Reactivity of n,π* Excited Singlet States of Alkanals[1]

J. Christopher Dalton,* Margaret W. Geiger, and John J. Snyder

Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627.
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Abstract: Relative quantum yields of fluorescence (Φ_f^{rel}) and fluorescence lifetimes (τ_f) have been determined in hexane for propanal, 1-butanal, 1-pentanal, 2-methylpropanal, and 2,2-dimethylpropanal. The reactivity of alkanal n,π* singlet states toward the unimolecular primary photochemical process of intramolecular γ-hydrogen abstraction is estimated from changes in the fluorescence decay rate (τ_f^{-1}) with alkanal structure. The electrophilic and nucleophilic reactivity of alkanal excited singlet states has also been investigated by studying the quenching of alkanal fluorescence by triethylamine (TEA) and *trans*-dicyanoethylene (*t*-DCE). A comparison of the quenching of alkanals and analogous alkanones indicates that alkanal ^{1}n,π* states are 5–10 times more reactive toward TEA quenching than alkanone ^{1}n,π* states, while the alkanone singlets are slightly more reactive toward quenching by *t*-DCE. These results are discussed in terms of electronic and steric effects on the reactivity of carbonyl n,π* states.

While there have been many reports of the chemical reactivity of excited electronic states of alkanones,[2] little quantitative information is available about the reactivity of n,π* excited states of simple alkyl aldehydes.[3] We report a study of the lifetimes, relative quantum yields, and quenching of the fluorescence of a series of alkanals. Our data provide insight into the reactivity of alkanal excited singlet states toward unimolecular and bimolecular primary photochemical processes and allow comparison of the electrophilic and nucleophilic reactivity of alkanal and alkanone ^{1}n,π* states.

Results and Discussion

The aldehydes studied include propanal, 1-butanal, 1-pentanal, 2-methylpropanal, and 2,2-dimethylpropanal. Relative quantum yields of fluorescence, Φ_f^{rel}, fluorescence lifetimes, τ_f, and fluorescence decay rates, τ_f^{-1}, determined for these aldehydes in hexane are given in Table I. Assuming the excited singlet state processes noted in Scheme I, kinetic expressions for the fluorescence lifetime, τ_f, and the fluorescence quantum yield, Φ_f, both in the absence of bimolecular reactant B, are given in eq 1 and 2, respectively.

$$\tau_f = \frac{1}{k_f + k_{st} + k_r^s} \qquad (1)$$

$$\Phi_f^0 = k_f\tau_f \qquad (2)$$

The quenching of alkanal fluorescence by triethylamine, TEA, and *trans*-dicyanoethylene, *t*-DCE, was also investigated. The fluorescence quenching data were analyzed by the standard Stern–Volmer treatment using eq 3 (see

$$\frac{\Phi_f^0}{\Phi_f} = 1 + k_b^s\tau_f[B] \qquad (3)$$

Scheme I). Linear Stern–Volmer plots were observed for the quenching of alkanal fluorescence. The observed bimolecular rate constants for fluorescence quenching, k_b^s, are given in Table II. These k_b^s values were obtained from the slopes of the fluorescence quenching plots ($k_b^s\tau_f$) and the measured fluorescence lifetimes.

Scheme I

$A \xrightarrow{h\nu} {}^1A$	Absorption
${}^1A \xrightarrow{k_f} A + h\nu_f$	Fluorescence
${}^1A \xrightarrow{k_{st}} {}^3A$	Intersystem crossing
${}^1A \xrightarrow{k_r^s}$ products	Unimolecular S_1 reaction
${}^1A + B \xrightarrow{k_b^s}$ products or quenching	Bimolecular S_1 reaction or quenching

