Chemiluminescent Recombination of Benzoyl Radicals

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Pyrolysis of di-t-butyl peroxyoxalate in the presence of benzaldehyde gives t-butyl alcohol and benzil as main products. Peroxide decomposition produces a visible chemiluminescence that can be attributed to triplet benzil emission. The excited triplet is produced in the benzoyl radical recombination ($2PhCO \longrightarrow {}^3[PhCOCOPh]$). For this process in benzene at 45 °C the specific rate constant is 7×10^5 $dm^3 mol^{-1} s^{-1}$.

Free-radical recombination and disproportionation are exothermic reactions that can be a thermal source of electronically excited states.[1-5] In spite of the fact that the expected rate constants for several of these reactions have been estimated from the rates of the opposite photochemical reactions and thermochemical considerations,[2] experimental determinations of excited-state formation yields are rare. Quinga and Mendenhall have evaluated the yield of ketone triplets produced in the dismutation of geminate alkoxyl radical pairs,[3] but no excited-state production was observed in the disproportionation of non-geminate radicals. De la Fuente *et al.* have presented evidence showing that the electroluminescence observed in the Kolbe reaction of pyruvic and phenylglyoxylic acids arises from excited diketones produced by acyl free-radical recombination,[4] but evaluation of a reliable quantum yield for the process was precluded by radical inhomogeneity and/or electrode adsorption. Furthermore, Huggenberger *et al.* failed to detect the formation of triplet benzil in the recombination of benzoyl radicals.[5] In the present work we report what we believe are the first conclusive data showing that excited molecules can be produced in the homogeneous recombination of non-geminate free acyl radicals.

Figure 1. Effect of di-t-butyl peroxyoxalate (PO) concentration upon the maximum photocurrent; [benzaldehyde] 0.1 mol dm^{-3}

Results and Discussion

Thermolysis of di-t-butyl peroxyoxalate (PO) at 45 °C in oxygen-free benzene solutions in the presence of an excess of benzaldehyde gives an almost quantitative yield of benzil (nearly 1.0 benzil molecules per PO molecule added) and t-butyl alcohol (0.87 molecules per PO reacted). The production of benzil can be explained in terms of Scheme 1.

$$[C(O)OOBu^t]_2 \longrightarrow 2 Bu^tO^{\cdot} + 2 CO_2 \qquad (1)$$

$$Bu^tO^{\cdot} + PhCH{=}O \longrightarrow Bu^tOH + PhCO^{\cdot} \qquad (2)$$

$$2 PhCO^{\cdot} \longrightarrow PhCOCOPh \qquad (3)$$

Scheme 1.

Luminescence is produced during the reaction. The relationships of the luminescence intensity with the PO and benzaldehyde concentrations are shown in Figures 1 and 2. The dependence of the luminescence intensity on reaction time is shown in Figure 3. The luminescence can be quenched by typical triplet quenchers. A plot of I°_{max}/I_{max} against anthracene concentration was linear over all the [anthracene] range considered (4.5 × 10^{-5} to 2.2 × 10^{-4} mol dm^{-3}). The slope of the Stern–Volmer plot (K_{SV}) obtained was 3.2 × 10^{-3}

The wavelength distribution of the emitted luminescence was evaluated by introducing 'cut-off' filters. The integrated (uncorrected) emission spectrum so obtained is given in Figure 4,
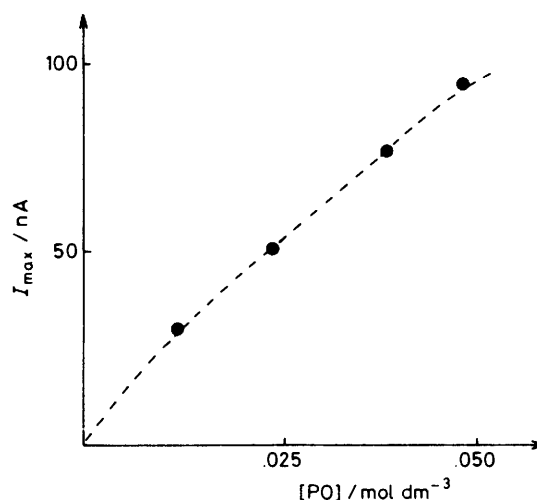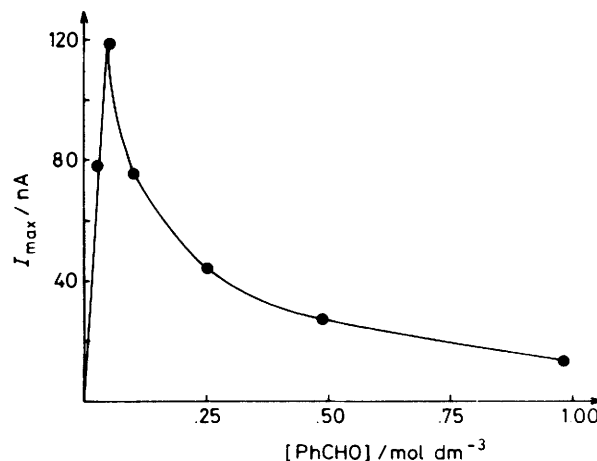

