

1033. *Electron Spin Resonance Studies of Radical Anions.
Part I. Aromatic Ketyls.*

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The electron spin resonance spectra observed during the reduction of some aromatic ketones are described and interpreted.

Electrolytic reduction of benzophenone and fluorenone in acetonitrile yields the corresponding ketyls. Photolytic reduction in alcoholic sodium methoxide or ethoxide also produces ketyls, though interaction with the solvent modifies the hyperfine spectra considerably. Reduction with sodium or potassium in 1,2-dimethoxyethane results in the formation of ion pairs in which the interaction of the unpaired electron with the metal is temperature-dependent. The paramagnetic species observed during reduction with lithium is probably dimeric.

THE formation of deeply coloured, highly reactive solutions when metallic sodium dissolves in anhydrous ethers containing aromatic ketones, was noted as long ago as 1891.¹ Numerous investigations² of these systems have established that they contain paramagnetic monomeric radical-anions (ketyls) in equilibrium with diamagnetic dianions, and that both species can initiate polymerisation. The products of hydrolysis include pinacols, ketones, and hydrols.³ However, uncertainty still exists regarding the detailed structure of the ketyls and their reactions in different solvents.

Electron spin resonance can provide information about the orbital of the unpaired electron and thus assist in establishing the structure of the ketyls. By the same means one can examine their stability as a function of temperature, solvent, pH, etc.

Earlier observations⁴ on the electron spin resonance spectra of the sodium ketyls of benzophenone and of fluorenone were only partially interpreted, although the interaction

¹ Beckmann and Paul, *Annalen*, 1891, **1**, 260.

² Schlenk and Weikel, *Ber.*, 1911, **44**, 1183; Schlenk and Thaal, *Ber.*, 1911, **46**, 2840; Schlenk Appenrodt, Michael, and Thal, *Ber.*, 1914, **47**, 473; Gomberg, *J. Amer. Chem. Soc.*, 1927, **49**, 236; Doescher and Wieland, *ibid.*, 1934, **56**, 2011; Sugden, *Trans. Faraday Soc.*, 1934, **30**, 19.

³ Backmann, *J. Amer. Chem. Soc.*, 1933, **55**, 1179.

⁴ Ovenall and Whiffen, *Chem. Soc. Special Publ.*, 1958, No. 12.

between the unpaired electron and a sodium atom in the benzophenone ketyl was observed and the rate of electron exchange between ketyl and ketone was determined.⁵ The use of electrochemical reduction to produce the ketyl without the alkali-metal counter ion was the key to the complete interpretation of the spectra of the sodium and the potassium ketlys already briefly reported.⁶ The present report amplifies the earlier Communication and extends the work to other ketones, other solvents, and a wider range of temperature. Kinetic aspects of the formation and disappearance of the ketlys will be treated in a later paper.

EXPERIMENTAL

Reagents.—Benzophenone (from British Drug Houses Ltd.), recrystallised twice from ethanol, had m. p. 49° (lit., 49°). 4,4'-Dichlorobenzophenone was prepared from benzophenone by Norris and Green's method.⁷ Fluorenone, supplied by Messrs. Light and Co., was not further purified. Tetraethylammonium bromide and hydroxide were supplied by British Drug Houses Ltd.; the latter was used in the preparation of the perchlorate by addition of the equivalent amount of perchloric acid, crystallisation from aqueous methyl cyanide, and drying over phosphorus pentoxide. Of the solvents used in electrolysis, methyl cyanide was purified by Wawzonek and Runner's⁸ method, and dimethylformamide was repeatedly shaken with phosphorus pentoxide and then fractionally distilled.

1,2-Dimethoxyethane needed extremely careful purification if stable solutions of the ketlys were to be obtained. The material provided by Eastman Kodak was refluxed, first, with benzophenone over sodium-potassium alloy, under a 2-ft. column packed with Fenske rings, for ~6 hr., fractionally distilled (b. p. 82°), and transferred to the apparatus used for the preparation of ketyl, degassed thoroughly *in vacuo*, and poured on fresh benzophenone and sodium. If a blue colour of the ketyl developed immediately the purity was generally satisfactory and the solvent was distilled off into a storage vessel, fitted with break-seals, etc. A similar procedure was used for purification of dioxan and tetrahydrofuran.

