(acac)_2$ by direct photolysis through a quartz filter.

8 J. J. Levison and S. D. Robinson, *J. Chem. Soc.* (*A*), 1970, 96; G. Wilke, E. W. Müller, and M. Kröner, *Angew. Chem.*, 1961, **73**, 33.

9 L. S. Meriweather and M. L. Fiene, *J. Am. Chem. Soc.*, 1959, **81**, 4200; P. C. Ellgen, *Inorg. Chem.*, 1971, **10**, 232; B. Corain, M. Bressan, and G. Favero, *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 197.

10 A. Tkâc and A. Staŝko, *Collect. Czech. Chem. Commun.*, 1972, **37**, 537; C. Amano, and S. Fujiwara, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 1817; E. Dinjus and R. Kirmse, *Z. Chem.*, 1976, **16**, 286; T. T. Tsou and J. K. Kochi, *J. Am. Chem. Soc.*, 1979, **101**, 6319.

11 P. Marathamuthu, L. K. Patterson, and G. Ferraudi, *Inorg. Chem.*, 1978, **17**, 3557.

12 A. Garner and F. Wilkinson, *J. Chem. Soc., Faraday Trans. 2*, 1972, **72**, 1010; J. C. Scaiano, *J. Am. Chem. Soc.*, 1980, **102**, 7747.