was catalyzed. In homogeneous solution, reaction 11 is

$$2\mathrm{Cu}^{+} \to \mathrm{Cu}^{0}(\mathrm{aq}) + \mathrm{Cu}^{2+}$$
(11)

highly endoergic, the standard potential of the  $Cu^+/Cu^0$ -(aq) redox system being as negative as -2.7 V.<sup>8</sup> A copper atom formed at the surface of a colloidal silver particle is expected to behave like an atom at the surface of a copper electrode in Cu<sup>+</sup> solution, the standard potential of the latter being 0.52 V.

4.4. General Conclusions. The reactions described resemble electrochemical reactions at compact metal electrodes. An essential feature of an ordinary electrochemical reaction is its dependence on the position of the Fermi level in the electrode, i.e., on the applied potential. For colloidal metal particles in solution, no outer potential can actually be applied. The position of the Fermi level in these particles is controlled by the ions that are present in the solution and, when radicals are produced, by the accumulation of electrons transferred to the colloid by shortlived reactive species. The catalyzed free-radical reactions observed are typical examples of the kind of electrochemistry occurring in colloidal solutions. They also highlight the need to use electrochemical considerations in order to understand them. The catalytic action of colloidal metals in redox processes was, in principle, recognized many decades ago. However, the chemistry of free radicals in solution had not been sufficiently developed at that time to allow one to discuss free-radical reactions in colloidal solutions in a detailed manner. The combination of modern free-radical chemistry and colloidal chemistry

should lead to a better understanding of the catalytic action of colloids, as well as to an extension of the chemistry that is known for radicals in homogeneous solution.

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# Self-Termination of Benzoyl Radicals to Ground- and Excited-State Benzil. Symmetry **Control of a Radical Combination**

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Benzoyl radicals ( $C_6H_5CO$ ) are generated in liquid solutions together with tert-butyl radicals by photocleavage of pivalophenone. The rate constant for their termination to benzil is determined by ESR and optical spectroscopy. It is well described by von Smoluchowski's equation employing a spin-statistical factor of 1/4. Energetically, the combination may lead to ground- and excited-state benzil. The latter reaction is ruled out by the kinetic data and the absence of recombination luminescence. Auxiliary data are presented on the photochemistry of pivalophenone and on the photophysics of benzil.

Many transient free radicals combine in solution with rate constants k of the order of magnitude expected for rate control by translational diffusion.<sup>1-4</sup> However, because of experimental and theoretical difficulties, the exact extent of diffusion control and the average number of unsuccessfull encounters have often been subject to speculation. Recently,<sup>5-7</sup> we have determined the rate constants for self-termination of two carbon-centered radicals, tert-butyl and benzyl, by kinetic ESR spectroscopy. For many solvents and over wide ranges of viscosity and temperature, the data were perfectly described by the von Smoluchowski equation (eq 1) within the error limits

> $2k = 8\pi (10^{-3}) N_{\rm L} \sigma D \rho$ (1)

 $(\pm 50\%$  absolute) when the following procedure for esti-

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mating the unknowns was applied.<sup>6,7</sup> The diffusion coefficient D of the radical R in the particular solvent was approximated by that of the hydrocarbon RH. The reaction distance  $\rho$  was estimated from molecular or molar volumes. Further, a spin-statistical factor  $\sigma = 1/4$  was adopted, since energetically the reactions considered can lead only to the formation of ground-state products, so that  $/_4$  of the encounters, i.e., those of triplet radical pairs, were considered unreactive. The same procedure has been applied successfully also by other authors to other systems<sup>8,9</sup> and indicates complete control by diffusion and spin statistics.

In this paper we consider the case of a radical self-termination where the product may also be formed in an excited triplet and possibly an excited singlet state. For

this situation we expect  $\sigma = 1$  in eq 1 and the appearance of recombination luminescence. In radical-ion reactions involving reverse electron transfer, the formation of excited triplet besides ground-state singlet products has amply been demonstrated.<sup>10,11</sup> In the field of neutral radicals, such terminations seem feasible for acvl radicals RCO, and, in fact, the formation of excited singlet<sup>12</sup> and/or triplet-state diketones<sup>13,14</sup> has been postulated<sup>12,13</sup> or mentioned as possible.<sup>14</sup> Of the possibly many suitable reactions, we have chosen the self-termination of benzoyl PhCO to benzil.<sup>15</sup> This radical is generated simultaneously with tert-butyl by photolysis of pivalophenone in non-hydrogen-donating solvents which provide a relatively simple reaction scheme. By ESR we determine the rate constant of benzoyl self-termination relative to that of tert-butyl, which has previously been shown<sup>5,6</sup> to obey eq 1 with  $\sigma =$  $1/_4$ , and combine the results with diffusion coefficients and reaction diameters to evaluate  $\sigma$  for the benzoyl termination. Energy estimates show that the reaction to the lowest triplet state of benzil should be exergonic by  $\simeq 10$  kcal/ mol, and it is known that this state phosphoresces.<sup>16</sup> Therefore, we also search for a luminescence due to radical termination by applying a modulated optical spectroscopy technique. This part of the study also yields the absorption spectrum of benzoyl, its termination kinetics, and some information on the photophysical behavior of benzil.