Sodium used in the preparation of the ketlys was purified by distillation *in vacuo* into another sample tube, also supplied with a break-seal. In order to obtain an active potassium mirror by the same procedure, the sample for distillation was cut from the centre of a block which had been washed in hexane for several days and then with sodium-dried ether before being transferred to the preparation tube. Lithium, supplied in paraffin by Messrs. Hopkins and Williams Ltd., cannot be distilled in glass, so after being washed as described for potassium, a small sample was placed in the preparation vessel and evacuated with heat but without melting.

The alkali-metal ketlys were then prepared by first sealing the tube containing the appropriate metallic mirror, *via* the break-seal on to the electron spin resonance (e.s.r.) sample-tube which had a side-arm into which solvent could be distilled from the vacuum-line. A weighed phial of ketone was placed in this side-arm before the whole apparatus was sealed on to the vacuum line and evacuated. Solvent was distilled in, the preparation apparatus sealed off, and solvent allowed to react with the mirror. The solution, then containing ketyl, was passed through a fine glass filter before entering the e.s.r. tube. Dilution could be effected by distilling in further solvent.

Electron Spin Resonance Observations.—Electron spin resonance spectra were recorded on a Varian V-4500 EPR spectrometer and a Mullard EM 133 10-inch electromagnet. The inhomogeneity of the magnetic field over the sample volume was approximately 50 milligauss, which is comparable with the broadening caused by the 100 kc./sec. modulation. The multi-purpose resonant cavity has provision for changing the temperature of the sample by means of a flow of dry nitrogen through a vacuum-jacketed sample holder, and for irradiating the sample through slots in the end of the cavity. Spectra were recorded as first derivatives. Line separations were determined by comparing spectra under "standard sweep" conditions with those obtained from triphenylmethyl or potassium peroxyaminedisulphonate under similar conditions. From these the hyperfine splitting constants were estimated with a precision of about

⁵ Weissman and Adam, *J. Amer. Chem. Soc.*, 1958, **80**, 1518.

⁶ Ayscough and Wilson, *Proc. Chem. Soc.*, 1962, 229.

⁷ Norris and Green, *Amer. Chem. J.*, 1901, **28**, 495.

⁸ Wawzonek and Runner, *J. Electrochem. Soc.*, 1952, **99**, 457.

2%. Spectroscopic g -factors were measured (± 0.0002) by superimposing a signal from solid diphenylpicrylhydrazyl on the radical-anion spectrum, g for this being assumed to be 2.0036.

Electrolysis.—The cell in which electrolytic reductions were carried out was similar in design to that described by Geske and Maki,⁹ consisting essentially of a narrow Pyrex tube, containing the solution, in the centre of the cavity, with a thin platinum wire as electrode inserted through the bottom into a drop of mercury. The other electrode consisted of a calomel cell dipping into the upper surface of the liquid. All solutions were deoxygenated by bubbling dry nitrogen through a fine capillary reaching the bottom of the sample tube. This capillary was raised above the top of the cavity while spectra were being recorded.

Photolysis.—Ultraviolet irradiation of the sample in the cavity was carried out by means of a medium-pressure mercury arc (250 w) placed about 20 cm. from the sample. The light was passed through a water filter to remove infrared radiation and then focussed by means of a quartz lens.

RESULTS

Benzophenone, 4,4'-dichlorobenzophenone, and fluorenone were examined in various solvents and by various reduction procedures. In addition, some of the systems were examined over a range of temperature. Electron spin resonance spectra were observed in most systems and were generally interpretable in terms of a single paramagnetic species. The results are summarised in the Table, which includes values of the hyperfine splitting constants of the interacting nuclei where these were determined.

Electron spin resonance spectra of reduced aromatic ketones.

Solvent	Reduction	Species formed	Hyperfine coupling constants (gauss)				
			a_1	a_2	a_3	a_4	a_m
Benzophenone							
MeCN	Electrol.	Ph ₂ CO ⁻	2.49	0.83	3.32	—	—
(CH ₂ -OMe) ₂	Na (20°)	Ph ₂ CO ⁻ Na ⁺	2.58	0.86	3.44	—	1.125
"	K (20°)	Ph ₂ CO ⁻ K ⁺	2.53	0.84	3.45	—	0.39
"	Li (20°)	(Ph ₂ CO) ₂ ^{-?}	2.1	1.3	—	—	—
NaOEt-EtOH	Photol.	Ph ₂ CO ⁻ _{solv}	2.80	1.03	3.46	—	—
Dioxan	Na	Asymm.					
Tetrahydrofuran	Na	Asymm.					
NaOEt-EtOH	Glucose	None					
4,4'-Dichlorobenzophenone							
MeCN	Electrol.	Ph ₂ CO ⁻	2.49	0.83	3.32	—	—
NaOEt-EtOH	Photol.	Ar ₂ CO ⁻ _{solv}	2.86	1.03	—	—	—
Fluorenone, C ₁₃ H ₈ O							
MeCN	Electrol.	C ₁₃ H ₈ O ⁻	2.00	3.01	0.64	<0.1	—
(CH ₂ -OMe) ₂	Na (10°)	C ₁₃ H ₈ O ⁻	2.01	3.01	0.67	0.17	0.35
NaOEt-EtOH	Photol.	C ₁₃ H ₈ O ⁻ _{solv}	2.61	3.34 ₂	0.73	0.38	—
"	Glucose	C ₁₃ H ₈ O ⁻ _{solv}	2.61	3.34 ₂	0.73	0.38	—

