CHEMILUMINESCENT RECOMBINATION OF ACETYL RADICALS

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RESUMEN

La pirólisis del di-tert-butilperoxioxalato a 45 °C en presencia de acetaldehido genera tert-butanol y biacetilo con rendimientos cercanos al 100%. Durante el proceso se observa luminiscencia que puede ser relacionada a la formación de biacetilo triplete en la recombinación de los radicales acetilo

$$2\ CH_3CO^{\cdot} \longrightarrow {}^3CH_3COCOCH_3 \qquad (1)$$

El rendimiento de biacetilos tripletes es de 1.3×10^{-4}.

SUMMARY

Pyrolysis of di-tertbutylperoxyoxalate at 45°C in the presence of acetaldehyde produces quantitative yields of tert-butanol and biacetyl. Luminescence arising from excited biacetyl is produced during the peroxide decomposition. The excited molecules are produced in the recombination of two acetyl radicals:

$$2\ CH_3CO^{\cdot} \longrightarrow {}^3CH_3COCOCH_3 \qquad (1)$$

The yield of excited molecules in the recombination of two acetyl radicals is 1.3×10^{-4}.

INTRODUCTION

Free radical recombination is an exothermic reaction that can be a thermal source of electronically excited molecules (1-5). Among the potentially more efficient chemiluminescent processes stand the recombination of acyl radicals to produce excited 1,2-dicarbonyl triplets (1). De la Fuente et al. (4) 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, but evaluation of reliable quantum yields were precluded by the complexity of the system. Recently, Lissi and De la Fuente have obtained more precise data regarding the triplet benzil yield in the recombination of benzoyl radicals (5). In this work, benzoyl radicals were produced by pyrolyzing di-tertbutylperoxyoxalate (PO) in presence of excess benzaldehyde (5). In the present work, we report the results obtained in the pyroly -

sis of PO in presence of acetaldehyde. The data obtained allow an evaluation of the yield of triplet biacetyl associated to the recombination of acetyl radicals.

RESULTS AND DISCUSSION

The pyrolysis of di-tertbutylperoxyoxalate (PO) at 45 °C in oxygen free benzene solutions in the presence of an excess of acetaldehyde produces nearly two molecules of tert-butanol and one molecule of biacetyl per PO added to the system. No other products than traces of methane were detected by gas-liquid chromatography and U.V. absorption. These products are compatible with the simple reaction scheme 1.

Scheme 1

$$PO \longrightarrow 2Bu^{t}O^{\cdot} + 2CO_2 \quad (1)$$

$$Bu^{t}O^{\cdot} + CH_3CHO \longrightarrow Bu^{t}OH + CH_3CO^{\cdot} \quad (2)$$

$$2CH_3CO^{\cdot} \longrightarrow CH_3COCOCH_3 \quad (3)$$

$$CH_3CO^{\cdot} \longrightarrow CH_3^{\cdot} + CO \quad (4)$$

$$CH_3^{\cdot} + CH_3CHO \longrightarrow CH_4 + CH_3CO^{\cdot} \quad (5)$$

Luminescence is produced during the reaction. The change in luminescence intensity with the PO and acetaldehyde concentrations are shown in Figs. 1 and 2. The dependence of the luminescence intensity with the reaction time is shown in Fig. 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 ($5x10^{-5}$ to $3x10^{-4}$ M). The slope of the Stern-Volmer plot (K_{sv}) obtained was $9.5x10^{+2}$ M^{-1}.

The wavelength distribution of the emitted luminescence was evaluated by introducing "cut-off" filters. The integrated (uncorrected) emission spectrum so obtained is given in Fig. 4. In this figure are also included the spectrum obtained in the presence of anthracene and that obtained when tetramethyldioxetane (TMD) (1.17×10^{-4} M) is decomposed in presence of an excess of biacetyl (3×10^{-2} M) at 45 °C in deaereated benzene. In this system, the luminescence can be explained in terms of Scheme 2.

