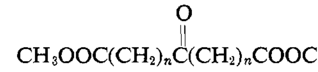
figuration conducive to photochemical reaction (a cyclic six-membered intermediate in the case of a type II reaction), while at the same time the probability of nonradiative decay of electronically excited states is increased by the increase in the number of vibrational and rotational modes in a macromolecule.

Conclusions

In conclusion, it is clear that in the photolysis of the three members of the homologous series



$$CH_3OOC(CH_2)_n\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_nCOOCH_3$$

there is a considerable difference in photochemistry depending on the value of n. When $n = 2$, there is a marked preference for radical reaction to occur either by the Norrish type I or photoreduction. When $n = 3$ the Norrish type II reaction occurs with a higher than normal quantum yield. When $n = 4$ both the type I and type II reactions occur with quantum yields similar to those expected from unsubstituted aliphatic ketones under similar photolysis conditions.

Regardless of the ketone structure, when the group is included in the backbone of a polymer chain, the quantum yield for scission is reduced by at least an order of magnitude to a value of about 0.01. This appears to be a general rule for polymeric ketones.

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Photochemistry of Ketone Polymers. VIII. Fluorescence and Energy Transfer of Aliphatic and Poly(vinyl ketones)

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ABSTRACT: The fluorescence of poly(methyl vinyl ketone), poly(methyl isopropenyl ketone), and aliphatic ketones R—C(=O)—R and Me—C(=O)—R excited at 310 nm has been studied in solution at 25°. The results reflect the dependence of radiationless processes from the singlet state on α-H and γ-H substitution and chain length. Comparison of absorption and fluorescence spectra of the polyketones with small ketones shows that there is probably some interaction of adjacent carbonyl groups in the polymers. The contrast between the relatively high transfer efficiency in the quenching of polyketone fluorescence by biacetyl and the low transfer efficiency in the analogous quenching of naphthalene fluorescence by the polyketones is consistent with the migration of singlet excitation energy in the carbonyl groups along the polymer chain. Measurements of fluorescence quenching in different solvents provide evidence that the efficiency of singlet–singlet energy transfer is not totally diffusion controlled in solvents of low viscosity.

Until recently, fluorescence studies of aliphatic carbonyl compounds have been rare because the very efficient intersystem crossing from the excited singlet state generally dominates all the processes from this state and very low fluorescence quantum yields are observed. Borkman and Kearns[1] estimated the quantum yield for acetone fluorescence at room temperature in solution to be $\phi_F \lesssim 0.01$. More recently O'Sullivan and Testa[2] obtained relative measurements of fluorescence yields at 313-nm excitation in different solvents. These authors found that for small aliphatic ketones in n-hexane $\phi_F \simeq 10^{-3}$ when normalized to the value of 0.09 for tryptophan. The maximum at 400–405 nm has been well characterized as normal carbonyl fluorescence with no unusual behavior attributable to variation in concentration of the ketone as had been suggested previously.[3] O'Sullivan and Testa also observed that fluorescence yields were increased relative to acetone by both deuteration and alkyl substitution at the α carbon and concluded that the α-C–H stretching mode is a factor in radiationless processes from the excited singlet state. Similar behavior has been observed by the same authors for the phosphorescence from the triplet state of these ketones.[4]

Several primary processes compete with radiative transitions for removal of excited-state energy (Figure 1), but quantum yields of chemical products for ketones[5] and ketone polymers[6] are generally quite low ($\lesssim 0.2$) at 310 nm. Radiationless processes compete effectively with both emission and chemical reaction from the excited singlet state so that further investigation of the factors which influence the rates of these processes become necessary for an understanding of the photochemistry of carbonyl compounds and, more particularly, of ketone polymers.

Energy transfer has proved to be a very useful method of studying the nature, lifetimes, and energy levels of excited states. Studies on ketones by the spectrofluorometric method were pioneered by Dubois and his coworkers.[7–9] The results have been adequately interpreted in terms of the mechanistic scheme summarized for convenience in eq 1–6. Equation

$$D + h\nu \longrightarrow {}^1D^* \tag{1}$$

$$^1D^* \longrightarrow D + h\nu_F \tag{2}$$

$$^1D^* \longrightarrow D \text{ or } {}^3D \tag{3}$$

$$^1D^* + O_2 \longrightarrow D + O_2^* \tag{4}$$

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[1] R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1965).

[2] M. O'Sullivan and A. C. Testa, *J. Amer. Chem. Soc.*, **92**, 5842 (1970).

[3] M. O'Sullivan and A. C. Testa, *ibid.*, **90**, 6245 (1968).

[4] M. O'Sullivan and A. C. Testa, *ibid.*, **92**, 258 (1970).

[5] J. C. Dalton and N. J. Turro, *Annu. Rev. Phys. Chem.*, **21**, 499 (1970).

[6] G. H. Hartley and J. E. Guillet, *Macromolecules*, **1**, 165 (1968).

[7] F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, **39**, 377 (1963).

