and the sodium tetrametaphosphate ion pair, $NaP_4O_{12}^{3-}$.[10]

The close agreement between the stability constant values for the $KATP^{3-}$ species obtained with the cationic glass electrode and the valinomycin electrode indicates that the latter might prove to be an excellent tool for thermodynamic studies involving changes in K^+ activity. While the present study was conducted with pure solutions, the excellent selectivity properties[11] of this electrode permit its use in the presence of a large excess of sodium ions as found in many biological systems.

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Fluorescence of Aliphatic Ketones[1]

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Abstract: The fluorescence of a series of aliphatic ketones excited at 313 nm has been studied at room temperature in *n*-hexane, cyclohexane, methanol, and acetonitrile. The results suggest that the α-CH stretching mode is a factor in radiationless processes from the excited singlet state. The fluorescence quantum yields of the carbonyl compounds were observed to increase with alkyl substitution at the α-carbon, and the fluorescence wavelength maxima remained constant at 405 ± 3 nm. The fluorescence yield of di-*tert*-butyl ketone in *n*-hexane at room temperature was determined to be larger by a factor of 4.41 than the value for acetone. Deuterated acetone exhibited enhanced fluorescence relative to ordinary acetone.

Recently we suggested that the 405-nm fluorescence band of acetone was due to an excimer based on concentration effects and its inability to respond to solvent effects.[2] Renkes and Wettack[3a] and Dalton[3b] have, since our initial report, each independently shown that the fluorescence wavelength maximum at 405 nm is normal fluorescence with no unusual behavior attributable to variation in concentration of the ketone. In view of our recent study on triplet deactivation of aliphatic ketones at 77°K[4] this report is presented with the aim of illustrating the effect of structure on the singlet deactivation of aliphatic ketones. The fluorescence of a series of aliphatic ketones, which may be considered derivatives of acetone in which the α-hydrogens are replaced with alkyl groups, have been investigated.

Experimental Section

Materials. The materials used in this study have been characterized elsewhere.[4]

Apparatus and Procedures. Absorption spectra were obtained with either a Bausch and Lomb Model 505 or a Beckman Model DU spectrophotometer. The natural radiative singlet lifetimes, τ_f^0, were estimated from the integrated absorption of the lowest transition of the ketone.

Fluorescence measurements were made with an Aminco grating monochromator equipped with a 1P21 photomultiplier tube and displayed on a Moseley Model 7030A XY recorder. The emission spectra were measured from air-saturated solutions, in view of the reported observations which indicate that the fluorescence of acetone and acetone-d_6 are unaffected by dissolved oxygen.[5,6]

All ketones were excited with 313-nm light which was isolated from an Osram HBO 100 W/2 high-pressure mercury lamp with a Schott interference filter. The monochromator entrance and exit slits were 1 mm and the emission was detected in a direction perpendicular to the exciting beam. Quartz spectrophotometric cells (1-cm path length) were used for absorption and fluorescence measurements, which were made at 25°. A planimeter was utilized to determine the relative fluorescence yield by integration of the emission spectra of all solutions, which were adjusted to have the same optical densities at the wavelength of excitation. The relative fluorescence quantum yield of acetone was determined relative to the value of 0.09 for tryptophan.[7]

Results

The most significant observations are that the spectral distribution of the fluorescence curves was identical for all the ketones studied and that the emission quantum yields increased when the α-hydrogens of acetone were replaced by various alkyl groups. A similar behavior was observed for the phosphorescence of these compounds.[4] The fluorescence wavelength maxima were in the range of 405 ± 3 nm for all the ketones in the four solvents employed, *i.e.*, *n*-hexane, cyclohexane, methanol, and acetonitrile. The relative fluorescence yield spectra of the compounds studied are shown in Figure 1, with the data normalized to acetone, which has the lowest fluorescence yield. Di-*tert*-butyl ketone has the largest fluorescence yield of the series and was found to be greater by a factor of 4.41 than acetone in *n*-hexane. A summary of the solvent effects on the

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(1) Presented in part at the Division of Physical Chemistry, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstract PHYS-166.

