Reactions of Radical Anions. Part XI.[1] Radical Anions of Substituted Fluorenones

By **Alwyn G. Evans,* Jeffrey C. Evans, Philip J. Emes,** and **Syed I. Haider,** Department of Chemistry, University College, Cardiff, P.O. Box 78, Cardiff CF1 1XL

The radical anions of substituted fluorenones have been studied by e.s.r. The disproportionation equilibria of the radical anions with the dianions and the neutral molecules have been examined and thermodynamic constants have been obtained for these systems in the presence of various gegenions.

WE have previously studied the disproportionation reactions of various radical anions.[2] We now report a similar study of radical anions of substituted fluorenones.

EXPERIMENTAL

Materials.—Dimethylformamide (B.D.H.) was distilled from sodium hydride and the fraction boiling at 153 °C was collected. Tetrahydrofuran was purified as described previously.[2]

1-Aminofluoren-9-one (Aldrich) crystallised as yellow needles, m.p. 118° (from ethanol) (lit.,[3] 118—118·5°). 2-Aminofluoren-9-one (Aldrich) crystallised as a violet-red compound, m.p. 162° (from ethanol) (lit.,[4] 163°). 4-Aminofluoren-9-one (Aldrich) crystallised as red needles, m.p. 144° (from ethanol) (lit.,[5] 145°). 4,5-Diazafluoren-9-one (K and K) crystallised from 95% ethanol, m.p. 212° (lit.,[6] 212—213°). 3-Aminofluoren-9-one was prepared by reduction of 3-nitrofluoren-9-one (Aldrich) with tin(II) chloride in concentrated hydrochloric acid and ethanol under reflux for 9 h. The insoluble tin complex was filtered from the cooled solution and decomposed with an excess of sodium hydroxide. The yellow base had m.p. 158—159° (from ethanol) (lit.,[7] 159°). 2,7-Diaminofluoren-9-one, obtained from 2,7-dinitrofluoren-9-one (Aldrich) by the method of Barker and Barker,[8] was purified by chromatography and recrystallised from xylene giving violet crystals, m.p. 283—284° (lit.,[8] 284—286°; lit.,[9] 290°). 1,8-Diazafluoren-9-one, obtained from 4,7-phenanthroline-5,6-quinone (CIBA) by the method of Druey and Schmidt,[10]

---

[1] Part X, A. G. Evans, J. C. Evans, P. J. Emes, C. L. James, and P. J. Pomery, *J. Chem. Soc.* (*B*), 1971, 1484.

[2] A. G. Evans, J. C. Evans, and E. H. Godden, *J. Chem. Soc.* (*B*), 1969, 546; A. G. Evans, J. C. Evans, C. L. James, *ibid.*, 1967, 652; A. G. Evans, J. C. Evans, E. H. Godden, *Trans. Faraday Soc.*, 1967, **63**, 136; A. G. Evans, J. C. Evans, *J. Chem. Soc* (*B*), 1966, 271; A. G. Evans, B. J. Tabner, *J. Chem. Soc.*, 1963, 4613; J. E. Bennett, A. G. Evans, J. C. Evans, E. D. Owen, and B. J. Tabner, *ibid.*, 1963, 3954; A. G. Evans, J. C. Evans, E. D. Owen, B. J. Tabner, and J. E. Bennett, *ibid.*, 1962, 226.

[3] G. Goldschmiedt, *Monatsh.*, 1902, **23**, 886.

[4] O. Diels, *Ber.*, 1901, **34**, 1764; C. W. Bennett and W. W. Muelder, *J. Amer. Chem. Soc.*, 1953, **75**, 6039.

[5] C. Courtot, *Ann. Chim.* (*France*), 1930, **14**, 5.

[6] G. E. Inglett and G. F. Smith, *J. Amer. Chem. Soc.*, 1950, **72**, 842.

[7] A. Eckerts and E. Langecker, *J. prakt. Chem.*, 1928, **118**, 267.

[8] A. Barker and C. C. Barker, *J. Chem. Soc.*, 1954, 870.

[9] J. Schmidt, F. Retzlaff, and A. Haid, *Annalen*, 1912, **390**, 224.

