Quenching of Excited States of Diethyl Ketone by Paramagnetic Metal Chelates

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Abstract: Diethyl ketone sensitized photooxidation of cumene can be effectively retarded by the addition of nickel chelate of 2,2′-thiobis[4-(1,1,3,3-tetramethylbutyl)phenol] (Ni–I). The retardation is attributed to the quenching of the excited states of diethyl ketone by Ni–I. The quenching efficiency could be obtained by comparing this effect with the effect of Ni–I on photooxidations initiated by di-*t*-butyl peroxide which is believed not to involve excited states. Ni–I also quenches the phosphorescence of diethyl ketone in EPA glass with the same efficacy. Resonance excitation energy transfer is probably the principal quenching mechanism.

Energy transfers involving electronic excited states may be broadly grouped into collisional processes and resonance excitation processes.[1] The latter are usually distinguished from the former if the quenching rate constant appreciably exceeds the estimated diffusion-controlled rate constant. Certain ambiguity is inherent in this comparison. In these nonequilibrium systems, nonrandom forces may exert unknown effects[2] at close approach of the collision partners. Furthermore, the calculation of diffusion-controlled rate constant using the Stokes–Einstein formula is often done without actual knowledge of the parameters. Together with the spherical particle approximation, the calculation is a crude one at best.

Oxygen has been shown to quench the triplet states of anthracene,[3] biacetyl,[4] and benzophenone[5] with diffusion-controlled rates. The results[6] of diethyl ketone sensitized photooxidation of cumene are also consistent with diffusion-controlled quenching of the triplet state of diethyl ketone (DEK) by oxygen. It appears that competitive quenching in photooxidation could be a useful method for direct comparisons of the efficiency of a quencher with that of oxygen. In this paper we describe how such experiments may be performed, the results of these experiments, and the information obtainable from them.

The quenchers chosen for this study are metal chelates of 2,2′-thiobis[4-(1,1,3,3-tetramethylbutyl)phenol] (I). Metal chelates of a variety of ligands have been reported[7,8] to be excellent quenchers of the excited states of benzophenone.

Experimental Section

Materials. The purification of cumene, chlorobenzene, DEK, and di-*t*-butyl peroxide (DTBP) have been given elsewhere.[9] The Ni, Cr, Yb, and Eu chelates of I were prepared by Dr. A. S. Matlack of Hercules Research Center. Octanoates of these metals were refluxed with I in chlorobenzene and the octanol formed was continuously removed by distillation. The complexes were repeatedly recrystallized from ethanol.

Photooxidation. Symmetrically placed on both sides of an AH-6 lamp are slits, filters, quartz water baths, magnetic stirrers, quartz reaction cells, and photomultiplier tubes. The filter system is the C′-band pass filter combination described by Kasha[10] for the transmission of 3130-Å light with a half band width of 150 Å. The water bath, which maintained the reaction cell immersed in it at constant temperature, was constructed from optical quarz provided with inlet and outlet for circulation of water to and from a heat exchange coil immersed in a constant temperature bath regulated at 62.5 ± 0.05°. The water in the quartz bath was stirred magnetically. The water loss due to evaporation was replenished from an overhead reservoir whose selenoid valve was operated by a resistive device placed in the quartz bath to sense the water level. The temperature of the quartz bath was thus maintained at 62.5 ± 0.5°.

The reaction cell was fabricated from a 1-cm path length Cary spectrophotometer cell and connected to a recording oxygen uptake measuring apparatus described elsewhere in detail.[9] Suitable precision burets with volumes ranging from 0.1 to 5 ml and maintained at constant temperature were used in experiments of different rates of oxidation.

The lengths of irradiation required in some experiments were quite long, from several hours to several days. The intensity of the lamp was measured at the beginning of each experiment by irradiating a solution of uranyl oxalate[11] in the reaction cell. This is then replaced by the cells containing the reaction mixtures for the actual experiment. The relative light intensity during the experiment was monitored by RCA 1P28 photomultiplier tubes. When the output of the photomultiplier dropped to 20% of the initial value, the lamp was replaced with a new one. The incident light intensity reported here represents the average intensity.

Spectroscopic Measurements. The electronic spectra were obtained with a Cary-14 spectrophotometer. The solvents used were either ethanol or isooctane. The spectra of DTPB, DEK, and the metal chelates are shown in Figures 1 and 2.

An Aminco–Bowman spectrometer with an Osram XBO-152 xenon arc lamp was used to measure phosphorescence at liquid nitrogen temperature. The EPA solvent was purchased from the American Instrument Co. without further purification.