[8] J. T. Dubois and M. Cox, *ibid.*, **38**, 2536 (1963).

[9] J. T. Dubois and R. L. Van Hemert, *ibid.*, **40**, 923 (1964).

$$^1D^* + D \longrightarrow D + D \qquad (5)$$

$$^1D^* + A \longrightarrow D + {}^1A^* \qquad (6)$$

6 describes the singlet–singlet transfer process which takes place in the presence of an acceptor with lower excitation energy. Under photostationary conditions, the ratio of donor fluorescence in the absence and presence of quencher molecules is given by

$$\frac{F^0}{F} = 1 + \left\{\frac{k_Q{}^1\tau^0}{1 + k_5{}^1\tau^0[D]}\right\}[A] \qquad (7)$$

In dilute solutions, plots of F^0/F *vs.* [A] are linear with slopes independent of [D], equal to

$$k_Q{}^1\tau^0 = K_Q \qquad (8)$$

where k_Q is the rate constant for singlet quenching by acceptor A (eq 6), $^1\tau^0$ is the singlet lifetime of the donor, and [D] and [A] are the donor and acceptor concentrations, respectively. K_Q is referred to as the Stern–Volmer constant. The quenching rate k_Q is usually equated with the rate of diffusion, k_{diff} which is calculated from the solvent viscosity η either from the Debye[10] equation (9) or more recently from the modified equation (10) of Osborne and Porter.[11]

$$k_{diff}' = \frac{8RT}{3000\eta} \qquad (9)$$

$$k_{diff} = \frac{8RT}{2000\eta} \qquad (10)$$

Equation 10 has proved to be more consistent with experimental results and is more reasonable theoretically than the traditional Debye equation.[12] Singlet lifetimes of small ketones measured by quenching fluorescence with biacetyl in hydrocarbon solutions[7,8] are in good agreement with similar measurements by the single photon counting and phase shifting techniques. Dubois, *et al.*, assumed that each donor–acceptor encounter led to singlet energy transfer, but Wagner and Kochevar[13] have shown that the rate of exothermic triplet energy transfer from aromatic ketones to conjugated dienes is not totally diffusion controlled in solvents of low viscosity. The probability that transfer takes place during the lifetime of a solution encounter may fall significantly below unity. In this study the question of singlet–singlet transfer efficiency has been reexamined by comparison of fluorescence quenching in different solvents.

Intermolecular energy transfer may also be affected by intramolecular exchange processes, since intuitively the migration of energy along the polymer chain increases the effective volume of the excited region or quenching sphere. For example, David, Demarteau, and Gueskens[14] have exploited the phosphorescence method of triplet transfer in low-temperature glasses following Terenin and Ermolaev[15] to show that the quenching spheres are significantly larger for poly(vinyl aromatic ketones) where intramolecular triplet migration may take place. One might therefore predict that a similar singlet migration may be reflected in increased efficiency of intermolecular transfer on each solution encounter in the case of polyketone donors. Such intramolecular processes when present in polymers can be of considerable importance. For example, intramolecular transfer to energy sinks may provide effective stabilization of the polymer molecules, whereas similar transfer to weak links could facilitate photodegradation. Either case may afford desirable properties in polymeric systems and may also relate to some important biological process.

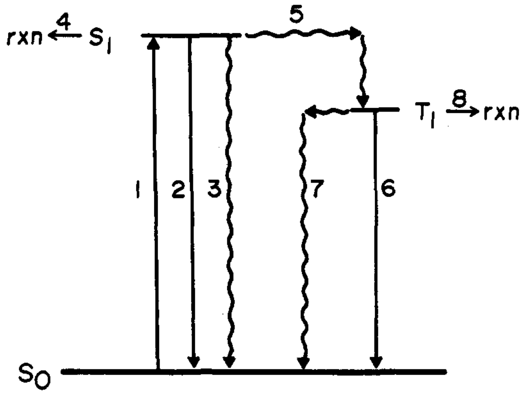

Figure 1. Modified Jablonski diagram: (1) absorption, (2) fluorescence, (3) internal conversion, (4, 8) chemical reaction, (5, 7) intersystem crossing, (6) phosphorescence. Wavy lines represent radiationless processes.

Experimental Section

Materials. Ketones. Fisher Spectranalysed acetone was used as received. Different authors[1,16] have attempted to further purify spectroquality acetone but have resorted to the starting material since no change was observed in the absorption or emission spectral properties in solution. 3-Pentanone, 4-heptanone, 5-nonanone, and 6-undecanone from Eastman Organic were purified on a Varian Aerograph Autoprep 700 preparative gas chromatograph. 8-Pentadecanone and 12-tricosanone were prepared by the method of David and Schultz.[17] 2-Butanone, 2-hexanone, and 2-heptanone were all reagent grade from Anachemia, Baker, and Kodak, respectively. 2-Pentanone, 2-octanone, 2-nonanone, and 2-undecanone were all purified on the Varian Autoprep 700. Pinacolane, 3-methyl-2-butanone, and 2,4-dimethyl-3-pentanone were all Baker reagent grade.