a_1 — a_4 refer to ring protons. a_m refers to the alkali metal.

Electrolytic Reduction.—The simplest spectra were obtained by electrolytic reduction of acetonitrile solutions. The concentration of ketone was about 2×10^{-3} M, and 0.1M-tetraethylammonium perchlorate was used as carrier electrolyte. The use of dimethylformamide and tetraethylammonium bromide as solvent and carrier, respectively, gave identical spectra apart from increased line-width. The blue colour of the benzophenone ketyl (or red for the fluorenone ketyl) became visible above the anode after about 5 minutes' electrolysis at a potential of -1.5 v with respect to the calomel electrode.

Benzophenone and its dichloro derivative gave identical spectra (see Fig. 1a), the interpretation of which has been described earlier.⁶ Twenty-three (under higher power, twenty-five) equally spaced lines are seen, corresponding to interaction with four *ortho*-, four *meta*-, and two *para*-protons. Considerable overlapping occurs since the hyperfine interaction constants are in the integral ratios $a_o : a_m : a_p = 3 : 1 : 4$. The chlorobenzophenone loses its chlorine atoms during electrolysis.

In the same way the spectrum observed in fluorenone is attributed to its anion, resulting from

⁹ Geske and Maki, *J. Amer. Chem. Soc.*, 1960, **82**, 2671.

addition of one electron to the π -orbital system. Interaction with six protons only (in pairs) is observed, and again considerable overlapping occurs to give the spectrum a deceptive simplicity (see Fig. 2a). The line-width is such that the fourth pair of protons must cause a splitting of less than 0.1 gauss. Without further experiment involving deuterium substitution it is not possible to correlate the observed splittings with specific positions in the molecule.

Photolytic Reduction.—Photolysis of the ketones in concentrated sodium ethoxide solutions gave more complex spectra, though attributable in each case to the ketyl (see Figs. 1e and 2b). The hyperfine splitting constants are, however, all larger than those observed from the species in acetonitrile or 1,2-dimethoxyethane (see below). The line-width is considerably reduced, so that all 75 lines of the benzophenone ketyl spectrum are observed, and 39 of those of the fluorenone ketyl. A curious feature of the spectrum of the fluorenone ketyl is that interaction

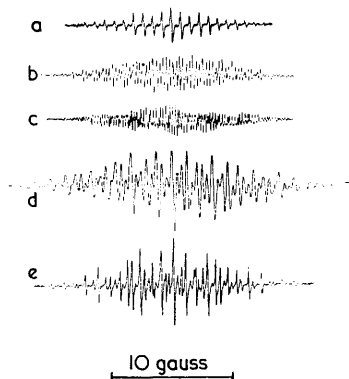


FIG. 1. Electron spin resonance spectra of benzophenone ketyls at 20°, after reduction by (a) electrolysis in acetonitrile, (b) sodium in $(\text{CH}_2\text{·OMe})_2$, (c) potassium in $(\text{CH}_2\text{·OMe})_2$, (d) lithium in $(\text{CH}_2\text{·OMe})_2$, (e) photolysis in ethanolic sodium ethoxide.