The nmr spectra were obtained with a Varian 60-Mc spectrometer using $CDCl_3$ and CCl_4 as solvent and $(CH_3)_4Si$ as internal reference.

Results

Measurement of the effect of Ni–I on photooxidation initiated by DEK suffers from the overlap of the strongly allowed absorption of Ni–I (ϵ_{3130} 4000) and the weak n–π* absorption of DEK. Whereas experiments under these conditions are usually avoided by photochemists, our choice of the system dictated the resolution of the complications inherent in these experiments.

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[2] P. J. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).

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[10] M. Kasha, *J. Opt. Soc. Amer.*, **38**, 929 (1948).

[11] P. A. Leighton and G. S. Forbes, *J. Amer. Chem. Soc.*, **52**, 3139 (1930).

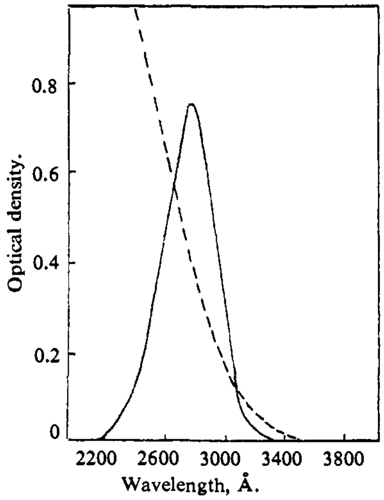

Figure 1. Electronic spectra at 1-cm path length of: ———, DEK (3.5×10^{-2} mol l.$^{-1}$ in ethanol); - - - -, DTBP (1×10^{-1} mol l.$^{-1}$ in ethanol).

The electronic spectrum of DEK, shown in Figure 1, is known to involve transition to metastable excited states. Its n–π^* triplet state has been postulated as the species which initiates photooxidation.[6] The addition of Ni–I should affect the reaction by screening the incident photon density available for absorption by DEK and by quenching the excited states of DEK. The primary objective of our experiments is to measure the quenching contribution to the inhibition of DEK-initiated photooxidation by Ni–I, and to determine the quenching efficiency as compared to that of oxygen.

A difference technique was used to attain maximum accuracy. A second initiator is needed which absorbs in the same wavelength region with nearly equal extinction coefficient as DEK, yet its excitation leads only to dissociation without the intermediacy of an excited state. DTBP appears to be an ideal candidate. The values of ϵ_{3130} of DTBP and DEK are 1.2 and 2.0, respectively. Yet the electronic spectrum of DTBP (Figure 1) is continuous. Even at the longest wavelength region of the DTBP absorption, the photon energy (>80 kcal/mol) is in excess of its bond energy of 40 kcal/mol. Photolysis of DTBP has been shown[12–15] to lead directly to radicals or hot radicals. In the following sections, the pure screening effect of Ni–I on DTBP-initiated photooxidation will be established. Consequently, the quenching effect of Ni–I on DEK-initiated photooxidations can be accessed by the comparison of the effects of Ni–I on the two systems assuming the same screening effect is also operative in the experiments involving DEK.

Ideally, this comparison should be made on solutions at initiator concentrations of equal absorption intensities. However, the quantum yield of initiation by DEK is only about $^1/_{20}$ of that by DTBP; the resulting differences in oxidation rates at equal absorption intensities could cause unforeseen complication. A compromise was made here, and stock solutions of DEK and DTBP were prepared such as to optimize the differences in absorption intensities and rates of oxidation.

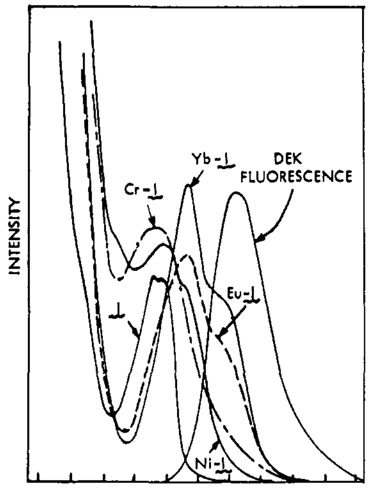

Figure 2. Absorption spectra of Ni–I, Cr–I, Yb–I, Eu–I, and I at 10^{-4} mol l.$^{-1}$; and fluorescence emission of DEK at 10^{-3} mol l.$^{-1}$

Varying amounts of Ni–I were added to the stock solutions to make up pairs of solutions. Each pair of solutions, which contain the same amount of Ni–I but slightly different amounts of the respective initiators, was irradiated simultaneously on two mirror image sections of the optical system. Their rates of oxidation were recorded and then compared.