Poly(methyl vinyl ketone) (poly-MVK) and poly(methyl isopropenyl ketone) (poly-MIPK) were prepared by free-radical polymerization of the distilled monomers and reprecipitated from benzene with methanol. The polymers were dried first in a vacuum oven at 50° and then on a high-vacuum line for several days. Naphthalene was a zone-refined "Ultrex" product obtained from Baker (purity >99.99%). Biacetyl from Fisher was freshly distilled under reduced pressure at room temperature and the middle fraction collected and stored in the dark.

Solvents. Ethyl acetate, cyclohexane, *n*-hexane, benzene, and carbon tetrachloride were all spectrograde quality from Fisher or Matheson Coleman and Bell. Decalin was purified by distillation, passed through a silica gel column, and filtered through a Millipore filter. Neat solvents showed no absorption or emission in the regions of excitation (310 nm). Solutions of ketones which are liquid at room temperature were made up volumetrically. Solid samples were measured gravimetrically and polymer solutions were tumbled for good dissolution. Ketone concentrations were adjusted to give optical densities identical with those for the acetone samples having the highest fluorescence yield upon excitation at 310 nm. All solutions were made up without degassing to remove dissolved oxygen,

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(10) P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).

(11) A. D. Osborne and A. Porter, *Proc. Roy. Soc., Ser. A*, (London), **284**, 9 (1965).

(12) H. J. V. Tyrell, "Diffusion and Heat Flow in Liquids," Butterworths, London, 1961, p 127.

(13) P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, **90**, 2232 (1968).

(14) C. David, W. Demarteau, and G. Genskens, *Eur. Polym. J.*, **6**, 537, 1397, 1405 (1970).

(15) A. N. Terenin and V. L. Ermolaev, *Sov. Phys.-Dokl.*, **6**, 600 (1962).

(16) J. Pavlik, M.Sc. Thesis, University of Toronto, 1970.

(17) R. Davis and H. P. Schultz, *J. Org. Chem.*, **27**, 854 (1962).

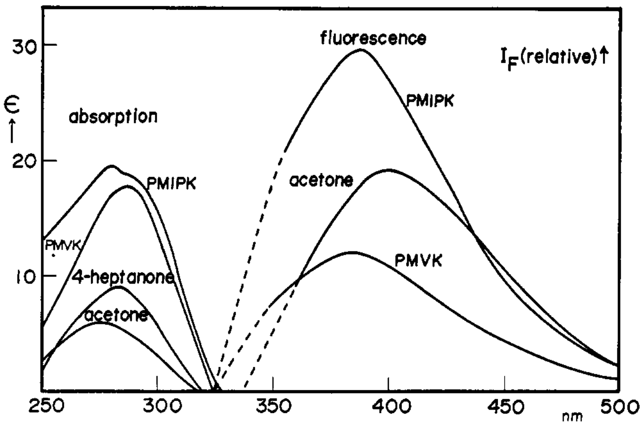

Figure 2. Absorption and fluorescence spectra of polyketones.

Table I

Relative Fluorescence Quantum Yields and Singlet Lifetimes of Me-Substituted Acetone Derivatives in Cyclohexane (λ_{ex} 310 nm)

Ketone	$\phi_F \times 10^3$ [a]	$\tau_R \times 10^6$ sec[b]	$^1\tau^0 \times 10^9$ sec[c]
$(CH_3)_2C{=}O$	1.00 (1.00)[d]	2.1 (2.5)	2.1 (2.5) **2.1**[e]
$CH_3CH_2COCH_3$	1.25 (1.27)	1.5 (2.3)	1.9 (2.9)
$(CH_3)_2CHCOCH_3$	1.36	2.0	2.7
$CH_3CH_2COCH_2CH_3$	1.49 (1.68)	1.9 (1.9)	2.8 (3.2)
$(CH_3)_3CCOCH_3$	2.49	1.8	4.5 **4.2**[e]
$(CH_3)_2CHCOCH(CH_3)_2$	2.62 (2.50)	1.7 (1.7)	4.5 (4.2)
$(CH_3)_3CCOC(CH_3)_3$	(4.41)	(2.0)	(8.8)
$(CD_3)_2C{=}O$	(1.36)	(2.5)	(3.4)

[a] Values normalized to value for acetone. [b] Radiative singlet lifetimes calculated from integrated absorption spectrum. [c] $^1\tau^0 = \phi_F\tau_R$ (eq 7) values in agreement with photon counting measurements. [d] Values in parentheses in *n*-hexane from M. O'Sullivan and A. C. Testa, *J. Amer. Chem. Soc.*, **92**, 5842 (1970). [e] Based on singlet–singlet energy transfer in solution (ref 7).

since it has been shown[1,2] that the fluorescence of aliphatic ketones, unlike phosphorescence, is not affected by the presence of oxygen.