Surprisingly, at first sight, the ESR and the optical work both indicate that the expected termination of benzoyl to triplet-state benzil does not occur to a measurable extent ( $\ll 3\%$ ). However, one may note that the lowest excited states of benzil have  $n\pi^*$  character<sup>16</sup> and are thus antisymmetric with respect to the dicarbonyl plane. On the other hand, benzoyl is a  $\sigma$ -type radical,<sup>17</sup> and the diradical states of two reacting benzoyls  $D_{\sigma\sigma}$  will be symmetric to this plane. Therefore, diradical and product excited states do not correlate, and our finding agrees with a state-symmetry control<sup>18</sup> of the reaction.

#### Results

Radical Reactions during Photolysis of Pivalophenone in tert-Butyl Alcohol. As has previously been shown from product studies,<sup>19</sup> from ESR observations of benzoyl and tert-butyl,<sup>20</sup> and by CIDNP,<sup>21</sup> pivalophenone excited in the  $n\pi^*$  transition band (310  $\leq \lambda \leq$  380 nm) undergoes  $\alpha$ cleavage from the triplet state in non-hydrogen-donor solvents with a quantum yield  $\phi \simeq 0.3$ .<sup>19b</sup> Thus, the following free-radical reactions occur:

$$PhCOC(CH_3)_3 \xrightarrow{h\nu} Ph\dot{C}O + \dot{C}(CH_3)_3$$
(2)

$$2\dot{C}(CH_3)_3 \xrightarrow{\kappa_{14}} HC(CH_3)_3 + CH_2 \xrightarrow{\kappa_{14}} C(CH_3)_2 \quad (3)$$

$$\xrightarrow{\kappa_{1c}} (CH_3)_3 CC(CH_3)_3 \tag{4}$$

$$2Ph\dot{C}O \xrightarrow{\kappa_2} PhCOCOPh \tag{5}$$

$$Ph\dot{C}O + \dot{C}(CH_3)_3 \xrightarrow{\kappa_{zd}} PhCHO + CH_2 = C(CH_3)_2 \qquad (6)$$

$$\xrightarrow{n_{\infty}} PhCOC(CH_3)_3 \tag{7}$$

The previous studies<sup>19</sup> indicate further reactions which could blurr our kinetic analysis. In particular, for high ketone conversion<sup>19a</sup> only traces of benzil and equal amounts of isobutene and isobutane were found, and a decrease of the yield of benzaldehyde with increasing ketone conversion was noted.<sup>19b</sup> Therefore, we have restudied the product distribution of a photolysis at 365 nm of pivalophenone 0.05 M in *tert*-butyl alcohol and at  $21 \pm 1$  °C for two ketone conversions. The results are given in Table

TABLE I:	<b>Reaction Products of Pivalophenone</b>	
Photolysis	in tert-Butyl Alcohol in mM $(\pm 0.01)$	



Figure 1. ESR spectrum obtained during photolysis of pivalophenone in 3-methyl-3-pentanol showing the presence of *tert*-butyl (sharp lines) and benzoyl (broad triplet) radicals.

I together with entries referring to the material balance of *tert*-butyl and benzoyl groups, and two product ratios which should be equal to one if reactions 2–7 are the only important ones. Obviously, for the higher (7%) conversion the consistency of the product distribution with the reaction scheme is poor though we have not detected further products by GLC.<sup>22</sup> The low yield of benzil indicates that this product is suppressed by further reactions. For low conversion (1%) the product distribution agrees fairly well with expectation, and reactions 2–7 are the only ones to be considered. Consequently, we have applied low conversions in all quantitative experiments.

Some features of the data deserve further comment. From the average ratio of isobutane to hexamethylethane, the ratio of disproportionation to combination of *tert*-butyl is 11, which compares favorably with values around 10 determined for solvents of similar viscosities.<sup>23</sup> The yield of benzaldehyde is ~20% smaller than twice the sum of the yields of isobutane and hexamethylethane. This reflects the disproportionation-to-combination ratio<sup>21</sup> of ~4-5 for the cross-terminations.<sup>6,7</sup> Finally, from the conversion the quantum yield for reaction 2 ( $\lambda = 365$  nm) is estimated as  $\phi = 0.38 \pm 0.06$ , which agrees with the literature data.<sup>19b</sup>

Ratios of the Self-Termination Rate Constants, Diffusion Coefficients, Reaction Diameters, and Spin-Statistical Factors of Benzoyl and tert-Butyl. Solutions of pivalophenone (0.05 M) in 3-methyl-3-pentanol were continuously photolyzed in the ESR flow arrangement described earlier.<sup>67,24</sup> Figure 1 shows an ESR spectrum which reveals the presence of tert-butyl and benzoyl radicals. Under the steady-state conditions employed the concentrations of the two radicals tert-butyl ( $R_1$ ) and benzoyl ( $R_2$ ) are governed by eq 8 and 9, where I is the rate of radical

$$d[R_1]/dt = 0 = I - 2k_1[R_1]^2 - k_x[R_1][R_2]$$
(8)

$$d[R_2]/dt = 0 = I - 2k_2[R_2]^2 - k_x[R_1][R_2]$$
(9)

formation 2, and  $k_1 = k_{1c} + k_{1d}$ ,  $k_x = k_{xc} + k_{xd}$ . Equations 8 and 9 lead to eq 10. Obviously, the determination of

$$[\mathbf{R}_1]/[\mathbf{R}_2] = (k_2/k_1)^{1/2}$$
 (10)

Self-Termination of Benzoyl Radicals



Figure 2. Expansions of parts of Figure 1: (a) second-order components of *tert*-butyl; (b) benzoyl spectrum.