[10] J. Druey and P. Schmidt, *Helv. Chim. Acta*, 1950, **53**, 1080.

afforded yellow crystals, m.p. 204° (from acetone) (lit.,[6] 205°).

Procedure.—Solutions of known concentrations of the fluorenone radical anions in tetrahydrofuran were prepared under high vacuum conditions by methods similar to those described earlier.[2] Samples of these solutions were transferred to e.s.r. tubes and examined on a Varian E-3 e.s.r. spectrometer at various temperatures between +20 and −60 °C. The temperature was controlled by a Varian temperature control system. Visible and u.v. spectra were also obtained for these solutions and the alkali metal concentration was determined by using a flame photometer.

TABLE 1

Results of studies on disproportionation equilibria at 0 °C

Fluoren-9-one	Gegenion	K_1	ΔG°_{1a}/ kcal mol^{-1}	ΔH°_{1a}/ kcal mol^{-1}	ΔS°_{1a}/ cal mol^{-1} deg^{-1}	$\lambda_{max.}$/nm radical anion	$\lambda_{max.}$/nm dianion
Unsubst.	Li$^+$	0·025	2·00	−3·57	−20·40	452	422, 600
	Na$^+$	0·063	1·49	−6·15	−27·91	458	434, 648
	K$^+$	0·049	1·64	−6·90	−31·28	476	465, 680
	Cs$^+$	0·210	0·85	−4·92	−21·13	530	474, 740
1-Amino	Li$^+$	0·058	1·55	−11·85	−49·1	446	364, 580
	Na$^+$	0·075	1·40	−3·86	−19·25	525	432, 630
	K$^+$	0·086	1·32	−3·98	−19·45	532	440, 650
	Cs$^+$	0·79	0·13	−2·64	−10·14	538	472, 660
2-Amino	Li$^+$	0·024	2·18	−0·555	−9·94	472	401
	Na$^+$	0·056	1·40	−3·86	−19·26	476	446
	Cs$^+$	21·37	−1·64	−1·67	−0·11	510	450, 630
3-Amino	Li$^+$	0·771	0·14	−5·27	−19·80	510	454
	Na$^+$	0·355	0·56	−3·38	−14·45	520	457
	K$^+$	0·133	1·09	−2·93	−14·72	530	465
	Rb$^+$	0·218	0·83	−1·62	−8·94	534	470
	Cs$^+$	25·29	−1·75	−1·44	1·16	538	474
4-Amino	Li$^+$	0·014	2·31	−1·03	−12·23	460	410
	Na$^+$	0·027	2·01	−4·21	−22·80	470	416
	K$^+$	0·035	1·84	−5·76	−27·84	467	436
	Cs$^+$	2·22	0·80	−0·60	−5·10	518	458
2,7-Diamino	Li$^+$	7·52	−1·10	−6·74	−20·65	474	308
	Na$^+$	0·98	0·012	−2·31	−8·50	477	317
	K$^+$	0·26	0·74	−2·69	−12·52	494	309
	Cs$^+$	92·9	−2·46	−3·82	−4·95	510	313
1,8-Diaza	Li$^+$	229·6	−2·95	−4·15	−4·39	437	427
	Na$^+$	19·5	−1·62	−3·66	−7·47	455	437
	K$^+$	157·8	−2·75	−3·66	−3·32	480	452
	Rb$^+$	285·1	−3·07	−4·09	−3·74	—	465
	Cs$^+$	175·4	−2·81	−3·88	−3·94	510	469
4,5-Diaza	Li$^+$	381	−3·23	−4·09	−3·14	—	334
	Na$^+$	3428	−4·42	−4·54	−0·43	—	337
	K$^+$	4688	−4·59	−3·45	4·18	—	337
	Rb$^+$	3145	−4·37	−2·11	8·28	—	336
	Cs$^+$	4571	−4·58	−3·15	5·21	—	338

Determination of the Radical Anion Concentration.—*Method* (*a*). E.s.r. absorption peaks of the radicals were integrated, and the integral count was compared with that obtained from a standard solution of diphenylpicrylhydrazyl under comparable conditions. This standard solution was made up under high vacuum conditions in the same rigorously purified tetrahydrofuran [2] as was the radical anion.

