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# Photoreactions of Biacetyl, Benzophenone, and Benzil with Electron-Rich Alkenes[†]

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**Abstract:** The rate constants ($k_q$) for fluorescence and phosphorescence quenching of biacetyl by electron-rich alkenes were measured in acetonitrile solution at room temperature. A weak dependence of log $k_q$ on the free enthalpy change ($\Delta G_2$) for electron transfer in the triplet state in the range $0 < \Delta G_2 < 1.0$ eV indicates formation of a polar exciplex. The strong enhancement of $k_q$ for $0 > \Delta G_2 > -0.70$ eV points to electron-transfer processes in singlet and triplet states. Quenching of the phosphorescence and the T–T absorption of benzophenone reveals larger (smaller) $k_q$ values in the endergonic (exergonic) region, as compared to the Rehm–Weller correlation. The slope of the plot of log $k_q$ vs. $\Delta G_2$ is similar to that of biacetyl in the endergonic region. The latter indicates that electron transfer in this instance is not the primary step. For benzil the plot of log $k_q$ vs. $\Delta G_2$ resembles more closely that of biacetyl, pointing to a similar mechanism. In the exergonic region electron transfer is observed for benzil (major process) and benzophenone (minor process) by detection of the radical anion with use of nanosecond laser flash photolysis. The yield and half-life of the radical anion depend on the nature of the electron donor and the ketone, the solvent polarity, and the additives (e.g., $LiClO_4$, special salt effect). The solvent effect on the photoproducts (oxetanes) is correlated with the free enthalpies of radical ion pair formation.

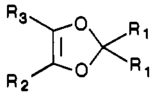
Charge transfer (CT) plays an important role for the interaction of electron donors (D) with photoexcited ketones.[1-5] Several groups have suggested the involvement of CT interaction in the quenching reaction of excited ketones by electron-rich alkenes.[6-8] A complete electron-transfer process, yielding the radical ions, has been observed less frequently; examples are the reduction of triplet benzophenone by methoxybenzenes,[9] 1,4-dioxene,[10] and amines.[11-13]

Especially in the case of electron-rich alkenes an electron-transfer step to the excited ketone under formation of radical ions can be an important competitive photoreaction to the formation of photoproducts such as oxetanes and H-abstraction products.[14-16] Whereas the detection of radical ions by means of ESR techniques[15a,b] provides information concerning the structure rather than dynamic properties,[14a] the quantum yields and half-lives of the radical ions in solution can be better obtained by ps and/or ns laser photolysis.[9-13] (For an example concerning conventional flash photolysis see ref 14a.) Moreover, electron transfer can be utilized to generate radical ions which can be intercepted by neutral alkenes or dienes by C–C bond formation.[14b] For this purpose it is desirable to optimize the conditions in order to obtain high quantum yields of radical ions with sufficiently long lifetimes.[14,17] In general, the feasibility of producing radical ions in polar solvents via photoinduced electron transfer can be predicted by using the well-known equation derived by Rehm and Weller:[18]

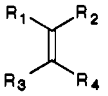
$$\Delta G_2 = E_{1/2}^{\text{ox}}(\text{D}) - E_{1/2}^{\text{red}}(\text{A}) - \Delta E_{\text{exc}}(\text{A}^*) + \Delta E_{\text{coul}} \quad (1)$$

The free enthalpy change ($\Delta G_2$) for the photoinduced electron transfer is related to the redox potentials of the acceptor ($E_{1/2}^{\text{red}}(\text{A})$) and of the donor ($E_{1/2}^{\text{ox}}(\text{D})$), the energy of the excited (singlet or triplet) state of the acceptor ($\Delta E_{\text{exc}}(\text{A}^*)$), and a term $\Delta E_{\text{coul}}$, which takes into account the solvent properties for ion separation ($\Delta E_{\text{coul}} = -0.055$ eV in acetonitrile[18c]).

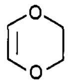
The present paper describes some properties of ketone/donor systems (cf. 17 and 19). For biacetyl and benzophenone the rate constants for luminescence quenching ($k_q$) by 1,3-dioxoles (**1a–e**), tetraethoxyethene (**2a**), and some other alkenes (**2b–6**) were determined over a wide range of $\Delta G_2$.



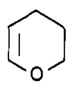
**1a**: $R_1 = R_2 = R_3 = H$
**1b**: $R_1 = CH_3; R_2 = R_3 = H$
**1c**: $R_1 = R_2 = H; R_3 = CH_3$
**1d**: $R_1 = H; R_2 = R_3 = CH_3$
**1e**: $R_1 = R_2 = R_3 = CH_3$



**2a**: $R_1 - R_4 = OC_2H_5$
**2b**: $R_1 = R_2 = H; R_3 = R_4 = OC_2H_5$
**2c**: $R_1 - R_3 = H; R_4 = OC_2H_5$
**2d**: $R_1 = R_3 = H; R_2 = R_4 = OSi(CH_3)_3$
**2e**: $R_1 - R_4 = CH_3$
**2f**: $R_1 = R_2 = C_6H_5; R_3 = H; R_4 = OCH_3$



**3**



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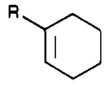
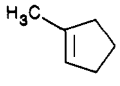


**5a**: R = H
**5b**: R = $CH_3$



**6**

With benzophenone and benzil the quantum yields of formation of the H-adduct (ketyl) radical ($\phi_{AH}$) and the radical anion ($\phi_{A^-}$)

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[†] Part 3 of the series Radical Ions. For parts 1 and 2 see ref 14a,b, respectively.

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**Table I.** Oxidation Potential of Alkenes, $\Delta G_2$, and Rate Constant for Fluorescence (F) and Phosphorescence (P) Quenching of Biacetyl[a]

| alkene | compd no. | $E_{1/2}^{ox}$, V | $10^{-9}k_q$,[b] $M^{-1}\,s^{-1}$ | | $\Delta G_2$,[c] eV |
|---|---|---|---|---|---|
| tetraethoxyethene | **2a** | 0.32 | 4.7 | F | −0.71 |
| tetramethyl-1,3-dioxole | **1e** | 0.42 | 4.4 | F | −0.61 |
| 4,5-dimethyl-1,3-dioxole | **1d** | 0.48 | 5.2 | F | −0.55 |
| 2,2-dimethyl-1,3-dioxole | **1b** | 0.69 | 1.8 | F | −0.34 |
| 1,3-dioxole | **1a** | 0.76 | 1.0 | F | −0.27 |
| 1,1-diethoxyethene | **2b** | 0.85 | 0.26 | F | −0.18 |
| 4-methyl-1,3-dioxole | **1c** | 0.60 | 0.21 | P | −0.17 |
| 1,3-dioxole | **1a** | 0.76 | 0.025 | P | −0.01 |
| (*Z*)-bis(trimethylsiloxy)ethene | **2d** | 0.77 | 0.039 | P | −0.004 |
| 1,1-diethoxyethene | **2b** | 0.85 | 0.0085 | P | +0.07 |
| dihydropyrane | **4** | 1.16 | 0.0048 | P | +0.39 |
| 2,3-dimethyl-2-butene | **2e** | 1.21 | 0.0025 | P | +0.43 |
| 1-methylcyclopentene | **6** | 1.40 | 0.0016 | P | +0.62 |
| ethyl vinyl ether | **2c** | 1.44 | 0.0018 | P | +0.67 |
| 1-methylcyclohexene | **5b** | 1.47 | 0.00085 | P | +0.69 |
| cyclohexene | **5a** | 1.72 | 0.00038 | P | +0.95 |

[a] In argon-saturated acetonitrile at 20 °C. [b] Obtained from steady-state emission (see Luminescence Quenching). [c] Calculated according to eq 1, using $E_{1/2}^{red} = -1.66$ V, $E_S = 2.64$ eV, and $E_T = 2.38$ eV.