Procedure. Absorption spectra were recorded at room temperature on a Bausch and Lomb Spectronic 505 double-beam recording uv–visible spectrophotometer. Neat solvents were used in the reference beam in stoppered quartz cells. Emission spectra were measured on a Hitachi Perkin-Elmer MPF-2A fluorescence spectrophotometer, and the output from the photomultiplier at high instrument sensitivity was recorded on a QPD-33 pen recorder. The spectra were ratio recorded to compensate for spectral distribution and fluctuations in the excitation source. Relative fluorescence yields were obtained from direct comparison of the spectral areas by use of a planimeter, by counting squares, or, as in the case of naphthalene, from sharp peak heights, all giving consistent results. Corrections were made in the quenching experiments for absorption of the exciting light by acceptor molecules. Curvature of uncorrected Stern–Volmer plots disappeared with the introduction of these corrections.

Relative quantum yields of fluorescence are normalized to a value $\phi_F = 1.00 \times 10^{-3}$ for acetone.[2] Radiative singlet lifetimes are calculated from absorption spectra using the expression[4,18]

$$\tau_R = \frac{3.5 \times 10^8}{\tilde{\nu}_{max}{}^2 \epsilon_{max} \Delta\tilde{\nu}_{1/2}} \qquad (11)$$

where $\tilde{\nu}_{max}$ is the frequency (cm^{-1}) of maximum absorption, ϵ_{max} is the maximum extinction coefficient, and $\Delta\tilde{\nu}_{1/2}$ is the half-width (cm^{-1}) of the absorption band.

Results and Discussion

The spectral distribution of the fluorescence curves was identical for all the simple ketones studied, with a maximum at 400 ± 5 nm. The similarity of the spectra suggests[2] that the emission is localized on the carbonyl chromophore of all the simple ketones. The band is broad and structureless, as is to be expected for a forbidden ($\pi^* \leftarrow n$) transition in solution. The large difference (12,000 cm^{-1}) between the Franck–Condon maxima for absorption and emission does suggest[1] a significant difference between the ground-state and excited-state geometries. No definite trends were observed in the various solvents, although it has been suggested[2] that the fluorescence quantum yields increase slightly in polar and hydrogen-bonding solvents for ketones.

In the case of the polymeric ketones poly-MVK and poly-MIPK, the maximum in fluorescence is blue shifted to 380–390 nm and the absorption is a factor of about 2 higher (Figure 2). The fluorescence band is easily extrapolated to eliminate scatter in the region of the Raman band to a minimum cutoff near 335 nm. The absorption band has a maximum wavelength cutoff near 325 mμ. The mirror image similarity is minimal and no overlap is observed, but the O–O transition is estimated at 325–335 nm, which shows that the first excited ketone singlet has an energy of about 86 ± 4 kcal mol^{-1} above the ground state. The difference observed in the distribution of the absorption spectra ($\lambda_{\epsilon_{max}}$ ~280 nm) and the excitation spectra ($\lambda_{F_{max}}$ ~310 nm) suggests that the quantum efficiency of fluorescence is dependent on wavelength.

Radiationless Processes. (i) α-Substituted Ketones. The numerical results are summarized in Table I, which also includes those of O'Sullivan and Testa.[2] The observation of the latter authors that fluorescence yields increase when the α hydrogens of acetone are replaced by various alkyl groups was confirmed. The actual singlet lifetime is defined as

$$^1\tau^0 = \frac{1}{k_F + k_d + k_{isc}} \qquad (12)$$

where k_d refers to possible internal conversion $S_1 \rightsquigarrow S_0$ and k_{isc} to $S_1 \rightsquigarrow T_1$ (Figure 1). The net monotonic increase of $^1\tau^0$ with substitution indicates that one of these rate constants must be decreasing. The radiative lifetimes $\tau_R = 1/k_F$ are not significantly different and may even show some increase in k_F on alkyl substitution, which we would attribute to increased allowedness of the radiative transition caused by distortion.[19] Yang, *et al.*,[20] suggest that α-C–H stretching may not be the only factor involved here, since similar results are observed by confining the carbonyl group in a cage-like system. The α-C–C out-of-plane bending is restrained in either case and in fact the total Franck-Condon factor may be a product of several terms. Product yields from the excited singlet likewise increase[5] with α substitution as reactions leading to photochemical adducts compete more effectively with radiationless processes.

(ii) Symmetric and Methyl Ketones. The radiative singlet lifetimes of ketones of the general structure $R_2C{=}O$ and $RC({=}O)CH_3$ decrease with the length of the R groups, suggesting, as before, an increase in radiative transition probability through distortion. The decrease relative to acetone

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(18) J. C. Dalton and N. J. Turro, *J. Amer. Chem. Soc.*, **93**, 3569 (1971).

(19) W. D. Chandler and L. Goodman, *J. Mol. Spectrosc.*, **37**, 33 (1971); **36**, 141 (1970).