Method (*b*). The differential spectra of the radical anion and of a standard solution of diphenylpicrylhydrazyl in tetrahydrofuran were obtained and a computer program was used to perform a double integration of the spectra; this gave the area under the absorption curve and hence the concentration.

Examination of Products.—Evaporation of the solution left a white residue and a coloured compound. The coloured crystals were dissolved in ether. The white residue was soluble in distilled water, and gave an alkaline solution and the typical alkali metal flame colour, which suggested the presence of a metal hydroxide. The ethereal extract and the original compound each gave a single spot on t.l.c., with the same R_F values. The m.p. of the coloured crystals, after recrystallisation from ethanol, was similar to that of the original compound. Thus the only products were the alkali metal and the neutral compound.

Electrolytic Reduction.—In some cases the electrolytic reduction technique [11,12] was used. This gave spectra of the radical anion in the absence of gegenion splitting. The compound was dissolved in dimethylformamide and a solution of tetra-n-butylammonium iodide in dimethylformamide was added as supporting electrolyte. The ratio of solution to carrier electrolyte was kept at 1 : 1. Soon after the initial passing of current the colour of the radical anion of the fluorenone became visible above the cathode and the tube was then placed in the e.s.r. cavity and the spectrum obtained.

RESULTS

Dianions of Fluorenones.—When the fluorenone dissolved in tetrahydrofuran was brought into prolonged contact with an alkali metal, the resulting solution had

---

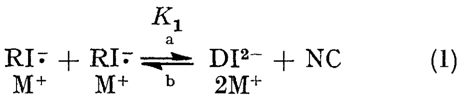
[11] D. H. Geske and A. H. Maki, *J. Amer. Chem. Soc.*, 1960, **82**, 2671.

[12] N. Steinberger and G. K. Fraenkel, *J. Chem. Phys.*, 1964, **40**, 723.

a [metal] : [fluorenone] ratio of 2 : 1 and gave no e.s.r. signal, showing that the fluorenone had been converted completely into the dianion. On opening the solution to air and examining the products, only the fluorenone and the alkali metal were found. The dianion absorption maxima for the various fluorenones and gegenions are given in Table 1.

Radical Anions of Fluorenones.—When the fluorenone dissolved in tetrahydrofuran was brought into contact with alkali metal for a short time, a solution was obtained which gave an e.s.r. spectrum showing that radical anions were present. On opening this solution to air and examining the product it was found that only the alkali metal and the original fluorenone were present. The radical anion absorption maxima for the various fluorenones and gegenions are given in Table 1.

Disproportionation Equilibrium.—The solutions were studied over the temperature range +20 to −60 °C. The changes over this range were completely reversible, and the solutions obeyed Beer's Law over a ten-fold dilution range. Thus we conclude that the disproportionation equilibrium shown in equation (1) occurs in these systems.



$$\underset{\mathrm{M}^+}{\mathrm{RI}^{\overline{\cdot}}} + \underset{\mathrm{M}^+}{\mathrm{RI}^{\overline{\cdot}}} \underset{\mathrm{b}}{\overset{K_1 \atop \mathrm{a}}{\rightleftharpoons}} \underset{2\mathrm{M}^+}{\mathrm{DI}^{2-}} + \mathrm{NC} \qquad (1)$$

where $\mathrm{RI}^{\overline{\cdot}}$ is the radical anion, DI^{2-} is the dianion, NC is the neutral compound, and M^+ is the alkali metal gegenion.

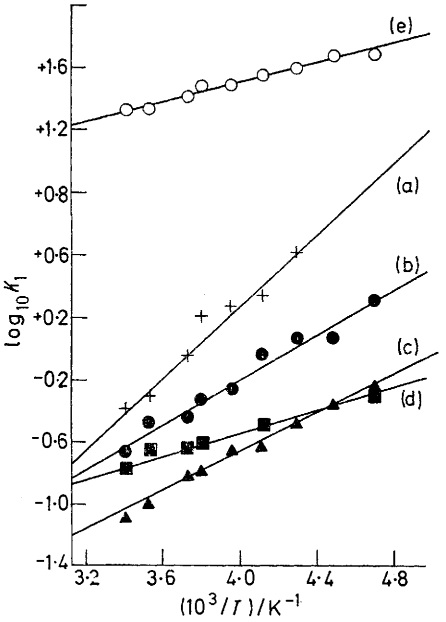


FIGURE 1 Temperature dependence of the equilibrium constant (K_1) for 3-aminofluoren-9-one system, with gegenions (a) lithium; (b) sodium; (c) potassium; (d) rubidium: and (e) caesium