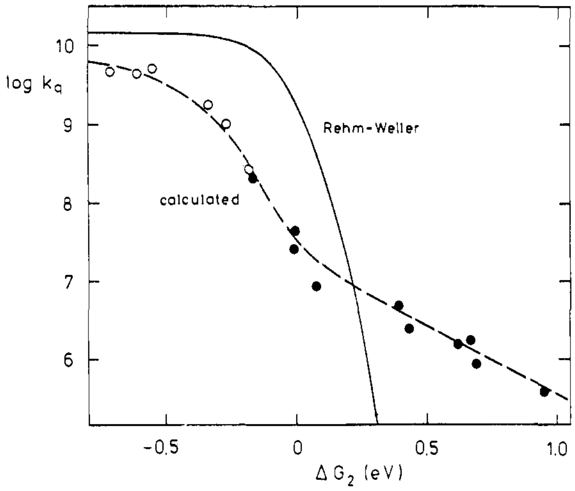
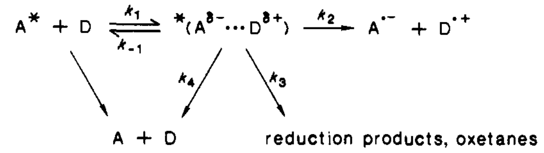


**Figure 1.** Semilogarithmic plot of the rate constant for luminescence quenching of biacetyl in acetonitrile at 20 °C as a function of the free enthalpy change for complete electron transfer (open and full circles refer to fluorescence and phosphorescence quenching, respectively); for calculation of the dashed line see text.

as well as the half-lives, both important to characterize the photoinduced electron transfer, were studied for **1a–e** and **2a**. Three amines, triethylamine (TEA), *N,N*-dimethylaniline (DMA), and 1,4-diazabicyclo[2.2.2]octane (DABCO), were used as electron donors, for the purpose of comparison.[11-13,20] Formation of products from benzophenone and benzil are described as well.

**Scheme I**



For preparative studies of biacetyl olefin systems see elsewhere.[15]

## Results and Discussion

**Relation between $k_q$ and $\Delta G_2$.** The fluorescence and phosphorescence of biacetyl were quenched by various alkenes in acetonitrile solution at room temperature. The $k_q$ values, obtained from linear Stern–Volmer relationships (Table I), reveal a strong dependence on $\Delta G_2$, reflecting the electron donor ability of the alkenes but no obvious correlation to the structure of D (e.g., allylic hydrogens). From the plot of log $k_q$ vs. $\Delta G_2$ (Figure 1), three different regions may be distinguished.

(1) For $\Delta G_2 > 0$ the slope ($s = -1.7$ eV$^{-1}$) is about 10% of that expected from the Rehm–Weller correlation[18] and of comparable size with that reported by Jones et al. for phosphorescence quenching of biacetyl by various unsaturated donors in benzene.[5a]

(2) For $\Delta G_2 < -0.4$ eV the $k_q$ values (obtained from fluorescence quenching) approach a limit which is smaller than that predicted by Rehm and Weller for an exergonic complete electron transfer process.[18]

(3) In the intermediate range, $0 > \Delta G_2 > -0.4$ eV, the dependence is almost linear with a slope of $-5.8$ eV$^{-1}$.

As compared to the Rehm–Weller correlation the $k_q$ values for the biacetyl/alkene system are larger in the endergonic and smaller in the exergonic $\Delta G_2$ region. Therefore, complete direct electron transfer from alkenes to the excited biacetyl molecule cannot be the rate-determining step of luminescence quenching. An "exciplex-biradical" mechanism, often formulated for endergonic ketone/alkene systems,[21] may be visualized. On the other hand, formation of radical ions has been observed by means of ESR spectroscopy or by scavenging with nucleophiles.[15] In Scheme I this mechanism is extended to formation of radical ions in a secondary step.

The exciplex is assumed to be formed reversibly ($k_1$, $k_{-1}$) with approximately 10% CT interaction; it may be deactivated via three pathways: by ion pair formation ($k_2$), by formation of oxetanes and/or H-abstraction (reduction) products ($k_3$), and by decay into the ground state ($k_4$). The respective rate equations are presented in the Appendix; $k_q$ is a function of the free enthalpy of exciplex formation ($\Delta G_{ex}$, eq 6 and 7), the free activation enthalpy for exciplex formation via reaction 1 ($\Delta G_1^{\ddagger}$, eq 8), and the free activation enthalpy for electron transfer ($\Delta G_2^{\ddagger}$, eq 9 and 10).

In order to obtain a good correlation with the results, some additional assumptions are necessary.

(1) For the calculation of $\Delta G_{ex}$ with eq 7[4a,22] we assume a slope set to $s = -1.7$ eV$^{-1}$, as found for the endergonic region.

(2) The free enthalpy of activation for exciplex formation (denoting $\Delta G_1^{\ddagger}$ for $\Delta G_1 = 0$) is $\Delta G_1^{\ddagger}(0) = 0.052$ eV (obtained from the best fit), i.e., smaller than $\Delta G_2^{\ddagger}(0)$ (denoting $\Delta G_2^{\ddagger}$ for $\Delta G_2 = 0$). This corresponds to a small reorganization energy according to the Marcus theory. Similar effects have been found with complexes for which partial CT interaction has been assumed.[22]

(3) $\Delta G_2^{\ddagger}(0) = 0.17$ eV; this value is larger than the lower Rehm–Weller limit but still smaller than related values for reorganization energies reported for other electron-transfer reactions.[23]

(4) Since $k_q$, even for the simplified Scheme I, is determined by four deactivation steps of the exciplex, the assumption was made that $k_3$ and $k_4$ do not depend on $\Delta G_2$. A much stronger influence

