Quenching of Biacetyl Fluorescence and Phosphorescence

Nicholas J. Turro and Robert Engel

Contribution from the Department of Chemistry, Columbia University,
New York, New York 10027. Received May 24, 1969

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 fluorescence 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 fluorescence (but not biacetyl fluorescence) by physical energy transfer. Mechanisms consistent with these results are discussed.

All of the previously reported photoreactions of biacetyl 1, in solution are thought to have originated from the triplet state. Theoretical evidence exists, and in some cases, experiments have shown that the n,$\pi^*$ singlet and triplet states of ketones have similar reactivities and are probably electronically similar. In the case of acetone, however, the n,$\pi^*$ triplet is apparently $10^3$ times more reactive toward intermolecular hydrogen abstraction from tri-n-butylstannane than the n,$\pi^*$ singlet. 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 Amino-Bowman spectrophotofluorometer have been reported previously. The rate constants for quenching were obtained by W. Robinson and V. E. DiGiorgio, J. Chem. Phys., 48, 2647 (1968); (c) For other examples of inertness of ketone singlets toward TBS see: K. Schaffner, Pure Appl. Chem., 16, 80 (1968).

Turro, Engel / Biacetyl Fluorescence and Phosphorescence Quenching

This major product was secured by preparative vpc and shown to be $\text{C}_3\text{H}_6\text{O}_2$: $C$, 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 into 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 stopped and shaken for 12 hr at room temperature. The reaction mixture was poured into ice-sulfuric acid solution of 4 ml of recovered 1-heptene, bp 30-35°C (200 mm), there was obtained 9 g of a clear liquid, bp 105-109°C (20 mm). Vpc analysis indicated that three products had been formed, one of which predominated to the extent of 60%.

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O} \]

in the terminal methyl group, the absorption of that substituent at 60.86 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.

-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 60-62°C, there was obtained 9.0 g of a clear liquid, bp 97-98°C (75 mm), there was obtained 9.0 g of a clear liquid, bp 22-23°C (15 mm), there was obtained 9.0 g of a clear liquid, bp 97-98°C (75 mm).

Quenching of Biacetyl Fluorescence and Phosphorescence

Nicholas J. Turro and Robert Engel

Contribution from the Department of Chemistry, Columbia University,
New York, New York 10027. Received May 24, 1969

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 fluorescence 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 fluorescence (but not biacetyl fluorescence) by physical energy transfer. Mechanisms consistent with these results are discussed.

All of the previously reported photoreactions of biacetyl 1, in solution are thought to have originated from the triplet state. Theoretical evidence exists, and in some cases, experiments have shown that the n,$\pi^*$ singlet and triplet states of ketones have similar reactivities and are probably electronically similar. In the case of acetone, however, the n,$\pi^*$ triplet is apparently $10^3$ times more reactive toward intermolecular hydrogen abstraction from tri-n-butylstannane than the n,$\pi^*$ singlet. 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 Amino-Bowman spectrophotofluorometer have been reported previously. The rate constants for quenching were obtained by W. Robinson and V. E. DiGiorgio, J. Chem. Phys., 48, 2647 (1968); (c) For other examples of inertness of ketone singlets toward TBS see: K. Schaffner, Pure Appl. Chem., 16, 80 (1968).

Turro, Engel / Biacetyl Fluorescence and Phosphorescence Quenching

This major product was secured by preparative vpc and shown to be $\text{C}_3\text{H}_6\text{O}_2$: $C$, 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 into 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 stopped and shaken for 12 hr at room temperature. The reaction mixture was poured into ice-sulfuric acid solution of 4 ml of recovered 1-heptene, bp 30-35°C (200 mm), there was obtained 9 g of a clear liquid, bp 105-109°C (20 mm). Vpc analysis indicated that three products had been formed, one of which predominated to the extent of 60%.

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O} \]
plotting peak-height ratios of biacetyl luminescence in the absence and presence of quencher against quencher concentration, as a Stern-Volmer plot. The slope of the plot, $k_{sv}$, is the product of the inimolecular quenching constant and the lifetime of the 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 plot was always linear ($\pm 40\%$) and the $k_{sv}$ values at each concentration agreed ($\pm 40\%$) with each other. $\tau$ was measured directly and independently and the $k_a$ values were thus obtained. Since $\tau$ for the triplet ($\tau_T = 0.46 \times 10^{-4}$ sec) of 1 is about 10 times larger than $\tau$ for the singlet ($\tau_s = 1.0 \times 10^{-6}$ sec) of 1, $k_{sv}$ values 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.  