Screening Effect of Ni–I on DTBP-Initiated Photooxidation. In the presence of Ni–I, DTBP-initiated photooxidation begins without an induction period; the rate of oxidation does not change with the length of irradiation at any Ni–I concentration. The results are summarized in Table I, column 3.

Table I. Effect of Ni–I on Photooxidations[a]

[Ni-I] $\times 10^2$, mol l.$^{-1}$	$I_0 \times 10^8$, einsteins cm^{-2} sec^{-1}	$-\frac{d[O_2]}{dt} \times 10_9$, mol l.$^{-1}$ sec^{-1} DTBP[b] initiated	DEK[c] initiated
0	1.26	31.0	5.83
0.0337	1.66	23.0	4.33
0.0753	1.45	21.8	3.89
0.102	1.94	16.0	2.55
0.141	1.94	12.9	1.63
0.222	1.52	10.3	0.88
0.337	1.66	8.03	0.438
1.01	1.26	3.61	0.034
3.03	2.04	1.92	0.004

[a] In 1:2 cumene–chlorobenzene at 62.5° and 3130 Å. [b] [DTBP] = 0.3 mol l.$^{-1}$. [c] [DEK] = 0.5 mol l.$^{-1}$.

Because of the low steady-state radical concentration and long chain lengths which prevail in these experiments, the rate of oxidation is given by $(\phi I_a/k_3)^{1/2}k_2 \cdot$[RH], where ϕ is the quantum yield, I_a is the light intensity absorbed by DTBP, and k_2 and k_3 are the rate constants of propagation and termination, respectively. If Ni–I functions solely as screener in these experiments as postulated, then a plot of the rates of oxidation *vs.* $I_a^{1/2}$ should be linear and the slope would correspond to $(\phi/k_3)^{1/2}k_2$[RH]. From the extinction coefficients (*vide supra*), the Ni–I concentrations, and the incident

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(12) L. M. Dorfman and Z. W. Salsburg, *J. Amer. Chem. Soc.*, **73**, 255 (1951).

(13) D. H. Volman and W. M. Graven, *ibid.*, **75**, 3111 (1953).

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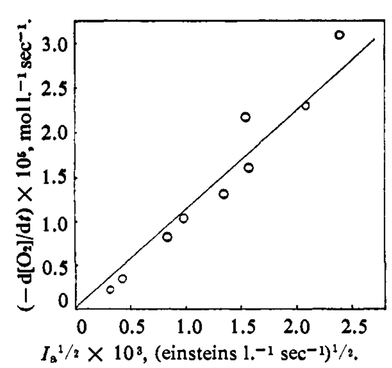

Figure 3. Photooxidation of cumene initiated by DTBP in the presence of Ni–I.

light intensities (Table I, columns 1 and 2), the values of I_a were calculated and plotted in Figure 3. The slope is 1.12×10^{-2} (mol l.$^{-1}$ sec^{-1})$^{1/2}$. The value of $k_2 k_3^{-1/2}$ has been given as 4.5×10^{-3} (l. mol^{-1} sec^{-1})$^{1/2}$. At the substrate concentration of 2.38 mol l.$^{-1}$, one obtains a quantum yield of 0.93.

The linear plot implies that the photooxidation is affected only by the screening of Ni–I but is otherwise independent of [Ni–I]. The values of I_a in these experiments differ by more than a factor of 60; the steady-state radical concentration in these experiments differ thus by a factor of up to 8. The linear plot of Figure 3 therefore also implies the absence of appreciable radical attack on Ni–I. The latter conclusion is supported by the following experiment. When 3×10^{-3} mol l.$^{-1}$ of Ni–I and 0.1 mol l.$^{-1}$ of α,α'-azo(bisisobutyronitrile) (AIBN) in cumene–chlorobenzene was heated at 62.5° (1 atm of oxygen), in 100 min 10% of the AIBN had decomposed to give about 0.013 mol l.$^{-1}$ of radicals.[16] The reaction mixture was continuously chromatographed by a mixture of ethanol and isooctane of increasing polarity on a silica gel column and the eluent analyzed continuously by ultraviolet spectrometry. More than 95% of the Ni–I present was found to be unchanged under these conditions.

Ni–I is also remarkably stable toward direct photolysis. Irradiation of Ni–I in chlorobenzene under nitrogen at 3130 Å and an intensity of 10^{-8} einstein cm^{-2} sec^{-1} for 2 weeks caused no appreciable spectroscopic changes. There were no photolysis products detected by gas chromatography. The results of Figure 3 show furthermore that Ni–I is also photolytically stable under oxidative conditions.

