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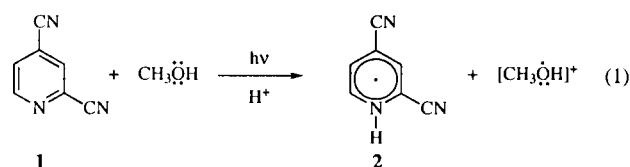
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When a 1° or 2° alcohol solution of benzophenone and 2,4-pyridinedicarbonitrile (**1**) is irradiated, the 2,4-dicyanopyridinyl radical (**2**) is formed immediately. When the irradiation is performed in the cavity of an ESR spectrometer, the spectrum amplitude increases to a near steady-state level, α . When the illumination is discontinued, a sharp rise in amplitude is observed to the β level. These results can be interpreted in terms of an equilibrium between free **2** and an ESR-silent complex of **2** (concentrations proportional to α and $\beta - \alpha$, respectively) with $K_{eq} = (\beta - \alpha)/\alpha$. The unprecedented increase in signal amplitude when irradiation is stopped requires an alcohol; the effect is not observed when other solvents are used. K_{eq} was found to correlate with the steric bulk of the alcohol solvent. These and other results lead to the conclusion that hydroxyalkyl radicals react reversibly with **2** to form the ESR-silent complex.

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As part of a study on the electron transfer reactions of six-membered monoazaaromatics, we reported that when 2,4-pyridinedicarbonitrile (**1**) is irradiated in alcohol solution, an intense signal for 2,4-dicyanopyridinyl radical is observed immediately [3]. The reaction involves electron transfer from the alcohol to the triplet state of the heterocycle, but the Rehm-Weller equation [4] predicts this transfer to be energetically unfavorable. However, the sensitivity of the reaction to acid concentration suggests a mechanism in which N-H bond forma-

tion is coupled to the electron transfer step, resulting in an exoergic process, equation (1).



In effect, N-H bond formation becomes the driving force for the reaction.

