$$CH_3CH_2CH_2CH_2CH_2CH-\overset{\displaystyle \overset{O}{\|}}{CHCOC(CH_3)_3}$$
$$\diagdown CH_2 \diagup$$

in the terminal methyl group, the absorption of that substituent at δ 0.88 should be greatly altered and the proton ratio should increase to 3.6:1. This was not the case. Rather, the methyl absorption was not perceptibly changed in the deuterated isomer and the proton ratio dropped to 2.7:1, in excellent agreement with the theoretical value of 2.8:1 demanded by structure **22**.

t-Butyl *trans*-2-(*n*-Pentyl)cyclopropanecarboxylate (16). Ethyl diazoacetate (11.4 g, 0.1 mole) was added slowly under nitrogen to a vigorously stirred slurry of 1-heptene (14.7 g, 0.15 mole) and powdered copper metal (1.0 g, 0.015 g-atom) heated to 90°. The addition required 1.5 hr. The mixture was cooled, filtered, and fractionated. In addition to 4.1 g of recovered 1-heptene, bp 30–35° (200 mm), there was obtained 9.0 g of a clear liquid, bp 105–109° (20 mm). Vpc analysis indicated that three products had been formed, one of which predominated to the extent of 60%.

This major product was secured by preparative vpc and shown to be **18**, ν_{max}^{neat} 1715 cm^{-1}.

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.55; H, 11.03.

This crude mixture of esters (1.84 g) was added dropwise to a solution of 4 g of sodium hydroxide dissolved in 25 ml of methanol. A vigorous exothermic reaction was observed together with a color change to yellow. After stirring for 3 hr at 40°, the reaction mixture was poured onto ice-sulfuric acid and the product was extracted with ether. The combined organic layers were dried and placed in a pressure bottle. After the addition of 11 ml (*ca.* 0.2 mole) of isobutylene and 1 ml of sulfuric acid, the bottle was tightly stoppered and shaken for 12 hr at room temperature. The reaction mixture was poured into an ice-cold sodium hydroxide solution and extracted with ether. The combined organic layers were dried and evaporated. Vpc analysis indicated the presence of three components in yields of 25, 35, and 20%, respectively. The first two components proved to be unsaturated esters which were not further characterized. The third component gave spectral characteristics in excellent agreement with those expected for **16** (see above).

Quenching of Biacetyl Fluorescence and Phosphorescence[1]

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Abstract: The quenching of biacetyl fluorescence and phosphorescence by alcohols, tri-*n*-butylstannane, aryl- and alkylamines, phenols, and aryl alkyl ethers has been studied in benzene and other solvents. Irreversible hydrogen abstraction appears to be the mechanism for quenching of biacetyl phosphorescence by alcohols and stannane, neither of which measurably quenches biacetyl fluorescence. Phenols quench both biacetyl fluorescence and phosphorescence but aryl alkyl ethers quench only biacetyl phosphorescence (at a rate 10^3 times slower than analogous phosphorescence quenching by phenols). Aryl- and alkylamines quench both biacetyl fluorescence and phosphorescence. The rates of phenol quenching are slower in solvents which are polar or hydrogen bonding, while the rates of quenching by amines are enhanced by increasing solvent polarity. Pyrene and acridine quench biacetyl phosphorescence (but not biacetyl fluorescence) by physical energy transfer. Mechanisms consistent with these results are discussed.

A ll of the previously reported photoreactions of biacetyl **1**, in solution are thought to have originated from the triplet state.[2-8] Theoretical evidence exists[9,10] and in some cases, experiments have shown[11-14] that

n,π^* singlet and triplet states of ketones have similar reactivities and are probably electronically similar. In the case of acetone, however, the n,π^* triplet is apparently $\sim 10^2$ times more reactive toward intermolecular hydrogen abstraction from tri-*n*-butylstannane than the n,π^* singlet.[15] Biacetyl, because of its relatively unique property of exhibiting phosphorescence as well as fluorescence in fluid solution at room temperature, allows the observation of both singlet and triplet quenching and direct determination and comparison of the reactivities of these two excited states. We have studied several types of quenchers and now report the quenching of biacetyl phosphorescence and fluorescence.

Experimental Section

The procedures for degassing and obtaining spectra on an Aminco–Bowman spectrophotofluorometer have been reported previously.[16] The rate constants for quenching were obtained by

(1) (a) Molecular Photochemistry. XVI. For paper XV, see N. J. Turro, E. Lee-Ruff, D. R. Morton, and J. M. Conia, *Tetrahedron Lett.*, 2991 (1969); we gratefully acknowledge the generous financial support of the Air Force Office of Scientific Research (Grants AFOSR-66-1000 and AFOSR-68-1381) and the National Science Foundation (Grant NSF-GP-4280). R. E. would like to thank the National Institutes of Health for a predoctoral fellowship (F1-GM-32,589). (b) For preliminary communications of this work, see N. J. Turro and R. Engel, *Mol. Photochem.*, 1, 143, 235 (1969).

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plotting peak–height ratios of biacetyl luminescence in the absence and presence of quencher against quencher concentration, as a Stern–Volmer plot.[18] The slope of the plot, $k_q\tau$, is the product of the bimolecular quenching constant and the lifetime of excited **1** in the absence of quencher. The minimum precision of the Stern–Volmer plots was $\pm 40\%$; more commonly precision of $\pm 20\%$ was achieved. For each type of quencher the initial biacetyl concentration was varied from 0.05 to 0.005. The Stern–Volmer plots were always linear ($\pm 40\%$) and the $k_q\tau$ values at each concentration agreed ($\pm 40\%$) with each other. τ was measured directly and independently[16] and the k_q values were thus obtained. Since τ for the triplet (τ_p 0.46 $\times$ 10^{-3} sec) of **1** is about 10^5 times larger than τ for the singlet (τ_f 1.0 $\times$ 10^{-8} sec) of **1**,[16] low concentrations of quencher are able to quench phosphorescence, yet leave fluorescence unaffected. When fluorescence quenching experiments were run, the solutions were aerated in order to quench all phosphorescence; the fluorescence of **1**, however, is essentially unaffected by aeration.[17]

Chemicals. Biacetyl, Matheson Coleman and Bell, was vacuum distilled before use; **isopropyl alcohol**, Fisher reagent, was used as received; **benzhydrol**, Matheson Coleman and Bell, was recrystallized twice from hot petroleum ether and dried under vacuum; **tri-n-butylstannane** was prepared by reduction of tri-n-butyltin chloride with LiAlH$_4$ using the procedure reported in the literature;[18] **phenol**, from Mallinkrodt, was sublimed before use; **resorcinol**, Fisher, was either used as received or sublimed first. No difference in quenching effect was noted. **Aniline**, Matheson Coleman and Bell, was distilled from zinc dust; **diphenylamine**, from Baker, was recrystallized from ethanol–water and dried under vacuum; **triphenylamine**, from Aldrich, was recrystallized from absolute ethanol; **anisole**, Amend Drug and Chem. Co., was vacuum distilled before use; **phenetole** (ethoxybenzene), N,N-dimethyl-aniline, and N,N-diethylaniline were from Matheson Coleman and Bell, and were all vacuum distilled before use; **deuteriophenol** and **dideuterioaniline** were prepared by exchange with D$_2$O. The extent of deuteration, as analyzed by nmr spectroscopy, was estimated at 90%; **tri-n-propylamine**, from Eastman, was distilled before use; **triethyl-, diethyl-, and isopropylamide** were from Matheson Coleman and Bell and were distilled before use; **ethylamine**, obtained in a 70% aqueous solution, from Matheson Coleman and Bell was purified by bulb-to-bulb vacuum distillation and subsequent drying over anhydrous Na$_2$SO$_4$; **diisopropylamine**, from Aldrich, was distilled before use; the N-substituted deuteriocompounds of diethyl-, diisopropyl-, and isopropylamine were prepared by exchange with D$_2$O. About 90% deuterium replacement was estimated by nmr spectroscopy. **1,4-Diazobicyclo[2.2.2]octane**, obtained from Matheson Coleman and Bell, was used as received; **benzene** was Baker Spectrograde, and the biacetyl phosphorescence lifetime in this solvent approached the highest values reported in the literature.[2] Distillation of the solvent before use afforded little change, so in most cases benzene was used without further purification; **acetonitrile** "chromatographic quality" was from Matheson Coleman and Bell; **pyrene**, from Baker, was recrystallized from ethanol; **acridine**, recrystallized and chromatographed, was provided by Dr. F. D. Lewis, **ferrocene**, recrystallized from n-hexane, was provided by Mr. R. Boecke.