Finally, Ni–I is not an inhibitor against thermal autoxidations. Thus when cumene was oxidized at 62.5° (1 atm of oxygen), initiated by 10^{-2} mol l.$^{-1}$ of AIBN, there was only a slight lowering of the initial rate of oxidation (Figure 4) when 3×10^{-3} mol l.$^{-1}$ of Ni–I was present. Subsequently, the rate of oxidation is the same with or without Ni–I. Similar results were obtained upon the addition of 0.5 mol l.$^{-1}$ of DEK.

Quenching Effect of Ni–I on DEK-Initiated Photooxidations. The results of DEK-initiated photooxidations in the presence of Ni–I are given in Table I, column 4. The oxidation is also without induction period and proceeds at constant rate. Comparison of columns

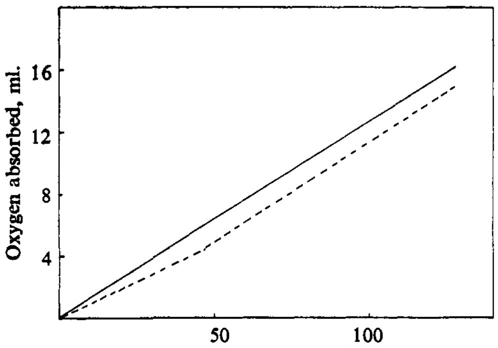

Figure 4. Cumene autoxidation: [AIBN] = 10^{-2} mol l.$^{-1}$, temperature = 62.5°, p_{O_2} = 1 atm, 1:2 cumene–chlorobenzene; ———, no additive; – – – –, [Ni–I] = 3×10^{-3} mol l.$^{-1}$.

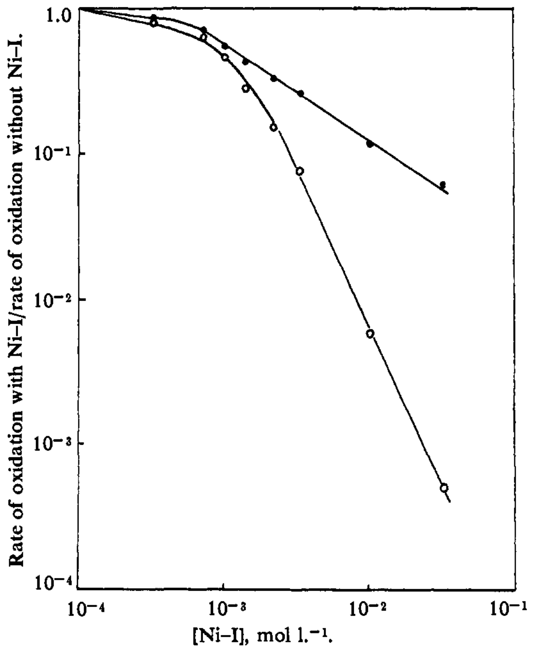

Figure 5. Differential protection against photooxidation by Ni–I initiated by ○, DEK; ●, DTBP.

3 and 4 shows that Ni–I is capable of providing additional inhibition to DEK-initiated photooxidation and this effect increases with increasing [Ni–I]. The relative rates of oxidation are plotted as a function of [Ni–I] in Figure 5.

We have already shown that radical attacks on and photolytic decomposition of Ni–I are unimportant. Furthermore, any subtle internal filtering effect or phototransformation is likely to be equally probable for the two systems under comparison. Therefore, the additional contribution to inhibition is attributed to quenching of DEK excited states by Ni–I.

That Ni–I is a more efficient quencher than oxygen is readily seen by considering the experiment which contains 3.37×10^{-3} mol l.$^{-1}$ of Ni–I and 5.5×10^{-3} mol l.$^{-1}$ of dissolved oxygen (Table I). The light intensity absorbed by DEK in this experiment is 5.1×10^{-7} einstein l.$^{-1}$ sec^{-1}. Using the expression given earlier,[6] we calculate a quantum yield, ϕ, of 0.0022 which is about ten times smaller than that obtained in the absence of Ni–I (ϕ_0 = 0.026).[6] The quantum yield was defined as

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(16) G. S. Hammond, J. N. Sen, and C. E. Boozer, *J. Amer. Chem. Soc.*, 77, 3244 (1955).

$$\phi_0 = \frac{k_r[\mathrm{RH}]}{\Sigma k} \approx \frac{k_r[\mathrm{RH}]}{k_{\mathrm{O_2}}[\mathrm{O_2}]} \tag{1}$$

where k_r is the rate constant of hydrogen abstraction, Σk contains all those terms for the reactions and decay of the excited states, and $k_{\mathrm{O_2}}$ is the oxygen quenching rate constant. Then

$$\frac{\phi}{\phi_0} = \frac{k_q[\mathrm{Q}] + k_{\mathrm{O_2}}[\mathrm{O_2}]}{k_{\mathrm{O_2}}[\mathrm{O_2}]} = \frac{k_q[\mathrm{Q}]}{k_{\mathrm{O_2}}[\mathrm{O_2}]} + 1 \tag{2}$$

Substituting the values of ϕ, ϕ_0, [Q] = [Ni–I], [O$_2$], and $k_{\mathrm{O_2}}$[6] into eq 2, one obtains the rate constant for quenching by Ni–I to be 1.9 × 10^{10} l. mol^{-1} sec^{-1} for this experiment. This value is about 20 times larger than $k_{\mathrm{O_2}}$.