**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 LiAIH$_4$ using the procedure reported in the literature; phenol, from Mallinckrodt, was sublimed before use; sec-butanol, Fisher, was either used 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 and ether; 3,4-dihydrobenzhydrol, Amend Drug and Chem. Co., was vacuum distilled before use; phenetole (ethoxybenzene), N,N-dimethyl-aniline, and N,N-diethyl-aniline were from Matheson Coleman and Bell, and were all vacuum distilled before use; deuteriophenol and dideuteriophenylamine 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 isopropylamine were prepared by exchange with D$_2$O; the water-cooled 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 $\AA$.

**Results**  

**Hydrogen Donors.** The quenching of biacetyl phosphorescence by known hydrogen donors (isopropyl alcohol (IPA), $^{4,5}$ benzhydrol (BZH), $^{10}$ and tri-$n$-butylstannane (TBS), $^{16,20}$ 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         | $k_{sv}$        | $k_a$           |
| (CH$_3$)$_2$CHOH        | CH$_3$CN        | $3.3 \times 10^4$ | $<-10^4$        |
| (C$_3$H$_7$)$_2$CHOH    | CH$_3$CN        | $7.0 \times 10^4$ | $<5 \times 10^4$ |
| (n-C$_3$H$_7$)$_2$SnH   | CH$_3$CN        | $1.3 \times 10^4$ | $<10^4$         |

$^a$ Data from Stern-Volmer luminescence quenching of 0.05 M 1 in benzene at 25°C. Maximum error limits $\pm 40\%$. $k_{sv}$ is the rate constant for quenching of biacetyl phosphorescence calculated from experimental $k_{sv}$ values and the assumption that $\tau_T = 0.46 \times 10^{-4}$ sec as found previously. $k_a$ is the rate constant for quenching of biacetyl fluorescence calculated from experimental $k_a$ values and the assumption that $\tau_T = 1.0 \times 10^{-6}$ sec as found previously. Units of $k_a$'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 (CH$_3$)$_2$CHOH.

$^d$ No quenching ($\pm 20\%$) of fluorescence in neat (<3 M) (n-C$_3$H$_7$)$_2$SnH.

The intensity and lifetime of biacetyl phosphorescence is formed in essentially quantitative yield. In 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. 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

OH $\rightarrow$ B$_3 + \text{RH} \rightarrow \text{CH}_3\text{COCOCH}_3$

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 ($\sim 10$ M) $k_{sv} < 10^7 M^{-1} sec^{-1}$, for 2.0 M benzhydrol in benzene $k_{sv} < 5 \times 10^7 M^{-1} sec^{-1}$, and for 1 M TBS in benzene $k_{sv} < 10^8 M^{-1} sec^{-1}$, since ($r_T$)$^{-1}$ 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 acetoniitrile. The intensity and lifetime of biacetyl phosphorescence in acetoniitrile were calibrated$^{22}$ by constructing a plot


(20) G. S. Hammond and P. A. Leermakers, ibid., 84, 207 (1962).  

(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 \( r_f \) to be used in calculation of the \( k_{qP} \) 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>
<thead>
<tr>
<th>Quencher</th>
<th>( k_{qP} ), M(^{-1}) sec(^{-1} )</th>
<th>( k_{qf} ), M(^{-1}) sec(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_6)H(_4)OH</td>
<td>3.4 ( \times ) 10(^8 )</td>
<td>2.0 ( \times ) 10(^9 )</td>
</tr>
<tr>
<td>C(_6)H(_4)OD</td>
<td>1.0 ( \times ) 10(^9 )</td>
<td>1.4 ( \times ) 10(^9 )</td>
</tr>
<tr>
<td>Resorcinol(^b)</td>
<td>2.5 ( \times ) 10(^8 )</td>
<td>6.5 ( \times ) 10(^8 )</td>
</tr>
<tr>
<td>C(_6)H(_4)OC(_6)H(_4)</td>
<td>1.3 ( \times ) 10(^8 )</td>
<td>(&lt;10^8)</td>
</tr>
<tr>
<td>C(_6)H(_4)OC(_6)H(_4)</td>
<td>1.2 ( \times ) 10(^9 )</td>
<td>(&lt;10^9)</td>
</tr>
</tbody>
</table>

a. Same as footnote a in Table I. b. 1,3-Dihydroxybenzene.