The fluorescence lifetime in CH$_3$CN was slightly different from that in benzene, so appropriate corrections were made. **Absolute ethanol** and **pyridine** (Fisher Reagent) were very poor solvents for biacetyl phosphorescence, so only fluorescence quenching studies were run.

Filter Devices. Photolyses were run with a 450-W Hanovia mercury lamp in a Pyrex immersion well with water-cooled jacket. The filter system was a Cu(NH$_3$)$_4$SO$_4$ solution prepared by dissolving 40 g of CuSO$_4$ in 68 ml of concentrated NH$_4$OH and diluting to 1 l. with water. The filter solution was placed in an outer jacket, so that the average path length of filter was about 7 mm. Between the lamp and the water-cooled jacket was placed a Norex glass sleeve to absorb light of wavelength less than 3400 Å. This ensured that the light which reached the samples was confined to the 3500–4500-Å region. Absorption spectra were taken on a Cary 14 recording spectrophotometer.

Results

Hydrogen Donors. The quenching of biacetyl phosphorescence by known hydrogen donors (isopropyl

alcohol (IPA),[4,8] benzhydrol (BZH),[19] and tri-n-butyl-stannane (TBS),[15,20] Table I) results in efficient photoreduction of **1**. In the case of IPA, the pinacol **2** and ace-

**Table I.** Quenching of Biacetyl Luminescence by Hydrogen Donors[a]

Quencher	Solvent	$k_q{}^p$	$k_q{}^f$
(CH$_3$)$_2$CHOH	C$_6$H$_6$	3.3 $\times$ 10^3	<10^5 [b]
	CH$_3$CN	1.3 $\times$ 10^4	
(C$_6$H$_5$)$_2$CHOH	C$_6$H$_6$	7.0 $\times$ 10^4	<5 $\times$ 10^6 [c]
	CH$_3$CN	1.3 $\times$ 10^6	
(n-C$_4$H$_9$)$_3$SnH	C$_6$H$_6$	1.5 $\times$ 10^7	<3 $\times$ 10^6 [d]

[a] Data from Stern–Volmer luminescence quenching of 0.05 M **1** in benzene at 25°. Maximum error limits $\pm 40\%$. $k_q{}^p$ is the rate constant for quenching of biacetyl phosphorescence calculated from experimental $k_q{}^p\tau_p$ values and the assumption that $\tau_p = 0.46 \times 10^{-3}$ sec as found previously.[16] $k_q{}^f$ is the rate constant for quenching of biacetyl fluorescence calculated from experimental $k_q{}^f\tau_f$ values and the assumption that $\tau_f = 1.0 \times 10^{-8}$ sec as found previously.[16] Units of k_q's are M^{-1} sec^{-1}. [b] No quenching ($\pm 10\%$) of fluorescence in neat (~ 10 M) (CH$_3$)$_2$CHOH. [c] No quenching ($\pm 10\%$) of fluorescence in 2.0 M (C$_6$H$_5$)$_2$CHOH. [d] No quenching ($\pm 20\%$) of fluorescence in neat (~ 3 M) (n-C$_4$H$_9$)$_3$-SnH.

tone are formed in essentially quantitative yield.[8] In

$$CH_3COCOCH_3 + (CH_3)_2CHOH \xrightarrow{h\nu}$$

1

2
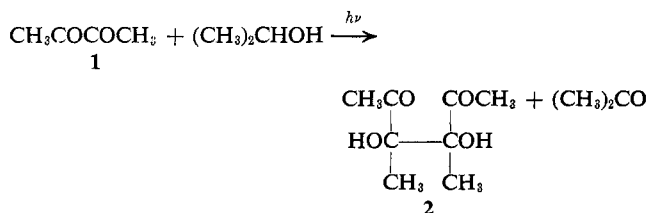
the case of BZH, both benzophenone and **2** were observed as products and for TBS a detailed product study was not made but **2** was a major product as determined by nmr and thin layer analysis.[21] Thus, it seems clear that each of the molecules listed in Table I quenches the biacetyl triplet, B$_3$, by hydrogen donation to yield the ketyl radical **3**. Since quenching of biacetyl fluorescence was not observed for the hydrogen donors in Table I, only a limit on the rate constant for

$$B_3 + RH \longrightarrow CH_3\overset{\overset{\displaystyle OH}{|}}{C}COCH_3$$

3
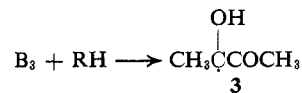
quenching of singlet biacetyl (B$_1$) is possible. The precision of our fluorescence intensity measurements is about $\pm 10\%$. Therefore, we can estimate that for neat IPA (~ 10 M) $k_q{}^f < 10^6$ M^{-1} sec^{-1}, for 2.0 M benzhydrol in benzene $k_q{}^f < 5 \times 10^6$ M^{-1} sec^{-1}, and for 1 M TBS in benzene $k_q{}^f < 10^7$ M^{-1} sec^{-1}, since $(\tau_f)^{-1}$ is known[16] to be equal to 1.0 $\times$ 10^8 sec^{-1} in purified benzene in the absence of quencher.

In order to determine the effect of solvent polarity on the rate constant for biacetyl phosphorescence, quenching by IPA and BZH was also studied in acetonitrile. The intensity and lifetime of biacetyl phosphorescence in acetonitrile were calibrated[22] by constructing a plot

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(21) T. J. Lee, Columbia University, unpublished results.
(22) See R. Engel, Ph.D. Dissertation, Columbia University, 1969, for further details.

of phosphorescence intensity (relative to fluorescence intensity) against phosphorescence lifetime. This calibration curve was then employed to determine the τ_p to be used in calculation of the k_q^p values given in Table I.

Phenol and Its Derivatives. Phenol and 1,3-dihydroxybenzene were found to quench biacetyl fluorescence with larger rate constants than they quench biacetyl phosphorescence. These quenchers did not decolorize benzene solutions of **1** when photolyzed at 4200 Å as did the hydrogen donors (Table I) studied, but rather the absorption spectrum of **1** remained virtually unchanged even after extended irradiation. Table II summarizes our quenching results for phenol and its derivatives.