Scheme 2

$$TMD \longrightarrow CH_3COCH_3 + {}^{3}CH_3COCH_3 \quad (6)$$

$${}^{3}CH_3COCH_3 + CH_3COCOCH_3 \longrightarrow CH_3COCH_3 + {}^{3}CH_3COCOCH_3 \quad (7)$$

$${}^{3}CH_3COCOCH_3 \longrightarrow CH_3COCOCH_3 + h\nu_{Ph} \quad (8)$$

The close agreement between the spectra obtained in the TMD-biacetil system and that observed in the PO decomposition in the presence of acetaldehyde would indicate that in this system most of the luminescence arises from triplet biacetyl. Significant contribution of excited singlet biacetyl can be further disregarded due to the fact that the spectrum shape does not change in the presence of typical triplet quenchers. The excited triplets are produced by process (9).

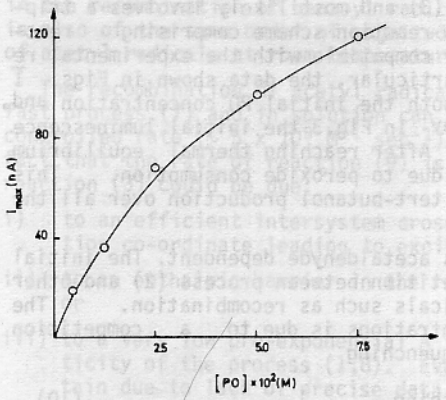

FIG. 1. Values of the maxima intensities as a function of added PO. Acetaldehyde: 0.25 M.

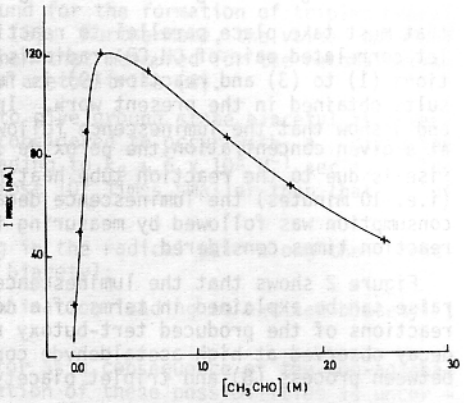

FIG. 2. Values of the maxima intensities as a function of the added acetaldehyde. PO = 5 x 10^{-2} M.

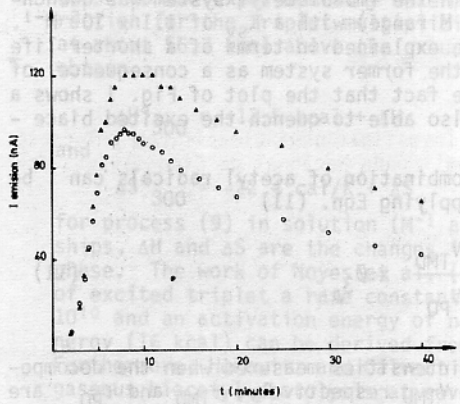

FIG. 3 Emitted intensity as a function of time. Acetaldehyde: 0.23 M; PO: 0.05 M. Acetaldehyde: 0.23 M; PO: 0.075 M.

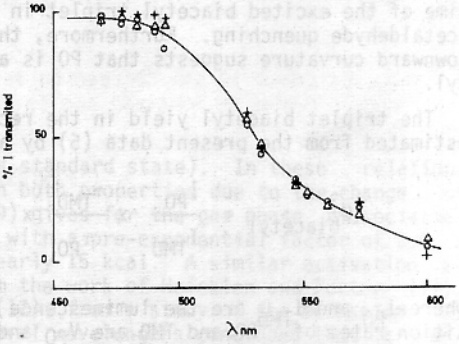

FIG. 4. Percentage of total light transmitted as a function of the cut-off wavelength of the filter.

