18,700 cm.$^{-1}$, and are readily assigned to be the $^4A_2 \rightarrow {}^4T_2$ and $^4A_2 \rightarrow {}^4T_1$ transitions, respectively; thus $Dq$ for the hexachlorochromate(III) ion is 1,318 cm.$^{-1}$. Using the experimental $Dq$ and the energy of the $^4A_2 \rightarrow {}^4T_1(F)$, the Racah parameter, $B'$, was calculated to be 575 cm.$^{-1}$ from the secular equation for $d^3$ in the weak field formalism. From this value $\beta$, the ratio of the Racah parameter for the complex to that of the free ion, was found to be 0.625. The magnitude of $\beta$ is indicative of covalent bonding[6] and determines the position of the chloride ion in the neuphelauxetic series.

In conclusion, we compare the ligand field of the hexachlorochromate(III) ion to those of chromium(III) chloride,[18] in which the chromium ion is also six coordinate,[19] and of the corresponding fluorides[20] in Table VII.

From Table VII, it can be seen that the ligand field parameters of the chloride ion in $CrCl_3$ and $[CrCl_6]^{3-}$ ion are not much different. However, the small differences which do exist have just the opposite trend expected and observed for the corresponding fluorides[20]; one would expect that, if the halide ion were exposed to the full polarizing effect of a single tripositive ion in a hexahalide ion, the ligand field strength would increase and $\beta$ would decrease.

TABLE VII

SPECTRAL DATA FOR SOME CHROMIUM(III) COMPLEXES

| Ligand | $Dq$, cm.$^{-1}$ | $\beta$ |
|---|---|---|
| $Cl^-(CrCl_6{}^{3-})^a$ | 1318 | 0.62 |
| $Cl^-(CrCl_3)^b$ | 1380 | .56 |
| $F^-(CrF_3)^c$ | 1460 | .81 |
| $F^-(CrF_6{}^{3-})^c$ | 1650 | .74 |
| $H_2O^b$ | 1740 | .79 |

$^a$ This work. $^b$ Ref. 6. $^c$ Ref. 20.

We have already pointed out that the chlorine-chlorine distance in the $[MCl_6]^{3-}$ ion is within the contact radius. Perhaps the large net negative charge on the $[CrCl_6]^{3-}$ ion and the larger size of the chloride ion enhance repulsion effects and hence decrease the ligand field as well as delocalized metal electron density onto the ligand.

**Acknowledgments.**—The authors wish to thank the National Science Foundation for a grant and for a fellowship to R. C. F. We also wish to thank Mr. R. Maguire for his assistance in the preparation of some of the compounds. We are indebted to the Charles F. Kettering Foundation for a grant to build the magnetic balance. T. S. P. is indebted to the Sloan Foundation for a fellowship.

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[CONTRIBUTION, ISSUED AS NO. 7221, FROM THE DIVISION OF PURE CHEMISTRY, NATIONAL RESEARCH COUNCIL, OTTAWA, CANADA]

# Free Radicals by Mass Spectrometry. XXIX. Ionization Potentials of Substituted Cyclopentadienyl Radicals

BY R. F. POTTIE[1] AND F. P. LOSSING

RECEIVED SEPTEMBER 22, 1962

The vertical ionization potentials of a number of substituted cyclopentadienyl radicals have been measured by electron impact. In order of decreasing ionization potential, the substituents are: CN, Br, F, Cl, H, $CH_3$, $C_2H_3$, $C_4H_4$ (indenyl radical), $NH_2$ and $(C_4H_4)_2$ (fluorenyl radical). A qualitative relationship between the ionization potential and substituent constants of the $\sigma$- and $\sigma^+$-type is found. Some modes of thermal decomposition of the radicals, and of their precursors the substituted phenoxyl radicals, are described.

## Introduction

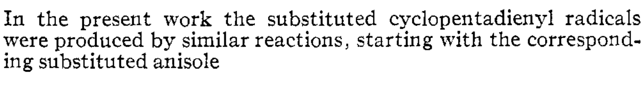
It recently has been shown[2] that the vertical ionization potentials of benzyl radicals substituted in the *p*- and *m*-positions by characteristic groups exhibit large differences which are generally in accord with the electron-releasing or electron-attracting powers of the substituents. A plot of the ionization potentials of the substituted benzyl radicals against $\sigma^+$-values showed a close correspondence from $\sigma^+ = -0.8$ to $\sigma^+ = +0.6$. In the present work the effect of substitution on a non-aromatic nucleus has been examined by measuring the vertical ionization potentials of a number of substituted cyclopentadienyl radicals.