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, \( k_{qP} \) and \( k_{qf} \) 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 \( k_{q} \) 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\(_6\)H\(_4\)ND\(_2\) relative to C\(_6\)H\(_4\)NH\(_2\), but no comparable isotope effect on fluorescence quenching was observed. Direct measurement\(^{16}\) of \( \tau_f \) (Table IV) in the presence of 0.01 M aniline, diphenylamine, and biphenylamine allowed direct calculation of \( k_{q} \). The agreement between these values and those determined from \( k_{q} \) \( r_f \) values and independent measurement of \( r_f \) is excellent (Table V).

<table>
<thead>
<tr>
<th>Quencher</th>
<th>( r_f ), nsec</th>
<th>( k_{q} ), M(^{-1}) sec(^{-1} )</th>
<th>( k_{q} ) from Table IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>10.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_6)H(_5)NH(_2)</td>
<td>5.7</td>
<td>7.5 ( \times ) 10(^9 )</td>
<td>1.1 ( \times ) 10(^9 )</td>
</tr>
<tr>
<td>(C(_6)H(_5))(_2)NH</td>
<td>6.5</td>
<td>6.5 ( \times ) 10(^9 )</td>
<td>7.4 ( \times ) 10(^9 )</td>
</tr>
<tr>
<td>(C(_6)H(_5))N</td>
<td>6.9</td>
<td>4.3 ( \times ) 10(^9 )</td>
<td>4.9 ( \times ) 10(^9 )</td>
</tr>
</tbody>
</table>

For three runs employing 0.05 M, 0.01 M, and 0.005 M biacetyl the \( k_{q} \) values are identical with the experimental error of \( \pm 40\% \).

**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. Deuteration 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\(_3\))\(_2\)CH]ND to [(CH\(_3\))\(_2\)CD]ND as quencher, a sharp drop in \( k_{q} \) 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 tripropylyamine.

**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 (\( E_f = 42 \) kcal/mol),\(^1\) 1,2-benzanthracene (\( E_f = 47 \) kcal/mol),\(^2\) and trans-stilbene (\( E_f = 50 \) 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 \( (E_2 = 53 \text{ kcal/mol}) \), pyrene \( (E_1 = 49 \text{ kcal/mol}) \), and acridine \( (E_1 = 45 \text{ kcal/mol}) \), linear Stern-Volmer plots were obtained with a precision of \( \pm 40\% \) (Table VI). These compounds did not measurably quench biacetyl fluorescence. Although ferrocene \( (E_2 \approx 50 \text{ kcal/mol}) \) 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 \( (k_{qF} \approx 4 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}) \).

Table VI. Quenching of Biacetyl Phosphorescence by Triplet Energy Acceptors

<table>
<thead>
<tr>
<th>Quencher</th>
<th>( E_a )</th>
<th>( k_{qP} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-Cyclohexadiene</td>
<td>53</td>
<td>( 2.9 \times 10^9 )</td>
</tr>
<tr>
<td>Pyrene</td>
<td>49</td>
<td>( 6.2 \times 10^9 )</td>
</tr>
<tr>
<td>Acridine</td>
<td>45</td>
<td>( 9 \times 10^8 )</td>
</tr>
</tbody>
</table>

\( ^a \) Values of \( k_{qP} \) in \( \text{M}^{-1} \text{sec}^{-1} \) are calculated from Stern-Volmer quenching constants, \( k_{qF, P} \), and measurement of \( \tau_p = 0.46 \times 10^{-3} \) sec. Biacetyl concentration 0.05 M. \( ^b \) Reference 23. \( ^c \) Reference 3. \( ^* \) Reference 24.

Solvatochrom 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 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.

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 \( \pm 20\% \) ) 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.

\( ^{24} \) D. F. Evans, ibid., 1351 (1957).

\( ^{a} \) Values of \( k_{qP} \) are calculated from Stern-Volmer quenching constants, \( k_{qF, P} \), and measurement of \( \tau_p = 0.46 \times 10^{-3} \) sec. Biacetyl concentration 0.05 M. \( ^{b} \) Reference 23. \( ^{c} \) Reference 3. \( ^{*} \) Reference 24.