Table II. Quenching of Biacetyl Luminescence by Phenol and Its Derivatives[a]

Quencher	k_q^p, M^{-1} sec^{-1}	k_q^f, M^{-1} sec^{-1}
C_6H_5OH	3.4×10^8	2.0×10^9
C_6H_5OD	1.0×10^8	1.4×10^9
Resorcinol[b]	2.5×10^9	6.5×10^9
$C_6H_5OCH_3$	1.3×10^5	$<10^6$ [c]
$C_6H_5OC_2H_5$	1.2×10^5	$<10^6$ [c]

[a] Same as footnote a in Table I. [b] 1,3-Dihydroxybenzene. [c] Fluorescence quenching not observed even in neat alkoxybenzene; values are upper limits assuming $\pm 10\%$ or more quenching was experimentally detectable.

The role that the phenolic hydrogen atom plays in the quenching by phenol was investigated by substituting deuterium and methyl and ethyl groups for the phenolic hydrogen in these compounds. For phenol-O-d, k_q^p and k_q^f were lower than the corresponding values for phenol by a factor of $\sim$2–3; but when methyl and ethyl groups were substituted for hydrogen in phenol *the rate constants were more than three orders of magnitude lower than for phenol.* In all these cases no net photoreaction was observed. Methoxybenzene and ethoxybenzene did not quench the fluorescence of biacetyl. Thus, only a maximum k_q^f can be calculated, as described above for TBS.

Aniline and Its Derivatives. Aniline and its derivatives were found to quench both biacetyl fluorescence and phosphorescence (Table III). The absorption spectrum of **1** was unchanged after extensive irradiation of biacetyl solutions containing the quenchers listed in Table III. An inverse isotope effect was found for phosphorescence quenching by $C_6H_5ND_2$ relative to $C_6H_5NH_2$, but no comparable isotope effect on fluorescence quenching was observed. Direct measurement[16] of τ_f (Table IV) in the presence of 0.01 M aniline,

Table III. Quenching of Biacetyl Luminescence by Aniline and Its Derivatives[a]

Quencher	k_q^p, M^{-1} sec^{-1}	k_q^f, M^{-1} sec^{-1}
$C_6H_5NH_2$[b]	5.0×10^8	1.1×10^{10}
$C_6H_5ND_2$	9.6×10^8	1.0×10^{10}
$(C_6H_5)_2NH$[b]	1.7×10^9	7.4×10^9
$(C_6H_5)_3N$[b]	3.1×10^7	4.9×10^9
$C_6H_5N(CH_3)_2$	2.7×10^8	1.2×10^{10}
$C_6H_5N(C_2H_5)_2$	8.4×10^8	1.1×10^{10}

[a] Same as footnote a in Table I. [b] For three runs employing 0.05 M, 0.1 M, and 0.005 M biacetyl the k_q values are identical within the experimental error of $\pm 40\%$.

Table IV. Direct Measurement of τ_f for Biacetyl in the Presence of Aniline, Diphenylamine, and Triphenylamine[a]

Quencher[b]	τ_f, nsec[c]	k_q^f [d]	k_q^f [e]
None	10.3		
$C_6H_5NH_2$	5.7	7.5×10^9	1.1×10^{10}
$(C_6H_5)_2NH$	6.1	6.5×10^9	7.4×10^9
$(C_6H_5)_3N$	6.9	4.5×10^9	4.9×10^9

[a] 0.05 M biacetyl in benzene at 25°. [b] 0.01 M. [c] Measured by single photon counting as described previously.[16] Error $\pm 10\%$. [d] Fluorescence quenching constant in M^{-1} sec^{-1} calculated from $(\tau_f)^{-1} = (\tau_f^0)^{-1} + k_q^f[Q]$ where τ_f = measured fluorescence lifetime of biacetyl in the presence of quencher and τ_f^0 = measured fluorescence lifetime of biacetyl in the absence of quencher. [e] Fluorescence quenching constant in M^{-1} sec^{-1} from Table III.

diphenylamine, and biphenylamine allowed direct calculation of k_q^f. The agreement between these values and those determined from $k_q^f \tau_f$ values and independent measurement of τ_f is excellent (Table V).

Table V. Quenching of Biacetyl Luminescence by Aliphatic Amines[a]

Quencher	k_q^p, M^{-1} sec^{-1}	k_q^f, M^{-1} sec^{-1}
$(CH_3)_2CHNH_2$	2.8×10^7	$<10^7$ [c]
$(CH_3)_2CHND_2$	2.4×10^7	$<10^7$ [c]
$(C_2H_5)_2NH$	2.2×10^7	1.7×10^9
$(C_2H_5)_2ND$	2.4×10^7	1.3×10^9
$[(CH_3)_2CH]_2NH$	2.5×10^7	1.3×10^9
$[(CH_3)_2CH]_2ND$	2.9×10^7	1.0×10^9
$[(CH_3)_2CD]_2ND$	2.9×10^7	$<10^8$
$(C_2H_5)_3N$[b]	5.0×10^7	2.4×10^9
$(n\text{-}C_3H_7)_3N$	8.0×10^7	3.1×10^9
DABCO	5.4×10^7	7.6×10^9

[a] Same as footnote a in Table I. [b] For three runs employing 0.05 M, 0.01 M, and 0.005 M biacetyl the k_q values are identical within the experimental error of $\pm 40\%$. [c] Accurate measurement not possible because of the high concentrations of primary amine required for measurable fluorescence quenching, biacetyl is noticeably consumed.

Aliphatic Amines. All of the aliphatic amines studied (except for primary amines) are quenchers of both the phosphorescence and fluorescence of **1** (Table V). The fluorescence quenching-rate constant decreases in going from tertiary to primary amines, but the phosphorescence quenching-rate constant is slightly lower for secondary amines than for primary or tertiary amines. Deuterium substitution for the amino hydrogens resulted in only small changes in the k_q's in all of the aliphatic amines studied. However, upon going from $[(CH_3)_2CH]_2ND$ to $[(CH_3)_2CD]_2ND$ as quencher, a sharp drop in k_q^f was found to occur. Decolorization of biacetyl solutions containing the quenchers in Table V occurred rapidly when irradiated at 4200 Å, in a similar way as for hydrogen donors, with the lone exception of 1,4-diazobicyclo[2.2.2]octane (DABCO). The pinacol **2** was isolated as a product of the photolysis of **1** with tripropylamine.[21]

Quenching by Electronic Energy Acceptors. The quenching of biacetyl phosphorescence by a number of compounds known to possess a triplet lower than 56 kcal/mol (the energy of biacetyl's lowest triplet level)[2] was studied. In the cases of anthracene (E_3 = 42 kcal/mol),[3] 1,2-benzanthracene (E_3 = 47 kcal/mol),[3] and *trans*-stilbene (E_3 = 50 kcal/mol)[3] the results were

complicated by photoreactions which caused destruction of 1 or the quencher or both, and nonlinear Stern–Volmer plots were observed. However, for 1,3-cyclohexadiene (E_3 = 53 kcal/mol),[23] pyrene (E_3 = 49 kcal/mol),[3] and acridine (E_3 = 45 kcal/mol)[24] linear Stern–Volmer plots were obtained with a precision of ±40% (Table VI). These compounds did not measurably quench biacetyl fluorescence. Although ferrocene (E_3 ∼ 50 kcal/mol)[25] quenched both biacetyl fluorescence and phosphorescence, the Stern–Volmer plots for phosphorescence quenching were not linear; the plots for fluorescence quenching by ferrocene were linear (k_q^f ∼ 4 × 10^{10} M^{-1} sec^{-1}).

