THE PHOTOCHEMISTRY OF α-ARYL CARBOXYLIC ANHYDRIDES

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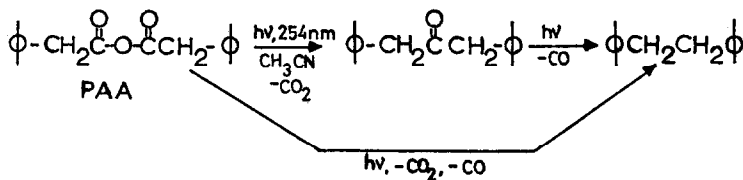Nieuwe Achtergracht 129, Amsterdam, The Netherlands

The gasphase photolysis of acetic anhydride has been investigated by Ausloos [1] and Taylor c.s. [2,3] Little is known about the photoreactivity of unsubstituted carboxylic anhydrides in the liquid phase, probably due to the lack of commercially available radiation sources for the absorption region of this class of compounds ($\lambda < 240$ nm).

We wish to report on the photolysis of α-phenyl substituted acetic anhydrides. The introduction of a phenyl group on the α-carbon atom enhances the absorption in the 254 region considerably ($\varepsilon_{254} = 520$). For these bichromophoric systems two modes of activation may be considered. Firstly, excitation of the aryl moiety, followed by intramolecular energy transfer. Such a process has been proposed by Brainard and Morrison [4] for the photoreaction of the 2-ethoxyethyl ester of phenylacetic acid. With this compound experimental evidence was found for a process of intramolecular singlet energy transfer from the phenyl to the ester group. Secondly, excitation of the anhydride function, with an enhanced possibility of occurrence of a Norrish Type I reaction, due to the reduced strength of the benzylic carbon-carbonyl bond.

We have found that photolysis of phenylacetic anhydride (PAA; 0.06M) in acetonitril with 254 nm radiation (Rayonet photochemical reactor) gives rise to elimination of CO_2 and CO with formation of dibenzyl along with some 1,3-diphenylpropanone, as shown in Scheme I. The ketone itself upon 313 nm irradiation is known to eliminate CO rather efficiently via a short lived triplet state. [5] At least part of the dibenzyl may thus originate from the ketone.
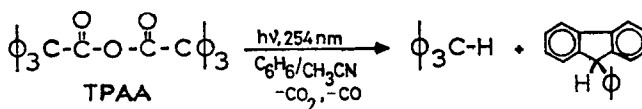
The importance of a close proximity of the two chromophores for reaction to occur at all, is demonstrated by the following observations. Irradiation of acetic anhydride in benzene as solvent and as possible sensitizer afforded no reaction products. In a comparative study of the homologues $C_6H_5-(CH_2)_n-$ $-CO-O-CO-(CH_2)_n-C_6H_5$ with n = 0, 1, 2, and 3, phenylacetic anhydride (PAA) is the only compound in this series showing photolytic reactivity.

$$\phi\text{-CH}_2\overset{\overset{O}{\|}}{\text{C}}\text{-O-}\overset{\overset{O}{\|}}{\text{C}}\text{CH}_2\text{-}\phi \xrightarrow[\substack{\text{CH}_3\text{CN} \\ -\text{CO}_2}]{h\nu, 254\text{nm}} \phi\text{-CH}_2\overset{\overset{O}{\|}}{\text{C}}\text{CH}_2\text{-}\phi \xrightarrow[-\text{CO}]{h\nu} \phi\text{CH}_2\text{CH}_2\phi$$

PAA

$$h\nu, -\text{CO}_2, -\text{CO}$$

Scheme I

It is noteworthy that the photoreactivity of PAA within the series of homo-
logues correlates with an increased UV-absorption in the 230-245 nm region
(e.g. $\varepsilon_{240} \sim 750$). This suggests some kind of interaction between the two
chromophores in the ground- or excited state of the molecule. Electronic inter-
action between the phenyl group and another chromophore has in fact been
established for α-phenyl substituted ketones,[6] carboxylic acids,[7] and
esters.[4] The photolysis of diphenylacetic anhydride gives essentially similar
results as depicted in Scheme I, although now only traces of the corresponding
ketone were detected.

In the case of triphenylacetic anhydride (TPAA) the distribution of photolytic
products is highly dependent on the presence of (traces of) oxygen. Irradiat-
ion of a thoroughly degassed solution of TPAA in benzene/acetonitril 1:1 v/v
(6×10^{-3}M) leads to the formation of triphenylmethane and 9-phenylfluorene in
a ratio of about 3:1 (Scheme II). This ratio is similar to that found by
Heine[8] in the photolysis of phenyl trityl ketone. The formation of 9-phenyl-
fluorene may be considered as arising from a photoreaction of the trityl
radical.[9-11]

$$\phi_3\text{C-}\overset{\overset{O}{\|}}{\text{C}}\text{-O-}\overset{\overset{O}{\|}}{\text{C}}\text{-C}\phi_3 \xrightarrow[\substack{\text{C}_6\text{H}_6/\text{CH}_3\text{CN} \\ -\text{CO}_2, -\text{CO}}]{h\nu, 254\text{nm}} \phi_3\text{C-H} +$$

TPAA

Scheme II

The presence of oxygen does not decrease the photoreactivity of TPAA. In ad-
dition to the products found in the anaerobic experiment, there is now also
formed benzophenone and biphenyl in a 8 to 1 ratio. Thus oxygen does not
quench the excited state but interferes chemically in a later stage.