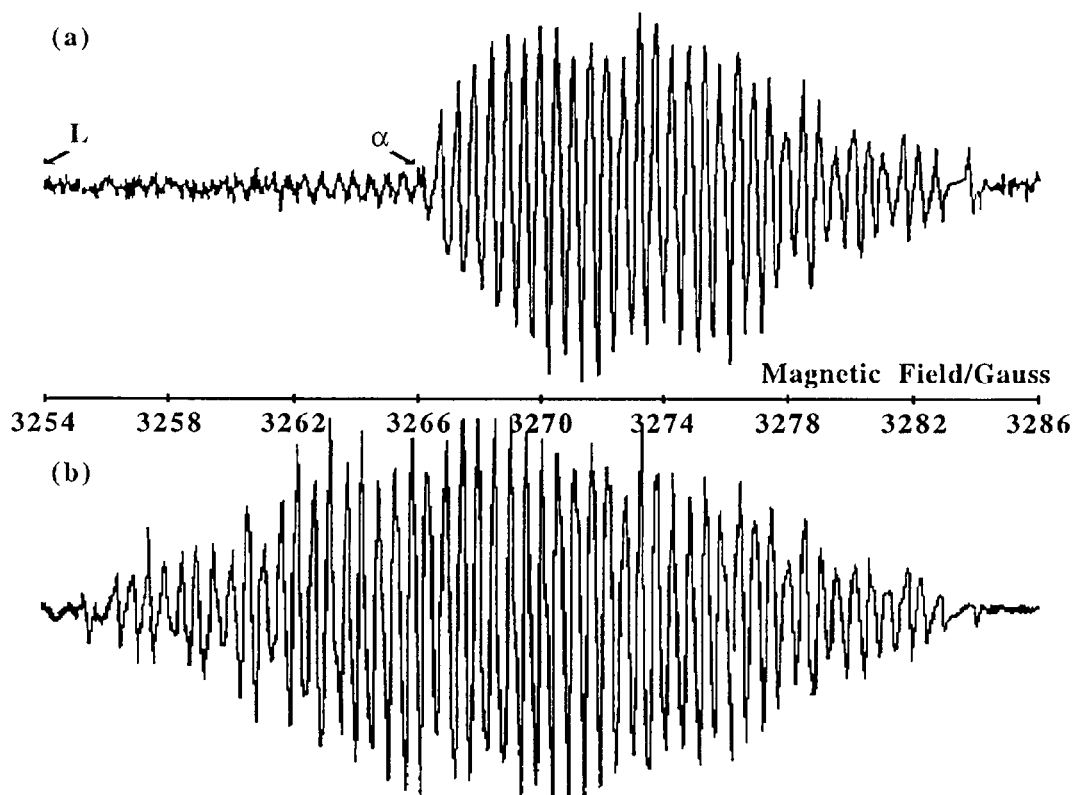


Figure 1. ESR spectrum of 2,4-dicyanopyridinyl radical (**2**) in ethanol taken at ambient temperatures. (a) Light is turned on at L and extinguished at α . (b) Second scan, taken with the light off.

Formation of the triplet state of **1** requires approximately 70 kcal/mol [3] so that benzophenone ($E_T = 69.2$ kcal/mol) [5] can be used as a photosensitizer. When benzophenone is used for this purpose, however, a surprising effect is observed: shortly after the light is turned on, the radical concentration reaches a near steady state (the α level) and immediately after the light is extinguished, a different approximate steady-state is attained (the β level). ESR spectra taken during and immediately after irradiation are virtually superimposable, Figure 1, and correspond to the reported spectrum of **2** [3]. In this paper we provide evidence for a mechanism for this effect involving the reversible formation of a σ -complex of two radicals.

EXPERIMENTAL

Materials.

Acetonitrile (hplc grade) was obtained from Aldrich; other solvents used were analytical grade. 4,4'-Dimethylbenzhydrol was prepared by a literature method [6,7]. The other alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, cyclohexanol 2-, 3- and 4-methylcyclohexanol and benzhydrol) were obtained from either Fisher, Aldrich, or Merck. 2,4-Pyridinedicarbonitrile (**1**) was obtained from ICN Pharmaceuticals and was recrystallized once from ethanol, mp 89-89.5° (lit 88-91°) [8]. Benzophenone (Fisher certified grade), 3-benzoylpyridine and 4-fluorobenzophenone (Aldrich) were used without purification. 4,4'-Dimethylbenzophenone (Eastman) and 4-methoxybenzophenone (Aldrich) were recrystallized from ethanol. 5,5-Dimethyl-1-pyrroline *N*-oxide was obtained from Aldrich.

ESR Spectrometry.

ESR spectra were recorded using Varian E104 or Bruker ER220D spectrometers. The radical **2** was generated *in situ* by the irradiation of a solution of **1** in the cavity of an ESR spectrometer using a 1000 W high-pressure mercury lamp; care was taken to

ensure the same lamp focus and orientation relative to the sample for each run. Solutions for room-temperature studies were deaerated by argon bubbling for at least 20 minutes and allowed to flow into a flat quartz cell under positive argon pressure before irradiation. Solutions for low-temperature studies were placed in 2-mm Pyrex tubes, deaerated by three freeze-pump-thaw cycles, sealed, mounted in the ESR cavity and irradiated. Unless otherwise stated, all solutions were 0.05 *M* **1** and 0.03 *M* ketone.

A Typical ESR Experiment.

A fresh solution was prepared with 0.05 *M* **1** and 0.03 *M* ketone in 25 ml alcohol. The cell was filled and mounted in the ESR cavity as described above. The beam of the lamp was then focused on the cavity and the ESR spectrum of the radical recorded. The derivative amplitude of a single spectral line was then measured as a function of time. When the α level reached near steady-state (10 s for methanol, 27 s for 2-propanol), the light was extinguished and the β level recorded (β level reached after 3 s for methanol, 11 s for 2-propanol) [9].

The Effect of Acidity and Solvent Polarity.