Table VI. Quenching of Biacetyl Phosphorescence by Triplet Energy Acceptors[a]

Quencher	E_3	k_q^p
1,3-Cyclohexadiene	53[b]	2.9 × 10^8
Pyrene	49[c]	6.2 × 10^9
Acridine	45[d]	9 × 10^9

[a] Values of k_q^p in M^{-1} sec^{-1} are calculated from Stern–Volmer quenching constants, $k_q^p \tau_p$, and measurement of τ_p = 0.46 × 10^{-3} sec. Biacetyl concentration 0.05 M. [b] Reference 23. [c] Reference 3. [d] Reference 24.

Solvent Effects on Quenching of Biacetyl Luminescence. In order to study further the phenomena of phenol and amine quenching of the luminescence of **1**, the effect of variation in solvent polarity on quenching constants was examined. If the mechanism for quenching is predominantly electron transfer in character, then the formation of charged intermediates should be enhanced in polar media[26] and the observed quenching constant should be raised relative to that in benzene, unless the diffusion-control limit has already been achieved in benzene. It should be noted that the triplet excitation energy of the amines and phenols studied are all at least 15–30 kcal/mol greater than that of biacetyl, so that quenching by excitation transfer is expected to be an insignificant quenching mechanism.[27]

The fluorescence quenching of **1** by phenols and amines was studied in pyridine, ethanol, and acetonitrile and compared to those previously obtained (Tables II, III, V) in benzene. The Stern–Volmer plots of quenching by phenol in dioxane were identical (within an experimental error of ±20%) with those obtained when the polar solvents listed in Tables VII and VIII were used. In addition the phosphorescence quenching in acetonitrile was compared to that in benzene. Tables VII and VIII summarize these results. As is shown for both singlet and triplet quenching, the rate constants are generally enhanced in polar solvents in the case of amine quenching, but a definite suppression effect is observed when phenol or resorcinol is the quencher.

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Table VII. Quenching of Biacetyl Phosphorescence in Benzene and Acetonitrile[a]

Quencher	Benzene k_q^p	Acetonitrile k_q^p
C_6H_5OH	3.4 × 10^8	7.9 × 10^6
Resorcinol	2.5 × 10^9	1.2 × 10^8
$C_6H_5NH_2$	5.0 × 10^8	1.5 × 10^9
$(C_6H_5)_2NH$	1.7 × 10^9	2.8 × 10^9
$(C_6H_5)_3N$	3.1 × 10^7	1.6 × 10^9
$(C_2H_5)_3N$	5.0 × 10^7	2.7 × 10^8

[a] Values of k_q^p are calculated from Stern–Volmer quenching constants, $k_q^p \tau_p$, and measurement of τ_p. The calculated (P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, **90**, 2232 (1968)) diffusion, controlled rate constant for benzene is 1.6 × 10^{10} M^{-1} sec^{-1} and for acetonitrile is 2.9 × 10^{10} M^{-1} sec^{-1}. In acetonitrile τ_p = 0.2 × 10^{-3} sec and in benzene τ_p = 0.46 × 10^{-3} sec.

Table VIII. Quenching of Biacetyl Fluorescence in Polar Solvents[a]

	k_q^f (× 10^{10} M^{-1} sec^{-1})			
Quencher	Benzene	Pyridine	Ethanol	Aceto-nitrile
C_6H_5OH	0.20	0.01	0.01	0.01
Resorcinol	0.65	0.15	0.14	0.04
$C_6H_5NH_2$	1.00	1.00	1.20	0.93
$(C_6H_5)_2NH$	0.74	1.20	1.30	1.20
$(C_6H_5)_3N$	0.49	1.00	1.30	1.30
$C_6H_5N(CH_3)_2$	1.20	1.60	1.60	1.60
$(C_3H_7)_3N$	0.24	0.52	0.12	0.29

[a] Values of k_q^f are calculated from Stern–Volmer quenching constants, $k_q^f \tau_f$, and measurement of τ_f by single photon counting.[16] In benzene, τ_f = 10.0 nsec, in pyridine τ_f = 5.7 nsec, in ethanol, τ_f = 7.7 nsec, and in acetonitrile τ_f = 8.2 nsec. Biacetyl concentration = 0.05 M. The calculated (P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, **90**, 2232 (1968)) values for diffusion-controlled quenching are benzene, 1.6 × 10^{10} M^{-1} sec^{-1}; pyridine, 1.1 × 10^{10} M^{-1} sec^{-1}; ethanol, 0.9 × 10^{10} M^{-1} sec^{-1}; acetonitrile, 2.9 × 10^{10} M^{-1} sec^{-1}.

The case of triphenylamine is particularly noteworthy in terms of the large increase in k_q^p upon going from benzene to acetonitrile.

Since in Tables VII and VIII we are comparing numbers which include a different variable (τ_f and τ_p) than was present when one solvent was used, we feel an absolute error of greater than ±50% must be considered when discussing rate constants derived from different solvents.

Discussion

The configuration of both B_1 and B_3 is best described as being derived from an n,π* excitation.[10b] It is thus to be expected that the photochemistry of biacetyl may parallel to some extent the known behavior of the n,π* states of monoketones. We shall keep in mind a comparison of the excited state behavior of **1** and that of monoketones during the discussion of our results.
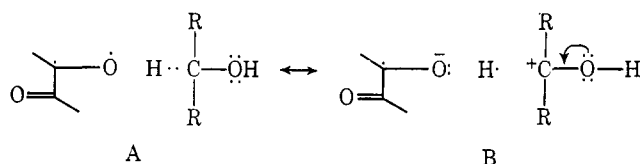
Quenching by IPA, BZH, and TBS. The photoreduction of **1** by IPA is well known[4,8] and the quenching constant for the phosphorescence of **1** has been reported.[2] The result presented in Table I is in good agreement with the reported value.[2] With BZH, k_q^p is more than 20 times larger than that for IPA. The experimental error in determining k_q^p is about 20%, so the increase in k_q of BZH over IPA is well beyond experimental error. TBS is known to quench acetone triplets with a rate constant close to that for diffusion-controlled reaction,[15] but for **1** the quenching constant appears to

be at least 100 times less than that expected for diffusion-controlled quenching.

The k_q^P values for IPA and BZH are orders of magnitude less than the intersystem-crossing rate constant as determined by the fluorescence lifetime of 1.[16] Therefore, if the singlet of biacetyl is comparable to biacetyl triplet in its reactivity toward hydrogen abstraction, it would not be possible to observe fluorescence quenching in neat isopropyl alcohol solution or in saturated benzhydrol solution. The *maximum* value estimated for k_q^f (Table I) is *larger* than k_q^P for IPA and BZH; as a result, no definite conclusions can be reached on relative singlet and triplet reactivities toward IPA and BZH in these cases.

The k_q^P obtained for TBS, on the other hand, is high enough so that in neat quencher solution the fluorescence of 1 should be about one-third as strong as that in C_6H_6 if the k_q^f is comparable to k_q^P. In 1 M TBS or in neat TBS, however, the biacetyl fluorescence intensity was unchanged within an error of $\pm 10\%$ from that in benzene, though after a short time some fluorescence was lost due to a dark reaction of biacetyl with the quencher. An attempt was made to measure the fluorescence lifetime of 1 in neat TBS, but the resulting decay curve was nonexponential with lifetimes ranging from 4 to 10 nsec. Thus it was possible to put only an upper limit on k_q^f, which is somewhat lower than k_q^P (Table I) for TBS. The reduced reactivity of a singlet n,π^* state toward hydrogen abstraction by TBS has also been observed for acetone.[15a,c] It is not expected that the reduced singlet reactivity is due to a heavy atom perturbation of singlet triplet intersystem crossing since such an effect does not occur to a significant extent with alkyl ketone n,π^* singlet states.[15b,28] The fact that the fluorescence intensity of 1 in neat TBS is essentially the same as it is in benzene allows us to conclude that the heavy-atom effect is negligible in our system also.