Like Ni–I, the chromium chelate of I is also effective in quenching the excited states of DEK as evidenced by its inhibiting effect on photooxidation. For instance, when a cumene–chlorobenzene solution of 0.5 mol l.$^{-1}$ of DEK and 3 × 10^{-3} mol l.$^{-1}$ of Cr–I, saturated with oxygen, was irradiated at 3130 Å and 62.5°, the rate of oxidation was 3.5 × 10^{-7} mol l.$^{-1}$ sec^{-1}. The rate obtained in the presence of Ni–I under nearly identical conditions was 4.38 × 10^{-7} mol l.$^{-1}$ sec^{-1} (Table I).

Unlike the transition metal chelates, the rare earth chelates of I are rather ineffective as quenchers. The results in Table II revealed very small effects when oxidations initiated by DEK and by DTBP are compared. Results similar to those for Eu–I given in Table II were obtained with Yb–I. Reactions in the presence of these chelates could only be studied and followed for a short time. They are apparently unstable toward photolysis under these conditions to give insoluble products deposited on the cell window.

Table II. Effect of Eu–I on Photooxidations[a]

[Eu–I] × 10^2, mol l.$^{-1}$	I_0 × 10^8, einsteins cm^{-2} sec^{-1}	$-\frac{d[\mathrm{O_2}]}{dt}$ × 10^6, mol l.$^{-1}$ sec^{-1} DTBP[b] initiated	DEK[c] initiated
0	1.37	32.1	5.92
0.061	1.26	22.0	4.11
0.10	1.65	16.6	2.95
0.15	1.75	13.0	2.25
0.30	1.90	9.2	1.73

[a] In 1:2 cumene–chlorobenzene at 62.5° and 3130 Å. [b] [DTBP] = 0.3 mol l.$^{-1}$. [c] [DEK] = 0.5 mol l.$^{-1}$.

Photooxidation could not be performed at all with I. Even under nitrogen, photolysis of I at 3130 Å caused immediate decomposition with the formation of a red precipitate. The major photolysis product has been identified as *p*-(1,1,3,3-tetramethylbutyl)phenol.

Quenching of DEK Phosphorescence by Ni–I. The emission spectrum of DEK is characterized by a narrow fluorescence band centered at 3400 Å with a half-width of 200 Å and a broad and intense phosphorescence band with peak at 4470 Å and a half-width of 1180 Å. The emission spectrum of Ni–I is very weak in comparison. At about the same absorption intensity and excitation wavelength, the fluorescence and phosphorescence of Ni–I, situated at 3650 and 4350 Å, respectively, are less than $^1/_{60}$ of the corresponding emission by DEK. The phosphorescence lifetime of DEK was found to be 18 msec.

The fluorescence emission of DEK occurs at a wavelength where Ni–I still has appreciable absorption. Therefore, meaningful fluorescence quenching cannot be measured spectroscopically.

On the other hand, the phosphorescence emissions of both DEK and Ni–I mostly lie beyond their absorptions. Phosphorescence quenching experiments were carried out in EPA glass at liquid nitrogen temperature on a series of solutions. Each set of solutions consisted of: (A) DEK, (B) Ni–I, and (C) a mixture of the two. The concentration of the components in the mixture is the same as those in the individual specimens. The emission spectra of these solutions were determined. The theoretical intensity for solution C in the absence of quenching was assumed to be

$$I_{\mathrm{C}}' = \frac{I_{\mathrm{A}}\epsilon_{\mathrm{A}}c_{\mathrm{A}} + I_{\mathrm{B}}\epsilon_{\mathrm{B}}c_{\mathrm{B}}}{\epsilon_{\mathrm{A}}c_{\mathrm{A}} + \epsilon_{\mathrm{B}}c_{\mathrm{B}}} \tag{3}$$