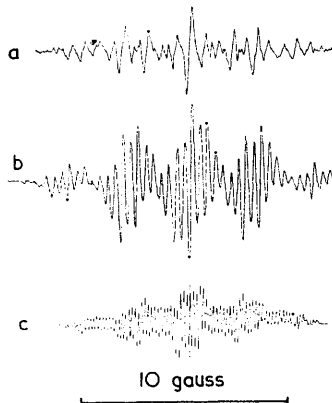


FIG. 2. Electron spin resonance spectra of fluorenone ketyls after reduction by (a) electrolysis in acetonitrile, (b) photolysis in ethanolic sodium ethoxide, (c) sodium in $(\text{CH}_2\text{·OMe})_2$. (a) and (b) recorded at 20°, (c) at 10°.

with the fourth pair of protons is now observed (cf. electrolytic reduction). This is not simply a result of better resolution: the distortion of the electronic orbitals caused by solvation must be much more pronounced than in the case of benzophenone. A further point of difference is that the chloro-derivative retains its chlorine during photochemical reduction though it loses them during electrolysis.

The spectrum of the benzophenone ketyl can be observed during ultraviolet irradiation: maximum intensity is reached in a few seconds and the signal disappears equally rapidly when the light source is removed. The ketyls of the chloro-derivative and of fluorenone are formed much more slowly (maximum concentration is attained in 5–10 min.) and disappear in a similar time.

Reduction with Glucose.—Of the ketones studied, only fluorenone showed evidence of the presence of an appreciable concentration of ketyl during reduction with glucose in ethanol and sodium ethoxide. The e.s.r. spectrum was identical with that observed on photochemical reduction in the same solvent.

Reduction with Alkali Metals.—Intensely coloured solutions were obtained by reaction of lithium, sodium, or potassium with ketones in a number of anhydrous ethereal solvents. Only with 1,2-dimethoxyethane as solvent has a satisfactory interpretation of the spectra been possible.

(a) *Benzophenone.* Electron spin resonance spectra of benzophenone reduced by lithium, sodium, and potassium are shown in Fig. 1. The spectra of the sodium and the potassium ketyl can be interpreted in terms of hyperfine splitting constants for the *ortho*-, *meta*-, and *para*-protons which are almost the same as those of the simple ketyl, with additional splitting by sodium or potassium, each with a nuclear spin of 3/2. Again the total number of observable

lines is much less than the maximum possible ($5 \times 5 \times 3 \times 4 = 300$) because of considerable superposition. Because of the complexity of the spectra, final assignments of splitting constants were made by computing parts of the spectra. Agreement was extremely good.

As in the sodium naphthalenide complex, the hyperfine splitting of the metal atom increases with temperature, and because of this the pattern changes very considerably. Spectra were examined between -50° and $+60^\circ$. The spectrum of the sodium ketyl became particularly simple at -34° and $+57^\circ$. This may be understood by reference to Fig. 3, in which the position of the lines obtained by superimposing an additional variable quaternary splitting on the basic ketyl spectrum is indicated. The position of the individual hyperfine lines are indicated along the horizontal lines marked -34° , $+20^\circ$, and $+57^\circ$ in this case, and the relative intensities of the lines can be obtained by adding the appropriate contributions from the relative values from the top line. Diagrams of this sort have been found useful in the analysis of complex spectra in which much overlapping of lines occurs.

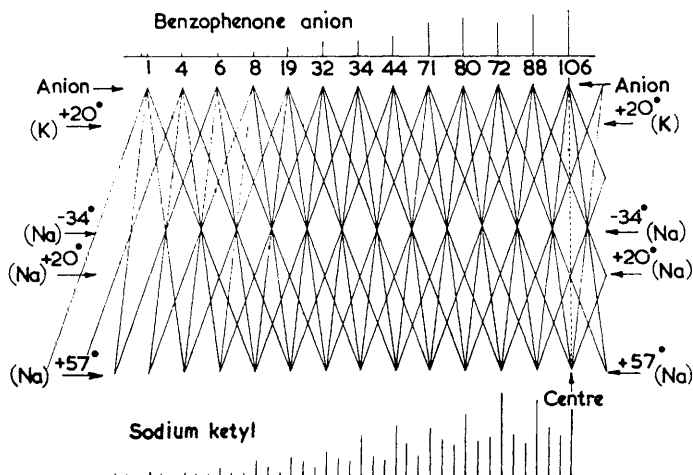


FIG. 3. Effect of an additional quaternary splitting (sodium or potassium) on the spectrum of the benzophenone anion. The constructed spectrum is that of the sodium ketyl in $(\text{CH}_2\cdot\text{OMe})_2$ at 20° .

The position of the potassium splitting at 20° is also shown on this diagram, but reference to the observed spectrum shows that most lines are further resolved because of the deviation from exactly integral ratios of the proton splittings in this ion-pair. The variation of the sodium and the potassium splittings with temperature is linear within experimental error over the range studied.