These data seem to require that quenching of biacetyl phosphorescence by IPA, BZH, and TBS is the result of hydrogen abstraction. The increase in k_q^P upon going from benzene to acetonitrile implies some polar character (as suggested by Cohen[29] for other n,π^* triplets) in the transition state for hydrogen abstraction. Presumably the bond energy of the H–X bond being broken, the degree of intermolecular hydrogen bonding (for the case of alcohols) and the stability of the radical pair produced by hydrogen abstraction also are influential in determining the transition state energy for quenching. Thus for IPA and BZH we may consider the following picture for the activated complex.

A   B

The analogy to these results with those reported for photoreduction of benzophenone[28] and acetone[15] argue strongly for a quenching mechanism which can validly be described as a hydrogen abstraction.

The failure of TBS to quench measurably biacetyl fluorescence demands that B_1 is at least five times less reactive toward hydrogen abstraction from TBS than is B_3. This result is analogous to the photoreduction of acetone[15a] by TBS for which it was found that TBS quenches acetone triplets with a rate constant of 8×10^8 M^{-1} sec^{-1} but that TBS does not measurably quench acetone singlets. This led Wagner to conclude that the n,π^* singlet of acetone is 10–100 times less reactive than its n,π^* triplet.

The rate constant for abstraction by B_3 from IPA and BZH is lower than that found for (a) photoreduction of benzophenone by IPA ($\sim10^6$ M^{-1} sec^{-1})[29] or BZH ($\sim10^7$ M^{-1} sec^{-1})[30] and (b) photoreduction of cyclohexanone by IPA ($\sim2 \times 10^6$ M^{-1} sec^{-1}).[31b] The reason for the lower reactivity of B_3 vis à vis other n,π^* ketone triplets probably results mainly from the lower triplet energy of B_3 relative to alkyl or aryl monoketone triplets, which cause the hydrogen-abstraction step to become relatively more endothermic. The possibility that the molecular orbital containing the n electron may be distributed over both carbonyl oxygen atoms[10b] of B_3 should also be considered, as this would also reduce reactivity.

Quenching by Phenol and Its Derivatives. The rate constants for quenching of the phosphorescence of 1 by phenol and resorcinol have been reported previously, and it was proposed that the quenching mechanism was hydrogen abstraction.[2] The k_q^P values for these two quenchers presented in Table II are within an order of magnitude of agreement with the previously published values.[2] The k_q^f values, which have not been reported previously, are three to ten times higher than the k_q^P values.

An irreversible hydrogen abstraction mechanism (analogous to that found for the compounds in Table I) for the quenching by phenols is ruled out since irradiation of solutions of 1 and phenol does not cause loss of 1.

The phenolic hydrogen must play an important part in the quenching mechanism based on the following observations: (a) an isotope effect on k_q^P ($k_H/k_D = 3.4$) and k_q^f ($k_H/k_D = 1.4$) for phenol; (b) a large suppression of k_q^P and k_q^f upon going from C_6H_5OH to $C_6H_5OCH_3$; and (c) suppression of k_q^P and k_q^f in polar *or* hydrogen bonding solvents. Becker[30,32] has proposed that acetophenone abstracts a hydrogen photochemically from phenol, but that the process is reversible giving the enol form of the ketone and phenol. This same process could be present in the quenching reaction of phenol and 1, giving the observed quenching with an apparent lack of photoreaction; evidence against such a mechanism was found, however, since irradiating 1 with phenol-O-d showed no deuterium incorporation in the methyl groups of 1.[22]

Other significant observations from Table II are (a) attachment of a second hydroxy group on phenol enhances k_q^P by a factor of ~10 and k_q^f by a factor of

(28) P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 13 (1968).

(29) S. G. Cohen, D. A. Laufer, and W. V. Sherman, *J. Amer. Chem. Soc.*, **86**, 3060 (1964); for direct (ESR) evidence that hydrogen abstraction results in formation of 3 see H. Zelder and R. Livingston, *J. Chem. Phys.*, **47**, 1465 (1967).

(30) H. D. Becker, *J. Org. Chem.*, **32**, 2140 (1967).

(31) (a) For example, IPA quenches B_3 ten times faster than does methanol.[2] Many other cases are known for which the quenching order tertiary > secondary > primary is followed for quenching of the n,π^* states of ketones;[28] (b) R. Simonaitis, G. W. Cowell, and J. N. Pitts, Jr., *Tetrahedron Lett.*, 3751 (1967).

(32) (a) T. Gramstad, *Acta Chem. Scand.*, **16**, 807 (1962); J. Robin and G. S. Panson, *J. Phys. Chem.*, **69**, 3089 (1965); A. Hall and J. L. Wood, *Spectrochim. Acta*, **24A**, 1109 (1968). (b) S. S. Mitra, *J. Chem. Phys.*, **36**, 3286 (1962); M. C. S. Lopes and H. W. Thompson, *Spectrochim. Acta*, **24A**, 1367 (1968).

~3; (b) k_q^P values for $C_6H_5OCH_3$ and $C_6H_5OC_2H_5$ are identical even though the latter possesses a potentially abstractable secondary hydrogen β to the oxygen and the former possesses a potentially abstractable primary hydrogen β to the oxygen;[31] and (c) the alkyl aryl ethers do not quench biacetyl fluorescence.

We conclude, on the basis of these data, that phenols quench both B_1 and B_3 via a reversible hydrogen abstraction mechanism, while alkyl aryl ethers quench via a reversible electron-abstraction mechanism. Thus for quenching by phenols we may envision the following picture for the activated complex
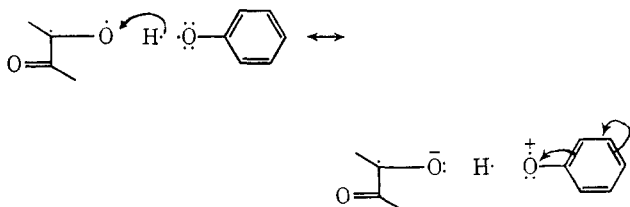
The effect of polar and hydrogen-bonding solvents in suppressing the rate constant for quenching can be attributed to hydrogen bonding between solvent and phenol and not to a polarity effect (e.g., equal suppression was found for acetonitrile or dioxane as solvent). It is known that phenol hydrogen bonds with pyridine[32a] and acetonitrile.[32b] Thus, our results suggest that (a) hydrogen bonding ties up a large fraction of phenol so that the concentration of free phenol is markedly decreased; (b) hydrogen-bonded phenol is less effective as a quencher than free phenol; and (c) polar stabilization of the transition state for quenching by phenols, if it occurs in polar solvents, is outweighed by hydrogen-bonding effects.