## Experimental

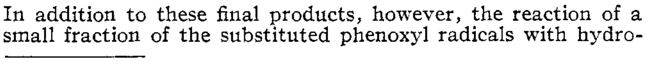
The radicals were produced by the thermal decomposition of suitable compounds in a fused-silica capillary reactor leading into the ionization chamber of a mass spectrometer.[3] The decomposition of the parent substance and the formation of stable products were followed by their mass spectra using 50-v. electrons. Observations on the production of radicals were made using electrons of energy sufficient to ionize the radical, but insufficient to form the radical ion by dissociative ionization of the parent substance.

The method used for comparing the ionization efficiency curves for a radical and the standard gas, usually xenon or krypton, has been described.[4,5] In some cases the net 50-v. peak for the radical could not be determined, since the spectra of one or more products of greater mass were unknown. The ionization efficiency curves were in these cases compared by matching the slopes of logarithmic plots by vertical displacement.[6,7]

**Production of the Radicals.**—The pyrolysis of anisole in a fused-silica capillary furnace at 950° was found in earlier[8] work to proceed by formation of methyl and phenoxyl radicals, followed by decomposition of the latter into CO and a cyclopentadienyl radical.



In the present work the substituted cyclopentadienyl radicals were produced by similar reactions, starting with the corresponding substituted anisole



In addition to these final products, however, the reaction of a small fraction of the substituted phenoxyl radicals with hydro-

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[1] National Research Council Postdoctorate Fellow 1958–1960. Present address: Engineering Research Laboratories, Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Del.

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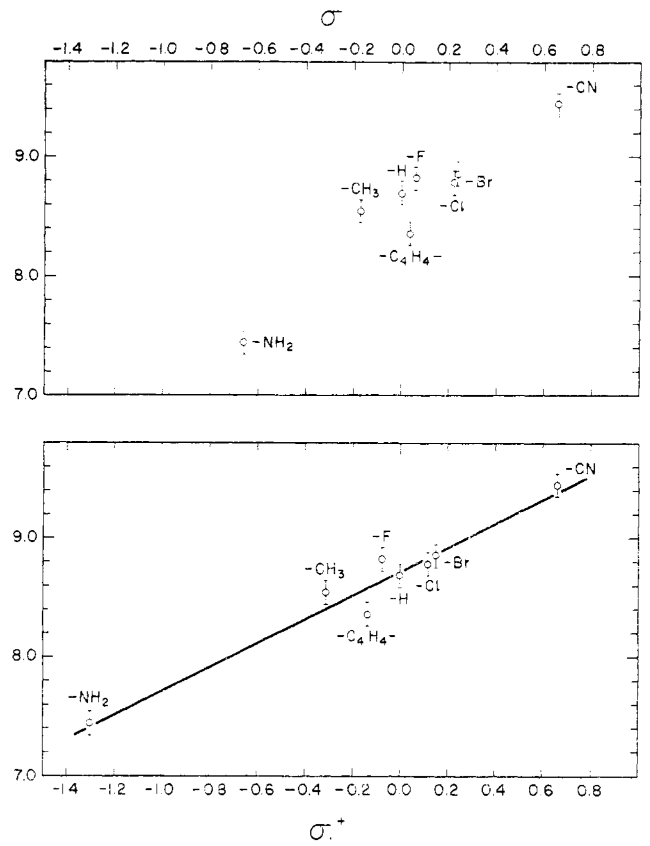
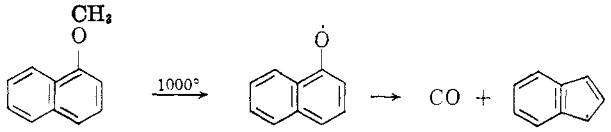


Fig. 1.—Ionization potentials of substituted cyclopentadienyl radicals plotted against $\sigma$-values (upper graph) and $\sigma^+$-values (lower graph).

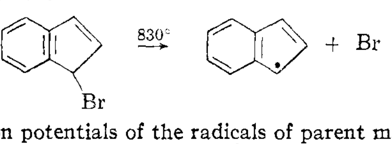
gen-containing materials adsorbed on the walls of the reactor or ionization chamber produced the substituted phenols $XC_6H_4OH$. A similar abstraction by the cyclopentadienyl radicals produced a small amount of the substituted cyclopentadienes $C_5H_5X$.

This method of preparation was found to be satisfactory for the cyclopentadienyl radicals substituted by F, Cl, Br, CN, $CH_3$, $C_2H_3$ and $NH_2$.

**Indenyl Radical.**—A radical of parent mass 115 was produced in good yield by the pyrolysis of 1-methoxynaphthalene

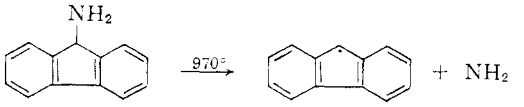


The identity of this radical was confirmed by measuring the ionization potential of indenyl radicals produced by the pyrolysis of indenyl bromide



The ionization potentials of the radicals of parent mass 115 produced from the two precursors were found to be the same within the experimental error.