Room-temperature ESR studies were performed using (i) ethanol solutions containing 0.03 *M* benzophenone and 0.012 or 0.036 *M* HCl; (ii) benzene/2-propanol or formamide/2-propanol (23/2 V/V) solutions containing 0.03 *M* benzophenone; (iii) acetonitrile solutions containing 0.03 *M* 4,4'-dimethylbenzophenone and 0.10 *M* 4,4'-dimethylbenzhydrol or 0.05 *M* benzophenone and 0.11 *M* benzhydrol. All solutions contained 0.05 *M* **1**.

Results and Discussion.

Irradiation of deaerated solutions of **1** in the presence of benzophenone as a photosensitizer produces **2**, equation (1). The amplitude of an ESR line in the spectrum of **2** increases to level α ; when the light is turned off, the ESR amplitude rapidly increases to level β by a first-order process [10].

When radicals are generated photochemically, one usually observes an increase in radical concentration when the light is turned on and a decrease when the light is extinguished. Peculiar behavior

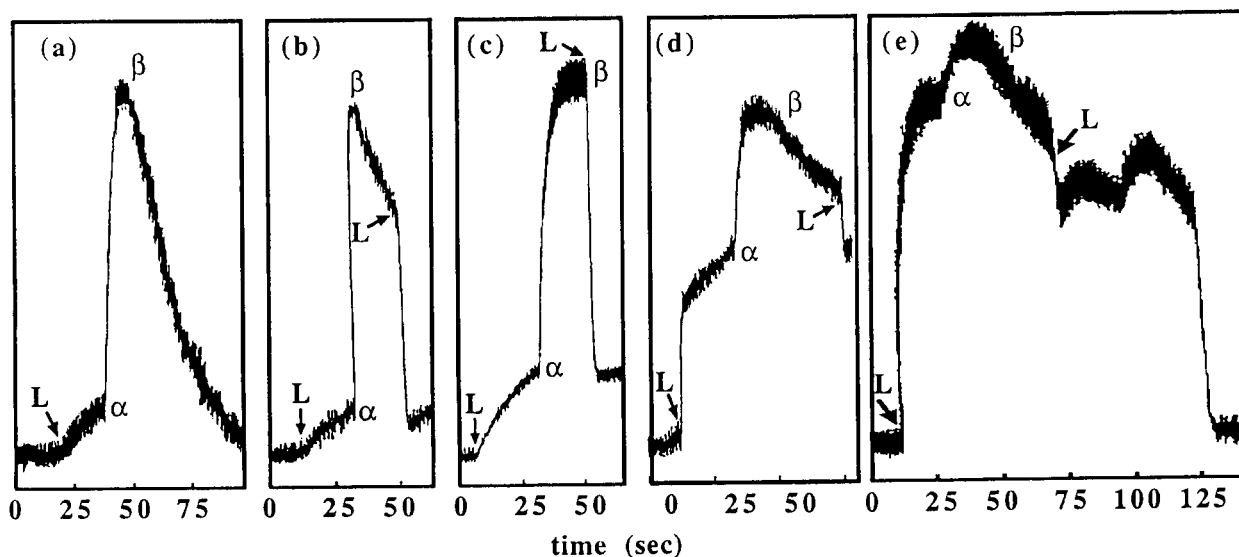


Figure 2. ESR derivative amplitude curves of one spectral peak as a function of time for the photoreaction of 0.05 *M* 2,4-pyridinedicarbonitrile with 0.03 *M* benzophenone in (a) methanol, (b) ethanol, (c) 2-propanol, (d) cyclohexanol, and (e) *t*-butyl alcohol solutions. The light is turned on at L and off at α . K_{eq} values are (a) 8.6, (b) 8.1, (c) 3.4, (d) 0.74, and (e) 0.17.

has been observed for pyridinyl radicals previously; when a dimer is photochemically dissociated, reversibility causes apparent changes in kinetic order of the dimerization process [11]. However we know of no literature example of an enormous increase in radical concentration when the light is turned off. The increase in signal intensity in the dark conceivably could be the result of increased T_2 relaxation time and consequent increase in signal amplitude without change in integrated intensity. Accordingly, we measured the line width with the light on and off, and found them to be virtually unchanged. This suggests that the signal enhancement effect is chemically based and not the result of spectroscopic changes.