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**Table II.** Rate Constant for Triplet Quenching of Benzophenone, $\Delta G_2$, and Quantum Yields and Half-Lives of the Radical Anion and the H-Adduct Radical[a]

| donor | solvent | $10^{-9}k_q$, $M^{-1}\,s^{-1}$ | $\Delta G_2$, eV | $\Phi_{A^-}$ | $t_{1/2}$,[b] $\mu s$ | $\Phi_{AH}$ | $t_{1/2}$,[b] $\mu s$ |
|---|---|---|---|---|---|---|---|
| **2a** | benzene | 4 (3.6) | | <0.05 | | <0.03 | |
| **2a** | acetonitrile | 6.1 (7.0) | −0.52 | 0.8 | 2 | <0.05 | ≥10 |
| **2a** | acetonitrile[c] | | | 0.7 | ≥10 | | |
| **1e** | acetonitrile | 5 (6.2) | −0.42 | 0.1 | | 0.4 | ≥20 |
| **1d** | benzene | 3.5 | | <0.05 | | 0.9 | ≥10 |
| **1d** | acetonitrile | 7.3 | −0.36 | <0.1 | 1 | 0.7 | ≈20 |
| **1c** | acetonitrile | 7 | −0.24 | <0.02 | | <0.05 | ≥10 |
| **1b** | acetonitrile | 6 (4.9) | −0.15 | <0.05 | 4 | ≤0.1 | >20 |
| **1a** | benzene | 3 | | <0.05 | | <0.05 | |
| **1a** | acetonitrile | 5.6 | −0.065 | <0.05 | | 0.1 | 30 |
| **3** | acetonitrile | 3 | −0.013 | <0.1 | | <0.1 | |
| **4** | acetonitrile | 1.0 (1.3) | +0.32 | <0.1 | | | |
| **2e** | acetonitrile | (5.1) | +0.36 | | | | |
| **2c** | acetonitrile | (1.2) | +0.54 | | | | |
| **5b** | acetonitrile | (0.3) | +0.59 | | | | |
| **5a** | acetonitrile | 0.08 (0.14) | +0.88 | | | | |
| DABCO | acetonitrile | | | 0.95 | 2 | ≤0.1 | ≥5 |
| DABCO | acetonitrile[c] | | | 0.9 | ≥5 | | |
| DMA | acetonitrile | | | 0.2 | 3 | 0.6 | ≥10 |
| TEA | acetonitrile | | | <0.05 | | 0.9 | ≥10 |

[a] In argon-saturated solutions using laser flash photolysis; values in parentheses were obtained by steady-state techniques; $E_{1/2}^{red} = -2.16$ V, $E_T = 2.95$ eV. [b] Half-life obtained for [donor] = $(2-5) \times 10^{-3}$ M; [benzophenone] = $(1-3) \times 10^{-2}$ M. [c] In the presence of about 0.4 M $LiClO_4$; $\lambda_{max} = 590$ and 600 nm for **2a** and DABCO, respectively.

of $\Delta G_2$ on $k_{-1}$ and $k_2$ than on $k_3$ seems to be justified by the solvent dependence (see below). For the pyrene/DMA system the rate constant for exciplex dissociation depends strongly on the solvent polarity whereas those for other deactivation processes are only slightly solvent dependent.[18c] Therefore, $k_2$ was calculated according to eq 9 and 10. However, also intraexciplex decay processes, such as proton transfer, may involve charge separation. An example, the photoreduction of phenyl ketones by alkylbenzenes, has recently been presented by Wagner et al.[4b]

(5) Setting the pre-exponential factor of $k_1$ to $k_{10} = 2 \times 10^{10}$ $M^{-1}\,s^{-1}$ (i.e., diffusion-controlled reaction)[18c] and that of $k_2$ to $k_{20} = 1 \times 10^{10}$ $M^{-1}\,s^{-1}$ and assuming $k_3 + k_4 = 2 \times 10^7$ $M^{-1}\,s^{-1}$, the calculated curve and the experimental data for the dependence of log $k_q$ on $\Delta G_2$ (Figure 1) are in good agreement.

In the range $-0.1 > \Delta G_2 > -0.7$ eV $k_2$ is $(0.1-5) \times 10^9$ $M^{-1}\,s^{-1}$ in acetonitrile at 25 °C, i.e., well below the diffusion-controlled limit. The exciplex lifetime, $(k_{-1} + k_2 + k_3 + k_4)^{-1}$, is calculated to be nearly constant in the whole $\Delta G_2$ range and smaller than 0.5 ns. For $\Delta G_2 < 0$ a decrease in $k_{-1}$ is essentially compensated for by an increase in $k_2$.[17a] If ion pair formation is ignored the exciplex lifetime continuously increases with $\Delta G_2$.[22]

In view of the suggestion of Freilich and Peters for quenching of triplet benzophenone[10] the proposed mechanism for quenching of the biacetyl luminescence needs some comments. According to both mechanisms formation of solvent separated ion pairs and products is the result of secondary events after the initial quenching step. However, they differ concerning the primary step. Freilich and Peters have suggested that initially a 1,4-biradical is formed which is in equilibrium with a contact ion pair.[10] On the basis of the correlation of log $k_q$ with $\Delta G_2$ (Figure 1 and Table I), we propose as primary step formation of an exciplex. The lifetime of the biacetyl exciplex should not vary significantly with the nature of the quencher (see above) whereas a $\sigma$-bond formation (1,4-biradical) should be more sensitive to structural variations of the quencher molecule than $\pi$-bonded complex formation involving CT interaction. As already mentioned by Freilich and Peters there is still evidence supporting initial CT to generate an exciplex even with aromatic ketones.[10b] On the basis of our results for biacetyl a clear distinction between formation of an exciplex with CT character and a contact ion pair is not possible even for the exergonic region.

For benzophenone in acetonitrile the $k_q$ values are close to the diffusion-controlled limit in the exergonic region, but in the endergonic region they are 2–3 orders of magnitude larger than those for biacetyl (Figure 2 and Table II). However, the slope of the linear part of log $k_q$ vs. $\Delta G_2$ ($s = -1.5$ $eV^{-1}$, i.e., 9% of the Rehm–Weller slope) is nearly the same as that for biacetyl triplet quenching. This is a typical value for luminescence quenching of ketones by electron-rich alkenes.[6b] Nevertheless, also for benzophenone it is still an open question whether formation of an exciplex according to Caldwell[7] and Wagner[8a] or a 1,4-biradical[10] is the initial step even under conditions where exergonic electron transfer is involved.

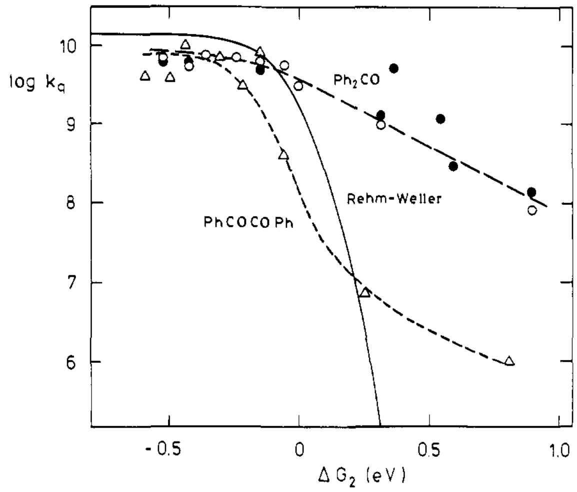

**Figure 2.** Semilogarithmic plot of the rate constant for triplet quenching of benzophenone (circles) and benzil (triangles) in acetonitrile at 25 °C as a function of the free enthalpy change for complete electron transfer; open and full symbols refer to T–T absorption and phosphorescence, respectively.