The τ_f values given in Table I are the first solution phase fluorescence lifetimes reported for these aldehydes[4] and are in the same range as τ_f values of simple alkanones.[2,5] The trends in the fluorescence decay rate, τ_f^{-1}, in hexane with aldehyde structure are interesting.[6] As the alkyl side chain changes from ethyl to 1-propyl to 1-butyl the rate of decay of the excited singlet state increases from 4.3×10^8 sec^{-1} (propanal) to 5.9×10^8 sec^{-1} (1-butanal) to 1.0×10^9 sec^{-1} (1-pentanal). The radiative rate constant for alkanal fluorescence is much less ($k_f \sim 10^5$ sec^{-1})[7] than τ_f^{-1}, and the intersystem crossing rate constant, k_{st}, would not be expected to be very sensitive to methyl substitution at the β and γ carbons.[8] Therefore, the increases in the excited singlet state decay rate in going from propanal to 1-butanal to 1-pentanal are consistent with the introduction of a primary photochemical process, such as intramolecular γ-hydrogen abstraction. Coyle[3a] has shown that both singlet and triplet n,π* states of 1-butanal and 1-pentanal undergo intramolecular γ-hydrogen abstraction processes. Triplet lifetimes, τ_t, of 35 and 6.2 nsec were determined for 1-butanal and 1-pentanal, respectively.[3a] These τ_t values suggest rate constants (k_r^t) for intramolecular γ-hydrogen abstraction from the ^{3}n,π* state of 2.9×10^7 sec^{-1} for 1-butanal and 1.6×10^8 sec^{-1} for 1-pentanal.[9] Assuming that the increases in τ_f^{-1} in going from propanal to 1-butanal to 1-pentanal are due to intramolecular γ-hydrogen abstraction, then k_r^s, the rate constant for this process from the aldehyde ^{1}n,π* state, is equal to $\sim 1 \times 10^8$ sec^{-1} for 1-butanal and $5\text{–}6 \times 10^8$ sec^{-1} for 1-pentanal. These rates are comparable to the reactivities of alkanone n,π* singlet states toward intramolecular γ-hydrogen abstraction of primary ($k_r^s = 1\text{–}2 \times 10^8$ sec^{-1}) and secondary ($k_r^s = 8\text{–}10 \times 10^8$ sec^{-1}) γ hydrogens.[5c,d] The greater reactivity of alkanal n,π* singlets than alkanal n,π* triplets toward intramolecular γ-hydrogen abstraction is also observed for alkanone n,π* states.[10]

We also note from Table I that increasing α-methyl substitution leads to a decrease in alkanal fluorescence lifetimes. The excited singlet state decay rate, τ_f^{-1}, thus increases in going from propanal (4.3×10^8 sec^{-1}) to 2-methylpropanal (7.1×10^8 sec^{-1}) to 2,2-dimethylpropanal (14.3×10^8 sec^{-1}). Increasing α-methyl substitution is known to reduce k_{st}, the intersystem crossing rate constant, and thus decrease τ_f^{-1} for alkanones.[5e,11] We observe, however, that τ_f^{-1} for alkanals increases as α-methyl groups are added. Unless α-methyl substitution has opposite effects on alkanal and alkanone k_{st} values, which seems unlikely, this suggests that a photochemical process, presumably α cleavage, is occurring from the alkanal ^{1}n,π* state. Simple alkanals are known to undergo α cleavage to alkyl and formyl radicals upon irradiation,[12] and the reactivity toward α cleavage would certainly be expected to increase with increasing α-methyl substitution.[2] While CIDNP studies[12a-c]

Table I. Fluorescence Characteristics of Alkanals

Aldehyde^a	$\Phi_f^{\mathrm{rel}\,b}$	τ_f, 10^{-9} sec^c	τ_f^{-1}, 10^8 sec^{-1}
Propanal	1.00	2.3	4.3
1-Butanal	0.98 (0.03)	1.7	5.9
1-Pentanal	0.55 (0.03)	1.0	10.0
2-Methylpropanal	0.82 (0.08)	1.4	7.1
2,2-Dimethylpropanal	0.49 (0.06)	0.7	14.3

^{a} Solutions approximately 0.1 M in hexanes. ^{b} Quantum yields of fluorescence relative to propanal measured at room temperature using Hitachi Perkin-Elmer MPF 2A spectrofluorometer. λ_{ex} 310 nm. Average of three determinations with standard deviation given in parentheses. ^{c} Fluorescence lifetimes measured by the single photon counting technique. Error ±20%.

