Photochemistry of Fluorene Derivatives

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Summary Excited-state pK values for fluorene and some 9-substituted fluorenes are reported.

IN our study of the photochemistry of fluorene derivatives, we have attempted to measure their acidity constants in the lowest singlet excited state (hereafter S_1) and in the lowest excited triplet state (hereafter T_1).

The ionic dissociation or formation of C–H bonds is usually a slow process. Excited-state pK's must therefore be estimated by use of the Förster cycle.[1,2] This technique has been described elsewhere.[3] Although the acidity constants obtained in this way may not always correspond to physically observable processes, the thermodynamic approach appears to be one of the only procedures for obtaining information on acid–base properties of carbon–hydrogen bonds when the rate of proton transfer is slow compared to the lifetime of the excited state. We report preliminary results for fluorene and three monosubstituted fluorenes. These derivatives are weak acids, but deprotonation is easily performed in mixtures of dimethyl sulphoxide–methanol–sodium methoxide or alcohols–sodium alkoxides of known H_- values.[4] From the results given in Table 1 it appears that the acidity in the S_1 state is increased by factors of 10^{22}—10^{29}. A smaller enhancement of the acidity is obtained in the triplet state (Table 2). This is to be compared with the results for prototropic equilibria involving protonation and deprotonation of hetero-atoms; in these systems, triplet-state pK's are also found between the ground state and the lowest singlet excited state pK's.[5] For the compounds studied in this work, p$K(G)$ is very sensitive to the substituent in position 9, but the opposite situation prevails in the S_1 and T_1 states. This suggests an increased delocalization of the negative charge in fluorenes in both excited states. Although the acidity is much increased in the S_1 state, the rate of deprotonation remains too slow for one to measure any significant fluorescence transformation between pH 0 and 12. A similar result has been obtained by Weller[6] for fluorene and has also been encountered when attempts have been made to protonate hydrocarbons on carbon atoms during the lifetime of the S_1 state.[2]

TABLE 1

	Ground state pK	ν_{00} (cm.$^{-1}$) Absorption	ν_{00} (cm.$^{-1}$) Fluorescence	$\Delta\nu_{00}$ (cm.$^{-1}$)	pK (S_1)	
Fluorene	20·5	33,300	32,780	14,115	− 8·5	Acid form
		19,600	18,250			Basic form
9-Phenylfluorene	18·6	32,840	32,470	14,110	−10·7	Acid form
		19,240	17,850			Basic form
9-Ethoxycarbonylfluorene ..	10·0	33,110	32,470	10,240	−11·8	Acid form
		23,150	21,950			Basic form
9-Cyanofluorene	11·4	33,300	32,410	10,605	−12·4	Acid form
		22,420	21,380			Basic form

TABLE 2

Molecules	ν_{00} (cm.$^{-1}$) Phosphorescence (acid)	ν_{00} (cm.$^{-1}$) Phosphorescence (base)	$\Delta\nu_{00}$ (cm.$^{-1}$)	p$K(T_1)$
Fluorene	23,720	16,400	7320	+5[a]
9-Phenylfluorene	23,530	16,660	6870	+4·2
9-Ethoxycarbonylfluorene ..	23,310	21,400	1910	+6·0
9-Cyanofluorene	23,390	20,320	3070	+5·0

[a] Phosphorescence of the anion of fluorene is very weak; therefore the ΔpK between the ground state and the lowest triplet state had to be measured from the phosphorescence maximum and is thus approximate.

Owing to the rather long lifetime of the triplet state of fluorene derivatives in solution, we tried to follow the acid–base equilibrium by conventional flash photolysis. The neutral forms of the derivatives examined give typical T–T absorption bands in dimethyl sulphoxide, whereas the transient spectra of the anions result essentially from the photo-ejection of an electron. This could be shown unambiguously for 9-ethoxycarbonylfluorene by comparison of the spectra obtained by flash-photolysis and by continuous irradiation of the anions in glassy Et_2O–isopentane–EtOH (5 : 5 : 2, v/v, E.P.A.) at 77°K. The radicals obtained in these conditions are stable and their visible spectra are similar to those observed by flash-photolysis (Table 3). The examination by e.s.r. spectroscopy of the glassy solutions of the irradiated anions proves the presence of trapped

TABLE 3

Wavelengths and relative intensities of the absorption maxima (nm) of 9-ethoxycarbonylfluorenyl radical

E.P.A. (77°K) Continuous irradiation		Dimethyl sulphoxide (room temperature) Flash-photolysis	
Position	Intensity	Position	Intensity
562	1·0	565	1·0
525	0·6	522	0·5
488	0·05	—	—

electrons in these systems. On the other hand, because of the very intense absorption of the fluorenyl radicals between 17,000 and 22,000 cm.$^{-1}$, it has not yet been possible to detect the trapped or solvated electrons by low-temperature or flash visible spectroscopy.

We thank Professor R. H. Martin for his interest, the Fonds National de la Recherche Collective and the Fonds National de la Recherche Scientifique Belge for financial support.

(*Received, June 23rd,* 1969; *Com.* 907.)

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