For benzil the plot of log $k_q$ vs. $\Delta G_2$ (Figure 2 and Table III) is reminiscent in some respects to the plots of the other two ketones. At $\Delta G_2 < -0.2$ eV the $k_q$ values of benzil are comparable to those for benzophenone, but they are significantly larger than those for biacetyl. On the other hand, at $\Delta G_2 > 0$ the $k_q$ values for benzophenone are similar to those for biacetyl but strikingly smaller than those for benzophenone. In particular, for benzil in the endergonic region the shape of the plot of $k_q$ vs. $\Delta G_2$ resembles that for biacetyl. The small solvent effect in the case of benzophenone, $k_q(CH_3CN)/k_q(C_6H_6) = 1.5-2.1$ for **2a**, **1a**, and **1d** (Table II) and benzil (2–2.7, Table III), supports the proposal that electron transfer is not the initial quenching step.

**Radical Anion and H-Adduct Radical.** In acetonitrile the transient absorption spectra of the triplet state of benzophenone ($^3A^*$), the diphenylhydroxymethyl radical ($A^{\bullet}H$), and the radical

**Table III.** Rate Constant for Triplet Quenching of Benzil, $\Delta G_2$, and Quantum Yield, Absorption Maximum, and Half-Life of the Radical Anion[a]

| donor | solvent | $10^{-9}k_q$, $M^{-1}\ s^{-1}$ | $\Delta G_2$, eV | $\Phi_{A^-}$ | $\lambda_{max}$, nm | $t_{1/2}$,[b] μs |
|---|---|---|---|---|---|---|
| **2a** | benzene | 2 | | <0.05 | | |
| **2a** | acetonitrile | 4 | −0.59 | 0.7 | 630 | 2 |
| **2a** | acetonitrile[c] | | | 0.7 | 550 | ≈30 |
| **1e** | acetonitrile | 4 | −0.49 | 0.5 | 630 | ≈2 |
| **1d** | benzene | 4 | | <0.05 | | |
| **1d** | tetrahydrofuran | 7 | | 0.08 | | |
| **1d** | acetone | 6 | | 0.3 | 620 | 2 |
| **1d** | acetone[c] | | | 0.5 | 550 | 20 |
| **1d** | propionitrile | | | 0.6 | 625 | 1 |
| **1d** | acetonitrile | 10 | −0.43 | 0.7 | 620 | 0.5 |
| **1d** | acetonitrile[c] | | | 0.9 | 550 | 8 |
| **1c** | acetonitrile | 7 | −0.31 | 0.2 | | 2 |
| **1b** | acetonitrile | 3 | −0.22 | <0.05 | | |
| **1a** | benzene | 3 | | <0.05 | | |
| **1a** | acetonitrile | 8 | −0.15 | 0.5 | | 1 |
| **3** | acetonitrile | 0.4 | −0.06 | <0.1 | | |
| **4** | acetonitrile | 0.007 | +0.25 | | | |
| **5a** | acetonitrile | 0.001 | +0.81 | | | |
| DABCO | acetonitrile | | | 0.6 | 630 | 2 |
| DMA | acetonitrile | | | 0.6 | 630 | 3 |
| TEA | benzene[d] | | | 0.3 | 600 | |
| TEA | acetonitrile | | | 1.0 | 610 | >50 |

[a] In argon-saturated solutions; $E_{1/2}^{red} = -1.50$ V, $E_T = 2.36$ eV; [benzil] = $(2-6) \times 10^{-2}$ M. [b] Minimum half-lives under our conditions, [donor] = $(2-5) \times 10^{-3}$ M. [c] In the presence of about 0.4 M $LiClO_4$. [d] A second transient with $\lambda_{max}$ = 490 nm is assigned to $A^{\bullet}H$.

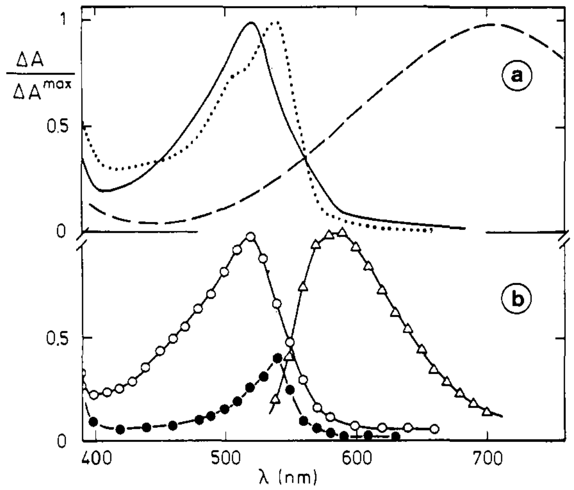

**Figure 3.** Absorption spectra with benzophenone in acetonitrile (a) of $^3A^*$ (solid line, end of pulse: ≲10 ns), of $A^{\bullet}H$ (dotted line, obtained after 1 μs in the presence of 2-propanol (≥1 M)), and of $A^{\bullet-}$ (dashed line, after 100 ns in the presence of **2a** (0.01 M)), and (b) in the presence of **1d** (0.02 M) after 20 ns (○) and 200 ns (●); fluorescence (uncorrected) of $A^{\bullet}H$ for [**1d**] = 0.2 M (△).

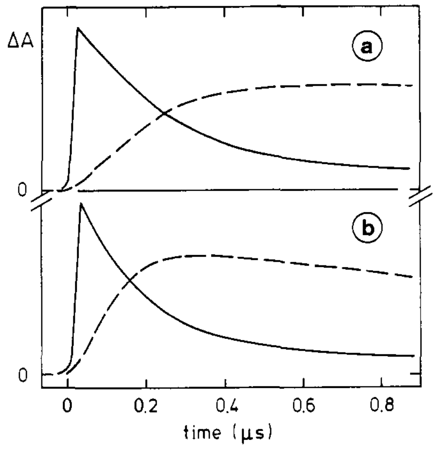

**Figure 4.** Time dependence of triplet decay (solid line) and formation of $A^{\bullet-}$ (dashed line) in acetonitrile (a) for benzophenone and **2a** ($10^{-3}$ M) and (b) for benzil and **1d** ($10^{-3}$ M).

anion ($A^{\bullet-}$) exhibit maxima at 522, 540, and 700 nm, respectively (Figure 3a). The rate constant for first-order decay of $^3A^*$ ($k_{obsd}$) depends linearly on the concentration of the donor (slope: $k_q$); for some cases (e.g., **1b** and **1e**) it is shown that the $k_q$ values, obtained from steady-state phosphorescence and pulsed laser excitation, are in good agreement (Table II). Depending on the solvent and the nature of the acceptor and the donor (HD), $A^{\bullet-}$, $A^{\bullet}H$, or both species were observed as remaining transients after triplet decay according to eq 2 and 3. The radical cation ($HD^{\bullet+}$)

$$^3A^* + HD \rightarrow A^{\bullet-} + HD^{\bullet+} \qquad (2)$$

$$^3A^* + HD \rightarrow A^{\bullet}H + D^{\bullet} \qquad (3)$$

and the radical ($D^{\bullet}$) would be expected to escape our observation due to their $\lambda_{max}$ in the UV and/or small molar absorption coefficients. For **2a** (Figure 4a) and DABCO it was shown that at a low donor concentration the rate constant for increase of the transient absorbance ($\Delta A$) of $A^{\bullet-}$ equals $k_{obsd}$. A corresponding increase of $\Delta A(A^{\bullet}H)$ is difficult to observe since the spectra of the H-addition product and $^3A^*$ are essentially overlapped. In some cases (e.g., **1d**) at high donor concentrations also the fluorescence of $A^{\bullet}H$[24] was observed (Figure 3b).