Table II. Quenching of Alkanal Fluorescence

Aldehyde^a	k_b^s, $10^9\,M^{-1}$ sec^{-1} TEA^b	t-DCE^c
2-Butanone	1.7	3.1
Propanal	8.9	1.7
1-Butanal	9.3	2.3
1-Pentanal	6.5	>1.8
2-Methylpropanal	7.2	1.0
2,2-Dimethylpropanal	6.5	1.4

^{a} Solutions approximately 0.1 M in hexanes for TEA quenching and 0.1 M in acetonitrile for t-DCE quenching. ^{b} Bimolecular rate constants for TEA quenching of carbonyl excited singlet states in hexane, determined from slopes of Stern–Volmer fluorescence quenching plots and τ_f values given in Table I. Error ±20%. ^{c} Bimolecular rate constants for t-DCE quenching of carbonyl excited singlet states in acetonitrile, determined from slopes of Stern–Volmer fluorescence quenching plots and the following τ_f values measured in acetonitrile: propanal (1.7 nsec), 1-butanal (1.5 nsec), 1-pentanal (<1 nsec), 2-methylpropanal (1.2 nsec), 2,2-dimethylpropanal (0.9 nsec), and 2-butanone (2.1 nsec). Error ±20%.

indicate that α cleavage occurs from the alkanal ^{3}n,π* state, our results suggest that α cleavage may occur from alkanal n,π* singlet states, as well.

We now want to consider the reactivity of alkanal excited singlet states toward bimolecular primary photochemical processes. By analogy with alkanones, alkanal n,π* excited states should have two reactive sites: the electrophilic half-vacant oxygen n_O orbital in the plane of the carbonyl; and the nucleophilic half-occupied delocalized π_{CO}* orbital above and below the plane of the carbonyl.[2] In order to assess the reactivity of these two sites for n,π* excited singlet states of alkanals we have studied quenching of alkanal fluorescence by (a) an electron-poor olefin, *trans*-dicyanoethylene (t-DCE), in acetonitrile, and (b) an aliphatic amine, triethylamine (TEA), in hexane. t-DCE has been shown to quench alkanone excited singlet states by interaction with the nucleophilic π_{CO}* orbital,[2,5a,11,13] while quenching of ketone n,π* states by aliphatic amines has been attributed to interaction of the electrophilic oxygen n orbital with the amine lone pair.[14]

Looking first at the quenching of alkanal fluorescence by TEA, we see that the bimolecular rate constants[15] given in Table II for quenching of alkanal excited singlet states by this tertiary amine ($k_b^s \sim$ 5-10 × $10^9\,M^{-1}$ sec^{-1}) are significantly greater than the rate constants for quenching analogous alkanone singlets, e.g., 2-butanone, and are close to the diffusion-controlled rate constant in hexane.[17] There is a modest dependence of reactivity toward TEA quenching on aldehyde structure, with increasing steric bulk of the alkyl side chain, particularly by α-methyl substitution, causing a decrease in k_b^s. The difference in reactivity of propanal (k_b^s = 8.9 × $10^9\,M^{-1}$ sec^{-1}) and 2,2-dimethylpropanal (k_b^s = 6.5 × $10^9\,M^{-1}$ sec^{-1}) singlets toward TEA quenching, however, is much less than the difference in reactivity of acetone (k_b^s = 2.7 × $10^9\,M^{-1}$ sec^{-1}) and *tert*-butyl methyl ketone (k_b^s = 6.8 × $10^8\,M^{-1}$ sec^{-1})[14g] singlets toward quenching by TEA. Thus, observed rate constants for TEA quenching of alkanal ^{1}n,π* states are both (a) 5 to 10 times greater and (b) significantly less sensitive to α-methyl substitution than rate constants for TEA quenching of analogous alkanone ^{1}n,π* states.

