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Photoinduced Electron- and Energy-Transfer Processes of Biacetyl Imprisoned in a Hemicarcerand

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Abstract: The energy- and electron-transfer quenching processes of the lowest triplet excited state of biacetyl (2,3-butanedione) imprisoned in a hemicarcerand have been systematically investigated in CH₂Cl₂ solution at room temperature. Twenty potential quenchers have been used, including ten triplet energy acceptors (mostly, aromatic hydrocarbons) and nine electron donors (mostly, aromatic amines). Bimolecular rate constants for the quenching processes were obtained by Stern–Volmer analysis and compared with those found for the quenching of free biacetyl. In the electron-transfer processes, aromatic amines with oxidation potential from +0.015 V (*N,N,N',N'*-tetramethyl-*p*-phenylenediamine) to +0.83 V (diphenylamine) quench free biacetyl at the diffusion-controlled limit, whereas for imprisoned biacetyl the rate constant decreases (roughly in a linear manner) from 4.0×10^8 to 1.2×10^5 M⁻¹ s⁻¹. As far as energy-transfer is concerned, the rate constant for the quenching of free biacetyl increases with decreasing ΔG° and reaches the diffusion-controlled plateau value ($k_q \sim 10^{10}$ M⁻¹ s⁻¹) for $\Delta G^\circ \sim -0.1$ eV, whereas for imprisoned biacetyl a scattered, bell-shaped log k_q vs ΔG° plot is obtained, with a maximum value ($\sim 10^6$ M⁻¹ s⁻¹) much below the diffusion-controlled limit. The results obtained show that the walls of the hemicarcerand allow only very weak electronic interaction between incarcerated triplet biacetyl and external quenchers. A brief discussion of the results obtained in the light of current energy- and electron-transfer theories is presented.

Introduction

Hemicarcerands^{2,3} (see, e.g., Figure 1) are cage-type molecules with large voids and with "portals" through which a variety of molecules can enter at high temperature and then remain imprisoned at room temperature for a more or less long period of time ("constrictive" binding⁴).

After the pioneering investigations of Turro and co-workers on the room temperature phosphorescence of luminophores enclosed in cyclodextrin (CD) cups,⁵ much work has been performed on the photochemical and photophysical properties of molecules enclosed in constrained media,^{6,7} particularly in CDs^{8,9} and zeolites.¹⁰ Hemicarcerands are species of great interest from this viewpoint since they offer the opportunity to study the excited state behavior of guest molecules isolated in a specific, discrete molecular inner phase. However, only a few studies have been reported so far on the photochemical and photophysical behavior of incarcerated molecules.^{11–15}

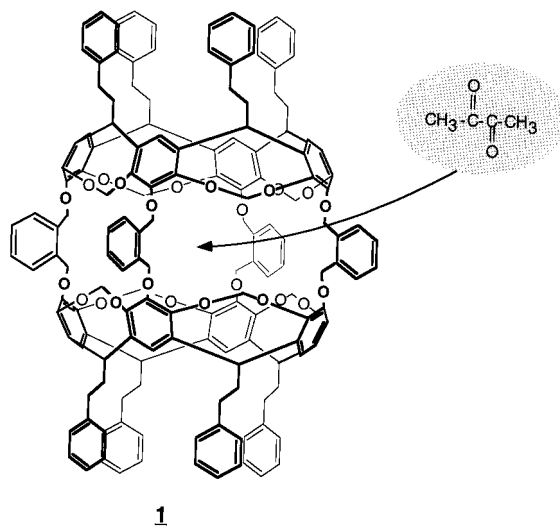


Figure 1. Structure formula of hemicarcerand **1** and of biacetyl.

Molecular models show that biacetyl (2,3-butanedione) fits well the cavity of hemicarcerand **1** (Figure 1). In a previous investigation¹³ we have shown that when biacetyl is imprisoned in **1**, its absorption, fluorescence, and phosphorescence maxima are red shifted compared to the values obtained for solutions of free biacetyl in any solvent. A very interesting feature of biacetyl is its strong and structured phosphorescence band (λ_{\max}

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= 518 nm in CH_2Cl_2) which originates from the lowest triplet excited state T_1 .^{16,17} The lifetime of the T_1 excited state is intrinsically long (millisecond time scale) but it is strongly affected by the presence of dioxygen (the bimolecular quenching constant for energy-transfer, k_{en} , is $8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in benzene). Actually, the phosphorescence band cannot be observed at all in air equilibrated solutions. However, when biacetyl is imprisoned into hemicarcerand **1**, the lifetime of the T_1 excited state (0.84 ms) is almost unaffected by the presence of dioxygen and a very intense phosphorescence band can be observed.¹³ Although the small size of dioxygen should at least allow the O_2 molecules to contact biacetyl through the portals, formation of an encounter complex of suitable distance/geometry to allow efficient energy-transfer is clearly prevented.

The above results prompted us to perform a systematic investigation on the effect of incarceration on photoinduced energy- and electron-transfer processes. When our studies were almost completed, Farran and Deshayes¹⁵ reported the results of an investigation on the energy-transfer quenching of triplet biacetyl incarcerated in **1**. They found a very interesting free energy dependence of the quenching constant, with evidence of a Marcus-type inverted region. In this paper we report the results of a systematic investigation on the electron-transfer quenching of triplet biacetyl incarcerated in **1**, and we also confirm and extend the results of Farran and Deshayes¹⁵ as far as quenching by energy-transfer is concerned.