The quantum yields of formation of $A^{\bullet}H$ ($\phi_{AH}$) and $A^{\bullet-}$ ($\phi_{A^-}$), obtained from $\Delta A$ values after decay of the benzophenone triplet (see Experimental Section), show the following trend. In acetonitrile $\phi_{A^-}$ is large for DABCO, DMA (cf. ref 9 and 12a), and **2a** but only approximately 0.1 or less for 1,3-dioxoles (Table II). $\phi_{AH}$ decreases in the order **1d**, **1e**, **1a** and is below the detection limit for the others. Since $\phi_{AH}$ and $\phi_{A^-}$ do not show a common trend, we conclude that hydrogen abstraction and electron transfer, although they may compete, are affected by different parameters. In solvents of lower polarity (benzene, 1,2-dichloroethane), $\phi_{A^-}$ (obtained with **1e**) is even smaller than in acetonitrile. Addition of 0.4 M $LiClO_4$ (special salt effect, cf. ref 13) to benzophenone and **2a** in acetonitrile leads to a longer half-life ($t_{1/2}$) of $A^{\bullet-}$ and causes a blue-shift of about 100 nm for the absorption maximum of $A^{\bullet-}$ without changing $\Delta A$ markedly. Similar results were found with DABCO (Table II) but no enhancing effect on $\Delta A(A^{\bullet-})$ with **1a**, contrasting the case of benzil and 1,3-dioxoles (see below). The hypsochromic shift and the prolonged half-life can be explained by the formation of a contact ion pair between $A^{\bullet-}$ and $Li^+$ (ion pair exchange).[13]

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(24) (a) Arimitsu, S.; Tsubomura, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1357. (b) Hodgson, B. W.; Keene, J. P.; Land, E. J.; Swallow, A. J. *J. Chem. Phys.* **1975**, *63*, 3671.

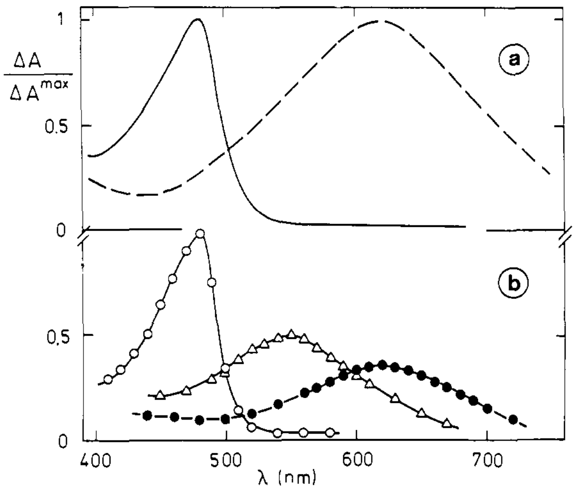


**Figure 5.** Absorption spectra with benzil (a) of $^3A^*$ (solid line, end of pulse) and of $A^{\bullet -}$ (dashed line, after 100 ns in the presence of **2a** (0.01 M)) in acetonitrile, and (b) in acetone in the presence of **1d** (0.02 M) (O, end of pulse) and after 200 ns in the absence (●) and presence (Δ) of $LiClO_4$ (0.4 M).

For benzil in acetonitrile $^3A^*$ and $A^{\bullet -}$ exhibit maxima at 480 and around 600 nm, respectively (Figure 5a).[25] The parallel behavior of the decay of triplet benzil and increase of $A^{\bullet -}$ is shown for quenching by **1d** (Figure 4b). The $k_q$ values are below the diffusion-controlled limit, and the solvent effect ($k_q(CH_3CN)/k_q(C_6H_6)$ = 2.0–2.7 for **1a**, **1d**, and **2a**) is comparable to the case of benzophenone. $\phi_{A^-}$ is set to unity for TEA (see: Laser Flash Photolysis) and is smaller but substantial for several electron-rich alkenes (Table III). Addition of $LiClO_4$ leads to higher $\phi_{A^-}$ values for alkenes and, as with benzophenone, to a blue-shift of $\lambda_{max}(A^{\bullet -})$ and a longer half-life of $A^{\bullet -}$ (Figure 5b). On decreasing the solvent polarity $\phi_{A^-}$ becomes much smaller. Because of the low solubility of $LiClO_4$ in less polar solvents a possible enhancement of $\phi_{A^-}$ by utilizing the special salt effect could not be verified either for benzophenone or for benzil. It should be emphasized that the effect of solvent polarity on $\phi_{A^-}$ (e.g., for **1d**) is markedly larger for benzil than for benzophenone.

Whereas $A^\bullet H$ (benzoylphenylhydroxymethyl) was observed for benzil and TEA in benzene ($\lambda_{max}$ = 490 nm),[17b] this species could not be detected with **1d** as donor, i.e., H-transfer plays virtually no role for the dioxoles. Furthermore, quenching of benzophenone triplet by 2-propanol yields in acetonitrile only $A^\bullet H$ (Figure 3a) but for benzil $A^\bullet H$ could not be detected even in pure 2-propanol. These observations are in accordance with the fact that benzil ($pK_a$ = 5.5) is a weaker H-abstractor than benzophenone ($pK_a$ = 9.3), as suggested by the difference in the $pK_a$ values for dissociation of the respective ketyl radicals.[17,25]

$$R_2\dot{C}{-}O^- + HD^{\bullet +} \rightleftharpoons R_2\dot{C}{-}OH + D^\bullet \qquad (4)$$

Corresponding electron-transfer and/or H-abstraction studies with biacetyl were unsuccessful under our conditions due to the overlap of the absorption spectra of eventual transients (e.g., $^3A^*$ or $A^{\bullet -}$)[26a] with that of the ground state.

In order to investigate the decay kinetics of radical anions and cations simultaneously, the triplet state of chloranil (tetrachloro-*p*-benzoquinone) in acetonitrile was quenched by 1-methoxy-2,2-diphenylethene (**2f**). The two species, observed after decay of the chloranil triplet ($\lambda_{max}$ around 500 nm), are assigned to its radical anion ($\lambda_{max}$ = 440 nm)[26b] and the radical cation of the ethene ($\lambda_{max}$ = 660 nm and a second one below 380 nm which was not kinetically evaluated). Thus, in this case both radical ions (eq 2) could be detected. A second-order decay law with identical half-lives for the two radical ions (in the $\mu$s range under our conditions) shows that their decay is coupled as expected for electron back-transfer. Addition of $LiClO_4$ (0.1 M) increases their half-lives by a factor of about 10. For benzophenone and benzil such effects with **2f** would be difficult to observe due to spectral overlap of $A^{\bullet -}$ and $D^{\bullet +}$.