The greater electrophilic reactivity of alkanal ^{1}n,π* states than alkanone ^{1}n,π* states toward amine quenching could a priori be due to either electronic or steric effects. The electronic effect could arise because substitution of an alkyl group for an α hydrogen in going from an aldehyde to a ketone makes the carbonyl reduction potential more negative,[18] an effect which may cause a decrease in the reactivity of the carbonyl n,π* state toward nucleophiles, such as amines (vide infra). Steric effects would, of course, favor reaction with aldehydes rather than the sterically more hindered ketones. Each of these effects will be discussed in more detail below.

The quenching of carbonyl n,π* states by amines appears to involve initial formation of a charge-transfer complex in which there has been a *partial* electron transfer from the amine to the ketone.[14] The half-vacant electrophilic oxygen n orbital of the carbonyl is the electron acceptor and the amine nonbonding nitrogen orbital is the electron donor. The free-energy change, ΔF, for formation of such a charge-transfer complex will clearly be a function of the reduction potential of the n,π* excited state (a measure of the energy released by the addition of an electron to the carbonyl excited state) and the oxidation potential of the ground state amine (a measure of the energy required for removal of an electron from the amine). The ΔF values for formation of charge-transfer complexes are commonly calculated using expressions similar to eq 4, where $E(\mathrm{D}|\mathrm{D}^+)$ is the

$$\Delta F = E(\mathrm{D}|\mathrm{D}^+) - (E(\mathrm{A}^-|\mathrm{A}) + \Delta E_{0,0}) + C \qquad (4)$$

amine oxidation potential, $E(\mathrm{A}^-|\mathrm{A})$ is the ketone reduction potential, $\Delta E_{0,0}$ is the carbonyl excited state energy, and C is a constant in a given solvent.[14,19,20] The term $(E(\mathrm{A}^-|\mathrm{A}) + \Delta E_{0,0})$ approximates the desired reduction potential of the carbonyl n,π* state. It has been observed that the bimolecular rate constants for charge-transfer quenching of excited states by electron donors increase with decreasing ΔF values, reaching a limiting value when $E(\mathrm{D}|\mathrm{D}^+) - (E(\mathrm{A}^-|\mathrm{A}) + \Delta E_{0,0})$ is less than about −5 kcal/mol.[14d,19,20] Now we might expect ΔF for TEA quenching to be more negative for alkanal ^{1}n,π* states than for alkanone ^{1}n,π* states because the less negative alkanal reduction potential may result in a greater ^{1}n,π* state reduction potential for alkanals.[21] More negative ΔF values for alkanal quenching, however, presumably would not cause k_b^s to be greater for alkanals than for alkanones because $E(\mathrm{D}|\mathrm{D}^+) - (E(\mathrm{A}^-|\mathrm{A}) + \Delta E_{0,0})$ for alkanone ^{1}n,π* states and TEA is nearly −10 kcal/mol,[14g,22] already well below the −5 kcal/mol value where bimolecular rate constants for quenching of carbonyl n,π* states by electron donors level off.[14d] Thus it seems unlikely that electronic effects are responsible for the greater reactivity of alkanal ^{1}n,π* states than alkanone ^{1}n,π* states toward quenching by triethylamine.

It is more probable that the greater reactivity of alkanal ^{1}n,π* states toward TEA is a steric effect, i.e., that interaction of the amine lone pair electrons with the electrophilic oxygen n orbital in the plane of the carbonyl is less sterically hindered in aldehydes than in ketones. This implies that attack of the alkyl amine on alkanal excited singlet states must occur predominantly from the aldehyde hydrogen side of the carbonyl, thus providing a ready explanation for why the effect of carbonyl α-methyl substitution on the reactivity toward TEA quenching (vide supra) is greater for alkanone S_1 states than alkanal S_1 states. If there is initially little approach to the aldehyde electrophilic oxygen n orbital from the side with the alkyl group (as opposed to the aldehyde hydrogen side), then clearly the effect of α substitution on the alkyl side chain on the overall quenching rate will be minimal.