TABLE II: Ratios of Radical Concentrations, Termination Rate Constants, Diffusion Coefficients, and Spin-Statistical Factors for *tert*-Butyl ( $R_1$ ) and Benzoyl ( $R_2$ ) in 3-Methyl-3-pentanol<sup>a</sup>

	10 °C	22 °C	34 °C
$[R_1]/[R_2]k_2/k_1106D_1, cm2/s106D_2, cm2/s\sigma_2/\sigma_1$	$\begin{array}{c} 0.90 \pm 0.10 \\ 0.81 \\ 3.62 \pm 0.13 \\ 2.95 \pm 0.13 \\ 0.95 \end{array}$	$\begin{array}{c} 0.91 \pm 0.10 \\ 0.83 \\ 5.77 \pm 0.10 \\ 4.60 \pm 0.18 \\ 0.99 \end{array}$	$\begin{array}{c} 0.79 \pm 0.10 \\ 0.62 \\ 8.67 \pm 0.39 \\ 6.62 \pm 0.33 \\ 0.77 \end{array}$

 $a k_{2}/k_{1}$  and  $\sigma_{2}/\sigma_{1}$ : ±25%.

the relative radical concentrations provides a convenient way for the determination of the ratio of self-termination rate constants.<sup>24,25</sup> To obtain these, the spectrum was expanded in the central portion (Figure 2). The two strongest second-order lines of tert-butyl (K = 3/2, M = $\pm 1/2$ ) and the benzoyl signal were recorded under conditions of negligible saturation and overmodulation (tertbutyl: power 0.036 mW, modulation amplitude  $4 \times 10^{-3}$ mT; benzoyl: power 10 mW, modulation amplitude  $2.5 \times$  $10^{-2}$  mT). The lines were then simulated and doubly integrated on a Varian 620i computer. From the average of the double integrals the ratios of radical concentrations were calculated by correcting for different modulation amplitudes, powers, scan ranges, and gains.<sup>6</sup> The procedure applied eliminates a CIDEP multiplet effect of tert-butyl. A possible net effect should be smaller than 10% under our conditions and is neglected.<sup>26</sup>

Table II shows that the concentrations of the two radicals and thus their self-termination rate constants are roughly equal.<sup>27</sup> From eq 1 we have

$$\frac{k_2}{k_1} = \frac{\sigma_2}{\sigma_1} \frac{D_2}{D_1} \frac{\rho_2}{\rho_1}$$
(11)

As previously,<sup>5,6</sup> we replace the reaction distances  $\rho$  by molecular diameters and estimate these as the average of the results of three methods.<sup>28</sup> This leads to  $\rho_1 = 5.63$  Å<sup>6</sup> and  $\rho_2 = 5.90$  Å; i.e.,  $\rho_2/\rho_1 = 1.05$  within an estimated error of ±10%. Finally, the diffusion coefficients of isobutane and benzaldehyde in 3-methyl-3-pentanol were determined (see Experimental Section) and are also given in Table II. Combining these data with  $k_2/k_1$  by eq 11 one obtains the ratios of spin-statistical factors  $\sigma_2/\sigma_1$ . Within the overall error of ±25%,  $\sigma_2/\sigma_1$  is equal to one for all three temperatures instead of four as expected (see Introduction);



Figure 3. Absorption spectrum of benzoyl radicals in 3-methyl-3pentanol.

i.e., termination of benzoyl to triplet-state benzil seems not to occur.

Absorption Spectrum and Termination Rate Constants of Benzoyl. In the optical studies we use an effect modulation technique<sup>29</sup> with photolysis by harmonically modulated intensity  $J = (J_0/2)(1 + \cos \omega t)$ .<sup>9,29c,30</sup> During photolysis the variation of the optical density of the sample is monitored by a polychromatic light beam which passes the reaction flow cell perpendicular to the photolysis beam and is transmitted via a monochromator to a photomultiplier. Its response varies linearly with the incident light intensity. Because of the modulated photolysis the optical density contains an ac component  $D_{\sim}$  from starting material, transient intermediates and products as well as a dc component  $D_{-}$  which give rise to components  $V_{\sim}$  and  $V_{-}$  of the photomultiplier response. Conditions of low optical densities and low excitation ( $D_{\sim} \ll 1$ ) lead by expansion of Beer's law to eq 12.  $V_{\sim}/V_{-}$  is formed in an

$$D_{\sim} = \frac{1}{\ln 10} \frac{V_{\sim}}{V_{-}}$$
(12)

analogue voltage divider, and  $D_{\sim}$  is analyzed by a superheterodyne lock-in amplifier. As will be shown elsewhere,<sup>31</sup> starting material and products contribute to the signal only at very low modulation frequencies ( $\omega/(2\pi) \leq 5 \text{ s}^{-1}$ ) under our conditions. For higher modulation frequencies the signal is governed by the optical density of transient species and appears within ~20% only on the modulation frequency  $\omega$ , even if the transients obey other than first-order kinetics.<sup>9,30</sup> Absorption spectra may thus be obtained by recording the amplitude  $\Delta D = |D_{\sim}|$  at constant  $\omega$  while scanning the monochromator. Kinetic information results from the dependence of amplitude and phase of  $D_{\sim}$  on the modulation frequency.