If, after achieving the β level, the light is turned on again, there is an immediate decrease in amplitude to slightly below the α level, Figure 2(a-e). If this process is repeated, the concentration of **2** eventually falls below detectable limits. This behavior suggests a rapid equilibrium in which, while the light is on, a significant fraction of radical **2** is converted to an ESR-silent form with concentration proportional to the difference in ESR amplitudes, $\beta - \alpha$. The remaining concentration of **2** is proportional to α , so that the apparent equilibrium constant for this process is $K_{eq} = (\beta - \alpha)/\alpha$.

This postulated equilibrium implies reversible reaction of **2** with another photo product. As shown in Table 1, K_{eq} depends on the alcohol used as solvent, suggesting that the second photo product is derived from the alcohol.

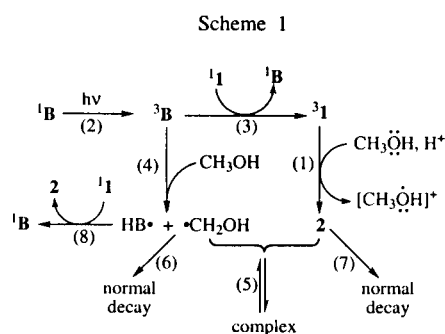
Table 1

Effect of alcohol on K_{eq} in benzophenone-sensitized reaction of **1** [a]

Solvent	Alcohol-derived radical (R_1R_2C-OH)		K_{eq}
	R_1	R_2	
Methanol	H	H	8.6
Ethanol	CH ₃	H	8.1
1-Propanol	CH ₃ CH ₂	H	4.4
1-Butanol	CH ₃ CH ₂ CH ₂	H	4.4
2-Propanol	CH ₃	CH ₃	3.4
Cyclohexanol	C ₆ H ₁₀	—	0.74

[a] We found that *t*-butyl alcohol, which does not have a hydrogen atom on the carbon bearing the OH group, has $K_{eq} = 0.17$. The mechanism that causes this enhancement must be different from that of the other reacting alcohols.

The mechanism postulated to explain these results is shown in the Scheme 1 below. In Scheme 1, singlet and triplet 2,4-pyridinedicarbonitrile and benzophenone are referred to as ¹**1** and ³**1**, ¹**B** and ³**B**, respectively, the 2,4-dicyanopyridinyl radical is **2** and the alcohol is methanol. K_{eq} refers to the equilibrium of reaction (5).



Scheme 1 incorporates our earlier understanding of the photosensitizer role of benzophenone and the key electron-transfer and proton-transfer steps of equation (1) to form **2**. The new element is the postulated formation of hydroxyalkyl radicals, equation (4), and the reversible reaction of these radicals with **2**. So long as the light is on and $\cdot CH_2OH$ is being formed, the concentration of **2** is suppressed: the α level. When the light is extinguished, $\cdot CH_2OH$ production ceases. These inherently short-lived radicals decay rapidly *via* eq (6) [12], shifting the equation (5) equilibrium so that the concentration of **2** increases rapidly to the β level, which slowly decreases as normal pyridinyl radical decay occurs [13]. If the light is turned on again, there is a very rapid decrease in the concentration of **2** as a result of complexation by the hydroxyalkyl radicals, formed photochemically by the reaction of benzophenone with alcohol, equation (4).

In the following, we discuss further experiments designed to test various aspects of this scheme.

Effect of Temperature.