Turning now to the data on quenching of aldehyde fluorescence in acetonitrile by the electron poor olefin *trans*-dicyanoethylene, *t*-DCE, we see from Table II that again the bimolecular quenching rate constants are close to the diffusion-controlled limit.[23] There is no discernible trend of reactivity as a function of alkanal structure. The observed rate constants for quenching of alkanal S_1 state by *t*-DCE are somewhat less than the $k_b{}^s$ values for quenching of the fluorescence of analogous alkanones, e.g., 2-butanone or acetone ($3.0 \times 10^9\ M^{-1}\ \text{sec}^{-1}$).[5a,24]

Considering electronic effects qualitatively, the fact that alkanals have a higher oxidation potential than alkanones[25] might be expected to result in the alkanone n,π^* state being more reactive than the alkanal n,π^* state toward electrophiles such as *t*-DCE (vide infra). Steric effects, on the other hand, would work in the opposite direction tending to make aldehyde n,π^* states more reactive than ketone n,π^* states. It is again instructive to look more quantitatively at the energetics of the quenching of carbonyl $^1n,\pi^*$ states by electron deficient olefins.

The quenching of carbonyl n,π^* states by electron-deficient olefins is thought to involve initial formation of an exciplex with partial charge-transfer character.[2,5a,13,26] Now, however, the ketone through its nucleophilic $\pi_{CO}{}^*$ orbital is the electron donor and the olefin $\pi_{CC}{}^*$ orbital is the electron acceptor. This suggests that the free-energy change, ΔF, for formation of the complex should be a function of the oxidation potential of the n,π^* state of the carbonyl ($E(D|D^+) - \Delta E_{0,0}$) and the reduction potential of the olefin ($E(A^-|A)$). The fact that the rate constants for quenching alkanone $^1n,\pi^*$ states by electron-deficient olefins correlates with the energy of the lowest vacant olefin MO[26] and, hence, olefin reduction potential implies that the reactivity of carbonyl $^1n,\pi^*$ states toward quenching by *t*-DCE should also reflect variations in the oxidation potential of the $^1n,\pi^*$ excited state unless the effect of changes in the value of $E(D|D^+) - \Delta E_{0,0}$ is balanced by steric effects. An apparent effect of $^1n,\pi^*$ excited state oxidation potential on the reactivity toward quenching by *t*-DCE is illustrated by comparing $k_b{}^s$ values for quenching fluorescence of acetone ($3.0 \times 10^9\ M^{-1}\ \text{sec}^{-1}$)[5a,24] and biacetyl ($\leq 1 \times 10^8\ M^{-1}\ \text{sec}^{-1}$).[27] The value of $E(D|D^+) - \Delta E_{0,0}$ is -25 kcal/mol for acetone $^1n,\pi^*$ states and -8 kcal/mol for biacetyl $^1n,\pi^*$ states, a difference due primarily to the lower excited singlet state energy ($\Delta E_{0,0}$) for biacetyl.[29] In our case, the fact that the alkanal oxidation potential is significantly greater than the alkanone oxidation potential[25] should be reflected in a less negative n,π^* state oxidation potential for alkanals than for alkanones.[34] The slightly lower reactivity of alkanal excited singlets than alkanone excited singlets toward *t*-DCE quenching presumably reflects primarily the combined effects of (a) the less negative alkanal $^1n,\pi^*$ state oxidation potential which tends to make alkanals less reactive toward charge-transfer complex formation with electrophiles and (b) the reduced steric hindrance to attack on alkanal $\pi_{CO}{}^*$ orbitals, which tends to make alkanal $^1n,\pi^*$ states more reactive than alkanone $^1n,\pi^*$ states.