Figure 3 shows an absorption spectrum of transient species observed at  $\omega/(2\pi) = 70 \text{ s}^{-1}$  during photolysis of 0.011 M pivalophenone in 3-methyl-3-pentanol at 13 °C (resolution 2 nm). The shape of the spectrum was independent of the wavelength of photolysis (316 or 365 nm), of the intensity of photolysis, and of the modulation frequency (70 or  $178 \text{ s}^{-1}$ ). This exludes contributions from stray light, impurities, or side products. Further, amplitudes and phase varied with  $\omega$  as expected for free-radical transients (vide infra). Therefore, we attribute the spectrum to tert-butyl and benzoyl radicals which should be present in about equal amounts. In an independent experiment<sup>31</sup> the spectrum of tert-butyl<sup>32</sup> was found to show a band at 307 nm and not to absorb above 350 nm. Thus, the bands at  $\lambda = 368$  and  $\simeq 460$  nm are assigned to the benzoyl radical, whereas the band at the low-wavelength end is probably mainly due to tert-butyl. It will be noted that the spectrum overlaps with the  $n\pi^*$  transition of pivalophenone (310  $\leq \lambda \leq$  380 nm) which, however, does

not disturb. The lower-wavelength limit is determined by the onset of the  $\pi\pi^*$  transitions of this compound which drastically lowers the transmission.

To our knowledge the optical spectrum of benzoyl in liquid or gaseous samples has not yet been reported, and there are conflicting reports on its appearance in solid media. An orange-red color has been claimed in early work.<sup>33</sup> Later, two bands at 320 and 460 nm were assigned to the radical,<sup>34</sup> but they were subsequently attributed to a radical anion, and a structureless absorption with an onset at  $\lambda \approx 380$  nm was reported.<sup>35</sup> Finally, a very weak band at  $\lambda \approx 700$  nm and a fairly light green color were claimed to be due to benzoyl.<sup>36</sup> The spectrum of Figure 3 does not support any of the previous claims. There is, however, some similarity to the spectra reported<sup>34</sup> for CH<sub>3</sub>CO and C<sub>6</sub>H<sub>5</sub>CH=CHCO which also show a weak band at  $\approx 500$  nm and a stronger absorption at 340 and 400 nm, respectively.

Lifetimes of benzoyl radicals in 3-methyl-3-pentanol containing 0.086 M pivalophenone were determined from the frequency dependence of the spectrum amplitude  $\Delta D$  at  $\lambda = 370$  nm. If the formation of the two radicals *tert*-butyl (R<sub>1</sub>) and benzoyl (R<sub>2</sub>) follows the excitation nearly instantaneously, which is true for our modulation frequencies  $\omega \leq 6 \times 10^3$  rad s<sup>-1</sup> since the lifetime of the pivalophenone triplet<sup>19</sup> is  $\sim 10^{-7}$  s, then the radical concentrations are described by eq 13 and 14. From the ESR

$$d[\mathbf{R}_1]/dt = \frac{1}{2}I_0(1 + \cos \omega t) - 2k_1[\mathbf{R}_1]^2 - k_x[\mathbf{R}_1][\mathbf{R}_2]$$
(13)

$$d[R_2]/dt = \frac{1}{2}I_0(1 + \cos \omega t) - 2k_2[R_2]^2 - k_x[R_1][R_2]$$
(14)

results we have  $k_1 = k_2$  within the experimental error limits (Table II). For this case eq 13 and 14 lead to the prediction that, after a short induction period of  $(4k[R])^{-1}$ ,  $[R_1] = [R_2]$ . Further, we assume  $k_x = 2(k_1k_2)^{1/2} = 2k_1$ , which reduces eq 13 and 14 to

$$d[R]/dt = \frac{1}{2}I_0(1 + \cos \omega t) - 4k[R]^2$$
(15)

with  $[R] = [R_1] = [R_2]$ ,  $k = k_1 = k_2 = 1/2k_x$ . Equation 15 is solved with the linear approximation<sup>9,30</sup>

$$[\mathbf{R}] = [\mathbf{R}]_0 + \Delta[\mathbf{R}] \cos(\omega t + \phi_{\mathbf{R}})$$
(16)

$$\Delta[\mathbf{R}] \ll [\mathbf{R}]_0 \tag{17}$$

and leads to

$$[R]_0 = (I_0/8k)^{1/2}$$
(18)

$$\Delta[\mathbf{R}] = \frac{1}{2} I_0 (\omega^2 + 1/\tau_{\mathbf{R}}^2)^{-1/2}$$
(19)

$$tg\phi_{\rm R} = -\omega\tau_{\rm R} \tag{20}$$

where  $\tau_{\rm R} = (8kI_0)^{-1/2}$ . As was shown by Paul<sup>9a</sup> these approximate solutions hold nearly exactly for  $\omega \tau_{\rm R} \ge 1$  and do not deviate grossly from the true solutions for all frequencies.  $\Delta[{\rm R}]$  is related to the observed  $\Delta D$  by

$$\Delta D = \epsilon l \Delta[\mathbf{R}] \tag{21}$$

where l is the length of the cell along the detection beam. Thus, a plot of  $(\Delta D)^{-2}$  vs.  $\omega^2$  should give a straight line with slope

$$a = 4/(\epsilon^2 l^2 I_0^2)$$

and intercept

$$b = \frac{4}{\epsilon^2 l^2 I_0^2} \frac{1}{\tau_{\rm R}^2}$$
(22)

from which  $\epsilon I_0$ ,  $\tau_{\rm R}$ , and  $2k/\epsilon$  may be determined. Figure



Figure 4. Determination of benzoyl lifetimes.