The fact that both methyl phenyl ether and ethyl phenyl ether are equally effective in quenching B_3 suggests that an α-hydrogen abstraction mechanism is *not* occurring since we would expect a secondary hydrogen to be abstracted at a measurably faster rate than a primary hydrogen.[31,33] There are at least two other attractive mechanisms for quenching of B_3 by aryl alkyl ethers which are consistent with our data: (a) reversible electron abstraction and (b) reversible addition to the aromatic nucleus, e.g.
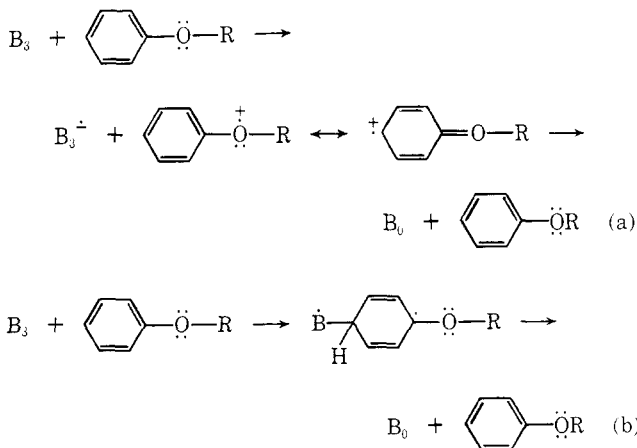
Mechanism a has analogy in the work of Guttenplan and Cohen[34] who have proposed a similar mechanism for the quenching of benzophenone reduction by ali-

(33) C. Walling and M. Gibian, *J. Amer. Chem. Soc.*, 87, 3361 (1965).
(34) J. Guttenplan and S. G. Cohen, *Chem. Commun.*, 247 (1969).

phatic sulfides, and b has analogy in the work of Baum and Norman[35a] who studied the biacetyl-sensitized decarboxylation of phenyl acetic acids. While we have no evidence to decide between these alternatives, it should be noted that the lifetime of B_3 in liquid benzene is considerably shorter than its inherent lifetime so that reversible addition to the benzene ring must be considered as a plausible quenching mechanism. Since ketone n,π^* states show electrophilic reactivity in general,[33] it would not be surprising if addition of B_3 to the benzene nucleus of an aryl alkyl ether occurred faster than addition to benzene.[35b] On the other hand, electron abstraction does seem to be a viable quenching mechanism in the case of amines (*vide infra*).

The generally lower k_q^P values relative to k_q^f for the phenols studied is interesting and contrasts with the situation for TBS discussed above. While the exact source of this differential quenching reactivity is not known, we suggest that it may arise from a greater polar character of B_1 relative to B_3. Singlet states are expected from theory to generally possess a greater polar character (Scheme I) than triplets because electron-

Scheme I
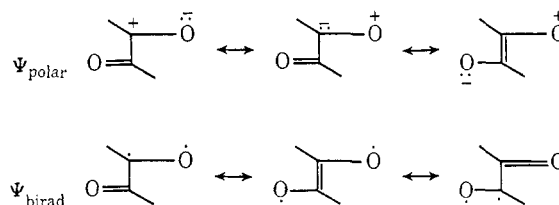
paired resonance structures are possible for the former, but not the latter; this results from the fact that two electrons in singly occupied orbitals tend to have a high probability of being in the same position in an excited singlet state, but tend to have a low probability of occupying the same region of space in a triplet.[36] In fact, this concept presumes greater biradical character for B_3 (Scheme I). Of course, the final states B_1 and B_3 will have character of both Ψ_{polar} and Ψ_{birad}, but B_1 may be weighted toward Ψ_{polar} while B_3 is weighted toward Ψ_{birad}.

It is also possible that a spin effect, rather than a polar effect, operates to enhance k_q^f over k_q^P. For example,[37] if the ion pair A in Scheme II is produced in a singlet

Scheme II
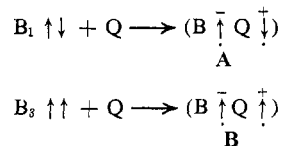
(35) (a) E. J. Baum and R. O. C. Norman, *J. Chem. Soc., B*, 227 (1968). (b) The high C–H bond strength (~112 kcal/mol) of benzene precludes hydrogen abstraction simply on the basis of energetics. However, in the cases where formal ketone photo hydrogen abstraction from benzene[8,35c] occurs, it seems likely that addition to the benzene nucleus actually occurs as a first step, followed by hydrogen abstraction from the intermediate(s) formed thereby. (c) A. Beckett and G. Porter, *Trans. Faraday Soc.*, 59, 2038 (1963); T. A. Claxton, T. E. Gough, and M. C. R. Symons, *ibid.*, 62, 279 (1966); J. A. Bell and H. Linschitz, *J. Amer. Chem. Soc.*, 85, 528 (1963); G. E. Greame, J. C. Paice, and C. C. R. Ramsay, *Aust. J. Chem.*, 20, 1671 (1967); M. B. Rubin and Z. Neuwirth-Weiss, *Chem. Commun.*, 1607 (1968).
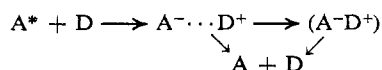(36) G. Jackson and G. Porter, *Proc. Roy. Soc.*, (London), A 260, 13 (1961); P. G. Dickens and J. W. Linnett, *Quart. Rev.* (London), 11, 291 (1957).
(37) For evidence that radical pairs maintain spin memory see ref 11; P. D. Bartlett and N. A. Proter, *J. Amer. Chem. Soc.*, 90, 5318 (1968); M. C. R. Symons, *Nature*, 213, 1226 (1967).

state, it may well have a lower energy content than the ion pair **B**, *i.e.*, the singlet radical pair can be stabilized by electron exchange of the unpaired odd electrons which contributes to bonding of B· $\uparrow^-$ and Q· $\uparrow^+$ but no such bonding stabilization is possible for B· $\uparrow^-$ Q· $\uparrow^+$. Thus, if the transition states leading to **A** and **B** reflect the lower energy content of **A**, **B₁** will be quenched faster than **B₃**. Finally, the fact that τ_f is decreased by addition of aniline derivatives rules out the existence of quenching by a species which precedes B₁, the fluorescing state, since the τ_f is independent of any precursor to B₁, but the intensity of fluorescence (used to measure $k_q^f \tau_f$) is not.[38]

Quenching by Aniline and Its Derivatives. It has been reported that aniline and diphenylamine quench biacetyl triplets with rate constants close to that for diffusion-controlled reaction.[2] The results for k_q^p presented in Table II are in agreement with the reported result. It was also reported[2] that triphenylamine quenched biacetyl triplets with a k_q^p 4 to 5 orders of magnitude less than diffusion controlled, so it was postulated that the quenching mechanism was hydrogen abstraction since aniline and diphenylamine have abstractable nonaromatic hydrogens, while triphenylamine does not. We have found that k_q^p for triphenylamine is only about 2 orders of magnitude less than k_q for diffusion-controlled quenching, and, in addition, fluorescence is significantly quenched by all three aromatic amines. There is also an apparent lack of disappearance of biacetyl when solutions are irradiated as with phenols. Substitutions of deuterium and methyl and ethyl groups for the amino hydrogens of aniline result in much smaller variations in k_q^p and k_q^f values than is found for phenols.

In fact, an *inverse* deuterium effect on k_q^p was found upon going from C₆H₅NH₂ to C₆H₅ND₂ as quencher. This result is consistent with enhancement of quenching by the more facile electron release from nitrogen of the –ND₂ group relative to –NH₂.[39] In contrast to the analogous cases for phenols, dimethylaniline is about three times less effective, as measured by k_q^p, than diethylaniline. On the other hand, the k_q^f values for all the compounds in Table III are nearly within experimental error of each other, with (C₆H₅)₃N being slightly less effective than the others. This lack of a clear-cut substitution effect and the absence of net photoreaction led us to reject a quenching mechanism involving hydrogen abstraction and to propose an electron (or charge) transfer quenching mechanism for aromatic amines similar to the type proposed by Weller.[26] In this mechanism the excited acceptor molecule A abstracts an electron from a donor D to give a complex or an ion pair which undergoes reverse electron transfer to give the two ground state molecules

$$A^* + D \longrightarrow A^- \cdots D^+ \longrightarrow (A^- D^+)$$
$$\searrow \quad \quad \swarrow$$
$$A + D$$

Such a mechanism predicts that k_q values should increase in a polar relative to a nonpolar medium since

charged intermediates are present, and this is found to be the case for the aromatic amines. However, the fact is that k_q^f is so close to the value for diffusion-controlled quenching in benzene that solvent polarity effects on k_q^f (Table VIII) are much less sensitive probes to mechanism than solvent effects on the k_q^p values (Table VII) which undergo substantial increases upon going from benzene to acetonitrile.