Experimental Section

Alkanals, quenchers, and solvents were monitored for purity by GLC, uv, and fluorescence spectroscopy. Alkanals were obtained commercially and purified by preparative GLC. Hexanes (Mallinckrodt Chemical Works, SpectrAR) were used as received. Acetonitrile (Mallinckrodt Chemical Works, SpectrAR) was distilled three times from P_2O_5 (0.5–1.0%, w/v) and then distilled from anhydrous K_2CO_3. Triethylamine (Eastman Organic Chemicals), bp 89°, was fractionally distilled. *trans*-Dicyanoethylene was purified by sublimation.

Preparative GLC work was done either on a Varian A-90-P or a Varian Model 920 chromatograph. Optical densities at λ_{ex} (310 nm) were obtained on a Beckman DU Spectrophotometer, equipped with Guilford Model 222 Photometer and Dual Lamp Source. Fluorescence spectra were measured on a Hitachi Perkin-Elmer MPF-2A spectrofluorometer. Relative quantum yields of fluorescence were estimated from the relative intensities of the fluorescence maxima since the position and shape of the fluorescence spectrum was very similar for all of the aldehydes studied. Full uv spectra were recorded using a Cary 118C spectrophotometer. Fluorescence lifetimes were measured using an Applied Photophysics Ltd. SP-1X single photon counting lifetime apparatus with an $f/4$ grating monochromator, an Amperex 56 DUVP/03 photomultiplier tube, and Ortec electronics.[35] The lifetime values were determined by convolution using a procedure similar to that of Stryer and coworkers.[36] The absolute error limits were qualitatively estimated to be ±20%.

The slope and intercept of each Stern–Volmer fluorescence quenching plot (eq 3) were determined by a least-squares analysis. The $k_b{}^s\tau_f$ value was then obtained by dividing the slope by the intercept. This procedure allows for error in the measurements of both $\Phi_f{}^0$ and Φ_f.

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(6) Qualitatively similar trends of τ_f values with aldehyde structure are observed in acetonitrile. See footnote c, Table II.

(7) Alkanal k_f values are estimated from integration of the alkanal electronic absorption spectrum ($\epsilon_{max} \leq 20$). See, for discussion, N. J. Turro, "Molecular Photochemistry", W. A. Benjamin, New York, N.Y., 1965, p 48.

(8) Yang, Elliott, and Kim have shown that k_{sl} values for acyclic alkanones are insensitive to γ-methyl substitution. See ref 5d.

(9) If radiationless deactivation occurs at comparable rates for alkanones and alkanals, then the reaction rate constants ($k_r{}^t$) should equal the triplet decay rate ($\tau_t{}^{-1}$) since photophysical decay of alkanone triplets, primarily by radiationless deactivation to S_0, occurs with a rate constant on the order of $10^5\ \text{sec}^{-1}$ (P. J. Wagner, *J. Am. Chem. Soc.*, **88**, 5672 (1966)).

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(15) The observed bimolecular rate constants for fluorescence quenching, $k_b{}^s$, given in Table II can also be considered to be the product of k_{diff}, the bimolecular rate constant for formation of an encounter complex, and $k_r/(k_r + k_{-diff})$, the probability that formation of the encounter complex results in quenching (k_r) rather than diffusion apart to regenerate ^{1}A and B (k_{-diff}).[14b,g,16] We assume thet k_{diff} and k_{-diff} do not vary with aldehyde structure, since the related rate constants for amine quenching of alkanone fluorescence do not appear to vary with alkanone or amine structure. Under these conditions, variations in $k_b{}^s$ reflect changes in k_r. See ref 14g for a more detailed discussion.

(16) See, for example, T. R. Evans, *J. Am. Chem. Soc.*, **93**, 2081 (1971).