TABLE III:Lifetimes, Termination Rate Constants, andExtinction Coefficients of Benzoyl Radicals in3-Methyl-3-pentanol

	0 °C	14 °C	33 °C
$10^{3}\tau_{\rm R}$ , s	$2.53 \pm 0.33$	$1.83 \pm 0.29$	$1.10 \pm 0.24$
$10^2 \epsilon I_{\rm O}, \ {\rm cm}^{-1} {\rm s}^{-1}$	$1.89 \pm 0.04$	$1.74 \pm 0.04$	$1.21 \pm 0.04$
$\frac{10^{-6}(2k)}{\mathrm{cm \ s^{-1}}}$	2.06 ± 0.27	$4.28 \pm 0.68$	14.6 ± 3.0
$10^{5}I_{O}$ , M s <sup>-1</sup>	≥3.8	≥4.5	≥5.1
$\epsilon (370 \text{ nm}), M^{-1} \text{ cm}^{-1}$	≤490	≤380	≤240
$10^{-9}(2k), M^{-1} s^{-1}$	≤1.0	≤1.7	≤3.5
$10^{-9}(2k^{calcd}), M^{-1} s^{-1}$	0.30	0.73	1.48
$\epsilon^{\text{calcd}} (370 \text{ nm}), \\ \text{M}^{-1} \text{ cm}^{-1}$	145	170	103

4 shows the plot for T = 14 °C, and similar ones were obtained for T = 0 and 33 °C. The values of  $\tau_{\rm R}$ ,  $\epsilon I_0$ , and  $2k/\epsilon$  are listed in Table III. Unfortunately, we were unable to measure  $I_0$  in this system as in others<sup>31</sup> from the amplitude of the spectrum of the starting ketone. A rough estimate, which is a lower limit, was determined by GLC analysis of the yields of isobutane and hexamethylethane and the dwell time of the solutions in the reaction zone. These data and the upper limits of 2k and  $\epsilon$  resulting from them are also given in the table. Further, we list 2k as calculated via eq 1 with  $\sigma = 1/4$ ,  $\rho = 5.9$  Å, and the diffusion coefficients extrapolated from Table II and give extinction coefficients obtained from these values. Of the two sets of termination constants and extinction coefficients, we consider the lower values more reliable. In fact, the higher rate constants of benzoyl would lead with  $k_2/k_1 \simeq 0.75$ (Table II) to termination constants for *tert*-butyl of 1.34, 2.27, and  $4.65 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for T = 0, 14, and 33 °C, whereas we interpolate from our previous data<sup>6</sup> 1.0, 1.7, and  $3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for a 3-methyl-3-pentanol solution of di-tert-butyl ketone with higher ketone content and lower viscosity. From both sets of data the extinction coefficients of benzoyl turn out to be rather low. This would agree with a forbidden  $\sigma \rightarrow \pi^*$  character of the two observed transitions.

Emission Characteristics and Phosphorescence Lifetimes of Benzil in 3-Methyl-3-Pentanol. Since one of the aims of this work is the detection of phosphorescence of benzil caused by the self-termination of benzoyl radicals, we show in this section that our modulation technique may be used to conveniently detect even weak emissions.

Solutions (0.003 M) of benzil in 3-methyl-3-pentanol were excited at  $\lambda = 365$  nm with harmonically modulated light. The emission was collected perpendicular to the incident light beam and focused onto the entrance slit of the monochromator. The ac component of the photomultiplier response was measured by phase-sensitive de-







520 560 Figure 7. Emission spectra of benzil (33 °C).

4.80

tection on the modulation frequency and was recorded as a function of the wavelength of detection. True emission spectra were obtained from the recorded curves after correcting for the spectral response function of the detection circuit.

600

640 nm

The photophysical behavior of benzil in liquid solution at room temperature has been studied by several authors previously.<sup>16,37</sup> Excitation of the  $n\pi^*$  transition is followed by a prompt fluorescence (lifetime  $\leq$  several ns,<sup>16</sup>  $\phi_{\rm F} \simeq$  $0.0012^{37b,c}$ , intersystem crossing with  $\phi_{\rm T} = 0.92$ , <sup>16,37a</sup> phosphorescence with a lifetime of typically several hundred microseconds and  $\phi_P \simeq 0.034$ ,<sup>87</sup> as well as thermal and P-type delayed fluorescence.<sup>16,37c</sup> From these data we expect a modulated prompt fluorescence in phase with excitation for all of our modulation frequencies  $\omega \leq 2$  $\pi 1000 \text{ rad/s}$ . Phosphorescence and delayed fluorescence should also follow the excitation at lower frequencies, but at the higher-frequency end a noticeable phase shift of

$$tg\phi_{\rm P} = -\omega\tau_{\rm P} \tag{23}$$

i.e., of  $-tg\phi_{\rm P} \lesssim 1.0$ , should occur. The experimental results (Figures 5-7) obtained for T = -1, 14, and 33 °C agree with this expectation. Curves B were taken at low modulation frequencies with in-phase detection and represent the total



Figure 8. Determination of benzil phosphorescence lifetimes.



Figure 9. Emissions during photolysis of pivalophenone in 3-methyl-3-pentanol.

emission. Curves F were observed in-phase at the same frequencies with nondeoxygenated solutions. Under these conditions the delayed emissions are completely quenched by oxygen,<sup>16</sup> so that curves F represent the prompt fluorescence. Curves P are the out-of-phase components detected at high modulation frequency and represent the delayed emissions. The bands at 564 and 625 nm are due to phosphorescence, while the shoulder at the position of the fluorescence maximum results from  $T_1 \rightarrow S_1$  delayed fluorescence.<sup>16</sup> In accord with our low excitation intensities, its relative increase with increasing temperature characterizes this emission as temperature-delayed fluorescence ( $\Delta E_{ST} = (5.4 \pm 0.4)$  kcal mol<sup>-1</sup>).<sup>16</sup> It should be noted that curves P and F in Figures 5-7 are scaled so that the sum of P and F is equal to B.