Figure 2. Effect of [benzaldehyde] upon the maximum photocurrent; [PO] 0.05 mol dm^{-3}

which also includes the spectrum obtained when tetramethyldioxetane (TMD) (1.17 × 10^{-4} mol dm^{-3}) is decomposed in the presence of an excess of benzil (0.2 mol dm^{-3}) at 45 °C in deaerated benzene. In this system, the luminescence can be explained in terms of Scheme 2.

The close agreement between the spectra obtained in the TMD–benzil system and that observed in the PO decompostion in the presence of benzaldehyde indicates that in this system
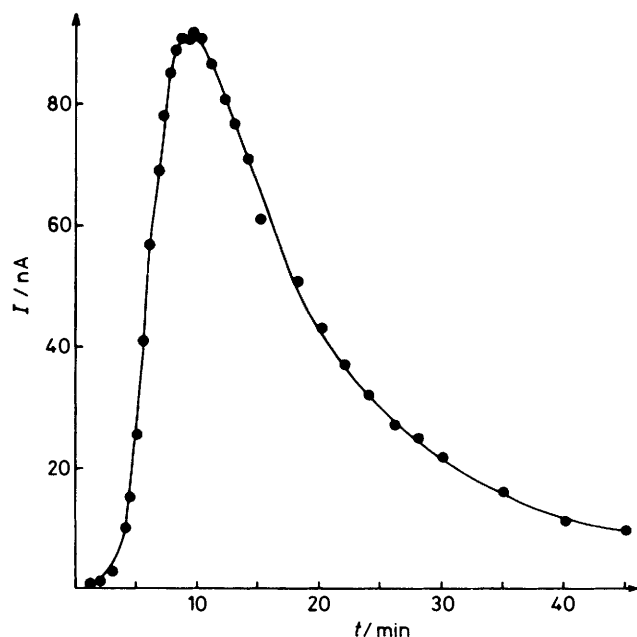
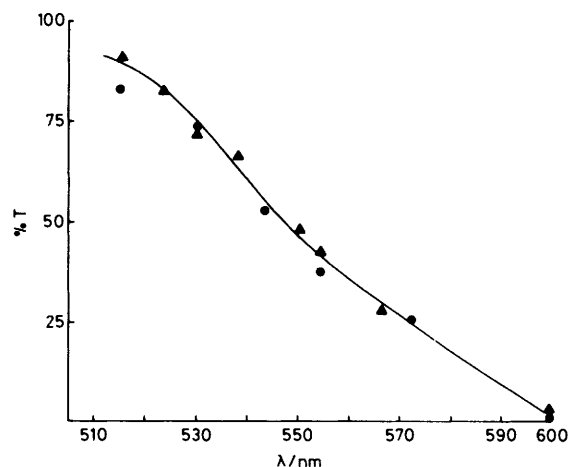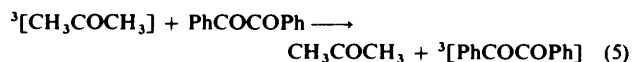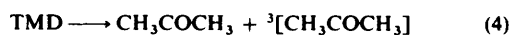**Figure 3.** Photocurrent as a function of reaction time; [PO] 0.05, [benzaldehyde] 0.1 mol dm^{-3}

Figure 4. Integrated uncorrected spectra in benzene at 45 °C; ● TMD–benzil, ▲ PO–benzaldehyde. Spectra were obtained by a comparison of intensity with and without filters (background 1 nA). TMD–benzil intensity without filters 200 nA; [benzil] 0.05; [TMD] 1.17 × 10^{-4} mol dm^{-3} (intensity was stable for long periods). PO–benzaldehyde maximum intensity without filters ca. 120 nA; [PO] 0.05; [benzaldehyde] 0.05 mol dm^{-3}. Measurements were carried out near the times of maximum intensity

$$TMD \longrightarrow CH_3COCH_3 + {}^3[CH_3COCH_3] \qquad (4)$$

$$^3[CH_3COCH_3] + PhCOCOPh \longrightarrow$$
$$CH_3COCH_3 + {}^3[PhCOCOPh] \quad (5)$$

$$^3[PhCOCOPh] \longrightarrow PhCOCOPh + h\nu \qquad (6)$$
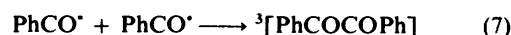
Scheme 2.

most of the luminescence also arises from triplet benzil. Furthermore, Figure 4 shows that more than 75% of the detected light has wavelength longer than 530 nm. On the other hand, and as a result of significant triplet quenching by

benzaldehyde, excitation of benzil in the reacted solution with light of 415 nm gives an emission dominated by fluorescence with more than 70% of the light of wavelength shorter than 530 nm.