When a methanol or ethanol solution of **1** and benzophenone was irradiated at -30 or -5° , no ESR signal is detectable with the light on or off; apparently K_{eq} is large enough at low temperature so that **2** is virtually completely converted to the complex. However, when the sample was warmed in the dark, the **2** signal began to appear at about -3° and increased in intensity with temperature, Figure 3. When samples were irradiated at -1° or above, both the α and β levels were observed, but with larger values of

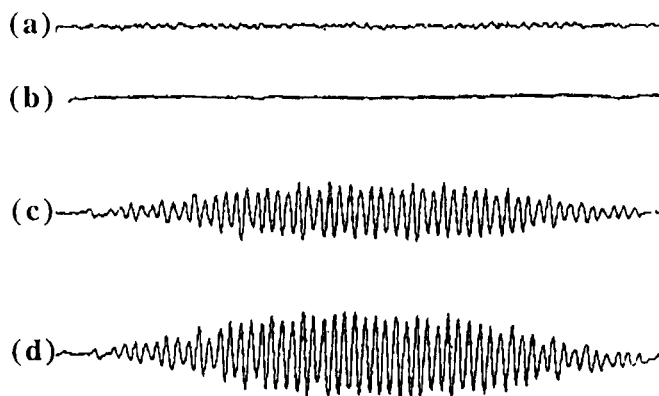


Figure 3. ESR spectrum of a solution of 0.05 *M* 2,4-pyridinedicarbonitrile with 0.03 *M* benzophenone in ethanol at: (a) -30° with the photolamp on; (b) -30° with the photolamp off; (c) after warming to 3° in the dark, and (d) after warming to 14° in the dark. The spectrum that appears on warming is that of **2**.

K_{eq} than were observed at room temperature. The activation energy for the reverse step of the complex formation equilibrium, equation (5), is expected to be significantly larger than that for the forward step, consistent with the temperature dependence of K_{eq} , but the activation energy for the forward step apparently is not negligible. When a sample is irradiated at 14° , a significant α level is achieved and, when the light is turned off, the signal grows very rapidly to a strong β level. At 3° , the α and β levels are much smaller, but if the temperature is increased to 14° , the signal becomes more intense. When the irradiation is carried out at -1° , very little signal could be detected. When the light is turned off, the signal intensity increases only slightly at this temperature.

When the temperature was raised to about 10°, the signal intensity increased to a maximum, but did not reach the level of the samples run at 14°. When the temperature was lowered to -9°, no signal was evident with the light on or off. At this temperature, few molecules have enough energy to pass over even the lower, forward energy barrier, so that much less complex is formed.

Samples which did not contain a photosensitizer did not show an ESR signal enhancement when the light was turned off. If the alcohol solution was frozen at -120° and then irradiated, with or without a photosensitizer, and warmed to room temperature in the dark, no radical was detected.

Other Photosensitizers.

A series of reactions was run in 2-propanol with other ketones used in place of benzophenone. Results are listed in Table 2.

Table 2

Results obtained at room temperature with 2-propanol and various ketones

Ketone	E_T (kcal/mol)	% Complex
Benzophenone	69.2	77
4-Acetylbenzoxazole	69.5	0
4-Acetylpyridine	70.3	0
Acetophenone	74.0	0
Durylphenyl ketone	80.0	0
4-Fluorobenzophenone	69.7	71
4-Methoxybenzophenone	69.0	75
4,4'-Dimethylbenzophenone	69.3	79
3-Benzoylpyridine	69.0	86

Ketones which could form ketyl radicals and which have triplet energies comparable to that of benzophenone gave similar results in the photochemical reaction.

In this photoreaction, benzophenone can act both as a photosensitizer, equation (3), and a chemical sensitizer by electron transfer from diphenyl ketyl, equation (8), both of which result in the formation of **2**. When the triplet energy of the ketone is substantially higher than that of the heterocyclic base, then the base quenches the ketone triplet and does not allow for the formation of ketyl. Thus when acetophenone was used instead of benzophenone, a strong signal was obtained for **2** with the same alcohols, but no enhancement of radical concentration is observed when the light is extinguished.

An n,π^* state, rather than a π,π^* state, is necessary to accomplish hydrogen atom abstraction, essential in the production of the alcohol-derived ketyl which in turn is required to form the σ -complex. In 4-acetylbenzoxazole the n,π^* and π,π^* states are closely spaced: increasing the solvent polarity can increase the energy of n,π^* and lower the energy of π,π^* . Hydrogen atom abstraction then becomes unfavorable. Benzophenone does not exhibit this behavior and the n,π^* state remains the lowest reactive state.