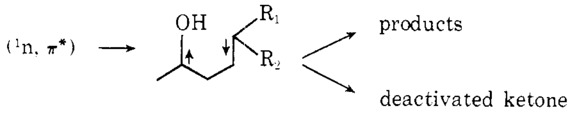
(20) N. C. Yang, E. D. Feit, M. H. Hui, N. J. Turro, and J. C. Dalton, *J. Amer. Chem. Soc.*, **92**, 6974 (1970).

TABLE II
RELATIVE FLUORESCENCE QUANTUM YIELDS AND SINGLET LIFETIMES OF KETONES IN CYCLOHEXANE (λ_{ex} 310 mμ)

Ketone	$\phi_F \times 10^3$	$\tau_R \times 10^6$ sec	${}^1\tau^0 \times 10^9$ sec
	$R_2C(=O)$		
Acetone	1.00	2.1	2.1
3-Pentanone	1.49	1.9	2.8
4-Heptanone	1.13	1.6	1.8
5-Nonanone	0.40	1.6	0.6
6-Undecanone	0.35	1.5	0.5
8-Pentadecanone	0.35	1.5	0.5
12-Tricosanone	0.35	1.5	0.5
	MeC(=O)R		
2-Butanone	1.25	1.5	1.9
2-Pentanone	1.28	1.4	1.8 (1.8)[a]
2-Hexanone	0.58	1.9	1.0 (0.81)[a]
2-Heptanone	0.54	1.7	0.9
2-Octanone	0.44	1.8	0.8
2-Nonanone	0.44	1.6	0.7
2-Undecanone	0.41	1.8	0.7
Acetone (in ETOAc)	1.10	2.1	2.3
Poly-MVK (in ETOAc)	0.75	1.1	0.8
Poly-MIPK (in ETOAc)	1.75	0.9	1.6

[a] See ref 18.

is at most 30% up to 12-tricosanone. However, the emission yields increase for α substitution initially and thereafter decrease, with no observed change above 12 or so carbon atoms. The chain length increase reduces the actual lifetime ${}^1\tau^0$ with a marked discontinuity on going from 4-heptanone to 5-nonanone and also from 2-pentanone to 2-hexanone (Table II and Figure 3). In each case γ hydrogens become secondary and would tend to indicate that these γ-hydrogen atoms might be important. The radiative lifetimes are not very different, whereas the emission decreases by a factor of 2–3 when the γ hydrogens go from primary to secondary. Yang and others[21] showed that the photolysis of alkanones with γ hydrogens proceeds with moderate quantum yields and the principal products are those derived from the type II process and cyclobutanols. They established the validity of a suggestion originally due to Wagner[22] that the triplet state will give a biradical intermediate first which may then revert to the starting ketone or proceed to give products. Their study of 2-pentanone, 2-hexanone, 5-methyl-2-hexanone, and optically active 5-methyl-2-heptanone showed that as the γ hydrogen goes from primary to tertiary, the value of k_{isc} remains essentially the same, whereas ϕ_{isc} decreases. The decrease in ϕ_{isc} was attributed to the increase in both the rate of chemical reactivity from the singlet k_s and the rate of radiationless decay, k_d, from the singlet. Both k_s and k_d vary together, which strongly implies that a chemical process may be involved in k_d for these alkanones



The observations of marked decrease in fluorescence yield as the γ hydrogens go from primary to secondary is therefore consistent with more efficient singlet radiationless deactivation *via* the biradical as observed by chemical methods.[23]

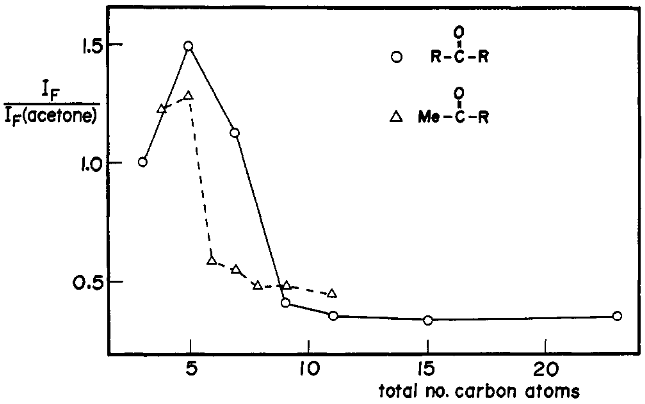
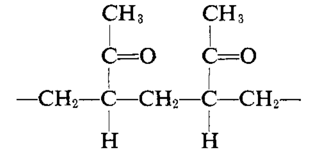


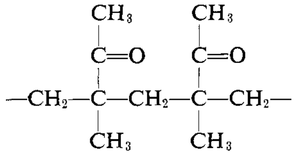
Figure 3. Relative fluorescence intensity of ketones.