Experimental Section

Hemicarcerand **1** (Figure 1) was obtained by the method described by Cram and co-workers.⁴ Under such conditions, one molecule of the solvent (namely, *N,N*-dimethylacetamide) remains encapsulated in the interior of the cage at room temperature. The species so obtained was characterised by ^1H NMR and elemental analysis. Inclusion of biacetyl in **1** was obtained following the procedure given to prepare hemicarceplexes of guests of similar size (e.g. 2-butanone).⁴ The isolated compound was purified by silica-gel chromatography and characterised by ^1H NMR (CDCl_3) on a Bruker ARX 400 spectrometer. ^1H NMR for **1**·biacetyl: δ -2.08 (s, 6H, $\text{CH}_3\text{COCOCH}_3$), 2.47 (m, 16H, $\text{CH}_2\text{CH}_2\text{Ph}$), 2.68 (m, 16H, $\text{CH}_2\text{CH}_2\text{Ph}$), 3.87 (d, 8H, inner OCH_2 , $J = 7.5 \text{ Hz}$), 4.71 (t, 8H, methine, $J = 7.8 \text{ Hz}$), 5.02 (s, 16H, benzylic), 5.46 (d, 8H, outer OCH_2 , $J = 7.5 \text{ Hz}$), 6.79 (s, 8H, ArH), 7.15–7.35 (m, ArH).

The hemicarceplex of biacetyl is moderately soluble in CH_2Cl_2 and benzene at room temperature and under such conditions it is stable for months. All the other chemicals were of reagent grade.

Absorption spectra, luminescence (emission and excitation) spectra, and excited state lifetimes were obtained by using equipment and procedures previously described.¹⁸

The experiments were carried out in CH_2Cl_2 solution at room temperature. Since biacetyl absorbs and emits in the visible spectral region, there is practically no interference with absorption and emission by the host.¹³ The experiments were carried out with excitation at 455 nm. We have measured the quenching of the phosphorescence lifetime of free or incarcerated biacetyl at different quencher concentrations. The lifetime of the T_1 excited state is 0.6 ms for free biacetyl (in carefully deaerated solutions) and 0.84 ms for incarcerated biacetyl.¹³ In some cases, the quenching of the phosphorescence intensity was also measured and the results obtained were the same as those obtained from lifetime measurements. The kinetic data were analyzed satisfactorily by the usual Stern–Volmer lifetime (τ) or intensity (I) equations, $\tau^0/\tau = I^0/I = 1 + k_q\tau^0[\text{Q}]$, where k_q is the quencher concentration and τ^0 and τ or I^0 and I are the emission lifetimes or intensities in the absence and presence of the quenchers. The rate constant for quenching

Table 1. Rate Constants for the Quenching by Aromatic Amines^a

	quencher	E_{ox}^b (V)	k_q ($\text{M}^{-1} \text{ s}^{-1}$) biacetyl	k_q ($\text{M}^{-1} \text{ s}^{-1}$) 1 ·biacetyl
a	diphenylamine	0.83	4.0×10^9	3.5×10^4
b	1-naphthylamine	0.54	1.2×10^5	
c	benzidine	0.46	1.0×10^{10}	4.2×10^5
d	<i>N,N</i> -diphenyl-1,4-phenylenediamine	0.34	2.0×10^9	1.9×10^7
e	4-aminodiphenylamine	0.27		1.2×10^7
f	1,4-phenylenediamine	0.18		5.0×10^6
g	<i>N,N,N',N'</i> -tetramethyl- <i>p</i> -phenylenediamine	0.015	5.0×10^9	4.0×10^8

^a CH_2Cl_2 solution. ^b Acetonitrile solution, *vs* SCE (from ref 21).

by dioxygen was evaluated by comparing the behavior of degassed, air-equilibrated, and oxygen saturated CH_2Cl_2 solutions. For the other quenchers, at least five different concentrations were used. In the case of the quenching of free biacetyl by amines, in view of the very low concentrations of amine needed, much care had to be taken to avoid the presence of impurities (e.g., water or acids) in the solvent. The concentration of incarcerated biacetyl was ca. $5 \times 10^{-4} \text{ M}$. Under these conditions, and because of the small electronic factor for the energy-transfer process (*vide infra*), correction¹⁶ for back energy-transfer in the case of the quenchers with high triplet energy (e.g., phenanthrene) was unnecessary. In fact, we have verified that changing the concentration of **1**·biacetyl of one order of magnitude had no effect on the measured quenching constants. For the experiments on free biacetyl, the solutions were degassed by repeated freeze-pump-thaw cycles. For the experiments on incarcerated biacetyl, degassing was not necessary (except, of course, for the quenching by dioxygen) because the phosphorescence intensity and lifetime are only very weakly quenched by O_2 .

The maximum error limits for the rate constants are estimated to be $\pm 30\%$ in all cases except for quenching by dioxygen ($\pm 50\%$).

Results

Quenching by Aromatic Amines. As shown in the fundamental papers by Turro and Engel,^{19,20} aromatic amines can quench the phosphorescent triplet excited state of biacetyl by an electron transfer mechanism. Therefore we have chosen a series of aromatic amines having known electrochemical properties to investigate in a systematic way electron-transfer quenching of incarcerated triplet biacetyl. The oxidation potentials of the amines²¹ and the quenching rate constants obtained from our experiments are given in Table 1.