(2) M. O'Sullivan and A. C. Testa, *J. Amer. Chem. Soc.*, **90**, 6245 (1968).

(3) (a) G. D. Renkes and F. S. Wettack, *ibid.*, **91**, 7514 (1969); (b) unpublished results from Professor Turro's group at Columbia University. We thank Dr. J. Christopher Dalton for providing us with sample fluorescence spectra of acetone at 10^{-3} *M* in hexane.

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(6) R. F. Borkman and D. R. Kearns, *J. Amer. Chem. Soc.*, **88**, 3467 (1966).

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Table I. Relative Fluorescence Quantum Yields of Aliphatic Ketones in Different Solvents[a]

	Solvent			
	n-Hexane	Cyclohexane	Acetonitrile	Methanol
1. CH_3-CO-CH_3	1.00	0.99	1.06	1.20
2. CH_3-CO-C_2H_5	1.27	1.32	1.38	1.56
3. C_2H_5-CO-C_2H_5	1.68	1.64	1.73	1.90
4. $(CH_3)_2CH$-CO-$CH(CH_3)_2$	2.50	2.57	3.19	3.13
5. $(CH_3)_3C$-CO-$C(CH_3)_3$	4.41	4.28	4.30	4.31
6. CH_3-CO-C_5H_9	1.47	1.38	1.57	1.50
7. CH_3-CO-C_6H_{11}	1.84	1.54	1.92	1.99
8. C_6H_{11}-CO-C_6H_{11}	2.83	2.66	3.12	3.35

[a] Quantum yield normalized to the value of unity for acetone in *n*-hexane.

fluorescence quantum yield, normalized to acetone, is given in Table I. It may be noted that the fluorescence yield increases slightly in polar and hydrogen-bonding solvents for all ketones, except di-*tert*-butyl ketone, which shows a small decrease. This behavior may be caused by steric hindrance to solvent–solute interaction.

The radiative singlet lifetimes of the ketones investigated are reasonably constant, as can be seen from the values presented in Table II. Although the methods for determining $\tau_f{}^0$ may not apply to forbidden transitions, the comparison between closely related molecules should be valid. It is interesting to note that the values for acetone and di-*tert*-butyl ketone are 2.5 and 2.0×10^{-6} sec, respectively, whereas the fluorescence quantum yields, given in Table II, are 1.00 and 4.41×10^{-3}. The actual singlet lifetime, defined as $\tau_f = 1/(k_f + k_{ds} + k_{isc})$, indicates that an increase in the lifetime of the singlet state can be attributed to a decrease in one or more of the following rate constants: fluorescence emission (k_f), internal conversion (k_{ds}), and intersystem crossing (k_{isc}). It is apparent from the data in Table II that the natural radiative lifetimes, $\tau_f{}^0 = 1/k_f$, are not significantly different. The fluorescence yield ratio for di-*tert*-butyl ketone to acetone is 4.41, while the ratio of the singlet lifetimes is estimated to be 3.5. The fair agreement between these values implies that the increase in fluorescence yield may be due to slowing down of internal conversion process, $S_1 \rightsquigarrow S_0$, assuming there is no significant variation in k_{isc}. An alternate possibility is that k_{isc} is slowing down with substitution at the α-carbon of the ketone. Determination of the singlet lifetimes of these molecules by other investigators are also included in Table II. The values determined for acetone and methyl *tert*-butyl ketone by the photon counting technique are in agreement with the results of the fluorescence yields reported in this study. The lifetime data determined from the sensitized fluorescence of biacetyl show more scatter and therefore make a comparison difficult.