Proof of Alcohol-derived Radical Involvement.

We have established that, in the presence of benzophenone and 1°, 2°, or 3° alcohols, **2** is normally formed by electron transfer from the alcohol to the triplet state of **1** or by electron transfer from diphenyl ketyl to **1** in its ground state [3]. In order to obtain further insight into the role of diphenyl ketyl in this process, the photoreaction was run with benzhydrol as the only alcohol. Under these conditions diphenyl ketyl would be the only radical present. A low level signal was obtained which disappeared when

the light was extinguished. A similar experiment with 4,4'-dimethylbenzophenone and 4,4'-dimethylbenzhydrol gave a strong signal, but very little signal growth when the light was extinguished, $K_{eq} = 0.10$. When 2-propanol was used in place of benzhydrol in acetonitrile with benzophenone, the signal increase was as strong as with 2-propanol as the solvent.

Experiments were performed to determine the importance of the hydroxyalkyl radical in the complex formation process. For these tests methanol was used as the solvent and the spin trap 5,5-dimethyl-1-pyrroline *N*-oxide was added to the reaction mixture. Under these conditions, K_{eq} was very much reduced and new features appeared in the spectrum, apparently due to the presence of 2,2-dimethyl-5-hydroxymethylpyrrolidine *N*-oxide, indicating the presence of hydroxymethyl radicals.

It seems clear that **2** is involved in the reversible formation of a rather stable, ESR-silent complex during the establishment of the α level, while the dissociation of this complex results in the formation of the β level (Figure 2). The most likely reaction partner is a radical. Since experiments performed with benzophenone/benzhydrol and 4,4'-dimethylbenzophenone/4,4'-dimethylbenzhydrol demonstrate that diphenyl ketyl and **2** alone do not show the enhancement effect, and since K_{eq} depends on the alcohol used as solvent, we conclude that the alcohol-derived hydroxyalkyl radical is the most likely reactant. Benzophenone thus serves two functions: to help populate the triplet state of **1**, equation (1), and to produce the active radical from the alcohol by a hydrogen abstraction process, equation (4). Irradiation of **1** in alcohol in the absence of benzophenone results in the formation of **2** without complex formation, undoubtedly because in the photochemical formation of **2** by electron transfer from the oxygen atom of the alcohol to **1**, the alcohol radical formed is only $[\text{CH}_3\text{OH}]^+$ with no $\cdot\text{CH}_2\text{OH}$.

The involvement of the hydroxyalkyl radical in the complex formation process explains why the α and β levels measured in the ESR spectrum changes with the alcohol that is used as solvent. We have considered several different structures for the complex, but a σ -complex seems the most logical.

Effect of Solvent.

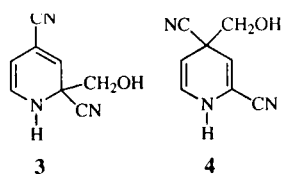
The effect of solvent polarity was then investigated using **1**, benzophenone and 2-propanol in benzene ($\epsilon = 2.3$) or formamide ($\epsilon = 110$). Radical **2** formed at a moderate level in both solvents but no signal enhancement was observed in either solvent when the light was turned off.

Effect of Benzophenone Concentration and Light Intensity.

Essentially the same results were obtained when the benzophenone concentration was 0.01, 0.03 or 0.06 *M* in ethanol [14]. Initial results indicate that, at least with ethanol, the complex is light sensitive. As the light intensity was decreased from 100 to 67 to 36%, K_{eq} increased from 8.1 to 10 to 17. This may be explained on the basis of a light induced dissociation of the complex resulting in an increase in the α level relative to the β level. As the light intensity is decreased, the equilibrium shifts toward the undissociated complex, the result being a higher K_{eq} .

Identity of the Complex.

