Photolysis of Triphenylmethyl Cations in Sulphuric Acid

By D. M. ALLEN and E. D. OWEN*

(Chemistry Department, University College, Cardiff CF1 1XL)

Summary Photolysis of triphenylmethyl cation in 99% sulphuric acid gave the 9-phenylfluorenyl and 9-hydroxy-fluoren-9-yl cations, both of which were formed *via* a common intermediate.

RECENT publications[1] have been concerned with the photolysis of triphenylmethyl cations in various sulphuric acid–acetic acid mixtures in the presence and absence of oxygen. In the absence of oxygen the mechanistic scheme suggested involved the abstraction of a hydrogen atom from a suitable donor by the excited triplet state of triphenylmethyl cation with the formation of the cation radical Ph_3CH^+. We have carried out experiments using 99% sulphuric acid but lower concentrations of carbonium ion *ca.* 10^{-5}M) than those employed previously (*ca* 10^{-3}M). Our systems also differed in that they contained no added hydrogen donors.

(II) by comparison of its u.v. and i.r. spectra with those of authentic material.[3] The visible and u.v. spectrum of a solution of compound (II) in 99% sulphuric acid *i.e.* of the carbonium ion (III) was identical with that of the $Ph_3C^+OH^-$ solutions after irradiation. The rate of disappearance of compound (I) was the same as the rate of appearance of the ion (lII) and this together with the sharpness of the isobestic points indicated a clean conversion of (I) into (III) with the absence of any detectable side reactions.

On adding varying amounts of oxygen two significant changes were observed compared with the oxygen-free systems. First, the overall rate of disappearance of the alcohol (I) was greatly reduced, falling by a factor of 40 as the partial pressure of oxygen was increased from zero to 450 Torr. Secondly, the percentage of the ion (III) in the product decreased and a new product was detected. U.v.
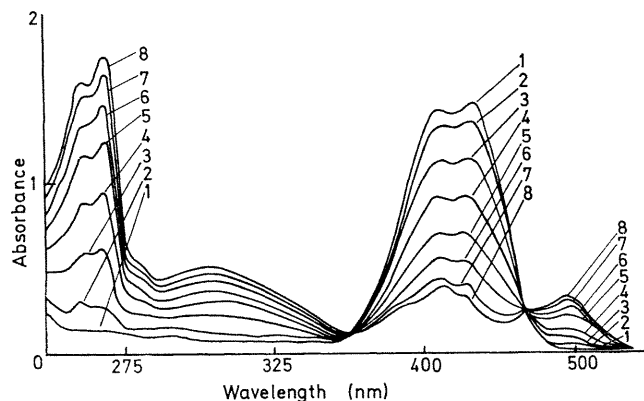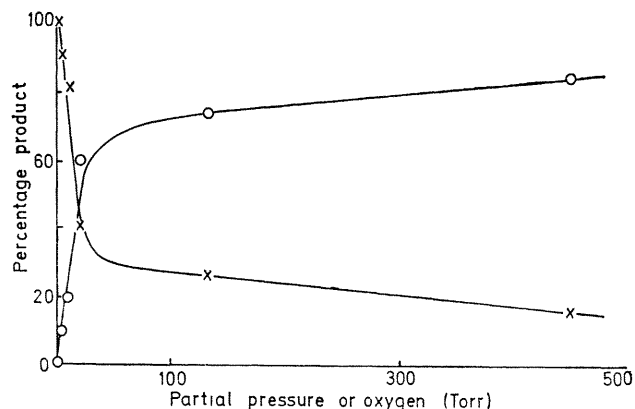

FIGURE 1. *Absorption spectra of solutions of triphenylcarbonium ion in 99% sulphuric acid open to the atmosphere after various times of photolysis* 1, 0; 2, 19; 3, 59; 4, 100; 5, 141; 6, 187; 7,269; and 8, 388 min.