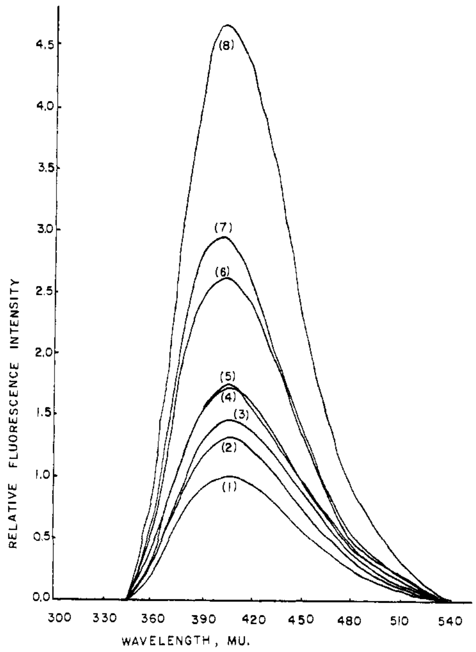

Figure 1. Fluorescence spectra of aliphatic ketones in *n*-hexane at 25° (λ_{exc} 313 nm): (1) acetone, (2) methyl ethyl ketone, (3) methyl cyclopentyl ketone, (4) diethyl ketone, (5) methyl cyclohexyl ketone, (6) diisopropyl ketone, (7) dicyclohexyl ketone, (8) di-*tert*-butyl ketone.

Table II. Relative Fluorescence Quantum Yields and Singlet Lifetimes of Aliphatic Ketones in *n*-Hexane (λ_{exc} 313 nm)

	$\Phi_F \times 10^3$ [a]	$\tau_f{}^0 \times 10^6$, sec[b]	$\tau_f \times 10^9$, sec[c]
1. CH_3-CO-CH_3	1.00	2.5	2.5 (2.1)[d] (3.9, 1.8)[e]
2. CD_3-CO-CD_3	1.36	2.5	3.4
3. CH_3-CO-C_2H_5	1.27	2.3	2.9 (2.8)[e]
4. C_2H_5-CO-C_2H_5	1.68	1.9	3.2 (4.4)[e]
5. $(CH_3)_2CH$-CO-$CH(CH_3)_2$	2.50	1.7	4.2
6. CH_3-CO-$C(CH_3)_3$			(4.2)[d]
7. $(CH_3)_3C$-CO-$C(CH_3)_3$	4.41	2.0	8.8
8. CH_3-CO-*c*-C_5H_9	1.38	2.0	2.8
9. CH_3-CO-*c*-C_6H_{11}	1.54	1.8	2.8
10. *c*-C_6H_{11}-CO-*c*-C_6H_{11}	2.83	1.3	3.7

[a] Relative fluorescence quantum yields normalized to the value of 0.09 for tryptophan; ref 7. [b] Radiative singlet lifetime calculated from integrated absorption spectrum; ref 4. [c] $\tau_f = \Phi_F \tau_f{}^0$. [d] Unpublished results from Professor Turro's group at Columbia University. [e] Based on singlet–singlet energy transfer experiments in solution: F. Wilkinson, *Advan. Photochem.*, **3**, 255 (1964).

Discussion

The unusual similarity of the fluorescence spectral distribution of all the carbonyl compounds investigated suggests that the emission process is localized in the carbonyl moiety. It is well known that aromatic ketones, such as acetophenone and benzophenone, do not fluoresce.[8]

The quantum yield for fluorescence is defined as $\Phi_F = k_f/(k_f + k_{ds} + k_{isc})$. In order to explain the trend in fluorescence, approximate values of these rate

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(8) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, Chapter 5.

constants must be known. The natural radiative lifetimes indicate relatively constant values for k_f, with possibly small variations with substitution, resulting from changes in ϵ_{max}.[4] Since the fluorescence yields of the compounds studied (Table II) are all low (<0.01) and the triplet yields, on the basis of available evidence,[5,6,9] can be assumed to be 1.00 ± 0.10, the intersystem crossing rates are expected to be faster, by factors of approximately 90–100, than the radiative singlet–singlet transition, *e.g.*, $k_{isc} \approx 100k_f$, assuming k_{ds} is negligible. This condition is not true, however, when internal conversion of the singlet occurs. Yang, *et al.*,[10] have recently reported that the triplet yield of alkanones containing a γ-hydrogen, which undergo the type II elimination, is less than unity; however, none of the compounds in the present study has γ-hydrogens. He reports that for 5-methyl-2-heptanone 78% of the electronic energy is dissipated in the process $S_1 \rightsquigarrow S_0$.