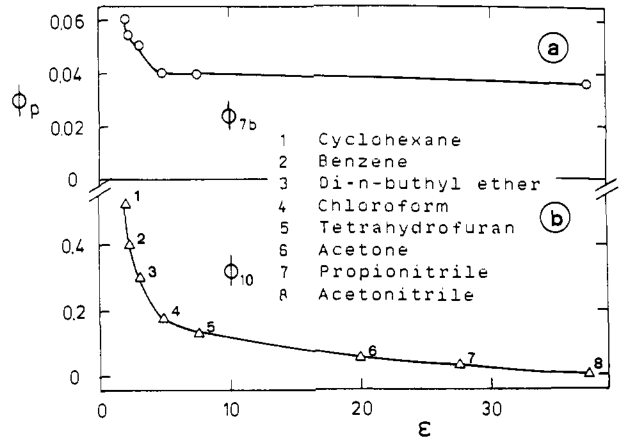
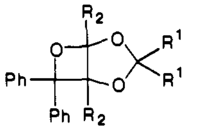
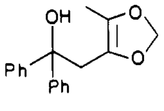


**Figure 6.** Dependence of the quantum yield of oxetane formation on the dielectric constant for triplet quenching of (a) benzophenone by **1b** ($\phi_{7b}$, O) and (b) benzil by **1d** ($\phi_{10}$, Δ).

**Solvent Effect on Product Formation.** Oxetanes and H-abstraction products are the photoproducts from biacetyl and olefins **1** and **2b**.[15b–d] The photoproducts of the reaction of 1,3-dioxoles with benzophenone are oxetanes and H-abstraction products as well. The solvent effect on the quantum yield ($\phi_p$) of oxetane formation from benzophenone is the same for **7a** (observed with **1a**) and **7b** (observed with **1b**). $\phi_7$ decreases by up to 60% with an increase in the solvent polarity (Figure 6a). Benzpinacole is another photoproduct from benzophenone and **1a** or **1d**, but it was not found for **1b**. In the case of **1d**, in addition to benzpinacole, only **8** and **9** were isolated. A solvent effect on the formation of H-abstraction products could not be detected. This indicates that CT is unimportant for the H-transfer to benzophenone and that proton transfer is not subsequent to electron transfer. This is further supported by the high $k_q$ values for 2,3-dimethyl-2-butene (**2e**) and 1-methylcyclohexene (**5b**) which do not fall on the log $k_q$ vs. $\Delta G_2$ correlation (Figure 2).



**7a**: $R_1 = R_2 = H$
**7b**: $R_1 = CH_3$; $R_2 = H$



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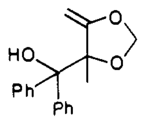
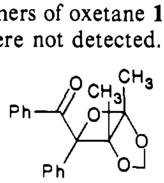
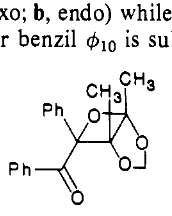


**9**

Singlet as well as triplet quenching of benzil by **1d** yields only the two isomers of oxetane **10** (**a**, exo; **b**, endo) while H-transfer products were not detected.[17] For benzil $\phi_{10}$ is substantial in



**10a**



**10b**

nonpolar solvents and decreases with an increase in the solvent polarity (Figure 6b) in a similar manner as $\phi_7$ in the case of benzophenone (Figure 6a), but the total change of $\phi_{10}$ is much larger than that of $\phi_{7b}$. This is in line with the result that the solvent polarity has a much larger effect on $\phi_{A^-}$ for benzil than for benzophenone (see above). Nevertheless, one should not expect a perfect relationship between $\phi_p$ and ($1 - \phi_{A^-}$) since other processes (e.g., electron back-transfer) may be involved.

The accordance of the solvent dependence on $\phi_p$ with the $\Delta G_2$ values is an indication for the competition between product for-

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mation and formation of radical ions. This is further supported by an analysis of the solvent dependence according to a method which has been described by Mashuhara et al.[27] For biacetyl/olefin systems the results of such an analysis have been recently reported.[16] In this respect benzophenone and benzil behave similarly.[17]

## Conclusion

Formation of a radical ion pair is an important pathway for the photoreactions of the three examined ketones with electron-rich alkenes if the free enthalpy for electron transfer in the triplet state ($\Delta G_2$) is smaller than zero. T–T absorption and luminescence quenching studies indicate that electron transfer is not the primary step. The assumption of an intermediate with less charge separation, such as an exciplex, may explain the correlation of log $k_q$ vs. $\Delta G_2$ for quenching of excited biacetyl and benzil. For the benzophenone/olefin system a clear distinction between an exciplex and a 1,4-biradical, as proposed by Freilich and Peters,[10] is not yet possible from our results. These intermediates may decay to either radical pairs or stable photoproducts. The competition between both processes is indicated by the solvent effect on their yields. We have measured on a nanosecond time scale the yields of H-adduct radical and radical anion formation and their half-lives. For benzophenone H-transfer is the dominant process for triplet quenching by most of the alkenes examined. For the benzil/olefin system the yield (up to unity) and the half-life (in the $\mu$s range) of the radical anion are large enough to allow interception of the radical ions in a bimolecular reaction[14b] (e.g., cycloaddition).

## Experimental Section

**Materials.** Alkenes **1a–e**, **2a–f**, and **3** were prepared according to literature procedures.[28] All other alkenes (Aldrich), TEA, and DMA were purified by distillation under nitrogen, and DABCO was sublimed. Biacetyl (Aldrich) was purified by distillation; benzophenone, benzil (both Aldrich), and chloranil (Fluka) were recrystallized twice from ethanol, methanol, and benzene, respectively; tetra-*n*-butylammonium tetrafluoroborate was recrystallized from ethyl acetate and dried at 0.1 Torr.

The following solvents were from Merck (Uvasol): tetrahydrofuran was freshly distilled from sodium before use, acetone and 1,2-dichloroethane were filtered over basic $Al_2O_3$, and cyclohexane, benzene, and acetonitrile were used as received. Propionitrile (Aldrich) was distilled from calcium hydride and passed through a column of basic $Al_2O_3$.

**Redox Potentials.** Half-peak redox potentials were obtained by cyclic voltametry at a platinum electrode and an Ag/0.1 M $AgNO_3$ reference electrode (concentration $10^{-3}$ M). Tetra-*n*-butylammonium terafluoroborate (0.1 M) was used as supporting electrolyte and acetonitrile as solvent was dried by filtration over basic $Al_2O_3$ (activated at 300 °C, 0.1 Torr). The scan speed was 100 mV/s; half-peak potentials were taken as the half-wave potentials [17] For **1d** and **1e** virtually total reversibility was obtained; the spacing between the peak and the half-peak potentials is 60 ± 5 mV.[29] While the multiple substituted 1,3-dioxoles exhibit at least the reduction peak, most of the other olefins examined show irreversible electrochemical oxidation curves. Nevertheless, according to Arnold and Humphreys the data are applicable for the correlation between log $k_q$ and $\Delta G_2$ since the electrochemical data show a deviation of only ±60 mV.[30]

**Luminescence Quenching.** The luminescence spectra were recorded on a spectrofluorimeter (Perkin-Elmer, MPF-3) at 20 °C. Samples containing a given ketone and quencher were deoxygenated by bubbling argon through the solutions in triangular cuvettes[31] for 5 min. Under our conditions the triplet lifetime of benzophenone (0.1 M) in acetonitrile, as measured by single photon counting (for a description of the setup, cf. ref 29b), is 3.5 ± 0.2 $\mu$s. A detailed determination of the luminescence lifetimes of biacetyl has been described elsewhere.[31c] The Stern–Volmer relationships have been measured over a concentration range with a factor of at least 10 for electron-rich and a factor of 50 for normal and electron-deficient olefins. No deviations other than statistical ones have been observed (maximum deviation ±10%). The limit for measuring the rate constants of quenching of the biacetyl phosphorescence was reached with **1c**. Attempts to determine $k_q$ values of even stronger donor olefins failed due to their fast reactions during irradiation in the spectrofluorimeter.