FIGURE 2. *Variation of the percentage of 9-phenylfluoren-9-yl cation* (III) (×) *and 9-hydroxyfluoren-9-yl cation* (V) (○) *in the product after photolysis with various partial pressures of oxygen.*

Thoroughly outgassed solutions of $Ph_3C\cdot OH$ (1) in 99% AnalaR sulphuric acid were irradiated (Pyrex filter; high-pressure mercury lamp) and the characteristic absorption of the carbonium ion[2] (λ_{max} 430 nm) decreased and was replaced by an absorption with a maximum at 493 nm. Isobestic points occurred at 453 and 340 nm. On completion of the reaction the sulphuric acid solution was diluted with a large excess of ice, extracted with benzene and the products separated by preparative t.l.c. on silica gel. The main product was found to be 9-phenylfluoren-9-ol

i.r., and mass spectra proved that this was fluoren-9-one (IV). Spectra of solutions photolysed while open to the atmosphere are shown in Figure 1. In this case the rate of increase of the peak at 493 nm was considerably reduced and new absorptions characteristic of the carbonium ion (V) formed by protonation of the ketone (IV) were observed.

In the presence of oxygen the rate of disappearance of the alcohol (I) is the sum of the rates of appearance of the ions (III) and (V) and in addition, as the concentration of oxygen is increased the percentage of (V) in the product increases as (III) decreases (Figure 2).

In the absence of oxygen our results substantially agree with those of previous workers. In the presence of oxygen, however, the simple distribution of products and the appearance of fluoren-9-one as a major product are a consequence of the low concentration of carbonium ion and the absence of added hydrogen donors.

The addition of oxygen to the degassed system reduces the rate of formation of the ion (III) about twenty times more than it affects the rate of formation of the ion (V), suggesting that the oxygen has a quenching effect as well as reacting with (III) to form (V). This in turn suggests that the triplet state of the ion is an important intermediate in the reaction since the oxygen has only a very small effect on the fluorescence of the alcohol (I).

The similarity of the two products, and the way in which their relative amounts vary with the concentration of dissolved oxygen suggests that they may be formed from a common intermediate such as (VI) (reaction 1).

(VI)
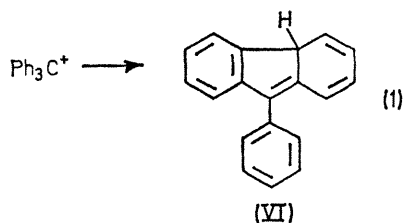
The carbonium ion (III) could arise by removal of an allylic hydride ion, a well known process in sulphuric acid[2] (reaction 2) or (VI) could undergo attack by molecular

(III)
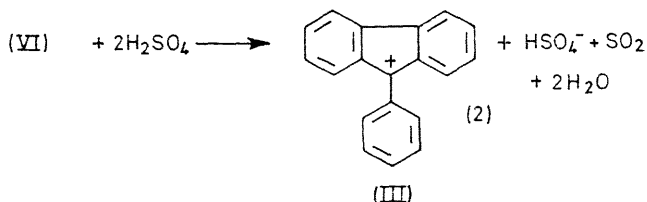
oxygen to form a hydroperoxide (VII) which would rearrange in acid solution to form the ion (V) (reaction 3).
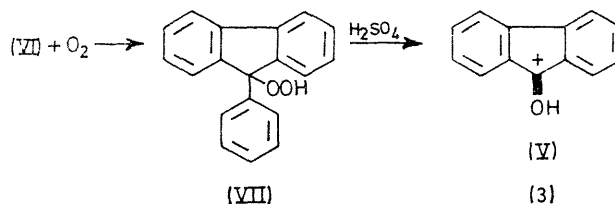
(VII)   (V)

[1] (a) E. E. van Tamelen, T. M. Cole, R. Greeley and H. Schumacher, J. Amer. Chem. Soc., 1968, 90, 1372; (b) E. E. van Tamelen and T. M. Cole, Jun., ibid., 1970, 92, 4123; (c) T. M. Cole, Jun., ibid., p. 4124.
[2] G. A. Olah and P. von R. Schleyer, 'Carbonium Ions,' Interscience, New York, 1968.
[3] W. E. Bachmann, J. Amer. Chem. Soc., 1930, 52, 3287.