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THE MULTIPLICITY OF THE PHOTO-FRIES REACTION(1)

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Trecker and coworkers(2) have recently reported preliminary results on the multiplicity of the photo-Fries reaction of p-tolyl acetate. They concluded from their results, inability to sensitize or quench the reaction, that the overall transformations occur from the singlet excited state or a very short-lived triplet state. In the present work, the photo-Fries reaction of phenyl benzoate was examined. Experiments designed to elucidate the excited state multiplicity of the reactive intermediate are described.

In preliminary sensitization experiments, solutions of phenyl benzoate in methanol containing acetophenone, xanthone, or benzophenone were irradiated. No triplet sensitized reaction could be detected. It was felt that the triplet energies of acetophenone and xanthone (E_t = 74 kcal/mole)(3) might be insufficiently high to achieve efficient energy transfer to the phenyl benzoate.(4) To determine if this was a factor in the lack of reaction, quenching studies were conducted on the photoreduction reaction of xanthone.(5)

Solutions of xanthone (1.0×10^{-2} M) in methanol, containing phenyl benzoate (1.1×10^{-2} M), phenyl acetate (1.7×10^{-2} M), and naphthalene (1.8×10^{-2} M), were irradiated (3500A).(6) Phenyl benzoate and phenyl acetate had no effect on the rate of photoreduction as compared to the unquenched reaction (18%, 9 hr.), while naphthalene completely quenched the reaction. Higher concentrations of phenyl benzoate (2×10^{-1} M) proved equally ineffective in quenching the reaction.

The efficient quenching of the photoreduction of xanthone by naphthalene (E_t = 61 kcal/mole)(3) implies that xanthone undergoes photoreduction via its triplet excited state, which is in accord with the commonly accepted mechanism for photoreduction of aryl ketones. The fact that phenyl benzoate does not quench the reaction of xanthone, even at high concentrations, suggests that the triplet energy of phenyl benzoate is greater than 74 kcal/mole.

Table I

Sensitized Photolysis of Phenyl Benzoate

[TPM] M x 10^2	% Reaction at Times (min.) 5	10	15	20
0	-	-	-	41
1.7^a	9	21	30	38
4.2^b	10	24	35	45

a. Absorbed 23% of incident light.

b. Absorbed 43% of incident light.

Solutions of phenyl benzoate in methanol (1.0 x 10^{-2} M) with triphenylmethane (TPM), E_t = 81 kcal/mole,(7) as the sensitizer were irradiated (2537A). The results (Table I) show that the rate of reaction in the presence of TPM was approximately equal to or greater than the rate without sensitizer, although the TPM absorbed a significant fraction of the light. The relative yields of products in the sensitized reactions were identical to those in the unsensitized runs. The apparent similarity of reaction rates in the presence of TPM compared to that of phenyl benzoate alone would suggest a fortuitous balancing of $\underline{k}_{ic}$ for phenyl benzoate and $\underline{k}_{ic}$ and $\underline{k}_q$ for TPM.(8) However, sensitization must have been achieved, since in the presence of TPM a significant rate decrease would have been expected if no sensitization had occurred. The demonstration of a triplet sensitized process with the product distribution identical to the unsensitized reaction is sufficient evidence that the triplet is the reacting species in the direct irradiations ("fingerprint method").(9) Therefore, we can conclude that the photo-Fries reaction of aryl esters is a triplet state reaction. These results also establish the triplet energy of phenyl benzoate as lying between 74 and 81 kcal/mole.(10)

Although the sensitization experiments indicate that the photo-Fries reaction proceeds *via* the triplet excited state, the reported lack of quenching of this reaction must be explained. Trecker(2) has shown that the photo-Fries reaction of *p*-tolyl acetate is not quenched by naphthalene (3.5 x 10^{-2} M) or by ferric acetylacetonate (1.5 x 10^{-3} M), both excellent triplet state quenchers. However, since the rearrangement products are formed in an intramolecular process, it is possible that the rate of reaction is sufficiently close to the rate of diffusion so as to preclude quenching at normal quencher concentrations. The lack of phosphorescence from these aryl esters(11) would support this view.

Preliminary results with p-tolyl benzoate indicate that at naphthalene concentrations greater than 0.3 M, the ratio of products 2-hydroxy-5-methylbenzophenone/p-cresol increases. Irradiation (3500A) of a solution of p-tolyl benzoate (0.5×10^{-1} M) in methanol with added naphthalene (0.31 M) at 40% reaction gave a yield of 2-hydroxy-5-methylbenzophenone comparable to that of the unquenched reaction. The yield of p-cresol was decreased by 50%, thus indicating that at least a portion of the reaction may be quenched under these conditions. Similar results were obtained with phenyl benzoate and 2,6-dimethylphenyl benzoate. Other quenchers are being investigated in an attempt to obtain more quantitative data.

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References

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(3) N. J. Turro, "Molecular Photochemistry", W. A. Benjamin, Inc., New York, N. Y., 1967, p. 132.

(4) This possibility has been discussed by Trecker. See ref. 2, footnote 26.

(5) This reaction has been studied by V. Fanker and E. Ehrhardt, *Bull. Chem. Soc. Jap.*, **39**, 1694 (1966).

(6) The reactions were carried out in sealed Vycor or Pyrex tubes (N_2 purged) using a Rayonet "merry-go-round" reactor. The analyses were accomplished by vpc using the internal standard method.

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(8) This apparent equivalence was brought to our attention by a referee.

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(10) Compare to methyl benzoate (E_t = 78 kcal/mole), Y. Kanda, R. Shimada, Y. Takenoshita, *Spectrochim. Acta*, **19**, 1249 (1963).

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