The case of triphenylamine is particularly noteworthy in terms of the large increase in \( k_{qP} \) upon going from benzene to acetonitrile.

Since in Tables VII and VIII we are comparing numbers which include a different variable \( (\tau_1 \) and \( \tau_p) \) than was present when one solvent was used, we feel an absolute error of greater than \( \pm 50\% \) must be considered when discussing rate constants derived from different solvents.

Discussion

The configuration of both B1 and B2 is best described as being derived from an n,\( \pi^* \) excitation. It is thus to be expected that the photochemistry of biacetyl may parallel to some extent the known behavior of the n,\( \pi^* \) 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 \( ^{28} \) and the quenching constant for the phosphorescence of 1 has been reported. \( ^{5} \) The result presented in Table I is in good agreement with the reported value. With BZH, \( k_{qP} \) is more than 20 times larger than that for IPA. The experimental error in determining \( k_{qP} \) is about 20\% so the increase in \( k_{qP} \) 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, \( ^{11} \) but for 1 the quenching constant appears to

<table>
<thead>
<tr>
<th>Quencher</th>
<th>Benzene ( k_{qP} )</th>
<th>Acetonitrile ( k_{qP} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_2\text{H}_5\text{OH} )</td>
<td>( 3.4 \times 10^4 )</td>
<td>( 7.9 \times 10^4 )</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>( 2.5 \times 10^5 )</td>
<td>( 1.2 \times 10^5 )</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_5\text{NH}_2 )</td>
<td>( 5.0 \times 10^5 )</td>
<td>( 1.5 \times 10^5 )</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_5\text{NH} )</td>
<td>( 1.7 \times 10^5 )</td>
<td>( 2.6 \times 10^5 )</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_5\text{N} )</td>
<td>( 5.1 \times 10^5 )</td>
<td>( 1.6 \times 10^5 )</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_5\text{N} )</td>
<td>( 5.0 \times 10^5 )</td>
<td>( 2.7 \times 10^5 )</td>
</tr>
</tbody>
</table>

\( ^{a} \) Values of \( k_{qP} \) are calculated from Stern-Volmer quenching constants, \( k_{qF, P} \), and measurement of \( \tau_p \) by single photon counting. \( ^{b} \) In benzene, \( \tau_1 = 10.0 \text{ nsec} \), in pyridine \( \tau_1 = 5.7 \text{ nsec} \), in ethanol, \( \tau_1 = 7.7 \text{ nsec} \), and in acetonitrile \( \tau_1 = 8.2 \text{ nsec} \). 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, \( 1.6 \times 10^{10} \text{ M}^{-1} \text{sec}^{-1} \); pyridine, \( 1.1 \times 10^{10} \text{ M}^{-1} \text{sec}^{-1} \); ethanol, \( 0.9 \times 10^{10} \text{ M}^{-1} \text{sec}^{-1} \); acetonitrile, \( 2.9 \times 10^{10} \text{ M}^{-1} \text{sec}^{-1} \).
be at least 100 times less than that expected for diffusion-controlled quenching.

The $k_{qP}$ values for IPA and BZH are orders of magnitude less than the intersystem-crossing rate constant as determined by the fluorescence lifetime of 1.14 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 benzyl alcohol solution. The maximum value estimated for $k_{qP}$ (Table I) is larger than $k_{qP}$ 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 $k_{qP}$ 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 C6H6 if the $k_{qP}$ is comparable to $k_{qP}$. 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 $k_{qP}$, which is somewhat lower than $k_{qP}$ (Table I) for TBS. The reduced reactivity of a singlet n, $\pi^*$ 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, $\pi^*$ singlet states.25,26 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 $k_{qP}$ upon going from benzene to acetonitrile implies some polar character (as suggested by Cohen29 for other n, $\pi^*$ 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.

The analogy to these results with those reported for photoreduction of benzophenone28 and acetone15 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 B3 is at least five times less reactive toward hydrogen abstraction from TBS than is B1. This result is analogous to the photoreduction of acetone3a by TBS for which it was found that TBS quenches acetone triplets with a rate constant of $8 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ but that TBS does not measurably quench acetone singlets. This led Wagner to conclude that the n, $\pi^*$ singlet of acetone is 10–100 times less reactive than its n, $\pi^*$ triplet.