Thermodynamic Constants for the Disproportionation Reaction.—Knowing the radical anion concentration from the e.s.r. experiments, the total gegenion concentration from flame photometry, and the total fluorenone concentration, we can calculate the equilibrium constant (K_1) of reaction (1):

$$K_1 = [\mathrm{DI}^{2-}2\mathrm{M}^+][\mathrm{NC}]/[\mathrm{RI}^{\overline{\cdot}}\mathrm{M}^+]^2$$

From the dependence of K_1 on temperature the values of ΔH°_{1a} were found (Table 1). We estimate the errors as $\pm 0{\cdot}5$ kcal mol^{-1} in ΔH°_{1a} and in ΔG°_{1a} and ± 1 cal deg^{-1} mol^{-1} in ΔS°_{1a}. The radical anion concentration values were accurate to $\pm 7\%$. An example of the temperature dependence results is shown in Figure 1. In all cases the system obeyed Beer's Law at room temperature over about a five-fold dilution range. Warhurst plots of $\tilde{\nu}$ against $1/(r_c + 2)$, where r_c is the cationic radius, are shown in Figure 2. Good plots were obtained for all except 2,7-diaminofluoren-9-one, in which $\tilde{\nu}$ for Li is larger than expected, showing that in this case the Li^+ (2,7-diaminofluoren-9-one)$^{\overline{\cdot}}$ ion pair has some solvent-separated character.

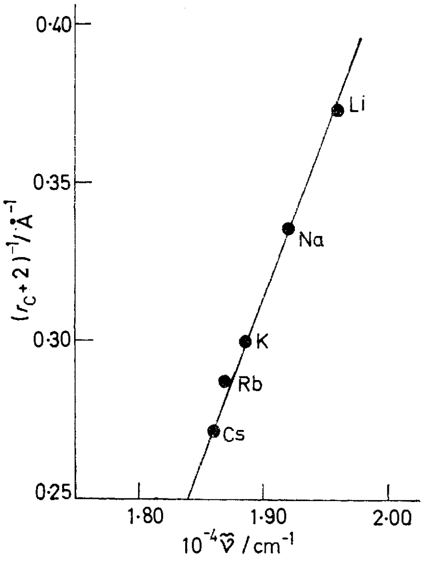


FIGURE 2 Plot of $\tilde{\nu}$ *vs.* $(r_c + 2)^{-1}$ for alkali metals with with 3-aminofluoren-9-one radical anion

E.s.r. Results.—In general good e.s.r. spectra of the radical anions were difficult to obtain and, where obtained, were complicated. Some of these spectra were obtained by electrolysing the solution of the neutral compound in dimethylformamide, but the majority came from the equilibrium mixtures of the compound in tetrahydrofuran after passing over the various alkali metal films. In the latter method the presence of neutral compound and the dianion affected the resolution of the spectra owing to the occurrence of exchange processes, and optimum conditions had to be sought. The splitting constants obtained are given in Table 2 (method of assignment is dealt with in the next section).

Molecular Orbital Calculations.—The following parameters were used (for notation see formula in Table 2):

$$\alpha_X = \alpha_C + 1{\cdot}0\beta_{C-C}; \quad \beta_{CX} = \beta_{C-C}$$

$$\alpha_O = \alpha_C + 1{\cdot}6\beta_{C-C}; \quad \beta_{CO} = 1{\cdot}5\beta_{C-C}$$

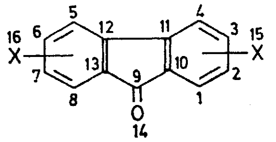
$$\beta_{11,12} = 0{\cdot}8\beta_{C-C}; \quad \beta_{9,10} = \beta_{9,13} = 1{\cdot}2\beta_{C-C}$$

The values for α_O, β_{CO}, $\beta_{11,12}$, and $\beta_{9,10}$ ($\beta_{9,13}$) were those used by Dehl and Fraenkel[13] for fluorenone. In addition, an auxiliary inductive parameter,[14] $\delta = 0{\cdot}10$, was introduced for the coulombic integral of C-9 to account for the electronic polarisation of C-9 by the oxygen atom.