Phosphorescence lifetimes were determined from the frequency dependence of the ratio of out-of-phase and in-phase components of the delayed emission at  $\lambda = 564$ nm and proper correction for the in-phase contribution of the prompt fluorescence. Figure 8 shows the plots according to eq 23 and gives lifetimes for the three temperatures. These are probably dominated by impurityand other quenching processes.

Emission of Benzil during Photolysis of Pivalophenone in 3-Methyl-3-pentanol. Using exactly the same photolysis conditions as for the determination of benzoyl lifetimes, we took emission spectra during the photoreactions of pivalophenone at 0, 15, and 33 °C. An example is given

by the upper trace of Figure 9, which reveals that benzil emissions are in fact observed. A comparison with Figure 6 shows, however, that besides benzil at least one other species contributes, particularly at the lower-wavelength end. Its emission increased with decreasing flow rate, i.e., larger conversion, indicating a reaction product. Since, besides benzil, none of the products listed in Table I absorbs at 365 nm, we attribute the additional emission to a fluororescence of the yellow side product mentioned previously.<sup>22</sup> Its contribution, shown as background in Figure 9, was determined as follows. The delayed emission of benzil (curve P in Figure 6) was subtracted, so that no extremum remained at the phosphorescence maximum (564 nm). In the same way the resulting trace was corrected for the prompt benzil fluorescence (curve F in Figure 6).

It is noteworthy that the emission spectrum during photolysis of pivalophenone contains contributions of benzil fluorescence and phosphorescence. Furthermore, within the error limits, their ratio is equal to that found with direct benzil excitation. This indicates that the benzil emission is caused by direct excitation of benzil formed in the reaction cell during the pivalophenone photolysis. It excludes energy transfer from pivalophenone to product benzil<sup>38</sup> as a source since the lifetime of the  $S_1$  state of pivalophenone is presumably very short. As a further possibility the formation of both excited singlet and triplet benzil in the self-termination of benzoyl radicals remains. This possibility is ruled out, however, by a kinetic study of the benzil phosphorescence.

We assume in the following that triplet benzil molecules are formed by direct excitation of benzil and by self-termination of benzoyl radicals. Their concentration, proportional to the phosphorescence intensity, then obeys

$$\frac{d[T]}{dt} = \frac{I_{A}}{2}(1 + \cos \omega t) + \kappa k[R]^{2} - \frac{1}{\tau_{P}}[T]$$
 (24)

where  $I_A$  is the production rate by direct excitation and  $\kappa$  is the efficiency of the termination to triplet benzil. Equation 24 is solved with the linear approximations 16 and 25

$$[T] = [T]_0 + \Delta[T] \cos(\omega t + \phi_T)$$
(25)

and leads to

$$-tg\phi_{\rm T} = \frac{\rho + \omega\tau_{\rm P}}{1 - \rho\omega\tau_{\rm P}} \tag{26}$$

where

$$\rho = \omega \tau_{\rm R} \Biggl\{ 1 + \frac{4I_{\rm A}}{I_0} \frac{1}{\kappa} (1 + \omega^2 \tau_{\rm R}^2) \Biggr\}^{-1}$$
(27)

For  $\kappa \to 0$ , we have  $\rho \to 0$ , and

$$-tg\phi_{\rm T} = \omega\tau_{\rm P} \tag{28}$$

For zero termination to triplet benzil we therefore expect a linear dependence of  $tg\phi$  for the phosphorescence on the modulation frequency. For an estimation of the deviations from this behavior for  $\kappa \neq 0$ , the ratio  $4I_A/I_0$  is approximated as follows. For small extinctions, monochromatic excitation (here 365 nm), and neclect of inner filter effects, we have from Beer's law

$$I_{\rm A} = 10^3 \ln 10 N_{\rm L}^{-1} \epsilon \phi_{\rm T} Q[\overline{\rm B}]_0$$
<sup>(29)</sup>

where  $\epsilon$  is the extinction coefficient of benzil at 365 nm ( $\epsilon$ (365) = 71 m<sup>-1</sup> cm<sup>-1</sup>),  $\phi_{\rm T}$  the quantum yield of triplet formation ( $\phi_{\rm T} = 0.92^{37}$ ), Q the quantum flux (6.4 × 10<sup>16</sup>



Figure 10. Emission kinetics during pivalophenone photolysis (0 °C).



Figure 11. Emission kinetics during pivalophenone photolysis (15 °C).



Figure 12. Emission kinetics during pivalophenone photolysis (33 °C).