The rate constant for abstraction by B3 from IPA and BZH is lower than that found for (a) photoreduction of benzophenone by IPA ($\sim 10^8 \text{ M}^{-1} \text{ sec}^{-1}$)29 or BZH ($\sim 10^7 \text{ M}^{-1} \text{ sec}^{-1}$)30 and (b) photoreduction of cyclohexanone by IPA ($\sim 2 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$).31 This result is analogous to the photoreduction of phenol and resorcinol have been reported previously, and it was proposed that the quenching mechanism was hydrogen abstraction.3 The $k_{qP}$ values for these two quenchers presented in Table II are within an order of magnitude of agreement with the previously published values.3 The $k_{qP}$ values, which have not been reported previously, are three to ten times higher than the $k_{qP}$ 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 $k_{qP}$ ($k_{H}/k_D = 3.4$) and $k_{qP}^*$ ($k_{H}/k_D = 1.4$) for phenol; (b) a large suppression of $k_{qP}$ and $k_{qP}^*$ upon going from C6H5OH to C6H5OCH3; and (c) suppression of $k_{qP}$ and $k_{qP}^*$ in polar hydrogen bonding solvents. Becker31,32 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 apparently 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 $k_{qP}$ by a factor of $\sim 10$ and $k_{qP}^*$ by a factor of $\sim 10$.


~3; (b) $k_{p}^*$ values for $\text{C}_6\text{H}_5\text{OCH}_3$ and $\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$ are identical even though the latter possesses a potentially abstractable secondary hydrogen $\beta$ to the oxygen and the former possesses a potentially abstractable primary hydrogen $\beta$ to the oxygen,\textsuperscript{31} and (c) the alkyl aryl ethers do not quench biaetyl fluorescence.

We conclude, on the basis of these data, that phenols quench both $\text{B}_1$ and $\text{B}_3$ via a reversible hydrogen abstraction mechanism, while alkyl aryl ethers quench a reversible electron-abstraction mechanism. Thus for quenching by phenols we may envision the following picture for the activated complex

\[
\begin{align*}
\text{O} & \quad \text{H} \\
\text{ phenol} & \quad \text{benzophenone} \\
\text{ArO}^{-} & \quad \text{H}^{+}
\end{align*}
\]

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\textsuperscript{32a} and acetonitrile.\textsuperscript{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 $\text{B}_1$ suggests that an $\alpha$-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.\textsuperscript{31,34} There are at least two other attractive mechanisms for quenching of $\text{B}_1$ by aryl alkyl ethers which are consistent with our data: (a) reversible electron abstraction and (b) reversible addition to the aromatic nucleus, e.g.

\[
\begin{align*}
\text{B}_1 & \quad + \quad \text{O} \quad \text{R} \\
\text{B}^{1+} & \quad + \quad \text{O} \quad \text{R} \\
\text{B}_1 & \quad + \quad \text{O} \quad \text{R} \quad \text{R} \\
\text{B}^{1+} & \quad + \quad \text{O} \quad \text{R} \quad \text{R} \\
\end{align*}
\]

Mechanism a has analogy in the work of Guttenplan and Cohen\textsuperscript{34} who have proposed a similar mechanism for the quenching of benzophenone reduction by alkyl esters of phosphoric sulfides, and b has analogy in the work of Baum and Norman\textsuperscript{35a} who studied the biaetyl-sensitized decarboxylation of phenyl acetic acids. While we have no evidence to decide between these alternatives, it should be noted that the lifetime of $\text{B}_1$ 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 $n,\pi^*$ states show electrophilic reactivity in general,\textsuperscript{33} it would not be surprising if addition of $\text{B}_1$ to the benzene nucleus of an aryl alkyl ether occurred faster than addition to benzene.\textsuperscript{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 $k_{p}^*$ values relative to $k_{p}^*$ 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 $\text{B}_1$ relative to $\text{B}_3$. Singlet states are expected from theory to generally possess a greater polar character (Scheme I) than triplets because electron-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.\textsuperscript{36} In fact, this concept presumes greater biradical character for $\text{B}_3$ (Scheme I). Of course, the final states $\text{B}_1$ and $\text{B}_3$ will have character of both $\Psi_{\text{polar}}$ and $\Psi_{\text{birad}}$, but $\text{B}_1$ may be weighted toward $\Psi_{\text{polar}}$ while $\text{B}_3$ is weighted toward $\Psi_{\text{birad}}$.