(iii) Polymeric Ketones. Data on emission quantum yields of poly-MVK and poly-MIPK are also shown in Table II. Three factors seem to be important. (1) There are fewer α hydrogens in polymeric ketones (relative to acetone) and this should reduce the radiationless decay of the singlet and increase the fluorescence yields. (2) The γ hydrogens of poly-MVK are tertiary, and, by analogy, singlet emission yields should be low, since radiationless deactivation can take place *via* the biradical. These two effects would favor a higher emission yield for poly-MIPK as compared to poly-MVK as observed. (3) The length of the polymeric chain contributes in two ways: (a) there is an increased density of vibrational states which would increase the Franck–Condon factors and facilitate radiationless processes and (b) there may be steric hindrance to formation of the biradical if this demands some specific geometry such as a six-membered ring. Heskins[24] and Golemba[25] have both assumed that the rate of formation of such a six-membered ring conformation would depend on the flexibility of the molecule. The two effects here are opposed in their influence and the net effect is not obvious.



$$-CH_2-\underset{\displaystyle H}{\overset{\displaystyle CH_3C{=}O}{C}}-CH_2-\underset{\displaystyle H}{\overset{\displaystyle CH_3C{=}O}{C}}-CH_2-$$

poly-MVK



$$-CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3C{=}O}{C}}-CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3C{=}O}{C}}-CH_2-$$

poly-MIPK

Energy-Transfer Studies. Naphthalene to Ketones. The low value of the extinction coefficient for the forbidden $\pi^* \leftarrow n$ transition in ketones implies that long-range, single-step transfer by dipole–dipole interactions may be neglected and collisional transfer by the exchange mechanism assumed for singlet quenching involving ketones. Naphthalene has been reported[26] to be a donor which can exhibit quenching *via* exciplex formation, but the only reported example for ketones[27] is the quenching by olefins and dienes which takes place at quencher concentrations very much higher than the range of concentrations in the present case. In any case, the precise details of the mechanism may not be important

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(21) (a) N. C. Yang and S. P. Elliott, *ibid.*, **91**, 7550 (1969); (b) N. C. Yang, S. P. Elliott, and B. Kim, *ibid.*, **91**, 7551 (1969).

(22) P. J. Wagner, *ibid.*, **89**, 5898 (1967).

(23) Since the completion of this work, Dalton and Turro have published similar results for the complete series of γ-methyl-substituted derivatives of 2-pentanone (see ref 18).

(24) M. Heskins, Ph.D. Thesis, University of Toronto, 1967.

(25) F. Golemba, Ph.D. Thesis, University of Toronto, 1970.

(26) S. Murov and G. S. Hammond, *J. Phys. Chem.*, **72**, 3797 (1968).

(27) (a) F. S. Wettack, G. D. Renkes, M. A. Rockley, N. J. Turro, and J. C. Dalton, *J. Amer. Chem. Soc.*, **92**, 1794 (1970); (b) N. C. Yang, M. H. Hui, and S. A. Bellard, *ibid.*, **93**, 4056 (1971).

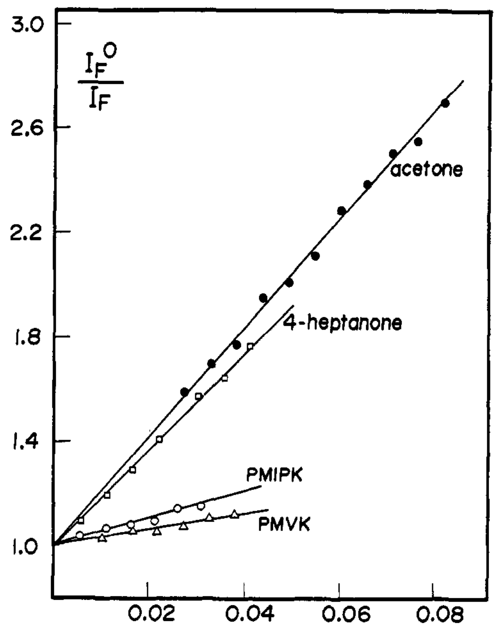

Figure 4. Fluorescence quenching of naphthalene by ketones in EtOAc.

TABLE III

FLUORESCENCE QUENCHING IN ETHYL ACETATE

Donor	Acceptor	$K_Q = k_Q{}^1\tau^0$	$k_Q \times 10^{-9}$	$k_{diff} \times 10^9$	p
Naphthalene	Acetone	21	2.5	23	0.11
Naphthalene	4-Heptanone	18	2.2	23	0.10
Naphthalene	Poly-MVK	3	0.36	11.5	0.032
Naphthalene	Poly-MIPK	5	0.60	11.5	0.05
Acetone	Biacetyl	11	4.8	23	0.21
3-Pentanone	Biacetyl	18	5.6	23	0.24
4-Heptanone	Biacetyl	10	5.3	23	0.23
Poly-MVK	Biacetyl	9	12	11.5	1.0
Poly-MIPK	Biacetyl	16	10	11.5	0.87

here. Dubois, *et al.*,[8] have shown that naphthalene fluorescence quenching by biacetyl is viscosity dependent, and Heskins and Guillet[28] have estimated the efficiency factors for quenching of naphthalene fluorescence by symmetric ketones and also by ethylene–carbon monoxide copolymers assuming that transfer was limited only by the diffusion constant. The parameter p is defined as the ratio of the quenching constant k_Q obtained from the Stern–Volmer equation ($K_Q = k_Q{}^1\tau^0$) to the diffusion constant k_{diff} obtained from eq 10. It is a measure of the efficiency of transfer on encounter of donor–acceptor pairs.