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(18) For example, the reduction potentials for acetone and acetaldehyde are −2.3 and −2.1 V, respectively.[14d]

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(20) Equation 4 calculates the ΔF values for formation of a charge-transfer complex in which there is full electron transfer from the donor (D) to the acceptor (A). The equation has, however, been usefully applied in cases where charge-transfer complexes are formed with only partial electron transfer.[14] In particular, although the slopes of plots of the log of the bimolecular rate constants for charge-transfer quenching (k_q) of excited states by electron donors vs. the calculated ΔF values vary with the extent of electron transfer in the complex, the k_q values appear to level off when $E(\mathrm{D}|\mathrm{D}^+) - (E(\mathrm{A}^-|\mathrm{A}) + \Delta E_{0,0})$ is less than −5 kcal/mol irrespective of the extent of electron transfer.[14a,d,19]

(21) It is difficult to determine the exact difference in alkanal and alkanone ^{1}n,π^* state reduction potentials as defined in eq 4 ($E(\mathrm{A}^-|\mathrm{A}) + \Delta E_{0,0}$) because the excited singlet state energies, $\Delta E_{0,0}$, are not precisely known. The ground state reduction potentials for model compounds ($E(\mathrm{A}^-|\mathrm{A})$ for acetone = −2.3 V; $E(\mathrm{A}^-|\mathrm{A})$ for acetaldehyde = −2.1 V)[14d] indicate that if the $\Delta E_{0,0}$ values are comparable, the ^{1}n,π^* state reduction potential will be around 5 kcal/mol greater for alkanals than alkanones. λ_{max} for $S_0 \rightarrow {}^1$n,π^* transitions is generally at somewhat longer wavelength for alkanals than alkanones (ref 12f, p 368–377) suggesting lower $\Delta E_{0,0}$ values for alkanals. On the other hand, we observe that λ_{max} for ^{1}n,$\pi^* \rightarrow S_0$ fluorescence transitions is generally at slightly shorter wavelengths for alkanals than alkanones, suggesting higher $\Delta E_{0,0}$ values for alkanals.

(22) $E(\mathrm{D}|\mathrm{D}^+)$ for TEA is 22.1 kcal/mol,[14d] $E(\mathrm{A}^-|\mathrm{A})$ for acetone is −53.2 kcal/mol,[14d] and $\Delta E_{0,0}$ for the acetone ^{1}n,π^* state is approximately 85 kcal/mol.

(23) The bimolecular rate constant for diffusion in acetonitrile has been estimated to be 2.7×10^{10} M^{-1} sec^{-1} (S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, N.Y., 1973, p 55).

(24) The k_q value given for *t*-DCE quenching of acetone S_1 states is obtained using a τ_f value of 1.7 nsec rather than the value of 2.0 nsec used in ref 5a.

(25) For example, the oxidation potentials of acetone and acetaldehyde are 2.59 and 3.03 V, respectively (R. O. Loutfy and R. O. Loutfy, *J. Phys. Chem.*, **77**, 336 (1973)).

(26) (a) N. J. Turro, *Pure Appl. Chem.*, **27**, 679 (1971); (b) N. J. Turro, C. Lee, N. Schore, J. Barltrop, and H. A. J. Carless, *J. Am. Chem. Soc.*, **93**, 3079 (1971); (c) M. P. Niemczyk, N. E. Schore, and N. J. Turro, *Mol. Photochem.*, **5**, 69 (1973).

(27) Reference 5a reports no quenching of biacetyl fluorescence in benzene with *t*-DCE concentrations greater than 0.1 *M*. Given a τ_f value of 10 nsec for biacetyl in benzene[28] and assuming that at most 10% quenching would go undetected yields 1×10^8 M^{-1} sec^{-1} as a limiting value of $k_b{}^s$ for *t*-DCE quenching of biacetyl singlets.

(28) N. J. Turro and R. Engel, *J. Am. Chem. Soc.*, **90**, 2989 (1968).