cm<sup>-2</sup> s<sup>-1</sup>), and  $[B]_0$  the average concentration of product benzil in the reaction volume. According to reactions 2-7,  $[B]_0$  is given by

$$\overline{[B]_0} = \frac{1}{2} k[R]_0^2 \tau \tag{30}$$

with  $[\mathbf{R}]_0 = (I_0/8k)^{1/2}$  (eq 18) and  $\tau$  the average dwell time of the solutions in the cell ( $\tau = 18$  s). Thus

$$\frac{4I_{\rm A}}{I_0} = 0.25 \times 10^3 \ln 10 N_{\rm L}^{-1} \epsilon \phi_{\rm T} Q \tau \tag{31}$$

which, with the apropriate data, is equal to

$$4I_{\rm A}/I_0 = 0.08 \pm 0.02 \tag{32}$$

Insertion into eq 27 with  $\tau_{\rm R} \gg \tau_{\rm P}$  shows that deviations from eq 28 are expected even for  $\kappa$  being small, not exceeding a few percent. Figures 10-12 give the experimental kinetics determined from the out-of-phase components of the phosphorescence as those of Figure 8. Obviously, the linear dependence is obeyed for all temperatures. The slopes of the lines lead to the phosphorescence lifetimes given in the figures. They are similar to those noted in Figure 8. Also drawn are curves calculated for  $\kappa = 0.03$  from eq 26, 27, and 32 and the values of  $\tau_{\rm R}$  from Table III. Clearly, if there is any termination to triplet benzil, its efficiency must be much smaller than 3% and kinetically unimportant. It should be noted that appreciable termination to the benzil S<sub>1</sub> state is likewise ruled out since it would have had to have the same phosphorescence behavior.

## Discussion

In the previous chapters we have shown that the selftermination of benzoyl radicals to excited-state benzil does not occur to a measurable extent, contrary to the common assumption that such reactions of acyl radicals should be possible because they seem energetically feasible.<sup>12-14</sup> Since the basis for this assumption may be wrong, we have to consider the thermochemistry of the reactions in detail. The gas-phase enthalpy

$$2Ph\dot{C}O \rightarrow PhCOCOPh (S_0) \tag{33}$$

$$\rightarrow$$
 PhCOCOPh (S<sub>1</sub>) (34)

 $\rightarrow$  PhCOCOPh (T<sub>1</sub>) (35)

of formation of benzil is  $H_f^{\circ} = -21.8 \text{ kcal mol}^{-1}$  with a possible error of  $\pm 1 \text{ kcal/mol}^{39}$  The absolute standard entropy was estimated<sup>40</sup> as 116.2 cal mol}^{-1} K^{-1}. The probably best values for benzoyl<sup>40,41</sup> are  $H_f^{\circ} = (26.1 \pm 2)$ kcal mol<sup>-1</sup> and  $S^{\circ} = 79.5$  cal mol<sup>-1</sup> K<sup>-1</sup>. This renders reaction 33 exergonic by 61.3 kcal mol<sup>-1</sup> with a possible error of  $\sim 5 \text{ kcal mol}^{-1}$ . From the emission spectra<sup>16</sup> the fluorescent  $S_1$  state lies ~57.0 kcal mol<sup>-1</sup> and the phosphorescent  $T_1$  state lies ~51.0 kcal mol<sup>-1</sup> above the benzil ground state. The entropies of ground and fluorescent  $S_1$ states are slightly different since the ground state assumes an average twisted conformation with a low barrier to internal rotation about the CO-CO bond,42 whereas the fluorescent state is transplanar<sup>43</sup> because of the stabilization of the lowest  $\pi^*$  orbital.<sup>44</sup> By standard procedures this difference is estimated as 3 cal mol<sup>-1</sup> K<sup>-1</sup>. The same difference lowers the entropy of the  $T_1$  state<sup>42d</sup> with respect to that of the ground state, but its effect is practically canceled by the contribution from the electronic degeneracy of  $T_1$ . With these data reaction 34 becomes exergonic to  $\sim 3$  kcal mol<sup>-1</sup>, and reaction 35 to  $\sim 10$  kcal mol<sup>-1</sup> with uncertainties of at most 6 kcal mol<sup>-1</sup>. Thus, termination to the  $S_1$  state is nearly thermoneutral, whereas that to the  $T_1$  state should be truly exergonic, and we do not think that solvation differences are large enough to alter this appreciably. Indirect evidence for the same conclusion arises from the photochemistry of benzil.<sup>45</sup> Photoreduction occurs efficiently from the  $T_1$  state in hydrogen-donor solvents,  $^{45,56}$  whereas  $\alpha$  cleavage to benzoyl radicals has never been directly observed and claims for this process<sup>4</sup> have been heavily criticized.<sup>45b</sup> By ESR we found a very weak signal of benzoyl during photolysis of benzil in 3methyl-3-pentanol at 20 °C. It was not quenched by  $3 \times$  $10^{-3}$  M pyrene which quenches the T<sub>1</sub> state completely,<sup>16</sup> and we presume that the cleavage occurs with a very low efficiency from an excited singlet state. In conclusion all available data suggest that two benzoyl radicals have a higher free enthalpy of formation than the phosphorescent  $T_1$  state of benzil.

As already mentioned in the Introduction the energetically feasible termination of benzoyl radicals to benzil in its lowest excited states is symmetry forbidden. The diradical states  $D_{\sigma\sigma}$  correlate with the ground state and with higher excited states; i.e., theory predicts a high activation energy for the termination to the lowest excited states, and this forms the reason for its nonoccurrence. Finally we remark that the rate constants of benzoyl again demonstrate the validity of eq 1.

### **Experimental Section**

Chemicals and Sample Preparation. 3-Methyl-3-pentanol, tert-butyl alcohol, benzaldehyde, benzil, and isobutane were purchased in the highest available purities from Fluka or Merck. Before use in ESR and optical studies, 3-methyl-3-pentanol was purified by distillation and benzil was recrystallized twice from ethanol. Pivalophenone was synthesized by standard methods<sup>48</sup> and purified by vacuum distillation on a spinning band column. NMR and GLC revealed a purity of 99.5%. All solutions were deoxygenated by purging with helium prior to use.