Comparison of the efficiency factors for the quenching of naphthalene fluorescence by small ketones and by the poly(vinyl ketones) (Figure 4 and Table III) shows that transfer to the ketone is less efficient in the polymeric systems. We have assumed the extreme case of negligible polymer movement (*i.e.*, of the center of mass of the polymer) in estimating the mutual diffusion coefficient for the naphthalene–polymer system. The other extreme would be to distinguish segment diffusion of the carbonyl groups within a small local environment due to conformational flexibility and thus estimate a diffusion coefficient for the polymer system similar to that for the small ketones. The choice between the two extremes is difficult, but in either case the efficiency for transfer to the polyketones is significantly less than for the small ketones. Heskins and Guillet[28] found that if one assumes that the polymers do not diffuse at all, the p values obtained for the quenching of naphthalene fluorescence by ethylene–carbon monoxide copolymers and by 6-undecanone were identical. They concluded that the collisional efficiency for the energy exchange process in their polymers containing isolated ketone groups was rather similar to that for small molecules. Since the present results differ, we have sought for a distinction and suggest that the interaction of the adjacent carbonyl groups in poly-MVK and poly-MIPK may be an important factor. Oster and Nishijima[29] have noted that when fluorescent species are attached to the polymer chain, the situation is more complicated than for small molecules in isolation, since now the quencher molecules must penetrate the polymer coil to encounter the excited molecule. Moldovan and Weill[30] have recently sought to distinguish between concentrations "inside" and "outside" the coil to account for the lower quenching of fluorescence when the chromophore is bound to a polymer. Structural differences in the ethylene–carbon monoxide copolymers and the poly(vinyl ketones) might make the steric inhibition more significant in the latter case.

Ketones to Biacetyl. The results in this case are quite different. The ketones are directly excited by the light source, and some excited molecules transfer energy to biacetyl on collision. Again we assume negligible polymer diffusion, and this time the quenching efficiency is about four times *greater* for the polymeric ketones than for the small ketones (Table III). Even if we allowed for segment diffusion and used the same k_{diff} for the case of the polymers, the quenching efficiency is still significantly higher for the polymers. This observation is most interesting. We will show later that the p values for the small ketones are very reasonable.

The fact that singlet energy transfer *from* the polymers is efficient, whereas the reverse process is not, suggests that the excitation energy on the polymer chain is somehow delocalized along the chain to facilitate transfer from the macromolecule by effectively increasing the probability of an encounter with a quencher molecule. That is, the delocalization or hopping of the excitation energy from one ketone group to another on the polymer chain permits quenching of the excitation at ketone groups other than the particular ketone group initially excited, and thereby increases the quenching cross section for energy transfer. The mechanism of intramolecular migration would involve some type of interaction of the ketone groups. That such interaction takes place is consistent with the changes observed in the absorption and emission spectra of the polymers compared to the small ketones (Figure 2). The absorption spectra show that the transition $S_1 \leftarrow S_0$ is much more probable for the polyketones than for small ketones. Symmetric ketones R—C(=O)—R for R = propyl or larger show a slightly more intense absorption than acetone or 3-pentanone, and the maximum is also red shifted. Both effects are pronounced in the polyketones. However, the polyketones show a shift to lower wavelengths in the fluorescence maxima, whereas all the other ketones have similar maxima at 400 nm. The evidence is ambiguous, since both ketone interaction and geometric distortion may account for the observed differences in the polymer spectra. The interaction of nonbonding orbitals in carbonyls has been examined recently by Swenson and Hoffmann.[31] Molecular orbital calculations on di-

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TABLE IV
FLUORESCENCE QUENCHING IN DIFFERENT SOLVENTS[a]

		n-Hexane			Ethyl acetate			Benzene			Cyclohexane			Decalin		
Donor	Acceptor	$k_Q{}^1\tau^0$	$k_Q \times 10^{-9}$	p	$k_Q{}^1\tau^0$	$k_Q \times 10^{-9}$	p	$k_Q{}^1\tau^0$	$k_Q \times 10^{-9}$	p	$k_Q{}^1\tau^0$	$k_Q \times 10^{-9}$	p	$k_Q{}^1\tau^0$	$k_Q \times 10^{-9}$	p
Acetone	Biacetyl	24	11.4	0.35	11	4.8	0.21	19	10.7	0.66	24	12.2	1.1			
3-Pentanone	Biacetyl	33	11.8	0.36	18	5.6	0.24	22	9.3	0.59	27	10.3	0.94			
4-Heptanone	Biacetyl	20	11.1	0.32	10	5.3	0.23	16.5	10.9	0.66	22	13.1	1.2			
Naphthalene	Acetone	36	4.3	0.13	21	~2.4	~0.10	32	1.5	0.09	66	3.1	0.29	34	~1.4	~0.34
Naphthalene	Biacetyl	163	19.7	0.60	148	~17.8	~0.74	250	11.9	0.73	213	10.1	0.92			
$\eta_{25°}$, cP			0.2923			0.426			0.603			0.898			2.42	
k_{diff}			3.3×10^{10}			2.3×10^{10}			1.64×10^{10}			1.1×10^{10}			0.41×10^{10}	