Our results suggest a σ -complex in which a hydroxyalkyl radical is reversibly attached to **2**. The most obvious possibilities are structures **3** and **4**. Calculations indicate that a higher spin density resides at position 4 than at position 2 [3]. However, in either



photochemical [15] reactions with benzophenone or thermal [16] reactions with benzhydrol and **1** in alcohol, substitution by diphenyl ketyl always occurred predominantly or exclusively at the 2-position. The mechanism of substitution at the 2-position in the photochemical reaction with benzophenone involves an electron transfer from the intermediary diphenyl ketyl to **1** in its ground state forming a transient radical anion intermediate. We proposed that substitution at the 2-position by diphenyl ketyl involves coordination with the negatively charged nitrogen atom of this intermediate which directs the ketyl group into the 2-position by way of a cyclic transition state. Substitution of the 4-cyano group with ketyl does not occur photochemically. Since in **2**, the nitrogen is protonated, coordination with this atom cannot occur, so that substitution at the 2-position is suppressed. Radical coupling then occurs at the 4-position, the position of highest spin density. The σ -complex which is formed cannot be very stable so that the reversibility of reaction (5) is not surprising. Accordingly, we propose that **4** is the σ -complex involved in the observed equilibrium.

Steric Constraints of the Hydroxyalkyl Radicals.

The data of Table 1 show a strong dependence of K_{eq} on alcohol solvent, ROH. Plots of K_{eq} versus solvent dielectric constant [17] or Kosower's solvent polarity parameter Z [18] give a reasonable correlation. However, we noticed that solvent dielectric constants are inversely proportional to the steric bulk of the R group. The K_{eq} values listed in Table 1 are plotted in Figure 4 versus Charton's steric constant ν [19] for the corresponding hydrocarbons. The very good correlation ($r^2 = 0.98$) indicates that the size of the alkyl group is a major factor determining the magnitude of K_{eq} .

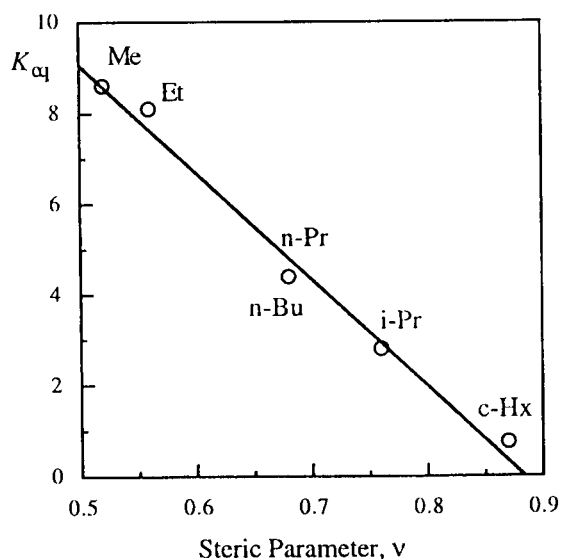


Figure 4. Plot of K_{eq} versus the steric parameter ν for the corresponding hydrocarbon without a hydroxyl group.

Effect of Acid.

Any factor that changes the rate of formation of either pyridinyl or hydroxyalkyl radicals will change the value of K_{eq} , all other things being equal. For example, in the reaction carried out in ethanol, if small amounts of acid are added to the reaction mixture, the rate of formation of **2** is greatly increased relative to the rate of complex formation, and K_{eq} is decreased accordingly, Figure 5 [3].

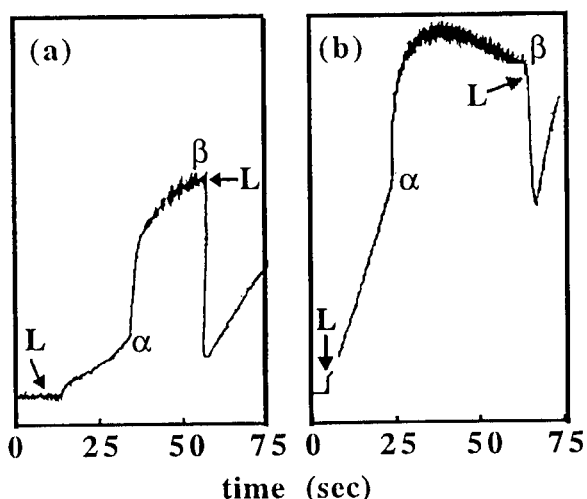


Figure 5. ESR derivative amplitude curves of one peak of the spectrum of the radical **2** in ethanol with (a) 0.012 M HCl and (b) 0.036 M HCl.