(29) The $\Delta E_{0,0}$ values for the ^{1}n,π^* states of biacetyl and acetone are 65[30] and 85 kcal/mol, respectively, while $E(\mathrm{D}|\mathrm{D}^+)$ is 60 kcal/mol for acetone and 57 kcal/mol for biacetyl.[31]

(30) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State", Prentice-Hall, Englewood Cliffs, N.J., 1969, p 84.

(31) Calculated from the biacetyl ionization potential (IP = 9.57 V)[32] using the following formula: $E(\mathrm{D}|\mathrm{D}^+) = 0.89\mathrm{IP} - 6.04$.[33]

(32) J. Kelder, H. Cerfontain, B. R. Higginson, and D. R. Lloyd, *Tetrahedron Lett.*, 739 (1974).

(33) L. L. Miller, G. D. Nordblom, and E. A. Mayed, *J. Org. Chem.*, **37**, 916 (1972).

(34) The difference in alkanal and alkanone excited singlet state energies, although not precisely known,[21] is surely less than the 10 kcal/mol difference in alkanal and alkanone oxidation potentials.[25]

(35) For a discussion of single photon counting techniques, see J. B. Birks and J. H. Munro, *Prog. React. Kinet.*, **4**, 215 (1967).

(36) L. Hundley, T. Coburn, E. Garwin, and L. Stryer, *Rev. Sci. Instrum.*, **38**, 488 (1967).

Electronic Structure of Dicarbonyls. Glyoxal Excited States[1]

Clifford E. Dykstra[2] and Henry F. Schaefer III*

Contribution from the Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720.

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Abstract: Excited electronic states of glyoxal, $(CHO)_2$, have been studied by ab initio self-consistent field (SCF) methods using a double ζ basis set of contracted Gaussian functions. The vertical excitation energies from the optimum ground state geometry were determined for 20 trans and 20 cis excited states. These included all singlet and triplet n → π^* and $\pi \rightarrow \pi^*$ excitations and the lowest n → σ^* excitations. Geometry optimization was performed for the three lowest cis and trans states. Two very low-lying unobserved triplet states, trans ^3B_u and cis $^3B_2$, are predicted by these calculations to be within about 15 000 cm^{-1} of the corresponding ground states, making them possibly the lowest excited states of glyoxal. The next lowest lying states were the observed trans ^3A_u, ^1A_u and cis $^1B_1$, for which the geometry optimization provides a basis for comparison with experiment. The experimentally observed states arise from an n → π^* excitation, but surprisingly the lowest triplets arise from $\pi \rightarrow \pi^*$ excitations. The geometry of these $\pi \rightarrow \pi^*$ triplets is strikingly different from that of the ground state and is in closer correspondence with a biradical structure.

While many excited states of carbon monoxide, formaldehyde, and other carbonyl molecules have been identified,[3a] fewer states of the simplest dicarbonyl, glyoxal, have been observed. Brand identified the first excited states of *trans*-glyoxal as ^1A_u and ^3A_u from his vibrational analysis of the 4550-Å absorption band.[3b] Following the description of McMurry,[3c] these states were associated with an n(a_g) → π^*(a_u) excitation. Extensive high-resolution spectroscopic studies have been made by Ramsay and coworkers.[4-6] In addition, they made the first observation of the cis form of glyoxal and identified the $^1B_1$ excited state in rotational analysis of a band at 4875 Å.[7-9] This state is associated with an n(a_1) → π^*(b_1) excitation and a $^3B_1$ state is presumed to occur in the same region. There has been no direct observation of other glyoxal excited states, though a simple molecular orbital picture suggests a total of 32 n → π^* and $\pi \rightarrow \pi^*$ states.

In addition to their spectroscopic interest, the excited states of glyoxal are important photochemically. Glyoxal has been found to photodissociate into hydrogen, carbon monoxide, formaldehyde, and CHO radicals.[10-14] And the dissociation product yields have been related to individual