Figure 2 shows the plot $\log k_q$ *vs* the oxidation potential of the quencher. The value of the rate constant found for the quenching of free biacetyl by diphenylamine is in good agreement with that reported by Turro and Engel^{19,20} in benzene. As one can see, the quenching of free biacetyl occurs at the diffusion-controlled limit. In the case of incarcerated biacetyl, however, the plot is quite different. One can notice that (i) the rate constants are smaller than those for free biacetyl; (ii) the points are considerably scattered; (iii) the rate constant decreases, roughly in a linear manner, as the amine becomes more difficult to oxidize.

Quenching by Triplet Energy Acceptors. For a systematic investigation of the energy-transfer process we have chosen a series of triplet-energy acceptors (Table 2) extensively used in this kind of experiments.^{19,20,22,23} Several of these molecules had already been used as quenchers of free biacetyl. The triplet

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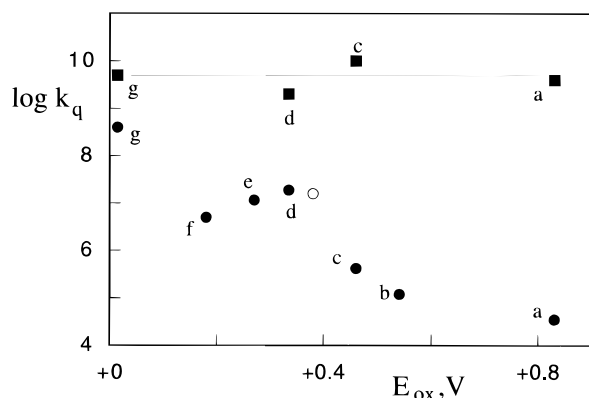


Figure 2. Plot of $\log k_q$ vs the oxidation potential of the quencher. Squares and circles refer to the quenching of free and incarcerated triplet biacetyl, respectively. The labels used for aromatic amines are those given in Table I. The empty circle refers to quenching by ferrocene.

Table 2. Rate Constants for Quenching by Triplet Acceptors^a

quencher	E_T^b (eV)	k_q^c ($M^{-1} s^{-1}$) biacetyl	k_q ($M^{-1} s^{-1}$) 1•biacetyl
1 phenanthrene	2.66		1.6×10^4
2 naphthalene	2.64	2.6×10^6	1.0×10^4
1-I-naphthalene	2.61	5.9×10^6	
1-Br-naphthalene	2.56	2.9×10^7	
1,8-dinitronaphthalene	2.48	2.6×10^9	
piperylene	2.46		
2,2'-dinaphthyl	2.42	2.9×10^9	
3 coronene	2.36		5.3×10^5
4 9-fluorenone	2.30		1.0×10^5
1,2-benzopyrene	2.29	5.9×10^9	
5 pyrene	2.09	5.0×10^9 ^d	1.0×10^6
6 benzanthrone	2.04		7.6×10^5
7 acridine	1.95	2.0×10^9 ^d	8.0×10^5
8 anthracene	1.84	7.0×10^9 ^d	8.5×10^5
9 cycloheptatriene	1.65		2.3×10^4

^a CH_2Cl_2 solution. ^b Energy of the lowest triplet state (from ref 23), unless otherwise noted. ^c In benzene, from ref 16, unless otherwise noted. ^d This work.

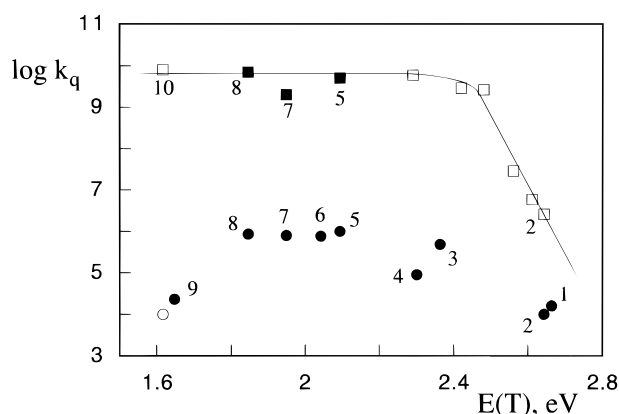


Figure 3. Plot of $\log k_q$ vs the triplet energy for the quenchers listed in Table 2. Squares and circles refer to the quenching of free and incarcerated triplet biacetyl, respectively. The empty circle refers to quenching by dioxygen to give the $^1\Sigma$ excited state.

energy of the quenchers ($E(T)$) and the quenching rate constants are given in Table 2. Figure 3 shows the $\log k_q$ vs $E(T)$ plot. For free biacetyl the rate constant increases with decreasing triplet energy of the acceptor and reaches a plateau for $E(T) \leq 2.4$ eV. The plot for incarcerated biacetyl is quite different: (i) the maximum value for the rate constant is about 4 orders of magnitude smaller than the diffusion-controlled rate; (ii) the points are considerably scattered; (iii) there is evidence of a decrease in the rate constant with increasing exoergonicity. In

spite of some nonnegligible differences in the numerical values of some rate constants, the plot shown in Figure 2 is similar to that obtained by Farran and Deshayes¹⁵ by using piperylene and five of the quenchers used in this work.