The calculated Hückel and McLachlan spin densities and the corresponding splitting constants obtained are shown in Table 2. The calculations provide information on all proton hyperfine splitting constants except those of the amino-protons.

Table 2

Splitting constants and calculated spin densities for the radical anions of fluorenones



Fluorenone radical anion	Position	Calculated spin densities		Calculated splitting constants (G)		Observed splitting constants (G)
		Hückel	McLachlan	Hückel	McLachlan	
1-Amino	2	0·063	0·054	1·57	1·35	1·20
	3	0·075	0·085	1·88	2·12	3·05
	4	0·039	0·013	0·98	0·33	0·64
	5	0·011	0·025	0·27	0·62	0·64
	6	0·081	0·107	2·03	2·68	3·05
	7	0·025	0·000	0·62	0·00	
	8	0·080	0·077	2·00	1·93	2·01
	15(X)	0·035	0·019	0·74	0·40	0·36(N)
2-Amino	1	0·112	0·144	2·80	3·60	5·00
	3	0·057	0·069	1·43	1·73	2·58
	4	0·009	0·020	0·23	0·49	0·49
	5	0·006	0·034	0·12	0·85	0·66
	6	0·088	0·116	2·20	2·90	
	7	0·017	0·016	0·43	0·40	0·49
	8	0·076	0·093	1·90	2·33	2·58
	15(X)	0·014	0·005	0·30	0·11	0·60(N)
3-Amino	1	0·062	0·078	1·56	1·95	1·60
	2	0·003	0·029	0·08	0·73	0·70
	4	0·045	0·023	1·13	0·58	1·60
	5	0·009	0·030	0·23	0·80	0·70
	6	0·088	0·116	2·20	2·90	1·60
	7	0·026	0·003	0·65	0·08	0·60
	8	0·069	0·083	1·73	2·08	1·60
	15(X)	0·046	0·036	0·97	0·75	2·50(N)
4-Amino	1	0·095	0·117	2·37	2·92	2·62
	2	0·20	0·015	0·49	0·38	0·95
	3	0·109	0·144	2·73	3·60	5·60
	5	0·007	0·030	0·18	0·80	0·10
	6	0·083	0·109	2·08	2·73	2·62
	7	0·017	0·013	0·43	0·33	
	8	0·072	0·088	1·77	2·20	0·95
	15(X)	0·006	0·006	0·13	0·13	0·48(N)
2,7-Diamino	1,8	0·111	0·146	2·79	3·65	2·84
	3,6	0·076	0·080	1·89	2·00	0·25
	4,5	0·005	0·028	0·13	0·70	0·25
	15,16(X)	0·011	0·001	0·23	0·02	0·70(N)
1,8-Diaza	1,8(X)	0·066	0·049	1·39	1·03	
	2,7	0·181	0·248	4·52	6·20	
	3,6	0·001	0·063	0·03	1·58	
	4,5	0·170	0·230	4·25	5·75	
4,5-Diaza	1,8	0·165	0·227	4·13	5·67	3·19
	2,7	0·040	0·001	1·00	0·03	0·21
	3,6	0·089	0·101	2·22	2·52	2·15
	4,5(X)	0·130	0·136	2·74	2·87	1·11(N)

Q = 25 for positions 1—8. Q = 21·1 for atom X.

DISCUSSION

The Disproportionation Reaction.—The e.s.r. signals produced when solutions of neutral molecules were passed over alkali metal films were studied. The change in e.s.r. spectrum with temperature was completely reversible, showing that a temperature-dependent equilibrium was involved.

Analysis of the solutions for metal gegenion by flame

---

[13] R. Dehl and G. K. Fraenkel, *J. Chem. Phys.*, 1963, **39**, 1793.