It is also possible that a spin effect, rather than a polar effect, operates to enhance $k_{p}^*$ over $k_{p}^*$. For example,\textsuperscript{37} if the ion pair A in Scheme II is produced in a singlet

\[
\begin{align*}
\text{B}_1 & \quad \downarrow+ \quad \Downarrow \quad \text{Q} \\
\text{B}_3 & \quad \downarrow+ \quad \Downarrow \quad \text{Q} \\
\text{A} & \quad \text{B}
\end{align*}
\]


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 $B::^\pm$ and $Q::^\pm$ but no such bonding stabilization is possible for $B::^\pm$ and $Q::^\pm$.

Thus, if the transition states leading to $A$ and $B$ reflect the lower energy content of $A$, $B_1$ will be quenched faster than $B_2$. Finally, the fact that $\tau_f$ is decreased by addition of aniline derivatives rules out the existence of quenching by a species which precedes $B_1$, the fluorescent state, since the $\tau_f$ is independent of any precursor to $B_1$, but the intensity of fluorescence (used to measure $k_q^{(f)}$) is not.

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 triphenylamidine 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 C$_6$H$_5$NH$_2$ to C$_6$H$_5$ND$_2$ as quencher. This result is consistent with enhancement of quenching by the more facile electron release from nitrogen of the -ND$_2$ group relative to -NH$_2$.\(^9\) In contrast to the analogous cases for phenols, dimethylamine is about three times less effective, as measured by $k_q^{(p)}$, than diethylamine. 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 (C$_6$H$_5$)$_3$N being slightly less effective than the others. This lack of a clear-cut substitution effect and the absence of net photooxidation 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.\(^24\) 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

$$A^* + D \rightarrow A\cdots D^* \rightarrow (A-D^*)$$

Such a mechanism predicts that $k_q$ values should increase in a polar relative to a nonpolar medium since $k_q^{(f)}$ values are already close to the expected value for diffusion-controlled quenching. Finally, it is noted (Table IV) 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 $B_1$ or $B_2$ by electron (or charge) transfer should depend on the quencher's ionization potential, since the energetics of the conversions to $B^-$ and $Q^{++}$ will probably 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 $k_q^{(f)}$ 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 $B_1$ is quenched by substituted anilines in the order 4-CH$_3$ > H > Cl.

Quenching by Aliphatic Amines. The aliphatic amines apparently photooxidize \(^1\) and also are effective quenchers of biacetyl phosphorescence. The results in Table IV show that while tertiary amines quench $B_1$ 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. Schulze-Frolshinde, Chem. Commun., 745 (1969); K. Musao and Y. Hiroshi, Z. Phys. Chem., 57, 103 (1968).

\(^{(39)}\) (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).

amines are less reactive, and primary amines do not measurably quench B1. The photoreduction of benzophenone and other ketones by aliphatic amines has been studied in great detail by Cohen and others. Two mechanisms have been proposed for these photo-reactions. 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 cation43 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 (kH/kD ~ 1.3) deuterium isotope effect on kqf on going from (CH3)2CHNH2 to (CH2)2CHND2; and (b) the general increase of kqf upon going from benzene to acetonitrile.

However, differences in behavior of B1 and B3 toward amine quenching is indicated by (a) the quenching of B1 by primary amines which fail to quench B2; (b) the occurrence of a strong isotope effect for quenching of B2 by [(CH3)2C(NH)2]Cl (es. [(CH3)2CH2]Cl) but the lack of a comparable effect on the quenching of B3; (c) the enhanced efficiency of singlet quenching by DABCO; and (d) the lack of net protoreaction with this quencher. The quenching of B1 (Table IX) may require an amine42 with an ionization potential of about 8 eV or less.

While further work is clearly required to disentangle the photochemistry of B1 and B2 with aliphatic amines (which should be possible by use of specific triplet energy transfer quenchers, vide infra), it seems that quenching of B1 and B2 by aliphatic amines is electron (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 B1. The rate constant for photoreduction of benzophenone44 by 2-butylamine has been estimated at ~ 5 x 10^7 M^-1 sec^-1, a value interestingly close to kqf for biacetyl triplet quenching. The uniformity of the kqf 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 kqf values show a dependence on amine structure.