**Laser Flash Photolysis.** The laser photolysis setup has already been described.[32] For excitation at 353 nm the third harmonic of a neodymium laser (J.K. Lasers, pulse width 10–15 ns) and for data analysis a transient digitizer (Tektronix R 7912) and a computer (PDP 11/04) were used. The measurements were carried out at 24 ± 2 °C; the samples were purged with argon before and after addition of a donor in appropriate concentrations.

The ketone concentrations were adjusted to an absorbance of 0.1–0.2 at 353 nm in 1 mm (range of overlap with the analyzing light beam). In the presence of a donor and (if necessary) after substraction of a constant $\Delta A$ (due to the contribution of a long-lived transient) the decay kinetics followed a first-order law throughout. Values of $k_q$ were obtained from linear plots of $k_{obsd}$ (at $\lambda_{max}$ of the T–T absorption, up to $3 \times 10^7$ $s^{-1}$) vs. [D] (typical error ±10%). The quantum yields were obtained after quenching the ketone triplet to 20–200 ns, i.e., under conditions where 90–99% of $^3A^*$ is quenched.

For benzophenone $\phi_{A^-}$ was calculated from the ratio of the absorptions of $A^{\bullet -}$ (at $\lambda_{max}$ after triplet decay and correction for 100% triplet quenching) and $^3A^*$ (<10 ns after the pulse) since the molar absorption coefficients are virtually the same; $\epsilon_{TT} = 7.6 \times 10^3$ and $\epsilon(A^{\bullet -}) = 7 \times 10^3$ $M^{-1}$ $cm^{-1}$: for $A^{\bullet}H$ $\epsilon_{540} = 3.2 \times 10^3$ $M^{-1}$ $cm^{-1}$ was assumed.[11c,12b] Although the absorption spectrum of $A^{\bullet -}$ extends also to <500 nm, the spectrum of $A^{\bullet}H$ which appears in some cases (e.g., for DMA) together with that of $A^{\bullet -}$ could be separated due to the generally longer half-life of $A^{\bullet}H$. For a typical case in acetonitrile the yields of $^3A^*$, $A^{\bullet -}$, and $A^{\bullet}H$ were measured (at the appropriate maxima) ≤10 ns, 200–500 ns, and 1–10 $\mu$s after the laser pulse, respectively. It should be noted that fluorescence from $A^{\bullet}H$[24] was only achieved at high [D] corresponding to a triplet lifetime of smaller than the laser pulse.

For benzil $\epsilon_{TT} = 8.4 \times 10^3$ $M^{-1}$ $cm^{-1}$ was used[25c] and $\epsilon(A^{\bullet -}) = 8 \times 10^3$ $M^{-1}$ $cm^{-1}$ was assumed on the basis of $\phi_{A^-} = 1$ for TEA (Table III). It was also assumed that $\epsilon(A^{\bullet -})$ is not changed on addition of $LiClO_4$. Since fluorescence quenching may contribute to the electron transfer for benzil at high [amine], e.g., Stern–Volmer constants of 20 (TEA) to 50 (DMA) $M^{-1}$ were obtained, $[D]^{-1} \gg K_{SV}$ was used.

**Photoproducts.** The photoproducts from biacetyl and 1,3-dioxoles **1** and **2b** are described in a full account elsewhere[15d] (see also ref 15a–c). For isolation of the photoproducts 0.1–0.3 M benzophenone or benzil and 0.3 M alkene were irradiated in benzene with a high-pressure mercury lamp (Philips HPK 125 W) under nitrogen and cooling with water. For benzophenone an UVW 55 Dema filter ($T_{max}$ = 360 nm) and for benzil a cut-off filter ($\lambda$ = 400 nm) were used. The product formation was monitored by GC: Carlo Erba Fractovap 2101, Spectra Physics Integrator SP 4000 and Interface Sp 4020, 4 m 5% OV 17 on Chromosorb WAW DMCS 80/100. **I**solation of products was by preparative HPLC: pump 303, manometric module 803, UV detector spectrochrome (all Gilson), differential refractometer (Bischoff), 26 cm column 7$\mu$ LiChrosorb Si 60 (Bischoff) using mixtures of *n*-hexane and ethyl acetate. The products were identified by $^1H$ NMR (Varian EM-390 and T-60) and $^{13}C$ NMR (Varian CFT-20).

Values of $\phi_p$ were determined with an irradiation setup and the potassium ferrioxalate actinometer.[33a] For the solvent dependence of $\phi_p$ a merry-go-round apparatus was used. The oxetane formation was measured by GC and H-abstraction products by analytic HPLC (Perkin-Elmer LC-65T detector/oven module, the corresponding microprocessor-controlled pump module (series 3), and differential refractometers). All products show the expected microanalytical data within ±0.25% for C and ±0.15% for H.

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**Benzophenone and 2,2-Dimethyl-1,3-dioxole (1b).** The reaction mixture contained only one product according to chromatographic analyses. Even benzpinacole was not formed as shown by comparison with an authentic sample.[33b] After filtration of a solution in *n*-hexane/ethyl acetate (98/2) over silica gel (Woelm, Si 100/200) the product was further purified by means of HPLC and identified as 3,3-dimethyl-7,7-diphenyl-2,4,6-trioxabicyclo[3.2.0]heptane, **7b**. $^1H$ NMR ($CCl_4$) $\delta$ 1.09 (s, 3 H, $CH_3$), 1.31 (s, 3 H, $CH_3$), 5.12 (d, $J = 3.2$ Hz, 1 H, OCH), 5.98 (d, $J = 3.2$ Hz, 1 H, $O_2CH$), 7.00–7.52 (m, 10 H, $C_6H_5$).

**Benzophenone and 1,3-Dioxole (1a).** The reaction mixture was composed of two photoproducts (0.97:1 in benzene; 0.69:1 in acetonitrile). Both products were isolated by means of HPLC with *n*-hexane/ethyl acetate (95/5) as eluate. The major product was identified as benzpinacole[33b] and the minor one as 7,7-diphenyl-2,4,6-trioxabicyclo[3.2.0]heptane, **7a**. $^1H$ NMR ($CCl_4$) $\delta$ 4.57 (d, $J = 2.7$ Hz, 1 H, OCH), 5.08 (s, 2 H, $OCH_2O$), 6.07 (d, $J = 2.7$ Hz, 1 H, $O_2CH$), 7.13–7.51 (m, 10 H, $C_6H_5$).