**Fluorenyl Radical.**—The fluorenyl radical was produced by the pyrolysis of 9-aminofluorene at 970°



The preparation of this radical from 9-methoxyanthracene, although feasible by analogy with the decomposition of 1-methoxynaphthalene, was not attempted.

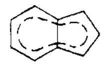
**Materials.**—Fluoro-, chloro- and bromoanisole, anisonitrile, *p*-methylanisole, *p*-anisidine, 4-methoxystyrene, 1-methoxynaphthalene, *p*-methoxyphenol and *m*- and *p*-dimethoxybenzene were commercial samples of good purity. Indenyl bromide was prepared from indene using N-bromosuccinimide in $CCl_4$ solution,[9] followed by bulb-to-bulb vacuum distillation. 9-Aminofluorene was prepared from fluorene through formation of the oxime and reduction with zinc and acetic acid.[10] It was purified by recrystallization of the hydrochloride and regeneration of the free amine.

## Results and Discussion

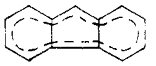
The vertical ionization potentials of the substituted cyclopentadienyl radicals are given in Table I. It can be seen that, as for benzyl radical,[2] substitution of H by CN raises the ionization potential by about 0.7 v. Substitution by $CH_3$ or $CH{=}CH_2$ causes a small decrease in ionization potential. Substitution by $NH_2$, on the other hand, causes a decrease of 1.1 v. in the ionization potential. In Fig. 1 the ionization potentials are plotted against substituent constants of the $\sigma$-type. The cyclopentadienyl cation, although not aromatic, is symmetrical, and the charge delocalization is shared equally by all five carbon atoms. In terms of substituent constants derived from substitution on phenyl derivatives the effect of a substituent would therefore be expected to be more closely analogous to that of a *p*-substituent than that of a *m*-substituent. The upper graph in Fig. 1 gives a plot of ionization potential against Hammett's $\sigma$-values,[11,12] the lower graph a plot against $\sigma^+$-values,[13] the *para* values being used in both cases. The value of $\sigma$ for 3,4-benzo- was taken as 0.04.[14] It can be seen from the upper graph that, although the ionization potential decreases as expected with increasing negativity of the $\sigma$-value, the scatter of points is so great that no quantitative relationship can be obtained. The lower graph, ionization potential as a function of $\sigma^+$, shows a closer proportionality, although even here the scatter of the points is much greater than in the corresponding relationship for substituted benzyl radicals.[2] Assuming that the experimental errors in the present measurements are no greater than those in the measurements on benzyl radicals, it appears that the effect of some substituents on the electronic distribution in cyclopentadienyl ions is different in detail from that in benzyl ions. For example, in contrast to the findings for the benzyl radicals, the ionization potentials for halogen-substituted cyclopentadienyl radicals are all essentially the same. Nevertheless, the slope of the line in the lower graph in Fig. 1 is nearly the same as that found for substitution in benzyl radicals,[2] showing that the effect of substitution is in general not greatly different. It is possible that a more detailed examination of substituent effects, such as that of Taft,[15] will allow a more exact prediction of the ionization potential of substituted cyclopentadienyl radicals.

An interesting sequence is given by successive substitution by $C_4H_4$ to give the indenyl and fluorenyl radicals

cyclopentadienyl
I.P. = 8.69



indenyl
I.P. = 8.35



fluorenyl
I.P. = 7.07

Substitution by the first $C_4H_4$ group brings about a reduction of 0.34 v., but substitution by the second $C_4H_4$ group brings about a very much greater reduction, 1.28 v. The ionization potential of fluorenyl radical is in fact not greatly different from that of diphenylmethyl radical, 7.32 v.[16]

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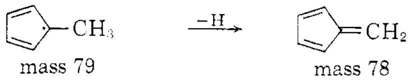
TABLE I

IONIZATION POTENTIALS OF SUBSTITUTED CYCLOPENTADIENYL RADICALS

| Radicals | Ionization potentials, volts Obsd. | Calcd. |
|---|---|---|
| cyc-$C_5H_4$—CN | 9.44 | |
| —Br | 8.85 | |
| —F | 8.82 | |
| —Cl | 8.78 | |
| —H | 8.69[8] | |
| —$CH_3$ | 8.54 | |
| —CH=$CH_2$ | 8.44 | |
| cyc-$C_5H_3C_4H_4$(indenyl) | 8.35 | |
| cyc-$C_5H_4NH_2$ | 7.55 | |
| cyc-$C_5H_2(C_4H_4)_2$(fluorenyl) | 7.07 | |
| Hydrocarbons | | |
| Indene | 8.81 | 8.63[17] |
| Fluorene | 8.63 | 8.56[17] |

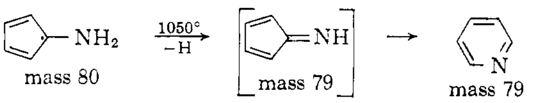
The vertical ionization potentials of indene and fluorene were also measured, and are given in Table I together with values calculated by Streitwieser.[17] The decrease in ionization potential between indene and fluorene is notably less than the difference between indenyl and fluorenyl radicals.