[14] G. W. Wheland and L. Pauling, *J. Amer. Chem. Soc.*, 1935, **57**, 2086.

photometry showed that the concentration of metal cation was in excess of that required by the radical anion concentration, which was found by e.s.r. measurements as described earlier. Further analysis of the products showed the presence of only the original neutral molecule and the appropriate alkali metal hydroxide.

These results indicate that the radical anions themselves undergo a disproportionation reaction according to equation (1). Several other observations support this conclusion. Beer's dilution law was accurately obeyed over an approximately five-fold concentration range, which shows that the equilibrium constant K_1 remains constant with change in reagent concentration; thus no dimerisation of the radical anions occurs in this system. Also the change in radical anion concentration was reversible with change in temperature.

U.v. and Visible Spectra.—The $\lambda_{\text{max.}}$ values for the various radical anions were found to increase with the size of the gegenion (Table 1). A plot of $\tilde{\nu}$ against $1/(r_c + 2)$ gave good straight lines in all cases. In the case of (4,5-diazafluoren-9-one)$^{\bar{\cdot}}$ the radical anion concentration was too small to be detected by the u.v. measurements. The results show that the ions formed exist as contact ion pairs except for Li^+ (2,7-aminofluoren-9-one)$^{\bar{\cdot}}$ which, as mentioned above, has some solvent-separated character. This has been shown earlier for the case of the fluorenone radical anion by using e.s.r. techniques.[15]

In the case of the dianions we have checked that the $\tilde{\nu}$ *vs.* $1/(r_c + 2)$ relationship holds for 3-aminofluoren-9-one and 1,8-diazafluoren-9-one, and have assumed that this is the case for all the other dianions.

E.s.r. Spectra.—The e.s.r. spectra showed that metal ion interaction is occurring, although the complexity of the spectra made it impossible to determine exactly the individual splitting constants.

As the temperature was reduced the splitting constants for nitrogen and protons remained constant. In these spectra there was no alternating line-width effect and also no line-broadening effect with change of temperature. This implies that the potential hollows associated with the oxygen and the nitrogen atoms are not comparable in depth, but that the gegenion is strongly attracted to one particular negative centre.

The nitrogen splitting constants decrease along the series 3- $\gg$ 4- $\approx$ 2- $>$ 1-aminofluoren-9-one (Table 2), concomitant with the decreasing extent of conjugation between the amino-group and the fluorenone system;[16] it would be expected that a high degree of conjugation would result in a high electron spin density on the nitrogen atom.

Thermodynamic Constants for the Disproportionation Equilibrium.—The thermodynamic quantities are given in Table 1. For the aminofluoren-9-ones K_1 is larger for Cs^+ than for the other gegenions, owing in the main, to the fact that ΔS°_{1a} is more positive. A detailed consideration of the relationship between changes in K_1, ΔH°_{1a}, and ΔS°_{1a} and change in gegenion is not warranted. For the change from radical anion to dianion, the value of ΔH°_{1a} (or ΔS°_{1a}) is the difference between two large numbers, and does not show a regular change with ion size. Similar behaviour is found in the change of solubility of salts with change in ionic radius.

For the monoaminofluoren-9-ones the value of K_1 is largest for the 3-aminofluoren-9-one, and it is for this monoaminofluorenone that the electron delocalisation is greatest. Thus the change from fluorenone to 3-aminofluoren-9-one (Table 1) is accompanied by an increase in K_1 due, in the main, to the ΔS°_{1a} term becoming more positive. The fact that this change accompanies electron delocalisation might be expected, since, other things being equal, the solvation of the dianion will be sterically more difficult than for the radical anion.

The large increase in K_1 in going from 1,8-diazafluorenone to 4,5-diazafluorenone is accompanied, in the main, by the ΔS°_{1a} term becoming more positive. We have not been able to determine the splitting constant for the nitrogen atom in 1,8-diazafluoren-9-one, but the thermodynamic results suggest that the electron delocalisation would be greater for the 4,5- than for the 1,8-diaza-compound.

We thank the S.R.C. for a research studentship (to P. J. E.), and the S.R.C. and U.G.C. for grants to buy the e.s.r. spectrometers.

[4/255 *Received*, 11*th February*, 1974]

---

[15] T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, 1966, **88**, 307.

[16] K. D. Warren, *J. Chem. Soc.* (*B*), 1968, 214; and personal communication.