The parallel effects of solvent (Tables VII and VIII) and structural changes (Table III) on k_q^p and k_q^f lead us to suggest the following description for the transition state for quenching of both B₁ and B₃ by aniline and its derivatives
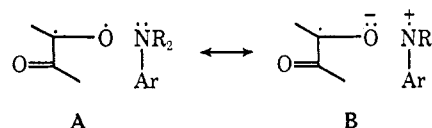
The slower rate of quenching by (C₆H₅)₃N in C₆H₆ may result from an early arrival at the transition state such that the electron-withdrawing effect of the third phenyl group (which can contribute to resonance structure **B** only to a minor extent because of the difficulty in achieving simultaneous planarity of all three phenyl groups) hinders electron withdrawal. Consistent with this notion is the fact that (Table VII) k_q^p for triphenylamine jumps nearly two orders of magnitude upon going from C₆H₆ to CH₃CN.

Further evidence for the electron (or charge) transfer mechanism for quenching by aniline derivatives is found in Tables VII and VIII, since polar solvents generally enhance k_q^p and k_q^f, although the values of the latter are already close to the expected value for diffusion-controlled quenching.[40] Finally, it is noted (Table IX) that reported ionization potentials for the anilines examined are all less than ~7.7 eV. From our data with aliphatic amines (*vide infra*) it seems that an amine ionization potential of <8 eV may be required for effective quenching by electron transfer.

It is reasonable that the ability of a compound to quench B₁ or B₃ by electron (or charge) transfer should depend on the quencher's ionization potential, since the energetics of the conversions to B·⁻ and Q·⁺ will prob-

$$B_1 + Q \longrightarrow B·^- + Q·^+$$
$$B_3 + Q \longrightarrow B·^- + Q·^+$$
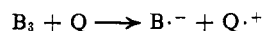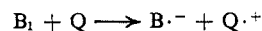
ably control to a large extent (see discussion for hydrogen donors above) whether electron-transfer quenching can compete with other quenching mechanisms.

The proposal given above to explain the greater values of k_p^f relative to k_q^p for quenching by phenols is applicable to our results with anilines which seem to quench fluorescence at close to the rate expected for diffusion-controlled reaction.[40] Consistent with an electron-abstraction mechanism are our preliminary findings[22] that B₃ is quenched by substituted anilines in the order 4–CH₃ > H > Cl.

Quenching by Aliphatic Amines. The aliphatic amines apparently photoreduce **1** and also are effective quenchers of biacetyl phosphorescence. The results in Table IV show that while tertiary amines quench B₁ singlets with k_q^f values close to those expected for diffusion-controlled quenching, secondary

(38) (a) For other examples of electron-transfer quenching for which the excited singlet is more effective than the triplet of the same molecule, see S. Ander, H. Blume, and G. Schulte-Frohlinde, *Chem. Commun.*, 745 (1968); K. Musao and Y. Hiroshi, *Z. Phys. Chem.*, **57**, 103 (1968). (b) Polar-solvent enhancement of electron-transfer quenching of the excited singlets of aromatic hydrocarbons by amines is known, ref 26 and W. R. Ware and H. P. Richter, *J. Chem. Phys.*, **48**, 1595 (1968).

(39) E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 181 (1963).

(40) F. Wilkinson, *Advan. Photochem.*, **3**, 241 (1964).

amines are less reactive, and primary amines do not measurably quench B_1. The photoreduction of benzophenone and other ketones by aliphatic amines has been studied in great detail by Cohen[41] and others.[42] Two mechanisms have been proposed for these photoreactions. One mechanism involves a hydrogen abstraction similar to that generally postulated for the quenching by alcohols and hydrocarbons, and the other involves quenching by an electron transfer from the amine to the ketone and then either (a) proton-back transfer to give the photoreduction products or (b) electron-back transfer to give back the starting materials. One may consider the electron-transfer mechanism as a modification of the mechanism in which the transition state for hydrogen abstraction is stabilized by delocalization of an electron of the heteroatom.

In fact, such a combination of hydrogen abstraction and electron-transfer mechanisms may well be operating in the quenching of the luminescence of 1 by aliphatic amines. While the quenching-rate constants of the triplets of 1 are relatively unaffected by the number of alkyl groups on the nitrogen, the fluorescence-quenching rate constants decrease as fewer electron-donating alkyl groups are present, presumably because the negative charge on the nitrogen decreases in the same order (Table V). In addition, 1,4-diazobicyclo[2.2.2]octane (DABCO) which has an especially stable cation[43] shows the highest singlet quenching constant compared to the other aliphatic amines (this may, however, simply be a statistical effect since DABCO has two nitrogens per molecule).

Evidence for an electron transfer or strongly polar nature of the transition state for quenching by aliphatic amines is provided by (a) the occurrence of a small $(k_H/k_D \sim 1.3)$ deuterium isotope effect on k_q^f and the lack of a significant deuterium isotope effect on k_q^p on going from $(CH_3)_2CHNH_2$ to $(CH_3)_2CHND_2$; and (b) the general increase of k_q^p upon going from benzene to acetonitrile.

However, differences in behavior of B_1 and B_3 toward amine quenching is indicated by (a) the quenching of B_3 by primary amines which fail to quench B_1; (b) the occurrence of a strong isotope effect for quenching of B_1 by $[(CH_3)_2CD]_2ND$ ($vs.$ $[(CH_3)_2CH]_2ND$) but the lack of a comparable effect on the quenching of B_3; (c) the enhanced efficiency of singlet quenching by DABCO; and (d) the lack of net protoreaction with this quencher. The quenching of B_1 (Table IX) may require an amine[42a] with an ionization potential of about 8 eV or less.

While further work is clearly required to disentangle the photochemistry of B_1 and B_3 with aliphatic amines (which should be possible by use of specific triplet energy transfer quenchers, $vide$ $infra$), it seems that quenching of B_1 and B_3 by aliphatic amines is electron

Table IX. Comparison between the Fluorescence Quenching Constant k_q^f and Amine Ionization Potentials

Amine	k_q^f ($\times 10^{10}$ M^{-1} sec^{-1})	IP, eV[a]
$C_6H_5N(CH_3)_2$	1.2	7.3[b]
$C_6H_5N(C_2H_5)_2$	1.1	7.2[b]
$C_6H_5NH_2$	1.0	7.9[b]
$(C_6H_5)_2NH$	0.7	7.4[b]
$(n\text{-}C_3H_7)_3N$	0.31	7.2[b]
$(C_2H_5)_3N$	0.2	7.5[c]
$(C_2H_5)_2NH$	0.17	8.0[c]
$[(CH_3)_2CH]_2NH$	0.13	7.7[c]
$(CH_3)_2CHNH_2$	0.1	8.7[c]

[a] Ionization potential. [b] Measured from charge-transfer complexes: G. Briegleb and J. Czeckulla, $Z.$ $Elektrochem.$, 63, 6 (1959). [c] Measured by photoionization: K. Wantabe and J. R. Mottl, $J.$ $Chem.$ $Phys.$, 26, 1773 (1957).