From the foregoing considerations, as well as from the fact that the chemiluminescence can be quenched by typical triplet quenchers such as anthracene, it can be concluded that the triplet is the main excited state involved. The triplet production can be attributed to the occurrence of process (7), that must take

$$PhCO^{\bullet} + PhCO^{\bullet} \longrightarrow {}^3[PhCOCOPh] \qquad (7)$$

place in parallel to reaction (3) and most likely involves a triplet-correlated pair of PhCO$^{\bullet}$ radicals. A reaction scheme comprising reactions (1)—(3) and reaction (7) is fully compatible with the experimental results shown in Figures 1—3. In particular, Figures 1 and 3 show that the luminescence follows both the initial PO concentration and, at a given concentration, the peroxide decay. The initial rise in luminescence is due to the fact that the reaction tube is, at $t = 0$, introduced at -15 °C. After reaching thermal equilibrium (10 min) the luminescence decays, owing to peroxide consumption. This consumption was followed by measuring the t-butyl alcohol produced. These measurements directly provide values of the peroxide decomposition rate over all the reaction times considered. The peroxide decomposition is faster than that previously reported at 45 °C in benzene,[6] probably as a consequence of partial catalysis by benzaldehyde.

Figure 2 shows that the luminescence is benzaldehyde-dependent. The initial rise can be explained in terms of a competition between process (2) and other reactions of the t-butoxyl radicals (i.e. recombination). The intensity decay observed at high benzaldehyde concentrations is due to a competition between process (6) and triplet benzil quenching.

$$^3[PhCOCOPh] + PhCOH \longrightarrow quenching \qquad (8)$$

The occurrence of reaction (8) is supported by the results obtained when benzil is irradiated in the presence of benzaldehyde under conditions similar to those employed in the chemiluminescence experiments. From these data it is concluded that benzaldehyde quenches benzil triplets with K_{SV} ca. 215 dm^3 mol^{-1} in benzene at 45 °C.

The luminescence observed in the PO–benzaldehyde system was quenched by anthracene with a Stern–Volmer constant of 3.2 × 10^{-3} dm^3 mol^{-1}. On the other hand, the benzil luminescence observed under similar conditions in the TMD–benzil system was quenched by anthracene (1.7 × 10^{-6} to 4.2 × 10^{-5} mol dm^{-3} range) with K_{SV} 1.6 × 10^5 dm^3 mol^{-1}. The difference can be explained in terms of a shorter lifetime of the excited benzil triplet in the former system. This shorter lifetime is a consequence of triplet benzil quenching by benzaldehyde [process (8)] and process (9), since it has been observed that,

$$^3[PhCOCOPh] + PO \longrightarrow quenching \qquad (9)$$
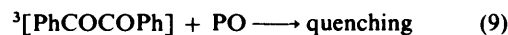
at room temperature, PO quenches the benzil phosphorescence with K_{SV} 120 dm^3 mol^{-1}.

The triplet benzil yields in the recombination of benzoyl radicals can be estimated from the present data by applying equation (10), where I_{PO} and I_{TMD} are the luminescence

$$\varphi(^3benzil) = (I_{PO}/I_{TMD})(\tau_{TMD}/\tau_{PO})(v_{PO}/v_{TMD})\varphi(^3A) \qquad (10)$$

intensities observed when the decomposition rates of PO and TMD are v_{PO} and v_{TMD} respectively; τ_{TMD} and τ_{PO} are the benzil triplet lifetimes under the experimental conditions employed in the PO and TMD experiments, respectively, and $\varphi(^3A)$ is the

acetone triplet yield in the TMD pyrolysis. The value of τ_{TMD}/τ_{PO} can be equated to the ratio of K_{SV} values obtained by employing anthracene as quencher in the chemiluminescence experiments [equation (11)].

$$\tau_{TMD}/\tau_{PO} = (K_{SV})_{TMD}/(K_{SV})_{PO} = 50 \qquad (11)$$

The values of v_{TMD} and $\varphi(^3A)$ were obtained from published data [7] and v_{PO} was obtained from the t-butyl alcohol production rate. This procedure gives $\varphi(^3\text{benzil}) = k_7/k_3 = 1.4 \times 10^{-4}$, compatible with the 3% upper limit mentioned by Huggenberger et al.[5]