Direct Photoactivation of **1**.

Since the triplet state of **1** and benzophenone lie close together, neither state is completely quenched and, thus each can participate in its own photochemistry as shown in Scheme 1. Under the conditions of the experiment, most of the light is absorbed by benzophenone which either transfers its energy to **1**, equation (3), or abstracts a H atom from the alcohol solvent, equation (4).

Photochemical Saturation Effect.

The molar absorption coefficients, ϵ_m , of 2,4-pyridinedicarbonitrile and benzophenone are $1 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1}$ at 280.5 nm [3] and $1 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ at 252 nm [5], respectively. With the concentrations on the order of 0.05 M, absorption of the incident light beam should be virtually complete in the outside 0.1 mm of solution. Thus a high concentration of radicals is produced in this outer layer of solution, enhancing the effect of bimolecular radical reactions relative to unimolecular reactions or diffusion. Thus the complex formation step (the key to the results reported here) would probably not be observable if the photolysis were carried out to produce more dilute radical solutions.

Other work.

Preliminary results obtained with other cyano substituted pyridines show that 2,4,6-pyridinetricarbonitrile loses the 4-cyano group on irradiation, and when the light is extinguished, the signal level rapidly loses one-third of its height and then begins to rise again. Under the same conditions, 2,6-pyridinedicarbonitrile showed little indication of complex formation with $K_{eq} = 0.23$ in ethanol solvent. The corresponding 3,4 isomer did

not form a complex. We are presently attempting to make direct measurements on the complex in frozen solution.

Conclusions.

When 2,4-pyridinedicarbonitrile and benzophenone are irradiated in 1° or 2° alcohol solution, a σ -complex forms. This complex forms when the triplet energy of the ketone is not much different from that of **1**, 70 kcal/mol. The other factor that is important is that the ketone must be able to extract a hydrogen atom from an alcohol molecule and form a hydroxyalkyl radical.

Another important factor in determining whether or not a complex will form is the steric factor. If we assume that the steric factors listed by Charton [19] for alkyl substituents also approximately apply to hydroxyalkyl radicals, then a complex will form when the alkyl group is not too bulky and has a steric constant not greater than approximately 0.89.

Acknowledgements..

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- [9] The time required to reach the α steady-state level ranged from 10 s for methanol to 27 s for 2-propanol. To reach the β level, the time required ranged from 3 s for methanol to 11 s for 2-propanol. All other alcohols tested had values within these ranges.
- [10] The kinetic order was determined with 4-methylcyclohexanol which is more viscous than the other alcohols used and has a hydroxyalkyl radical that makes a complex that has a more gradual slope to the β level than do the radicals derived from the other alcohols. The estimated rate constant is about 0.01 s^{-1} .
- [11] For examples see K. Akiyama, S. Tero-Kubota, and Y. Ikegami, *J. Am. Chem. Soc.*, **105**, 3601 (1983).
- [12] The hydroxymethyl radical, $\bullet\text{CH}_2\text{OH}$, may decay by disproportionation, dimerization, or reaction with benzophenone.
- [13] One decay route of **2**, equation (7), is substitution of the cyano groups in the 2 and 4 positions by diphenylmethanol groups.
- [14] With the concentration of benzophenone at 0.01 M K_{eq} was 2.8 at the usual time interval of 19 seconds, reaching 10.3 at 66 seconds and remaining at this value in subsequent on-off light cycles. The lower concentration seems to yield a higher K_{eq} value, an observation that is under further study.
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