Quenching by Other Species. We have also investigated the quenching of free and incarcerated biacetyl by a few other molecules (Table 3).

Dioxygen is known to quench the triplet state of free biacetyl at a diffusion-controlled rate.¹⁶ In the case of incarcerated biacetyl, however, the quenching constant is of the order of $10^{-4} M^{-1} s^{-1}$.

For the aliphatic amine DABCO (1,4-diazobicyclo[2.2.2]-octane), a rate constant $1.5 \times 10^7 M^{-1} s^{-1}$ was obtained by Turro and Engel¹⁹ for free biacetyl in benzene. For incarcerated biacetyl we have found that the rate constant has an upper limit of $5 \times 10^3 M^{-1} s^{-1}$.

Quenching of free biacetyl by ferrocene in benzene solution apparently does not give linear Stern–Volmer plots.¹⁹ In CH_2Cl_2 solution we have found a rate constant at the diffusion-controlled limit. For incarcerated biacetyl in the same solvent, the Stern–Volmer plot was linear and the rate constant was found to be $1.7 \times 10^7 M^{-1} s^{-1}$.

Quenching of free biacetyl by resorcinol in benzene occurs with rate constant $2.5 \times 10^9 M^{-1} s^{-1}$ in benzene and $1.2 \times 10^8 M^{-1} s^{-1}$ in acetonitrile.¹⁹ We have found that in CH_2Cl_2 the upper limit of the rate constant for the quenching of incarcerated biacetyl by resorcinol is $10^3 M^{-1} s^{-1}$.

Discussion

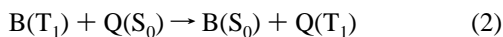
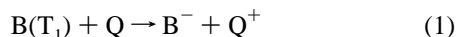
Biacetyl was chosen as a guest because of its size, which was expected to fit well the cavity of **1**,¹³ and its well known strong and long-lived phosphorescence in fluid solution at room temperature¹⁷ which makes possible (and also relatively easy) the measurements of quenching constants even for poorly efficient quenchers.

In a previous paper,¹² we incarcerated 9-cyanoanthracene in a hemicarcerand where the two halves were connected by $-CH=N-(m-C_6H_4)-N=CH-$ instead of $-O-CH_2-(o-C_6H_4)-CH_2-O-$ bridges. In that case we found NMR evidence of a C_{2v} symmetry, suggesting that 9-cyanoanthracene occupies a fixed position in the hemicarcerand cavity. This is likely related to the presence of the nitrile substituent which, as suggested by CPK models, can find a place in one of the four portals of the hemicarcerand structure, thereby preventing rotation of the guest. In the case of **1**•biacetyl, the 1H NMR spectrum does not show any signal splitting of host OCH_2O protons because the guest is symmetric. No signal splitting is observed also in the case of non symmetric guests of comparable size and shape (2-butanone, *N,N*-dimethylacetamide, 1,1,2,2-tetrachloroethane). These results suggest that biacetyl rotates freely inside the cavity.⁴ For **1**•acetophenone, a single conformation along the long axis of **1** was evidenced.¹⁴ Regardless of the detailed structure of **1**•biacetyl, the results of a previous investigation¹³ clearly show that biacetyl (i) is contained in a not-too-tight cavity where no specific host-guest interaction takes place, and (ii) is shielded by the wall of the hemicarcerand from direct interaction with solvent molecules.

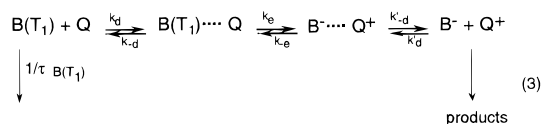
For free biacetyl, quenching of the triplet excited state can take place by electron transfer, energy-transfer, and reversible and irreversible H abstraction.^{19,20} In view of the shielding effect of the hemicarcerand, it seems likely that quenching of incarcerated biacetyl by solute molecules can only take place by electron- or energy-transfer processes, “mediated” by the interposed walls of **1**, during an encounter between **1**•biacetyl and the quencher. Since direct orbital overlap between triplet

biacetyl and quencher is prevented, it can be expected that both electron^{24–28} and energy^{28–31} transfer have to be nonadiabatic in character.

Kinetic Analysis. Quenching of the triplet excited state of biacetyl, B(T₁), by electron and energy-transfer can be schematically indicated as in eqs 1 and 2, respectively:³²



Since these processes require diffusion and formation of encounters, the following kinetic scheme can be used (for the sake of simplicity, in the following we give equations only for the case of an electron transfer quenching; the same equations can be used for energy-transfer^{29,30}):



The general rate law for this kinetic scheme is given by³³

$$k_q = \frac{k_d}{1 + \frac{k_{-d}}{k_e} + \frac{k_{-d}}{k'_d} \frac{k_{-e}}{k_e}} \quad (4)$$

In the frame of a classic treatment, $k_e = k_e^\circ \exp(-\Delta G^\ddagger/RT)$, $k_{-e} = k_e \exp(-\Delta G^\circ/RT)$, and eq 4 can be transformed into

$$k_q = \frac{k_d}{1 + \frac{k_{-d}}{k_e^\circ} e^{\Delta G^\ddagger/RT} + e^{\Delta G^\circ/RT}} \quad (5)$$