[a] Values for k_Q were obtained from the numerical values for the Stern–Volmer slopes ($k_Q{}^1\tau^0$). $^1\tau^0$ values for ketones in different solvents were obtained as in Table I, making corrections for the refractive index of each solvent. $^1\tau^0$ values for naphthalene in aerated solutions have been measured for hexane (8.3 nsec), benzene (21 nsec), and cyclohexane (21 nsec). We have assumed $^1\tau^0$ values for EtOAc (as for hexane and for decalin ($\leq$25 nsec). See T. V. Ivanova, P. I. Kudriashov, and V. I. Sveshnikov, *Sov. Phys.-Dokl.*, **6**, 407 (1961); I. B. Berlman and A. Weinreb, *Mol. Phys.*, **5**, 313 (1962).

and tricarbonyls show that the interaction of the nonbonding "lone-pair" orbitals by direct through-space and indirect through-bond mechanisms is significant in these molecules. However, to what extent these interactions are operative in the poly(vinyl ketones) which contain many equivalent carbonyl groups remains an open question.

Singlet transfer along polymer chains has been inferred from studies on excimer fluorescence of polystyrene,[32] poly(1-vinylnaphthalene),[32,33] poly(*N*-vinylcarbazole),[34] and poly(vinyltoluene).[35] Singlet transfer in molecules containing both an energy donor and an energy acceptor has also been studied[36] in oligomers of poly(L-proline) with the donor, a naphthal group, and the acceptor, a dansyl group, separated by distances up to 46 Å. The results are consistent with Forster's dipole–dipole resonance mechanism. Other similar studies of intramolecular singlet energy transfer, as monitored by fluorescence spectroscopy, have been well documented.[37] These studies show that transfer is dependent on the distance between the chromophores as well as the orientation and relative energies of the donor–acceptor pair. The oscillator strength for the $\pi^* \leftarrow$ n ketone transition is small, and we would suspect that any intramolecular singlet transfer in the polyketones would take place by the exchange mechanism when the carbonyl groups are in close proximity.

The Factors Involving S–S Transfer Efficiency. Results summarized in Table IV are consistent with the overlap criterion of the Dexter exchange mechanism[38] which implies that the rate of transfer varies with the integrated overlap of the normalized donor emission and acceptor absorption spectra. Thus S–S transfer efficiency decreases in the series naphthalene → biacetyl > acetone → biacetyl > naphthalene → acetone, which is the order of decreasing spectral overlap. Variations in transfer efficiency have already been observed to depend on the nature of the chromophoric groups. Herkstroeter and Hammond[39] observed a *p* factor 0.50 for quenching of a number of donors by piperylene, and Schuster and others[40] observed that cyclohexadiene was more efficient by a factor of 1–20 than piperylene in quenching α-santonin and related compounds in benzene.

The results in Table IV also show that the efficiency of singlet energy transfer increases with the viscosity of the solvent. Wagner and Kochevar[13] made similar observations for the quenching of the triplet-state photoelimination of valerophenone by a diene and obtained values ranging from 0.3 to 1. In the less viscous solvents, the efficiency of energy transfer is determined by the rate k_{et} at which energy is transferred once donor and acceptor have diffused together and the rate k_{diff} at which the two species diffuse apart. It is reasonable to assume that k_{diff} is a solvent parameter and is common for tranfer *to* or *from* the ketone in the various solvents. However, k_{et} may very well vary with the donor–acceptor pair so that we notice consistently larger values for the efficiency of transfer from ketones to biacetyl compared to that from naphthalene to ketone. If we assume that

$$p = \frac{k_{\mathrm{et}}}{k_{\mathrm{et}} + \dfrac{1}{^1\tau^0} + k_{\mathrm{diff}}} \qquad (13)$$

for short singlet lifetimes, there is a greater probability that normal deactivation of the excited state during an encounter may take place before energy transfer. This factor may be important for singlet ketones ($^1\tau^0 \sim 10^{-9}$ sec) but is usually ignored for triplet transfer ($^3\tau^0 \sim 10^{-6}$ sec).

The practical implications of the conclusions that $k_Q < k_{\mathrm{diff}}$ in nonviscous solvents are at best disappointing. At present, quenching of the Stern–Volmer type is the usual way of ascertaining the reactivity of excited ketones[5] and ketone polymers,[6] since the short lifetimes generally restrict direct measurements of decay kinetics. But such studies can provide accurate knowledge of the lifetimes and reactivities of excited states only if reliable values for quenching rate constants are known. Much care is therefore demanded in the choice of a particular system for quenching studies and similarly of the method for determining quenching constants.

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