There was no evidence for dissociation of the ion-pairs this temperature range, or at concentrations varying from 10^{-3}M to 10^{-4}M .

In striking contrast are the results obtained for the lithium ketyl. The spectrum shown in Fig. 1d is slightly asymmetrical and, although no more complex than the others, has not been fully interpreted. The positions and intensities of the lines are not correctly reproduced by superimposing the quartet splitting of lithium on the basic ketyl spectrum; moreover, there is no change with temperature between -50° and $+60^\circ$. It is, therefore, presumed that the paramagnetic species does not contain lithium; that the lithium hyperfine splitting is extremely small is untenable since a large hyperfine interaction with the lithium nucleus has been observed¹⁰ when lithium atoms are deposited in an inert matrix at 4°K . Nor can the spectrum be interpreted in terms of interaction with four *ortho*-, four *meta*-, and two *para*-protons only, and one must therefore conclude that the species responsible contains more protons. Reasonably good agreement can be obtained with a spectrum formed by primary interaction with sixteen protons, six with $a = 2.1$ gauss and ten with $a = 1.3$ gauss. Such a spectrum could

¹⁰ Jen, Bowers, Cochran, and Foner, *Phys. Rev.*, 1962, **126**, 1749.

arise from a dimeric structure such as $\text{Ph}_2\text{C}\cdot\text{O}\cdot\text{Ph}_2\text{C}\cdot\text{O}^-$ formed by condensation of one ketyl and one ketone molecule, though one cannot identify the interacting protons with any assurance.

(b) *Fluorenone*. Only the sodium ketyl was examined, at temperatures between -50° and $+68^\circ$. As expected, marked changes in appearance occurred but attempts to interpret these in terms of basic pattern of the simple ketyl further split by interaction with sodium failed, except for the spectrum observed at 10° (see Fig. 2c). In this case agreement with the computed spectrum leaves little doubt that the interpretation is correct, and we conclude that the failure to interpret spectra at other temperatures means that one or more of the proton splittings is also temperature-dependent. Again deuterium substitution would probably help to identify the variable protons, but it is likely, in view of the much greater sensitivity of this system to changes in local environment, that more drastic changes in electron distribution occur.

DISCUSSION

It has been established that relatively stable solutions of the ketyls of benzophenone and fluorenone can be prepared by electrolytic or photochemical reduction in alkaline alcoholic solutions, and by reduction with alkali metals in ethereal solvents. The fluorenone ketyl can also be observed during reduction with glucose in alkaline alcoholic solution. The presence of sodium or potassium hyperfine splitting indicates some interaction between the ketyl anion and the metal. The unpaired-spin density on the metal ion is very small, probably less than 1% on the basis of the hyperfine splitting of sodium in inert matrices at 4°K .¹⁰ The configuration of the ion pairs is still a subject for conjecture. Calculations by McClelland¹¹ suggest that the metal ion is close to the oxygen atom above the plane of the aromatic rings. If so, the temperature variation of the metal hyperfine splitting could be attributed to changes in the extent of oscillation about the mean position, permitting greater penetration of the π -orbitals. Although the hyperfine interaction is about the same as that in the sodium naphthalenide ion-pair, the energy of interaction must be greater as there is no evidence of dissociation in the systems examined. The change in electron distribution caused by formation of the ion pair is small for benzophenone, but marked in the case of the fluorenone ketyl. The change is much greater when the aprotic solvent is replaced by a protic solvent such as water or alcohol, as shown by the results of the photolytic and chemical reductions in ethanol. The increase in unpaired-spin density in the aromatic rings is probably a consequence of hydrogen-bonding between the carbonyl-oxygen atom and the ethanol. A much smaller effect is seen in the anions of aromatic nitro-compounds, though in these cases there is a large increase in the nitrogen hyperfine splitting. By analogy one would expect a considerable change in electron distribution in the carbonyl group of the ketyls. Unfortunately this cannot be observed since neither carbon nor oxygen has a nuclear spin, and it would be necessary to introduce ^{13}C or ^{17}O .

The reason for the appearance of asymmetric and variable spectra when dioxan or tetrahydrofuran is used as solvent for the sodium reductions is not established. The effect is not simply a variation in line-width which can often result in asymmetric spectra, and it must be presumed that more than one paramagnetic species is present. The general appearance of the spectra suggests that these may be dimeric or polymeric species similar to those postulated in the solutions reduced by lithium.

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¹¹ McClelland, *Trans. Faraday Soc.*, 1961, **57**, 1459.