In the nonadiabatic limit,²⁴ the pre-exponential factor k_e° can be expressed by $\kappa \nu_n$ (where κ is the electronic transmission coefficient and ν_n an effective frequency for nuclear motion) and the free activation energy ΔG^\ddagger can be expressed by classical Marcus equation^{24,34}

$$\Delta G^\ddagger = \lambda \left(1 + \frac{\Delta G^\circ}{4\lambda} \right)^2 \quad (6)$$

where λ is the so called intrinsic nuclear barrier which receives contribution from the inner-sphere (intramolecular) λ_i and outer-sphere (solvent) λ_o reorganizational energies. Therefore, the

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rate constant for the process within the encounter is given by

$$k_e = \kappa \nu_n e^{-\Delta G^\ddagger/RT} \quad (7)$$

For a homogeneous series of reactions,²⁵ such as those between the same oxidant *A and a series of structurally and electronically related reductants Q₁, Q₂, Q₃,... that have variable redox potential but the same size, shape, electronic structure and electric charge,³⁵ one can assume that throughout the series the reactions parameters k_d and k_{-d} in eq 5, λ in eq 6, and κ and ν_n in eq 7 are constant. Under these assumptions, k_q in eq 5 is only a function of ΔG° and a log k_q vs ΔG° plot is a bell-shaped curve involving (i) a “normal” region for endoergonic or slightly exoergonic reactions, where log k_q increases with increasing driving force, and (ii) an “inverted” region for strongly exoergonic reactions, in which log k_q decreases with increasing driving force.

In a quantum mechanical approach, the rate constant k_e can be expressed as the product of an electronic and a nuclear term^{36,37}

$$k_e = \left(\frac{2\pi}{\hbar} \right) |\langle \nu | \rangle|^2 FCWD \quad (8)$$

where $\langle \nu |$ is the electronic exchange matrix element and $FCWD$ is the Franck-Condon weighted density of states. In a simple approximation in which the solvent modes (average frequency, ν_o) are thermally excited and treated classically and the internal vibrations (average frequency, ν_i) are frozen and treated quantum mechanically, the $FCWD$ is given by

$$\begin{aligned} FCWD = & \frac{1}{(4\pi\lambda_o RT)^{1/2}} e^{-S} \sum_m \frac{S^m}{m!} \exp \left[- \frac{(\Delta G^\circ + \lambda_o + m\hbar\nu_i)^2}{4\lambda_o RT} \right] \quad (9) \\ S = & \lambda_i / \hbar\nu_i \end{aligned}$$

In eq 9, λ_o and λ_i are the outer and inner reorganizational energies and the summation extends over m , the number of quanta of the inner vibrational mode in the product state.

If $\langle \nu |$, λ_o and S are relatively constant in a series of reactions, k_q in eq 5 is again only a function of ΔG° and a log k_q vs ΔG° plot is a curve similar to the classical Marcus curve except that the parabolic branch in the strongly exoergonic region (Marcus inverted region) is substituted by a linear decrease of log k_q with increasing driving force (energy-gap law).^{24,37,38}

It should also be noted that for adiabatic reactions (i.e. when the classical transmission coefficient κ is close to unit, or the electronic exchange matrix element $\langle \nu |$ is relatively high (even a few cm⁻¹), differences in electronic interactions may be masked by the diffusion-controlled limit.^{25,28}

Analysis of the Experimental Results. The driving force ΔG°_{el} for electron transfer quenching processes can be obtained from the equation³⁹

$$-\Delta G^\circ_{el} = E_{\text{B(T}_1\text{)}} - E_{\text{B/B}^-} - E_{\text{Q}^+/\text{Q}} + W_r \quad (10)$$

where $E_{\text{B(T}_1\text{)}}$ is the energy of the triplet excited state of biacetyl

(35) In the case of energy-transfer, a homogeneous series of reactions is similarly defined as the energy-transfer from the same excited state of a molecule to a series of structurally and electronically related acceptors which have variable excited state energy.^{29,30}

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Table 3. Quenching Rate Constants by Other Quenchers^a

quencher	E_T^b (V)	E_{ox}^c (V)	k_q^d (M ⁻¹ s ⁻¹) biacetyl	k_q^e (M ⁻¹ s ⁻¹) 1•biacetyl
dioxygen	1.62 ^f	8.0×10^9 ^g	1.0×10^4	
DABCO	<i>h</i>	0.57	5.4×10^7	$\leq 5 \times 10^3$
ferrocene	1.0 ⁱ	0.34	1.7×10^{10} ^e	1.7×10^7
resorcinol	3.35 ^l	<i>m</i>	2.5×10^9 ⁿ	$< 1 \times 10^3$

^a CH₂Cl₂ solution. ^b Energy of the lowest triplet state, unless otherwise noted. ^c Oxidation potential in acetonitrile *vs* SCE, from ref 21. ^d Benzene solution from ref 19 and 20. ^e This work. ^f Energy of the ¹Σ excited state. The ¹Δ excited state lies 0.65 eV below the ¹Σ excited state (from ref 17). ^g From ref 16. ^h Unknown, but certainly higher than 3 eV. ⁱ From ref 29. ^j From the emission maximum (370 nm) at 77 K. ^m Unknown, but presumably higher than 1.3 eV (for 1,2- and 1,4-dimethoxybenzenes, oxidation potentials are 1.45 and 1.34, respectively).²³ ⁿ Mechanism: H abstraction.