The formation of these products may be explained as follows (Scheme III).
The triphenylmethyl radicals react with oxygen with formation of triphenyl-
methylperoxy radicals which in a bimolecular process yield oxygen and tri-
phenylmethoxy radicals. These radicals then decompose to phenyl radicals and
benzophenone. [12-14] The phenyl radicals in benzene as solvent will yield in
part biphenyl. Experiments performed by Hey c.s. [15] have shown that in the
decomposition of benzoylperoxide in benzene approximately 1 out of 6 phenyl
radicals ends up as biphenyl. In our experiment the observed benzophenone/
biphenyl ratio is higher than would be expected if the dephenylation of the
triphenylmethoxy radical were the only route to benzophenone. This suggests
that benzophenone is also formed by another route.
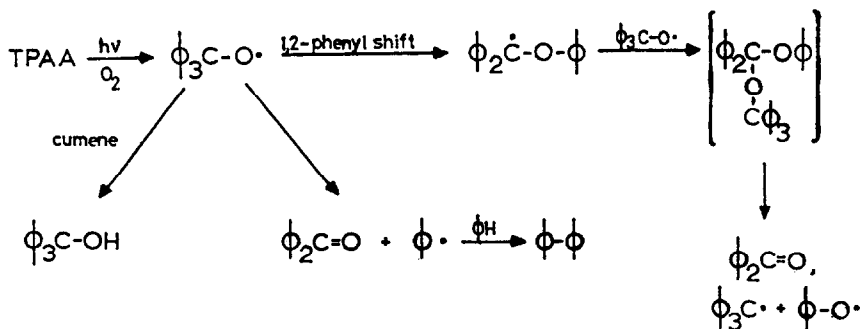
Scheme III

It is known from the literature [16] that the triphenylmethoxy radical can
undergo a 1,2-phenyl shift with formation of a phenoxydiphenylmethyl radical.
Recombination of this radical with a triphenylmethoxy radical leads to the
formation of (presumably) unstable phenoxydiphenyltriphenylmethoxymethane
which decomposes to form benzophenone and a trityl and phenoxy radical
(Scheme III).

The presumed intermediacy of triphenylmethoxy radicals is supported by photo-
lytic experiments of TPAA using cumene as hydrogen-donating solvent. In fact,
some triphenylmethanol is then observed as a product along with a large ex-
cess of acetophenone. The excess of acetophenone arises from the direct
photo-oxidation of cumene, as was shown in a separate experiment.

Further study, also on the substituted phenylacetic anhydrides, is in progres

REFERENCES

1. P. Ausloos, Can. J. Chem., 34, 1709 (1956).
2. R.J. Kandel, H.A. Taylor, J. Chem. Phys., 19, 1250 (1951).
3. H. Burwasser, H.A. Taylor, ibid., 23, 2295, (1955).
4. R. Brainard and H. Morrison, J. Amer. Chem. Soc., 93, 2685 (1971).
5. W.K. Robbins and R.H. Eastman, ibid., 92, 6076 (1970).
6. W.D. Kumler, L.A. Strait, and E.L. Alpen, ibid., 72, 1463 (1950).
7. M.L. Yarchak, J. Christopher Dalton, and W.H. Saunders jr., ibid., 95, 5228 (1973).
8. H.G. Heine, Tetrahedron Letters, 1473 (1971).
9. S.T. Bowden and W.J. Jones, J. Chem. Soc., 1149 (1928).
10. R.L. Letsinger, R. Collat, and M. Magnusson, J. Amer. Chem. Soc., 76, 4185 (1954).
11. H.G. Lewis and E.D. Owen, Chem. Comm., 216 (1966).
12. H. Wieland, Ber., 44, 2550 (1911).
13. M.S. Kharasch, A.C. Poshkus, A. Fono, and W. Nudenberg, J. Org. Chem., 16, 1458 (1951).
14. S.J. Cristol and J.E. Leffler, J. Amer. Chem. Soc., 76, 4468 (1954).
15. D.H. Hey, M.J. Perkins, and G.H. Williams, J. Chem. Soc., 3412 (1964).
16. M.A. Spielman, J. Amer. Chem. Soc., 57, 1117 (1935).