(or charge) transfer in character, but that the nature of the hydrogen on the α-carbon and the electron density on the nitrogen atom is more important in the quenching of B_1. The rate constant for photoreduction of benzophenone[41e] by 2-butylamine has been estimated at $\sim 5 \times 10^7$ M^{-1} sec^{-1}, a value interestingly close to k_q^p for biacetyl triplet quenching. The uniformity of the k_q^p values upon going from primary to secondary to tertiary amines is curious and difficult to explain. We are presently studying the cause of this "leveling" effect.

The possibility that this effect may result from the immediate formation of some diffusion-controlled quenching impurity (such as an α-ketoimine) is rendered unlikely by the following observations: (a) no evidence could be found for a measurable dark reaction during the time required for analysis; (b) tertiary amines would not be expected to react with biacetyl in the same manner as primary or secondary amines; (c) DABCO behaves analogously to acyclic amines; and (d) the k_q^f values show a dependence on amine structure.

Cohen and Stein[41h] have proposed that triplet benzophenone undergoes a rapid charge-transfer interaction with the n electrons of amines, and that this interaction leads to partial quenching and partial reduction. In our systems similar behavior may be operating but we cannot differentiate at this point between a common transition state which then partitions between physical and chemical quenching or two independent physical and chemical quenching paths.

Quenching by Triplet Energy Transfer. Previous work on the quenching of biacetyl phosphorescence in benzene by triplet energy acceptors has shown that the quenching rate constant approaches the value expected for diffusion-controlled reaction when the quencher triplet energy is several kcal/mol below 56 kcal/mol, the value assigned to the energy of B_3.[3] The highest values for k_q^p in benzene for quenching of B_3 obtained in previous studies[3,44] are in the range 5–8 $\times$ 10^9 M^{-1} sec^{-1}. Our data (Table VIII) are consistent with this work.

The calculated value from the Debye equation[44] for k_{dif} in benzene is 1.0×10^{10} M^- sec^{-1}. If we assume that k_{dif} in benzene is $\sim 10^{10}$ M^{-1} sec^{-1}, then we see that fluorescence quenching by resorcinol (Table II), anilines (Table III), and DABCO (Table V) is within ex-

(41) (a) S. G. Cohen and R. Baumgarten, $J.$ $Amer.$ $Chem.$ $Soc.$, 87, 2996 (1965); (b) $ibid.$, 89, 3471 (1967); (c) S. G. Cohen and J. I. Cohen, $ibid.$, 89, 164 (1967); (d) S. G. Cohen and J. I. Cohen, $J.$ $Phys.$ $Chem.$, 72, 3782 (1968); (e) S. G. Cohen and H. M. Chao, $J.$ $Amer.$ $Chem.$ $Soc.$, 90, 165 (1968); (f) S. G. Cohen and J. B. Guttenplan, $Tetrahedron$ $Lett.$, 5353 (1968); (g) S. G. Cohen, N. Stein, and H. M. Chao, $J.$ $Amer.$ $Chem.$ $Soc.$, 90, 521 (1968); (h) S. G. Cohen and N. Stein, $ibid.$, 91, 3690 (1969).

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perimental error of the diffusion controlled rate in benzene.[40,44]

Conclusion

No one mechanism appears to be capable of explaining the quenching of biacetyl luminescence by the quenchers studied in this work, which appears to be one of the few detailed studies of direct bimolecular quenching of the singlet and triplet states of the same molecule.[45] It appears that quenching may involve either electron or hydrogen abstraction by B_1 or B_3 and that either of these processes may be reversible. The results of our study are summarized in Table X. Some of the significant points revealed by this work are (a) the n,π^* triplet of biacetyl shows considerably less reactivity toward hydrogen abstraction than the n,π^* triplet states of monoketones; (b) reversible electron and reversible hydrogen abstraction can operate as mechanisms for quenching B_1 and B_3; (c) a generally greater enhancement of $k_q{}^t$ over $k_q{}^p$ is found for quenching involving polar electron or charge-transfer transition states; (d) $k_q{}^t$ values approach the magnitude expected for diffusion-controlled quenching for phenols, aromatic amines and tertiary amines; and (e) the rate of quenching by

(45) Comparisons of intramolecular photoreactions are known[12-14] but only recently has a comparison between the reactivity of an excited singlet and triplet of the same molecule toward a bimolecular reaction been studied; ref 11, ref 42, and L. A. Singer, G. A. Davis, and V. P Muralidharan, *J. Am. Chem. Soc.*, 91, 897 (1969).

Table X. Summary of $k_q{}^p$, $k_q{}^t$ and Probable Quenching Mechanisms

Quencher	$k_q{}^p$	$k_q{}^t$	Probable quenching mechanism
Alcohols	10^3–10^7	$<10^6$	Irreversible H abstraction
Phenols	10^6–10^9	10^9–10^{10}	Reversible H abstraction
Aromatic amines	10^7–10^9	10^9–10^{10}	Reversible e abstraction
Trialkyl-amines	10^7–10^8	10^9–10^{10}	Irreversible H or e abstraction
Dialkyl-amines	10^7–10^8	10^9	Irreversible H or e abstraction
Monoalkyl-amines	10^7–10^8	10^7	Irreversible H or e abstraction

hydrogen abstraction can be suppressed (phenols) or enhanced (alcohols) by increasing solvent polarity. Finally, it should be stated that although it was not possible to devise a single mechanism consistent with all of our data, the mechanism of the primary photochemical act which quenches the n,π^* states of biacetyl may be similar for all of the quenchers studied in Tables I–III, V; *i.e.*, the transition state for quenching may at one extreme be considered as an electron abstraction and the other extreme as a hydrogen atom abstract. Transition states in which the movement of the electron and a proton (to various degrees) toward the n,π^* states would then be conceptually intermediate to these two extremes.

The Electrochemical Reduction of Nitrobenzyl Halides in Acetonitrile

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Abstract: The electrochemical reduction of nitrobenzyl chlorides and bromides has been studied in acetonitrile solution. Electrochemical and spectroscopic methods show that the reduction of a nitrobenzyl halide is initially a one-electron process which gives the corresponding anion radical. In the case of an anion radical of either *o*- or *p*-nitrobenzyl halide, halide ion is rapidly lost to give the neutral nitrobenzyl radical. Although the principal pathway for the reaction of the nitrobenzyl radical is dimerization, a small amount of the product of hydrogen atom abstraction is also observed. The subsequent reduction of the corresponding dinitrobibenzyl and nitrotoluene to the dianion and the anion radical, respectively, completes the over-all two-electron process. Decomposition of an anion radical of either *m*-nitrobenzyl chloride or *m*-nitrobenzyl bromide occurs more slowly than in the case of the *ortho* and *para* isomers. Although the short-term chronoamperometric and cyclic voltammetric results are consistent with a reaction pathway involving hydrogen atom abstraction and *m*-nitrotoluene formation, controlled-potential coulometry indicates that less than 40% of the theoretical amount of *m*-nitrotoluene is actually present. No other products, including a dimer, could be found electrochemically or by gas chromatography.

Numerous reports have appeared recently concerning the chemical,[1-5] photochemical,[6] and electrochemical[7-12] reduction of halogenated nitroaromatics to

anion radicals in nonaqueous solvent systems. While several of the anion radicals are sufficiently stable so as to permit the recording of their electron spin resonance

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