(taken as the energy of the onset of the first vibrational feature of the phosphorescence spectrum: 2.59 eV for free biacetyl; 2.52 eV for incarcerated biacetyl),¹³ $E_{B/B-}$ is the one-electron energy corresponding to reduction of biacetyl (-1.03 V *vs* SCE for free biacetyl in EtOH–H₂O;⁴⁰ unknown for incarcerated biacetyl), $E_{Q^+/Q}$ is the one-electron energy corresponding to oxidation of the quencher (Table 1),²¹ and $w_r = (z_A - z_B^+)e^2/r(A-B^+)\epsilon_s$ is the work term.²⁴ For $z_A = -1$ and $z_B^+ = +1$, in CH₂Cl₂ solution ($\epsilon_s = 8.9$), $w_r = 0.27$ eV for $r(A-B^+) = 6$ Å, an estimated average value for the encounter between free biacetyl and an aromatic molecule.

The driving force ΔG_{en}° for energy-transfer quenching processes can be simply taken as the difference between the energy of triplet biacetyl (*vide supra*), and the energy of the triplet (or another relevant) excited state of the quencher.^{29,30}

$$-\Delta G_{en}^\circ = E_{B(T_1)} - E_{Q^*} \quad (11)$$

Aromatic amines (Table 1) and DABCO (Table 3) can be easily oxidized, but do not have low energy excited states. In other words, for these quenchers ΔG_{el}° is negative and ΔG_{en}° is positive: therefore, quenching can only take place by electron transfer.

The quenchers listed in Table 2 and dioxygen (Table 3) cannot be easily oxidized, but their lowest excited state lies below the biacetyl triplet. Therefore for these quenchers ΔG_{en}° is negative and ΔG_{el}° is positive, so that quenching occurs by energy-transfer.

For ferrocene, both ΔG_{el}° and ΔG_{en}° are considerably negative (the potential of the Fc⁺/Fc couple is $+0.34$ V *vs* SCE in acetonitrile;²¹ the lowest excited state of ferrocene is around 1 eV²⁹) so that both electron- and energy-transfer quenching processes are plausible. As far as quenching of incarcerated biacetyl is concerned, the value of the rate constant found for ferrocene fits well the trend shown by the log k_q vs E_{ox} plot (Figure 2), whereas it would appear anomalously high if inserted in the log k_q vs $E(T)$ plot of Figure 3. Therefore it seems likely that ferrocene operates by an electron-transfer mechanism. This is in agreement with theoretical expectations since the electronic matrix element is a one-electron exchange integral in the case of electron transfer and a two-electron exchange integral (which, of course, implies less overlap at the same distance) in the case of energy-transfer.^{41,42}

Finally, resorcinol has neither low energy excited states nor an accessible oxidation potential. Therefore neither an energy- nor an electron-transfer quenching mechanism is likely. In the case of free biacetyl, in fact, quenching by resorcinol occurs via hydrogen abstraction.¹⁹ The lack of any measurable quenching effect for resorcinol on incarcerated biacetyl confirms

that energy- and electron-transfer mechanisms are not thermodynamically accessible, and shows that hydrogen abstraction is prevented because resorcinol cannot approach the excited triplet state of incarcerated biacetyl.

Quenching by Electron Transfer. For aromatic amines and ferrocene the electron transfer quenching of free biacetyl occurs at the diffusion-controlled limit (Figure 2). This suggests that the electronic exchange matrix element is relatively large. In the case of incarcerated biacetyl, the rate constants are much smaller than those for free biacetyl (Table 1, Figure 2). In principle, this could be due to (i) a smaller electronic exchange matrix element, (ii) a less negative free energy change or (iii) a larger reorganizational barrier for the reaction of incarcerated biacetyl.

As mentioned above, the spectroscopic study described in a previous paper¹³ showed that, when incarcerated in **1**, biacetyl occupies a not-too-tight cavity where it experiences a dielectric constant smaller than that of cyclohexane. This can lead to a less favorable free energy change for a charge-separation reaction.^{33,43} A quantitative evaluation of the shift in the reaction free energy, however, is precluded because the two reaction partners are located into different microenvironments (the quencher is surrounded by CH₂Cl₂ molecules, whereas biacetyl is inside the hemicarcerand cavity). It should also be noted that in passing from the quenching of free biacetyl to the quenching of incarcerated biacetyl, the work term stabilization should decrease because of the larger distance of the two reactants in the case of incarcerated biacetyl. This should in part compensate the previous effect, but any quantitative evaluation is again precluded by the complexity of the system.

As to the reorganizational energy, the intramolecular contribution λ_i should be the same for free and incarcerated biacetyl, whereas the solvent contribution λ_o should be smaller for incarcerated biacetyl because of the smaller dielectric constant of its environment (*vide supra*). It should be noted, however, that there can be a contribution from the hemicarcerand, because of vibrational rearrangements caused by the presence of the negative charge inside the cavity and solvent rearrangement around the charged hemicarcerplex.