+ PO-acetaldehyde system.
o PO-acetaldehyde-anthracene-system
Δ TMD-biacetyl system.

$$CH_3CO^{\cdot} + CH_3CO^{\cdot} \longrightarrow {}^3CH_3COCOCH_3 \qquad (9)$$

that must take place parallel to reaction (3) and most likely involves a triplet correlated pair of $CH_3CO^{\cdot}$ radicals. A reaction scheme comprising reactions (1) to (3) and reaction (9) is fully compatible with the experimental results obtained in the present work. In particular, the data shown in Figs. 1 and 3 show that the luminescence follows both the initial PO concentration and, at a given concentration, the peroxide decay. In Fig.3 the initial luminescence rise is due to the reaction tube heating. After reaching thermal equilibrium (i.e. 10 minutes) the luminescence decays due to peroxide consumption. This consumption was followed by measuring the tert-butanol production over all the reaction times considered.

Figure 2 shows that the luminescence is acetaldehyde dependent. The initial raise can be explained in terms of a competition between process (2) and other reactions of the produced tert-butoxy radicals such as recombination. The decay observed at high acetaldehyde concentrations is due to a competition between process (8) and triplet biacetyl quenching

$$^3CH_3COCOCH_3 + CH_3CHO \longrightarrow \text{quenching} \qquad (10)$$

The occurrence of reaction (10) is supported by the quenching observed when biacetyl is irradiated in the presence of acetaldehyde under conditions similar to those employed in the chemiluminescence experiments. From these data it is concluded that acetaldehyde quenches acetyl triplets with a $K_{SV} \approx 8.2 \times 10^{-1}\ M^{-1}$ in benzene at 45 °C.

The luminescence produced in the PO-acetaldehyde system was quenched by anthracene with a K_{SV} of $9.5 \times 10^2\ M^{-1}$. On the other hand, the biacetyl luminescence produced under similar conditions in the TMD-biacetyl system was quenched by anthracene (5×10^{-5} M to 3×10^{-4} M range) with a K_{SV} of $1.1 \times 10^5\ M^{-1}$. The difference between both values can be explained in terms of a shorter lifetime of the excited biacetyl triplet in the former system as a consequence of acetaldehyde quenching. Furthermore, the fact that the plot of Fig. 1 shows a downward curvature suggests that PO is also able to quench the excited biacetyl.

The triplet biacetyl yield in the recombination of acetyl radicals can be estimated from the present data (5) by applying Eqn. (11)

$$\phi^3_{\text{biacetyl}} = \frac{I_{PO}}{I_{TMD}} \times \frac{\tau_{TMD}}{\tau_{PO}} \times \frac{V_{TMD}}{V_{PO}} \times \phi_{3_A} \qquad (11)$$

where I_{PO} and I_{TMD} are the luminescence intensities measured when the decomposition rates of PO and TMD are V_{PO} and V_{TMD} respectively; τ_{TMD} and τ_{PO} are the triplet biacetyl lifetimes under the experimental conditions employed in the experiments respectively, and ϕ_{3A} is the acetone triple yield in the pyrolysis of TMD. The value of τ_{TMD}/τ_{PO} can be equated to the ratio of K_{SV} values obtained employing anthracene as quencher in the chemiluminescence experiments

$$\tau_{TMD}/\tau_{PO} = (K_{SV})_{TMD}/(K_{SV})_{PO} = 1.2 \times 10^2$$

V_{TMD} and ϕ_{3A} can be obtained from published data (6), and V_{PO} is directly measured from the tert-butanol production rate. By this procedure it is obtained that

$$\phi_{3_{biacetyl}} = 1.3 \times 10^{-4}$$

This value is almost equal to that found for the formation of triplet benzyl in the recombination of benzoyl radicals (5). Furthermore, the value obtained is also of the same order of magnitude than that measured for the recombination of acetyl radicals at room temperature in acetonitrile (4).