where the I's are the integrated intensities of the phosphorescence emissions, ϵ's are the extinction coefficients, and c's are the concentrations. The quenching efficiency is then given as $(I_{\mathrm{C}}' - I_{\mathrm{C}})/I_{\mathrm{A}}'$ where I_{C} is the observed emission intensity and $I_{\mathrm{A}}' = I_{\mathrm{A}}\epsilon_{\mathrm{A}}c_{\mathrm{A}}/(\epsilon_{\mathrm{A}}c_{\mathrm{A}} + \epsilon_{\mathrm{B}}c_{\mathrm{B}})$. In this calculation the additional emission from Ni–I, which results from excitation accompanying the quenching of the DEK excited states, has been neglected. The error thus introduced is probably small because the emission of Ni–I is weak, implying that the decay of the Ni–I excited states is predominantly nonradiative. The assumption could give lower quenching efficiencies than the true values. The results of these experiments, summarized in Table III, show efficient quenching of DEK phosphorescence by Ni–I.

Table III. Phosphorescence Quenching by Ni–I[a]

[Ni–I] × 10^2, mol l.$^{-1}$	Phosphorescence intensity Without DEK	With DEK	I_{C}', calcd	Quenching efficiency, %
0.003	60	3100	3000	0
0.01	110	2400	2520	4.5
0.03	162	1700	1940	12
0.1	55	510	1030	49
0.3	45	55	545	90

[a] Measured at −195° in EPA glass with 0.95 mol l.$^{-1}$ DEK which has a phosphorescence intensity of 3000 arbitrary units.

The phosphorescence emission of I at 4250 Å is 10 to 200 times more intense than that of Ni–I depending upon the concentration. The emission intensities of mixtures of I and DEK exceed the values calculated from eq 3 by 0.4- to 1.8-fold, increasing with the increase of the phenol concentration. The first excited singlet states of DEK and I are 33,000 and 29,500 cm^{-1} above their respective ground states; the first triplet states of DEK and I are found at 29,500 and 27,000 cm^{-1}, respectively. These energies were estimated from the absorption and emission spectra of these compounds. The observed enhancement in emission of the DEK–I mixtures implies sensitization processes such as

$$^3\mathrm{DEK} + \mathrm{I}^0 \longrightarrow \mathrm{DEK}^0 + {}^3\mathrm{I} \tag{4}$$

and/or

$$^1\mathrm{DEK} + \mathrm{I}^0 \longrightarrow \mathrm{DEK}^0 + {}^1\mathrm{I} \tag{5}$$

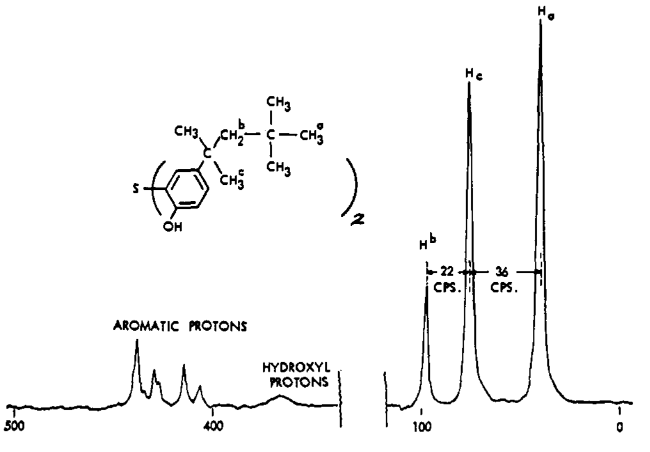

Figure 6. Nmr spectrum of I, 14% in $CDCl_3$.

Paramagnetism of Ni–I. The nmr spectrum of I is shown in Figure 6 together with the proton-shift assignments. The corresponding spectrum of Ni–I (Figure 7) contains only one broad triplet, centered at about 74 cps to the high-field side of $(CH_3)_4Si$. From the integrated intensity and the separation among the peaks, the broad triplet is assigned to the aliphatic protons. Compared to the spectrum of I the aliphatic proton resonances are broadened and shifted by about 140 cps upfield in Ni–I. The aromatic protons were not detected with field sweeps of ±5000 cps on both sides of $(CH_3)_4Si$.

The paramagnetic proton resonance shift for transition metal complexes was first noted by McConnell and Holm[17] for nickelocene. Subsequently, examples[18,19] were found which exhibit either large positive or large negative paramagnetic shifts depending upon the signs of the spin density at the protons

$$\Delta H = \rho Q(\gamma_e/\gamma_H)g\beta S(S + 1)H/6\mathbf{k}T \qquad (6)$$

where $g = 2$, $Q = -22.5$ gauss, ΔH is the proton shift, γ's are the gyromagnetic ratios, β is the Bohr magneton, S is assumed to be one for Ni–I, $H = 60 \times 10^6$ cps, and $\mathbf{k}$ is the Boltzmann constant. The observed paramagnetic shift of 140 cps corresponds to a negative spin density, ρ, on the carbon atoms of the alkyl group of about 7.5×10^{-4}.