At least in part, the different behavior between free and incarcerated biacetyl is expected to come from different electronic interaction. CPK molecular models show that even in the closest approach configuration the distance between incarcerated biacetyl and an external electron donor cannot be smaller than *ca.* 7–8 Å because of the interposition of the walls of the hemicarcerand. Furthermore, owing to the protruding benzene ring in the equatorial plane and the presence of -CH₂-CH₂-C₆H₅ substituents on the two halves of the hemicarcerand surface (Figure 1), close approaches are unlikely and their frequency will strongly depend on the dimension and structure of the electron donor. A small electronic interaction accounts not only for the low values of the rate constants, but also for the large scattering of the data. A large scattering has in fact been observed for other nonadiabatic electron-transfer reactions.²⁷ It should be pointed out that the value of the electronic exchange matrix element ψ is very sensitive to the nature of

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the donor and the reciprocal orientation of the two reaction partners. This means that data reported in Figure 2 do not correspond to a homogeneous series of reactions in the sense described above. This may be the reason why there is no evidence of an inverted region. It should also be recalled that detection of the inverted behavior has most often been an elusive task for bimolecular electron transfer reactions,^{25,44–47} although some clear-cut examples have recently been reported.^{48,49} One reason is that electronically more efficient channels can come into play at high exoergonicity, thereby masking the expected inverted behavior. This could be due to the formation of more intimate encounters at the expenses of a larger reorganizational energy,²⁷ or to higher lying, accessible excited states.^{50,51} Lacking fundamental parameters like the free energy change and considering the dispersion of the data, it seems worthless to fit the experimental values by a curve based on the theoretical equations described above. It seems also difficult to associate a clear meaning to the roughly linear increase in the rate constant with increasing exoergonicity. It cannot be excluded that the considerably high value of the rate constant for tetramethyl-*p*-phenylenediamine involves formation of an excited state of reduced biacetyl.

Quenching by Energy Transfer. As shown by the data reported in Table 2 and Figure 3, the behavior of free and incarcerated biacetyl is quite different also for quenching by energy-transfer. Such a different behavior cannot be attributed to differences in reaction free energy, since the triplet energy of free (2.59 eV) and incarcerated (2.52 eV) biacetyl is almost the same. It should also be recalled that for energy-transfer processes the solvent contribution to the reorganizational energy is very small, and there is no reason why the intramolecular contribution should be different for free or incarcerated biacetyl. Therefore the different behavior shown by free and incarcerated biacetyl in energy-transfer quenching processes (Figure 3) cannot be due to the Franck-Condon factor. We conclude that such a difference has to be related to differences in the electronic exchange matrix elements (eq 8).

Since the excited state energies of free and incarcerated biacetyl and of the quenchers are known, we can calculate the free energy change (eq 11) and plot the rate constants as a function of $\Delta G^\circ_{\text{en}}$. As shown by Figure 4, the $\log k_q$ vs $\Delta G^\circ_{\text{en}}$ plot, as well as the analogous plot reported by Farran and Deshayes,¹⁵ exhibits an “inverted region”, as expected on the basis of eqs 5–7 or 5, 8, and 9. It should be noted that the rate constants relative to quenching by dioxygen has been placed at a free energy change corresponding to formation of the $^1\Sigma$ excited state since it has been shown that an upper excited state can be involved when there is enough driving force in the process.^{52–54} The free energy change for formation of the lower lying $^1\Delta$ excited state is 0.65 eV more negative.

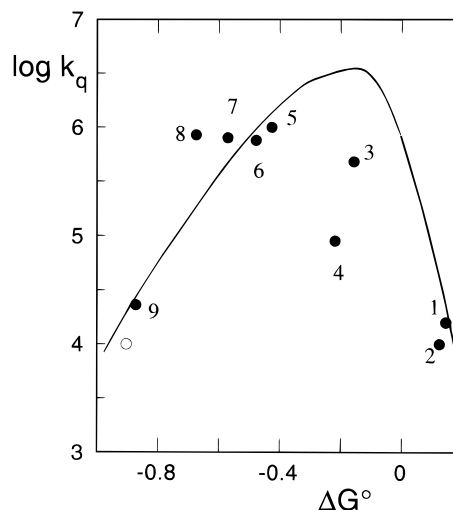


Figure 4. Plot of $\log k_q$ vs $\Delta G^\circ_{\text{en}}$ for the quenching of incarcerated biacetyl by the quenchers listed in Table 2 (solid circles) and dioxygen (empty circle). In the case of dioxygen, the free energy is that concerning the formation of the $^1\Sigma$ excited state. The $\Delta G^\circ_{\text{en}}$ value for formation of the lowest energy excited state, $^1\Delta$, would be -1.54 eV. The solid line is a theoretical curve based on the following parameters: $h\nu_i = 1300$ cm^{-1} ; $S = 0.75$; $\lambda_s = 1000$ cm^{-1} ; $\nu = 0.1$ cm^{-1} .