The fluorescence quantum yields in this study indicate the ratio k_{isc}/k_f to be larger by a factor of 4 for acetone than for di-*tert*-butyl ketone, while k_f is found to be constant, as seen from the integrated absorption spectra; consequently, it would appear that the intersystem crossing rate constant is faster in acetone. Although this prediction rests on the fact that k_{ds} is negligible and $\Phi_F + \Phi_T = 1$, this interpretation is consistent with recent studies by Turro, *et al.*[11] They reported that the singlet lifetime of cyclic alkanones is primarily determined by k_{isc}, which varies with substitution at the α-carbon. A recent study from this laboratory on the phosphorescence of aliphatic ketones is also consistent with variation of k_{isc} with structural changes at the α-carbon of the ketone.[4] In addition, Yang and Feit[12] have shown that while acetone does not undergo appreciable photochemistry from the singlet state, methyl *tert*-butyl ketone reacts from the single and triplet excited states.

The constancy of the fluorescence spectral distribution of these compounds is unexpected in view of the red shift in absorption spectra with alkyl substitution. Formaldehyde, the simplest carbonyl compound, has been reported to possess a pyramidal geometry in the equilibrium excited singlet and triplet states.[13,14] If this concept is extended to other carbonyl compounds, it would require that the fluorescence emission arises from a transition between a pyramidal excited state and a pyramidal ground state, followed by nonradiative relaxation to the equilibrium ground state. Kearns, *et al.*,[6] have suggested that the large difference in energy (12,000 cm^{-1}) between the Franck–Condon maxima for absorption and emission in acetone implies that there is a significant difference between the geometry of the ground and excited states. Although the Franck–Condon principle requires preservation of geometry in the absorption process, the excited molecule survives long enough to relax to a pyramidal geometry before emission occurs.

It seems reasonable to assume that the introduction of bulky alkyl groups at the α-carbon would tend to decrease the energy difference between the equilibrium Franck–Condon state and the pyramidal equilibrium state from which emission occurs. In contrast to the reorganization in the excited state, the energy difference between the Franck–Condon ground state and the equilibrium ground state would require a larger change for di-*tert*-butyl ketone relative to acetone, since the former has the lower energy singlet and, therefore, the larger stokes shift. The energy change associated with the geometrical rearrangement in the excited state may then be considered a dominant factor in the determination of fluorescence transition frequency. A similar explanation could also account for the constancy of the phosphorescence spectra of these molecules.[4] It should be noted that the effect of structure on radiationless decay is not as pronounced in the singlet manifold as it is in the triplet manifold, since the triplet yields of these molecules are essentially unity. A referee has commented that the high triplet yield of the ketones investigated cannot account for the greater effect of $T_1 \rightsquigarrow S_0$ relative to the $S_1 \rightsquigarrow T_1$ with variation of the molecule at the α-carbon. In addition to structural effects on radiationless processes, this consideration suggests that radiationless processes from singlets and triplets may be different.

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(9) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(10) N. C. Yang and S. P. Elliott, *J. Amer. Chem. Soc.*, **91**, 7550 (1969); N. C. Yang, S. P. Elliott, and B. Kim, *ibid.*, **91**, 7551 (1969).

(11) J. C. Dalton, D. M. Pond, D. S. Weiss, F. D. Lewis, and N. J. Turro, *ibid.*, **92**, 2564 (1970).

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