Discussion of Results

The results presented above are now analyzed according to the known kinetics of photooxidation. Let us assume the reaction sequences in the DTBP-initiated oxidation to be

$$\left.\begin{array}{lr} \mathrm{DTBP} + h\nu \longrightarrow 2\mathrm{R}\cdot & \phi I_a \\ \mathrm{R}\cdot + \mathrm{O_2} \longrightarrow \mathrm{ROO}\cdot & k_1 \\ \mathrm{ROO}\cdot + \mathrm{RH} \longrightarrow \mathrm{ROOH} + \mathrm{R}\cdot & k_2 \\ 2\mathrm{ROO}\cdot \longrightarrow \text{products} + \mathrm{O_2} & k_3 \end{array}\right\} \qquad (7)$$

In the presence of an excess of DTBP and for long radical chain lengths,[20] steady-state approximation yields for the rate of oxidation

$$R = (\phi I_a/k_3)^{1/2}k_2[\mathrm{RH}] \qquad (8)$$

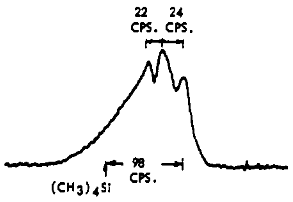

Figure 7. Nmr spectrum of Ni–I, 15% in CCl_4.

A similar sequence can be written for the DEK-initiated reactions

$$\left.\begin{array}{lr} K^0 + h\nu \longrightarrow K^* & \phi I_a' \\ K^* \longrightarrow K^0 & k_d \\ K^* + \mathrm{O_2} \longrightarrow K^0 + \mathrm{O_2} & k_{\mathrm{O_2}} \\ K^* + \mathrm{sol} \longrightarrow K^0 + \mathrm{sol} & k_{\mathrm{sol}} \\ K^* + \mathrm{RH} \longrightarrow 2\mathrm{R}\cdot & k_r \\ K^* + Q \longrightarrow K^0 + Q & k_q \end{array}\right\} \qquad (9)$$

where the reactions of R· have been omitted. The rate of oxidation is

$$R' = (\phi' I_a'/k_3)^{1/2}\frac{k_2k_r^{1/2}[\mathrm{RH}]^{3/2}}{(\Sigma k + k_q[\mathrm{Q}])^{1/2}} \qquad (10)$$

Denoting those experiments without added quencher by a subscript 0 and those initiated by DEK by a prime, we write for the ratio of rates of oxidation with and without quencher

$$\left(\frac{R_0'}{R'}\right)^2 = \frac{(\phi' I_a')_0}{(\phi' I_a')}\left(1 + \frac{k_q[\mathrm{Q}]}{\Sigma k}\right) \qquad (11)$$

Under the experimental conditions used in this work and the assumption that Ni–I functions solely as light screener in the DTBP-initiated photooxidations

$$\frac{(\phi' I_a')_0}{(\phi' I_a')} = \frac{(\phi I_a)_0}{(\phi I_a)} = \left(\frac{R_0}{R}\right)^2 \qquad (12)$$

Substitution of eq 12 into 11 gives

$$\frac{(R_0'/R')^2}{(R_0/R)^2} = 1 + \frac{k_q[\mathrm{Q}]}{\Sigma k} \qquad (13)$$

The results of Table I however do not fit eq 13 if k_q is concentration independent. The ratio on the left-hand side of the equation increases rapidly with the increase of Ni–I concentration. However, if quenching occurs *via* a resonance excitation transfer mechanism,[21,22] the rate constant as a function of distance is given by

$$k_q = (1/\tau)(r_0/r)^6 \qquad (14)$$

where τ is the actual mean lifetime of the donor and r_0 is the "critical" distance separating the donor and the acceptor. The r^{-6} dependence of the rate constant is equivalent to a dependence on the square of the Ni–I concentration. Accordingly, a log–log plot of the function on the left-hand side in eq 13 *vs.* [Ni–I] should yield a line with a slope of 3. Figure 8 shows the experimental data and the theoretical line with a slope of 3. A more conventional plot is that of quenching efficiency *vs.* log of quencher concentration (Figure 9). The quenching efficiency is given by $1 - (R'/R_0')^2(R/R_0)^{-2}$. The figure shows 50% quenching efficiency at 1.5×10^{-3} mol l.$^{-1}$.