**Benzophenone and 4,5-Dimethyl-1,3-dioxole (1d).** After irradiation the solvent was removed by distillation. Three products were formed in a 25:5:1 ratio. Benzpinacole[33b] (main product) crystallized upon addition of *n*-hexane/ethyl acetate (95:5) to the residue and was removed by filtration. After filtration over basic aluminum oxide (Woelm) the products were isolated by HPLC. 4-(2,2-Diphenyl-2-hydroxyethyl)-5-methyl-1,3-dioxole, **8** (minor component of mixed adducts): $^1H$ NMR ($CDCl_3$) $\delta$ 1.36 (s, 3 H, $CH_3$), 1.74 (s, 2 H, $CH_2$), 2.40 (s, 1 H, OH), 5.09 and 5.38 (2 s, 2 H, $OCH_2O$), 7.07–7.80 (m, 10 H, $C_6H_5$).

**4-(Diphenylhydroxymethyl)-4-methyl-5-methylene-1,3-dioxolane (9)** (main component): colorless oil; $^1H$ NMR ($CDCl_3$) $\delta$ 1.48 (s, 3 H, $CH_3$), 2.81 (s, 1 H, OH), 4.02 and 4.38 (2 d, $J = 1.8$ Hz, 2 H, $=CH_2$), 4.47 and 4.90 (2 d, $J = 1.2$ Hz, 2 H, $OCH_2O$), 7.03–7.83 (m, 10 H, $C_6H_5$).

**Benzil and 4,5-Dimethyl-1,3-dioxole (1d).** Only two products were formed in a 3.5:1 (1:0.9) ratio in benzene (acetonitrile). A pinacole from benzil could not be detected, even by comparing with an authentic sample.[33c] The products were identified as oxetanes. The stereochemistry was assigned in analogy to the exo and endo oxetanes which had been obtained from **1d** and 1-phenyl-1,2-propandione.[17b]

**7-(*exo*-Benzoyl)-7-phenyl-1,5-dimethyl-2,4,6-trioxabicyclo[3.2.0]heptane (10a)**: major adduct in benzene; colorless oil; $^1H$ NMR ($CDCl_3$) $\delta$ ($CCl_4$) 1.40 (s, 3 H, $CH_3$), 1.53 (s, 3 H, $CH_3$), 4.55 and 4.90 (2 s, 2 H, $OCH_2O$), 7.15–7.73 (m, 8 H, $C_6H_5$), 7.92–8.13 (m, 2 H, *o*-$C_6H_5$). **7-(*endo*-Benzoyl)-7-phenyl-1,5-dimethyl-2,4,6-trioxabicyclo[3.2.0]heptane (10b)**: minor adduct in benzene; colorless oil; $^1H$ NMR ($CDCl_3$) $\delta$ 1.10 (s, 3 H, $CH_3$), 1.54 (s, 3 H, $CH_3$), 4.70 and 5.09 (2 s, 2 H, $OCH_2O$), 7.07–7.47 (m, 6 H, $C_6H_5$), 7.59–7.93 (m, 4 H, *o*-$C_6H_5$).

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## Appendix

According to Scheme I the rate constant for quenching of the excited ketone is given by eq 5.

$$k_q = \frac{k_1(k_2 + k_3 + k_4)}{k_{-1} + k_2 + k_3 + k_4} \tag{5}$$

The free enthalpy for exciplex formation is defined by eq 6.

$$K_{ex} = \frac{k_1}{k_{-1}} = \exp\frac{-\Delta G_{ex}}{RT} \tag{6}$$

$\Delta G_{ex}$ depends on $\Delta G_2$ and the slope of the plot of log $k_q$ vs. $\Delta G_2$ according to eq 7.[4a,22]

$$\Delta G_{ex} = s\Delta G_2/17 \text{ eV}^{-1} \tag{7}$$

The free activation enthalpy for exciplex formation ($\Delta G_1^{\ddagger}$) which is needed for the calculation of $k_q$ according to eq 5 was obtained in analogy with the calculation of $\Delta G_2^{\ddagger}$ by Rehm and Weller.[18a]

$$\Delta G_1^{\ddagger} = \frac{\Delta G_{ex}}{2} + \left[\left(\frac{\Delta G_{ex}}{2}\right)^2 + \Delta G_1^{\ddagger}(0)^2\right]^{1/2} \tag{8}$$

$$k_2 = k_{20} \exp(-\Delta G_2^{\ddagger}/RT) \tag{9}$$

$$\Delta G_2^{\ddagger} = \frac{\Delta G_2}{2} + \left[\left(\frac{\Delta G_2}{2}\right)^2 + \Delta G_2^{\ddagger}(0)^2\right]^{1/2} \tag{10}$$

**Registry No. 1a**, 288-53-9; **1b**, 22945-10-4; **1c**, 14738-96-6; **1d**, 85976-13-2; **1e**, 85976-14-3; **2a**, 40923-93-1; **2b**, 2678-54-8; **2c**, 109-92-2; **2d**, 26327-98-0; **2e**, 563-79-1; **2f**, 40237-72-7; **3**, 543-75-9; **4**, 110-87-2; **5a**, 110-83-8; **5b**, 591-49-1; **6**, 693-89-0; biacetyl, 431-03-8; benzophenone, 119-61-9; benzil, 134-81-6.

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# External Heavy-Atom Effects on First and Second Order Decay Rate Constants of Anthracene Triplets

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**Abstract:** Second order rate constants for quenching of anthracene triplets, $^3A^*$, by methyl iodide, MeI, in benzene and ethyl iodide, EtI, in methylcyclohexane, determined flash kinetically, are $(3.3_0 \pm 0.2_7) \times 10^2$ and $(4.4_6 \pm 0.3_2) \times 10^2$ $M^{-1}$ $s^{-1}$ at 25 ± 2 °C. Use of ferrocene, Fe, as a second quencher in methylcyclohexane leads to strictly additive quenching, $k_{Fe} = (5.0_8 \pm 0.14) \times 10^9$ $M^{-1}$ $s^{-1}$, and, contrary to an earlier report, provides no kinetic evidence for the intervention of an A/EtI triplet exciplex. $^3A^*$ quenching by ground-state anthracene (self-quenching), $k_{sq} = (2.77 \pm 0.09) \times 10^5$ $M^{-1}$ $s^{-1}$, and by MeI are also strictly additive processes in benzene, providing no kinetic evidence for the intervention of a sufficiently long-lived triplet excimer in the self-quenching process. A pronounced increase in the efficiency of A triplet–triplet annihilation observed with [MeI] $\gtrsim$ 2 M in benzene provides strong evidence for interconversion of quintet, triplet, and singlet sublevels of the triplet encounter pairs through heavy–atom enhanced spin–orbit coupling.

It is well established by spectroscopic observations that interaction of solute molecules with molecules containing heavy atoms increases the probabilities of radiative and nonradiative singlet-triplet transitions.[1] This phenomenon is known as the external heavy-atom (Kasha[2]) effect and is attributed to enhanced spin-orbital coupling. In photochemistry, the external heavy-atom (H-A) effect on $S_1 \rightarrow T$ intersystem crossing has been shown to reduce yields of singlet-derived products while enhancing yields of triplet-derived products.[3] At high mol % of H-A addend, triplet product quantum yields decrease due to significant, though less

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