Cohen and Stein41h have proposed that triplet benzophenone undergoes a rapid charge-transfer interaction with the n electrons of amine, 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 B3. The highest values for kqf in benzene for quenching of B3 obtained in previous studies44,44 are in the range 5-8 x 10^9 M^-1 sec^-1. Our data (Table VIII) are consistent with this work.

The calculated value from the Debye equation44 for kqf in benzene is 1.0 x 10^10 M^-1 sec^-1. If we assume that kqf in benzene is ~ 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-

<table>
<thead>
<tr>
<th>Amine</th>
<th>kqf (× 10^10)</th>
<th>IP, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6H6(N(CH3)2)</td>
<td>1.2</td>
<td>7.3</td>
</tr>
<tr>
<td>C6H6(N(CH3)H)</td>
<td>1.1</td>
<td>7.2</td>
</tr>
<tr>
<td>C6H6(NH2)</td>
<td>1.0</td>
<td>7.6</td>
</tr>
<tr>
<td>[(CH2)2CH2]2</td>
<td>0.7</td>
<td>7.4</td>
</tr>
<tr>
<td>(µ-C(NH)2)N</td>
<td>0.31</td>
<td>7.2</td>
</tr>
<tr>
<td>[(CH2)2N]H</td>
<td>0.2</td>
<td>7.5</td>
</tr>
<tr>
<td>[(CH2)2NH]</td>
<td>0.17</td>
<td>8.0</td>
</tr>
<tr>
<td>[(CH2)2CH2]2</td>
<td>0.13</td>
<td>7.7</td>
</tr>
<tr>
<td>[(CH2)2CHNH2]</td>
<td>0.1</td>
<td>8.7</td>
</tr>
</tbody>
</table>


Experimental error of the diffusion controlled rate in benzene.  

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.  

It appears that quenching may involve either electron or hydrogen abstraction by B\textsubscript{1} or B\textsubscript{2}, 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,\pi* triplet of biacetyl shows considerably less reactivity toward hydrogen abstraction than the n,\pi* triplet states of monoketones; (b) reversible electron and reversible hydrogen abstraction can operate as mechanisms for quenching B\textsubscript{1} and B\textsubscript{2}; (c) a generally greater enhancement of k\textsubscript{p} over k\textsubscript{q} is found for quenching involving polar electron or charge-transfer transition states; (d) k\textsubscript{p} values approach the magnitude expected for diffusion-controlled quenching for phenols, aromatic amines and tertiary amines; and (e) the rate of quenching by 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,\pi* 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,\pi* states would then be conceptually intermediate to these two extremes.

<table>
<thead>
<tr>
<th>Quencher</th>
<th>k\textsubscript{p}</th>
<th>k\textsubscript{q}</th>
<th>Probable quenching mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohols</td>
<td>10\textsuperscript{-10}</td>
<td>&lt;10\textsuperscript{-4}</td>
<td>Irreversible H abstraction</td>
</tr>
<tr>
<td>Phenols</td>
<td>10\textsuperscript{-10}</td>
<td>10\textsuperscript{-10}</td>
<td>Reversible H abstraction</td>
</tr>
<tr>
<td>Aromatic amines</td>
<td>10\textsuperscript{-10}</td>
<td>10\textsuperscript{-10}</td>
<td>Reversible e abstraction</td>
</tr>
<tr>
<td>Trialkylamines</td>
<td>10\textsuperscript{-10}</td>
<td>10\textsuperscript{-10}</td>
<td>Irreversible H or e abstraction</td>
</tr>
<tr>
<td>Dialkylamines</td>
<td>10\textsuperscript{-10}</td>
<td>10\textsuperscript{-8}</td>
<td>Irreversible e abstraction</td>
</tr>
<tr>
<td>Monoalkylamines</td>
<td>10\textsuperscript{-9}</td>
<td>10\textsuperscript{-9}</td>
<td>Irreversible H or e abstraction</td>
</tr>
</tbody>
</table>

The Electrochemical Reduction of Nitrobenzyl Halides in Acetonitrile

James G. Lawless, Duane E. Bartak, and M. Dale Hawley

Contribution from the Department of Chemistry, Kansas State University, Manhattan, Kansas 66502. Received May 28, 1969

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 dinitrobenzyl and nitrotoluene to the dianion and the anion radical, respectively, completes the overall 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

(2) N. Kornblum, R. E. Michel, and R. C. Kerber, ibid., 88, 5562 (1966).

Lawless, Bartak, Hawley / Nitrobenzyl Halides