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THE NATURE OF THE PHOTOREACTIVE TRIPLET STATE OF 9-ANTHRALDEHYDE

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The photoreduction of aromatic ketones normally occurs via the intermediacy of an n, π^* triplet state (1) although in certain cases the reduction can proceed via a π, π^* triplet state (2). The photoreactive triplet state may not necessarily be the lowest energy state of the triplet manifold. In the case of 9-anthraldehyde the triplet sate of lowest energy is π. π^* in character (3) and non-reactive with respect to photoreduction (4), and it has been deduced (4) that the higher energy photoreactive state is n,π^* in character. 9-anthraldehyde is photoreduced in the presence of toluenes (4), and the results given below for comparative reductions in toluenes provide further evidence that the photoreactive state is n, π^* in character.

Comparative experiments were performed by irradiating at 366nm sealed, degassed solutions of 9-anthraldehyde (0.01M) and toluene or substituted toluene (0.1 - 0.5M) in benzene. The photolysis were carried out in an apparatus previously described (5) and the quantum yields for the photoreduction of 9-anthraldehyde by toluene, Φ_o, and by substituted toluenes, Φ, were calculated after allowance had been made for the consumption of 9-anthraldehyde by photo-dimerisation and for the different numbers of ' reactive ' protons in the toluenes used. The plot of $\log_{10} \Phi/\Phi_o$ against the Hammett σ^+ constants for the substituents is shown in Fig. 1.

The value for the reaction constant ρ^+ derived from the straight line plot is -1.31. This value is to be compared with the corresponding value of -1.16 for the photoreactive triplet state of benzophenone (6). Since it has been well established that the photoreactive triplet state of benzophenone is n, π^* in character, the similarity between two values indicates that the reactive triplet state of 9-anthraldehyde is also n, π^* in character.

It is to be expected that the n, π^* triplet states of 9-anthraldehyde and benzophenone would have similar electronegativities, and hence the slightly larger negative value of σ^+ for the triplet state of 9-anthraldehyde may reflect a decreased reactivity of this triplet state as compared to that of benzophenone. This would be in accord with the lower energy (58 - 64 Kcal/mole) of the triplet state of anthraldehyde (4) compared to the higher energy (69 Kcal/mole) of the triplet state of benzophenone (7).

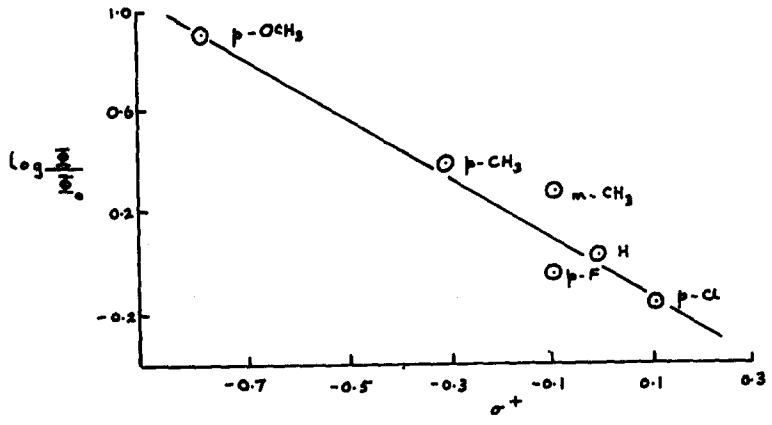

Fig. 1. Relationship between relative reactivities of toluenes and Hammett σ^+ constants.

REFERENCES

1. W.M. Moore, G.S. Hammond and R.P. Foss, J.Am. Chem. Soc. 83, 2789 (1961); G.S. Hammond, W.P. Baker and W.M. Moore, ibid. 83, 2795 (1961).

2. G.S. Hammond and P.A. Leermakers, ibid. 84, 207 (1962).

3. D.A. Warwick and C.H.J. Wells, Spectrochim. Acta, 24A, 589 (1968).

4. D.A. Warwick and C.H.J. Wells, Tetrahedron Letters, 4401 (1968).

5. D.A. Warwick and C.H.J. Wells, J.Sci.Instruments, 44, 483 (1967).

6. C. Walling and M.J. Gibian, J.Am. Chem. Soc., 87, 3361 (1965).

7. W.G. Herkstroeter, A.A. Lamola and G.S. Hammond, ibid. 86, 4537 (1964).