An “inverted region” for energy-transfer quenching has been found in other cases, including the bimolecular quenching of excited Os(II)-bpy complexes by anthracene and 2,3-benzanthracene,^{53,54} the intramolecular energy-transfer in a series of compounds containing a triplet energy donor and an acceptor separated by a rigid spacer,⁵⁵ and the intramolecular energy-transfer in a series of Re(I) complexes linked to anthracene.⁵⁶ In all these cases, attempts have been made to fit the experimental $\log k_q$ vs ΔG° plot by the theoretical quantum mechanical equations. We have tried to fit the data obtained for incarcerated biacetyl by using eqs 5, 8, and 9 and we have found that no set of the $h\nu_i$, S , λ_o , and ν parameters gives a really good fit. The curve shown in Figure 4 corresponds to the following, reasonable^{53–56} set of values: $h\nu_i = 1300$ cm^{-1} ; $S = 0.75$; $\lambda_o = 1000$ cm^{-1} ; $\nu = 0.1$ cm^{-1} .

In some previous work,^{53,54,56} it has been found that the agreement between experimental and calculated values was fairly good. However, in the case of energy-transfer from 4-benzophenonyl or 4-acetophenonyl moieties rigidly linked by a *cis*-1,4-cyclohexanediyl spacer to a variety of triplet acceptors, no clear and simple correlation between the rates and the free energy change was found.⁵⁵ The authors pointed out that this finding was not surprising if the diversity of the structural variations of the compounds was taken into account. A great scattering of the data was also found for the same reason in the quenching of three different aromatic triplets by a variety of Cr(III) complexes.⁵⁷ Admittedly, one cannot hope that the electronic exchange matrix element is constant throughout the series of the energy-transfer processes whose rate constants are reported in Figure 4. This is particularly true if we compare quenchers as different as an aromatic hydrocarbon and dioxygen.⁵⁸ As discussed by Sigman and Closs,⁵⁵ also the electronic

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(58) Besides a different electronic exchange matrix element, the reorganizational energy is also expected to be different for quenching by an aromatic hydrocarbon or dioxygen. In fact, the $^1\Sigma$ excited state of dioxygen is an intraconfigurational excited state and therefore there is no intramolecular reorganizational energy upon excitation, (see also ref 59).

character of the excited state of the acceptor can play an important role in determining the electronic interaction. Among our quenchers, there are aromatic hydrocarbons as well as aromatic ketones. One could think that a homogeneous subset of data (Table 2) could be that concerning quenching by aromatic hydrocarbons. However, because of the different size of the various aromatic hydrocarbons, their encounters with $1\cdot$ biacetyl can be characterized by different donor-acceptor distances and/or orientations, resulting in different values for the electronic exchange matrix element. Therefore it is not at all surprising that even if we consider only aromatic hydrocarbon quenchers, the free energy correlation is not particularly good. Because of the reasons discussed above, we believe that even the claim that the plot shown in Figure 4 (as well as the analogous plot reported by Farran and Deshayes¹⁵) can be taken as evidence of an inverted behavior should be taken with caution since it could simply reflect the non-homogeneity of the various energy-transfer processes.

An important results is that, even changing drastically the values of the other parameters, reasonable curves can only be obtained for values of $\nu \leq 0.1 \text{ cm}^{-1}$. The electronic interaction between incarcerated biacetyl and external quenchers is therefore very small, as expected because the excited state and the quencher are separated by the walls of the hemicarcerand. A much larger value ($\nu = 2.5 \text{ cm}^{-1}$) was found by Meyer, *et al.*,⁵⁴ for the bimolecular quenching of a series of excited Os(II)-bpy complexes by anthracene and 2,3-benzanthracene, where the excited state and the quencher can directly collide in encounters. Our ν value is closer to that found by Sigman and Closs⁵⁵ for the intramolecular energy-transfer between triplet energy donors and acceptors separated by a rigid *cis*-1,4-cyclohexanediyl spacer ($\nu = 0.3 \text{ cm}^{-1}$).

Conclusions

The lowest triplet excited state of biacetyl imprisoned in a hemicarcerand is very long lived (0.84 ms) and gives a very intense phosphorescence. By a systematic investigation carried

out in CH_2Cl_2 solution at room temperature, we have shown that such an imprisoned excited state can undergo energy and electron transfer processes with species present in solution. The rate constants of these processes are orders of magnitude smaller than those of the processes involving free biacetyl, but can nevertheless be measured with good accuracy because of the very long lifetime of the excited state. Quenching by hydrogen abstraction can occur for free biacetyl, but not for incarcerated biacetyl. In the case of quenching by electron transfer of incarcerated biacetyl, the rate constant increases from 1.2×10^5 to $4.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ as the oxidation potential decreases from +0.83 V (diphenylamine) to +0.015 V (*N,N,N',N'*-tetramethyl-*p*-phenylenediamine), but no clear correlation has been found. For energy-transfer quenching, a bell-shaped $\log k_q$ vs ΔG° plot was obtained, with a maximum value ($\sim 10^6 \text{ M}^{-1} \text{ s}^{-1}$) which is much below the diffusion-controlled limit. The data are much scattered and difficult to fit with a unique set of parameters, indicating that structural and electronic differences among the family of quenchers play an important role. For the energy-transfer process the value of the electron exchange matrix element is $\nu \leq 0.1 \text{ cm}^{-1}$, indicating that the electronic interaction between incarcerated biacetyl and external quenchers is very small, as expected because the excited state and the quencher are separated by the walls of the hemicarcerand.

The interpretation of these new types of energy and electron transfer processes, which involve two partners in different "phases of matter"³ (namely, the interior of a hemicarcerand for the excited biacetyl, and the CH_2Cl_2 solution for the quencher) poses several new problems.

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