Benzoyl recombination is a diffusionally controlled process,[5] and its rate constant can be taken as nearly 5×10^9 dm^3 mol^{-1} s^{-1}, leading to $k_7 = 7.0 \times 10^5$ dm^3 mol^{-1} s^{-1} for the recombination to triplet benzil. This value is considerably smaller than that estimated from the electrogenerated luminescence.[4] Nevertheless, in this system the reported k_3 value (ca. 4×10^7 dm^3 mol^{-1} s^{-1}) was bound to have large errors, owing to the difficulty in evaluating the phosphorescence efficiency of the electrogenerated triplet. For the benzil triplet photocleavage at 45 °C, a value of ca. 10^3 s^{-1} can be obtained by extrapolating data obtained in dodecane at higher temperatures.[8] By combining this value with k_7, a ΔG° value for the cleavage of triplet benzil of ca. 4.5 kcal can be derived. This value, although smaller than that estimated by Huggenberger et al.,[5] is within the uncertainty of the thermochemical data.

The formation of triplet benzil from benzoyl radicals is an exothermic process.[5] The fact that k_7/k_3 is considerably smaller than unity, in spite of the favourable statistical factor expected from the different multiplicities of the two processes, implies that triplet recombination must have an extra thermodynamic barrier[2] and/or a very low pre-exponential A factor. These restrictions could be explained in terms of the symmetry-forbidden character of the process.[2,5]

Experimental

Di-t-butyl peroxyoxalate (PO) was synthesized by the method of Bartlett et al.[6] from oxalyl chloride (Sigma) and t-butyl hydroperoxide (Aldrich 70%; dried over magnesium sulphate) in n-pentane (Merck, puriss). After recrystallization from n-pentane the solid obtained had m.p. 51 °C. The compound can be safely stored at low temperature (ca. −20 °C) for several weeks without significant decomposition. On the other hand, extreme care must be taken when the solid is handled since it is occasionally explosive.

Anthracene (Fluka, puriss) was sublimed at reduced pressure. Benzaldehyde (Fischer, certified) was vacuum-distilled twice.

Benzene (Merck, Uvasol), was employed as solvent. Tetramethyldioxetane was kindly supplied by Dr. E. Bechara, University of Sao Paulo.

Luminescence measurements were carried out in cylindrical Pyrex cells (diameter 1 cm) sealed under vacuum after two freeze-thaw cycles. The reaction tubes were kept at −15 °C. To initiate a run the tube was introduced into a glass jacket thermostatically controlled at 45 ± 0.5 °C. The jacket window was placed in front of a EMI-9502-S photomultiplier. The photocurrent was measured at various times with a Keithley 414-A picoamperimeter. Cut-off filter solutions were prepared with sodium picrate or sodium dichromate solutions of various concentrations.[4]

Quenching experiments were performed over the chemiluminescence or the phosphorescence observed after benzil irradiation at 415 nm. The phosphorescence quenching experiments were carried out employing a Perkin-Elmer LS-5 spectrofluorimeter. Quenching by anthracene and benzaldehyde was carried out at 45 ± 0.5 °C. Quenching by PO was carried out at room temperature to avoid peroxide decomposition. All measurements were carried out under nitrogen. Luminescence quenching experiments were performed by adding to the reaction tubes various anthracene concentrations prior to oxygen evacuation. The anthracene quenching efficiency was estimated from its effect upon the maximum intensity observed during the PO decomposition.

t-Butyl alcohol production was measured by g.l.c. after decomposing the excess of PO in the presence of styrene. Benzil was identified by g.l.c. and by its absorption in the u.v.–visible region. Its production was quantified spectrophotometrically from the thermolysed sample absorption at 415 nm.

References

1 H. W. Holden and K. P. Kutschke, Can J. Chem., 1961, 39, 1552.
2 E. B. Abuin and E. A. Lissi, Photochem. Photobiol., 1979, 30, 59.
3 E. M. Y. Quinga and G. D. Mendenhall, J. Am. Chem. Soc., 1983, 105, 6520.
4 J. De la Fuente, E. A. Lissi, and R. Rozas, Can. J. Chem., 1984, 62, 2117.
5 C. H. Huggenberger, J. Lipscher, and H. Fischer, J. Phys. Chem., 1980, 84, 3467.
6 P. D. Bartlett, E. P. Benzing, and R. E. Pincock, J. Am. Chem. Soc., 1960, 82, 1762.
7 H. C. Steinmetzer, A. Yekta, and N. J. Turro, J. Am. Chem. Soc., 1974, 96, 282.
8 T. Cáceres, M. V. Encinas, and E. A. Lissi, J. Photochem., 1984, 27, 109.