**Thermal Decomposition of Radicals.**—Most of the substituted cyclopentadienyl radicals were found to be quite stable at furnace temperatures around 1000°. For these radicals the parent peak measured with low energy electrons showed little or no decrease as the temperature was raised to 1050–1075°. Some of these radicals, however, were found to decompose above 1000° by loss of a hydrogen atom, as shown by the decrease in the radical parent peak at low electron energies and the increase of the peak at one mass unit below the parent. Since the pressure in the reactor was $\sim 10^{-3}$ mm., these reactions may have occurred mainly on the walls. One of the radicals decomposing in this way was the methylcyclopentadienyl radical. Between 1000° and 1050°, the parent mass 79 peak decreased appreciably, and a mass 78 peak appeared. The structure of the radical suggests that the hydrogen atom lost must come from the $CH_3$ group. The expected product of mass 78 would therefore be fulvene

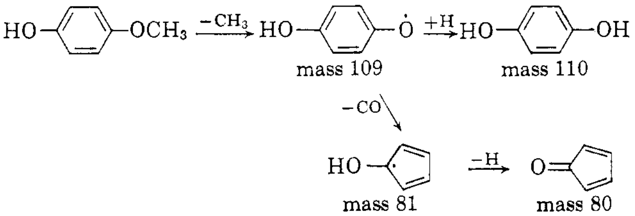


A measurement of the ionization potential of the product at mass 78, however, gave 9.57 v., in close agreement with the vertical ionization potential of benzene, 9.52 v.[18] No experimental ionization potential for fulvene is available, but M.O. calculations give 8.84–9.07 v.,[17] appreciably lower than that of benzene. It seems quite clear therefore that the observed product of mass 78 is benzene and not fulvene. If fulvene is formed as an intermediate, as seems probable from the structure of the radical, its rearrangement to benzene at 1050° must be very fast.

A similar rearrangement occurred in the decomposition of the amino-cyclopentadienyl radical. At 1050° this radical (parent mass 80) lost a hydrogen atom to give a compound of mass 79. The ionization potential of this product was 9.59 v., which is the same as that of pyridine, 9.70 v.,[19] within the experimental error. The corresponding intermediate in this case would be cyclopentadienyl imine, the nitrogen analog of fulvene.

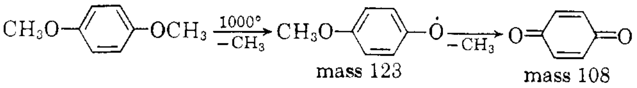


Attempts to prepare the -OH and -$OCH_3$ substituted radicals were unsuccessful, owing to their thermal instability. In the thermal decomposition of *p*-methoxyphenol, a small maximum at 925° was found for the *p*-hydroxyphenoxyl radical at mass 109. A product at mass 110, presumably quinol, was also formed. Above 925°, the peak at mass 109 decreased again, and a large increase in ion current at mass 80 was produced. A very slight net increase for the hydroxycyclopentadienyl radical at mass 81 was found, but the amount was insufficient to permit an ionization potential measurement. Although no identification of the species other than their parent masses was made, the following reactions are consistent with the observations

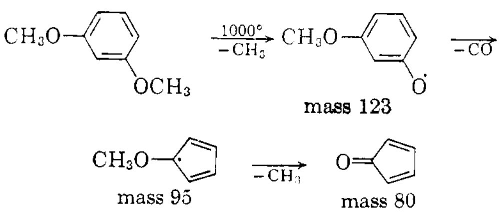


The final product of mass 80, cyclopentadienone, cannot be isolated under normal reaction conditions since it polymerizes very rapidly.[20] [21] Its existence in the gas phase at $10^{-3}$ mm., however, is not improbable.

The thermal decomposition of *p*-dimethoxybenzene did not yield any 5-membered ring derivatives. Instead of eliminating CO from the ring, the $CH_3O$-substituted phenoxyl radical lost a $CH_3$ group to give quinone



Evidently the stability of the quinone structure causes the O–$CH_3$ bond in the radical to be greatly weakened, so that this mode of decomposition is favored over loss of CO from the ring. With *m*-dimethoxybenzene this alternative mode to form a quinone was not possible and the radical dissociated by loss of CO. The resulting $CH_3O$-substituted cyclopentadienyl radical, like the OH substituted radical mentioned above, was insufficiently stable to permit an ionization potential to be measured. The final product was again a substance of mass 80, presumably cyclopentadienone



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