One important characteristic of resonance excitation transfer is the invariance of quenching efficiency with

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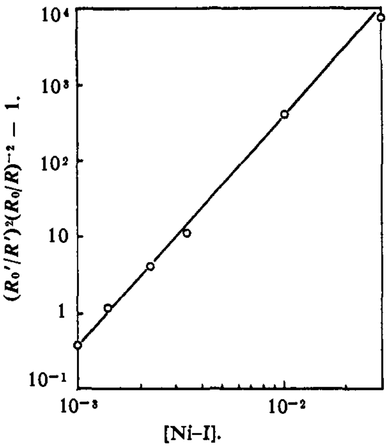

Figure 8. Inhibition of photooxidation by quenching.

temperature and viscosity. Since photooxidation can be conveniently measured only at moderate temperatures, the quenching efficiency of phosphorescence by Ni–I was determined at liquid nitrogen temperature in EPA glass instead. The half-quenching concentration thus obtained is about 10^{-3} mol $l.^{-1}$ (Table III).

The ground state of Ni–I has been shown to be paramagnetic; it is probably a triplet state. The first absorption band is apparently an allowed transition. It is not yet clear whether this transition involves the excitation of an electron from a ligand bonding molecular orbital to an unfilled d orbital of the metal or to a ligand antibonding molecular orbital. In any case, the first excited state is probably also a triplet state. The most probable resonance-transfer process is

$$^1\text{DEK} + {}^3\text{Ni–I}^0 \longrightarrow \text{DEK}^0 + {}^3\text{Ni–I} \qquad (15)$$

This process conserves the spin multiplicity,[3] and Figure 2 shows appreciable donor–acceptor spectral overlap. Therefore, the critical quenching radius, r_0, could be comparable to those found for other allowed energy-transfer processes,[23–25] which range from 38 to 84 Å. The value for r_0 can be calculated from the quenching data using the relationship[21]

$$r_0 = (3000/4\pi N[\text{Q}]_0)^{1/3} \qquad (16)$$

where N is the Avogadro's number, and $[\text{Q}]_0$ is the reference quencher concentration corresponding to an average of one Ni–I molecule in a sphere of radius r_0. In a system of rapidly rotating molecules, $[\text{Q}]_0$ is the concentration at 75% quenching efficiency. The value of r_0 is calculated to be 57 Å.

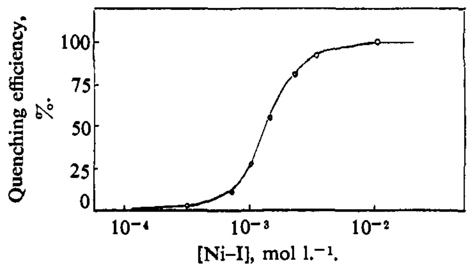

Figure 9. Quenching efficiency of Ni–I.

Whereas all the experimental phenomena appear consistent with resonance excitation transfer, quantitative agreement with the theory is less satisfactory. According to Förster's theory, the critical quenching radius is primarily a function of donor–acceptor spectral overlap and of emission quantum yield of the donor

$$r_0^6 = \frac{9000 \ln 10\ \chi^2\phi_\text{D}}{128\pi^6 n^4 N}\int_0^\infty F_\text{D}(\nu)\epsilon_\text{A}(\nu)\frac{\text{d}\nu}{\nu^4} \qquad (17)$$

where n is the refractive index, ϕ_D is the emission quantum yield of the donor, χ^2 is the orientation factor, and the integral gives the spectral overlap; these quantities have values of 1.5428, 0.01,[26] 1, and 2.66×10^{-12}, respectively. The theoretical value for r_0, calculated from eq 17, is 25 Å. This value is about one-half as large as the experimental value. The source of this discrepancy is not obvious to us and is being further investigated. There appears to be a similar discrepancy of about a factor of 1.5 to 2.0 between the theoretical and experimental values of r_0 in all the systems studied by Ware,[23] with the latter having the larger values.

On the basis of spectral overlap alone (Figure 2), Yb–I and Eu–I may be expected to be efficient quenchers. However, rare earth ions[3] and their chelates[7] have been found consistently to be ineffective quenchers of triplet molecules. The photolytic instability of these chelates could also be a contributory factor to the low efficiencies observed.

The principal contribution of the paramagnetism to the quenching action of Ni–I and Cr–I appears to be one of imparting photolytic stability to the otherwise unstable ligand. Paramagnetic catalysis of intersystem crossing[3] could provide a path for rapid radiationless decay of the electronic excitation energy. The ease of occurrence of these radiationless decays is also indicated by the weak luminescence emissions from these chelates. In this context, these paramagnetic chelates are superior stabilizers against photooxidations initiated by aliphatic carbonyl compounds.[27]

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