The recombination of acetyl radicals to give ground state biacetyl is a very fast process (7) and in solution can be considered to occur with a diffusion controlled rate ($\sim 5 \times 10^9$ M^{-1} sec^{-1}) leading to $k_3 \approx 6 \times 10^5$ M^{-1} sec^{-1}. The fact that the rate of reaction (9) is almost 10^4 times smaller than that of reaction (3) could be due:

i) to an efficient intersystem crossing in the radical pair along the reaction co-ordinate leading to excited biacetyl;

ii) to an enthalpic barrier in the recombination leading to excited biacetyl ; or

iii) to a very low pre-exponential A factor as a consequence of the non-adiabaticity of the process (1,8). Evaluation of these possibilities is uncertain due to lack of precise data on the photodissociation yield of biacetyl in solution and on the thermochemistry of the process. Reasonably well stablished data are at present only available for the processes in the gas phase. For process (3), the data reported by Benson (9) leads to

$$\Delta H^\circ_{300} = -67.8 \text{ kcal/mol}$$

$$\Delta S^\circ_{300} = -37.4 \text{ cal/mol K}$$

for the gas phase process at 1 atmosphere of pressure. The ΔH obtained is close to the experimentally determined value of 70 kcal (10). After correction for the triplet multiplicity and considering that the triplet lies at about 56.3 kcal above the ground state in non-polar solvent (11), we obtain

$$\Delta H^\circ_{300} = -11.5 \text{ kcal} + \Delta H$$

and

$$\Delta S^\circ_{300} = -22.4 \text{ cal/K} + \Delta S$$

for process (9) in solution (M^{-1} as standard state). In these relationships, ΔH and ΔS are the changes in both properties due to the change of phase. The work of Noyes et al. (9) gives for the gas phase dissociation of excited triplet a rate constant with a pre-exponential factor of 1.8×10^{10} and an activation energy of nearly 15 kcal. A similar activation energy (16 kcal) can be derived from the work of Heicklen and Porter (11). Furthermore, Horowitz and Calvert (12), from a study of the mechanism of gaseous biacetyl photolysis at several wavelengths concluded that it appears that the minimum energy for the decomposition of both singlet and triplet states of biacetyl lies very near the 70 kcal/mole required to disrupt the weakest bond in the ground-state biacetyl molecule. All these data, in spite of the uncertainty introduced by the unknown enthalpy change introduced by the solvent, would be compatible with a very small enthalpic barrier and a low pre-exponential A factor in the acetyl recombination leading to the excited triplet. In fact, if the thermochemical data is coupled with the kinetic data (1), the expected value of k_3 is near 10^4 M^{-1} sec^{-1}, a value that is fully compatible with that found in the present work.

EXPERIMENTAL

The pyrolysis of PO was carried out at 45 ± 0.5 °C in benzene in presence of acetaldehyde. Luminescence emitted was measured by carrying out the pyrolysis in cylindrical Pyrex cells (1 cm diameter) sealed under vacuum placed in front of an EMI-9502-S photomultiplier. The reaction tubes were kept at -15°C and the measurements started after their introduction into a glass jacket thermo - statized at the working temperature. In order to obtain the luminescence spec tra, cut-off filter solutions were introduced between the sample and the photo multiplier window (4). Tert-butanol production was measured by gas-liquid chromatography. Biacetyl was identified and measured by its near U.V.-visible absorption spectra. The full absorption band was identical to that of a standard biacetyl solution, showing that formation of other near U.V. absorb - ing compounds can be disregarded.

Luminescence measurements in the tetramethyldioxetane-biacetyl system were performed under identical conditions than those described for the PO-acetalde- hyde system. Quenching experiments were performed in both systems by adding to the reaction tubes different anthracene concentration prior to oxygen eva - cuation. In the PO-acetaldehyde system, the anthracene quenching efficiency was estimated from its effect upon the maximum intensity observed during the PO decomposition.

Ditertbutylperoxyoxalate (PO) was synthesized by the method of Bartlett et al. (13), and stored as a solid at low temperature (~ -20°C). Acetaldehyde was washed with sulfuric acid and twice destilled prior to its use. Its puri- ty was checked by gas chromatography. Anthracene (Fluka, Puriss) was sublima- ted at reduced pressure. Tetramethyl dioxetane was kindly supplied by Dr. E. Bechara, University of Sao Paulo. Benzene (Merck, Uvasol) was employed as solvent.

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