GLC Determination of Reaction Products. Solutions (0.05 M) of pivalophenone in tert-butyl alcohol were photolyzed in 1-mm quartz cells at  $\lambda = 365$  nm in an arrangement described earlier.<sup>49</sup> GLC analysis was performed on Perkin-Elmer Sigma 3 (2-m glass column) and Carlo-Erba Fractovap 2101 (glass capillaries, i.d. 0.3 m, length 50 m, coatings UCON HB 5100 and OV 1) gas chromatographs with a Perkin-Elmer M2 integrator. Calibrations were performed by using aliphatic hydrocarbons (C<sub>5</sub>-C<sub>8</sub>) as internal standards.

ESR Measurements. The solutions flowed continuously through a flat cell of 1-mm optical path length within the cavity of the spectrometer.<sup>5,24</sup> Polychromatic photolysis with  $305 \le \lambda \le 360$  nm was employed. In this region the absorbance was  $\le 0.58$ . Ketone conversion during the dwell time in the region of photolysis ( $\simeq 1.5$  s) was  $\lesssim 2\%$ .

Diffusion Coefficients. We use a comparatively rapid and accurate method for the determination of diffusion coefficients<sup>50</sup> based on the pioneering work of Taylor<sup>51</sup> on the axial dispersion of a solute in a laminar flow. A  $\delta$  pulse of solution is injected into a flow of solvent in a long narrow tube. The combined effects of transport and diffusion result at long distance from the injection point in a Gaussian concentration profile with a variance  $\sigma^2$  related to D by eq 36, where r is the inner radius of the tube and

$$D = \frac{r^2}{24\sigma^2}t\tag{36}$$

t is the time between injection and appearance of the concentration maximum at the detector. Our apparatus consists of a Varian 8500 isochratic pump delivering a pulseless solvent flow. It is connected via a Rheodyne 7120 injector with a  $10-\mu$ L loop to a 316 stainless steel capillary (length 10 m, i.d. 0.566 mm,<sup>52</sup> o.d. 1.6 mm) wound to a helix of 300-mm diameter. This helix is thermostated to  $\pm 0.05$  °C. The concentration is monitored by an Optilab 902 differential refractometer with microcells of 0.2-mm optical path length. The outlet of the sample cell is connected to the inlet of the reference cell via a 7-m Teflon tubing of 1.6-mm i.d. By this connection base-line drifts are avoided.

In all measurements the conditions were chosen such that known errors of the method<sup>53</sup> were avoided. Typically, 10  $\mu$ L of solutions containing 125  $\mu$ g of solute were injected into the solvent streaming with flow rates of 3–6 cm<sup>3</sup>/h. Typical diffusion times were 20–40 min. For isobutane, solutions were prepared by bubbling the gas through the solvent. Values of diffusion coefficients given in Table II are averages of nine independent runs at three different flows. The accuracy of the method was checked by remeasuring a number of well-known diffusion coefficients. Further, the data given in Table II did not depend on the pivalophenone concentration for  $c \leq 0.086$  M.

Optical Modulation Spectroscopy. The photolysis beam consists of a 1-kW Xe/Hg short arc lamp (Hanovia 977B-1)

driven by a stabilized power supply (Heinzinger TNX 977B-1), the light being transmitted to the sample by a Suprasil lens. Harmonic modulation of the light intensity (phase accuracy better than  $\pm 0.5^{\circ}$ ,  $(\sum_{n>1} J_{n\omega}^2)^{1/2}/J_{\omega} < 3\%$ ) is achieved by specially shaped slots<sup>30</sup> close to the lens and the rotating sector of a light chopper (Ortec Brookdeal 9479). The frequency could be varied from 10 to  $10^3$  s<sup>-1</sup>. In kinetic experiments the wavelength region of excitation was limited to the 365-nm band by filtering with an aqueous CuSO<sub>4</sub>-CoSO<sub>4</sub> solution (0.4 M CuSO<sub>4</sub>, 0.28 M  $CoSO_4$ , 0.56 ppt concentrated  $H_2SO_4$ ) and glass filters (Schott UG 11 and WG 345). The quantum flux in the sample cell was determined by ferrioxalate actinometry. For the measurement of the absorption spectrum a NiS- $O_4$ -CoSO<sub>4</sub> filter solution (225  $\leq \lambda \leq$  340 nm) was employed to achieve a higher quantum flux.

The solutions flow through a rectangular  $(5 \times 5 \text{ mm}^2)$ microcuvette (Starna Type 43) within a Dewar arrangement with a flow rate of  $0.5 \text{ cm}^3/\text{min}$ . Ketone conversion in this reaction cell was less than 0.5%.

The detection light of a Xe arc (Osram XBO 450W) driven by a stabilized power supply (Heinzinger TNX 450) is lead through the sample in a direction perpendicular to the excitation beam and is focused onto the entrance slit of a grating monochromator (linear dispersion 2 nm/mm, aperture 1:8). Higher-order light is eliminated by suitable glass filters. For the detection of emissions, the mono-chromator is placed closer to the sample cell. The signal of the photomultiplier (Hamamatsu R 955) is transferred via an analog voltage divider or directly (emission studies) to the lock-in amplifier (Ortholoc-SC 9505, sinetrac response mode) triggered by the light chopper and is recorded. In determinations of signal amplitudes, an integrator served to improve the signal-to-noise ratio. In all experiments due care was taken to obtain correct zerophase adjustments and optically homogeneous light distributions in the sample cell. A full description of the arrangement and its principles of operation will be given elsewhere.

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