

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 β , the ratio of the Racah parameter for the complex to that of the free ion, was found to be 0.625. The magnitude of β is indicative of covalent bonding⁶ and determines the position of the chloride ion in the nephelauxetic 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 fluorides²⁰ in Table VII.

From Table VII, it can be seen that the ligand field parameters of the chloride ion in CrCl_3 and $[\text{CrCl}_6]^{3-}$ ion are not much different. However, the small differences which do exist have just the opposite trend expected and observed for the corresponding fluorides²⁰; one would expect that, if the halide ion were exposed to the full polarizing effect of a single tripositive ion in a

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TABLE VII
SPECTRAL DATA FOR SOME CHROMIUM(III) COMPLEXES

Ligand	Dq, cm^{-1}	β
$\text{Cl}^-(\text{CrCl}_6^{3-})^a$	1318	0.62
$\text{Cl}^-(\text{CrCl}_3)^b$	1380	.56
$\text{F}^-(\text{CrF}_6)^c$	1460	.81
$\text{F}^-(\text{CrF}_6^{3-})^c$	1650	.74
H_2O^b	1740	.79

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

hexahalide ion, the ligand field strength would increase and β would decrease.

We have already pointed out that the chlorine-chlorine distance in the $[\text{MCl}_6]^{3-}$ ion is within the contact radius. Perhaps the large net negative charge on the $[\text{CrCl}_6]^{3-}$ 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.

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

By R. F. POTTIE¹ AND F. P. LOSSING

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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_5 , C_6H_5 (indenyl radical), NH_2 and $(\text{C}_6\text{H}_4)_2$ (fluorenyl radical). A qualitative relationship between the ionization potential and substituent constants of the σ - and σ^+ -type is found. Some modes of thermal decomposition of the radicals, and of their precursors the substituted phenoxy radicals, are described.

Introduction

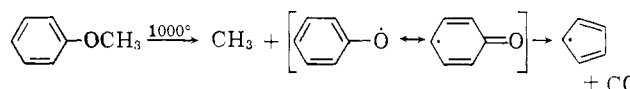
It recently has been shown² that the vertical ionization potentials of benzyl radicals substituted in the p - and m -positions by characteristic groups exhibit large differences which are generally in accord with the electron-releasing or electron-attracting powers of the substituents. A plot of the ionization potentials of the substituted benzyl radicals against σ^+ -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

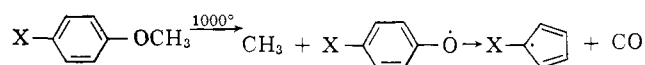
The radicals were produced by the thermal decomposition of suitable compounds in a fused-silica capillary reactor leading into the ionization chamber of a mass spectrometer.³ The decomposition of the parent substance and the formation of stable products were followed by their mass spectra using 50-v. 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 earlier⁸ work to proceed by formation of methyl and phenoxy 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 phenoxy radicals with hydro-

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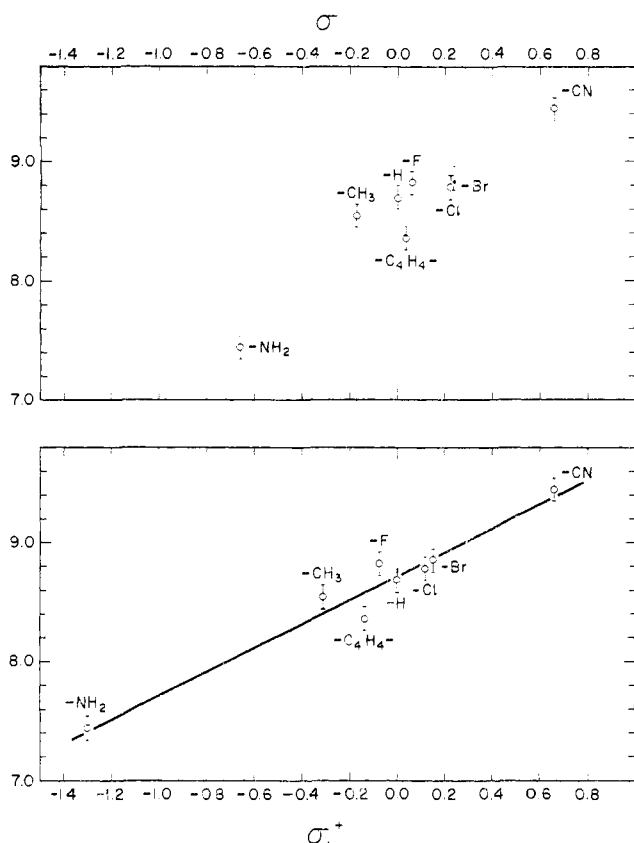
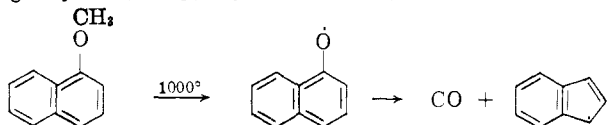


Fig. 1.—Ionization potentials of substituted cyclopentadienyl radicals plotted against σ -values (upper graph) and σ^+ -values (lower graph).

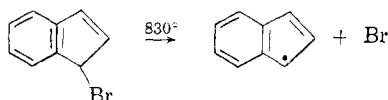
gen-containing materials adsorbed on the walls of the reactor or ionization chamber produced the substituted phenols $\text{XC}_6\text{H}_4\text{OH}$. A similar abstraction by the cyclopentadienyl radicals produced a small amount of the substituted cyclopentadienes $\text{C}_5\text{H}_6\text{X}$.

This method of preparation was found to be satisfactory for the cyclopentadienyl radicals substituted by F, Cl, Br, CN, CH_3 , C_2H_5 and NH_2 .

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

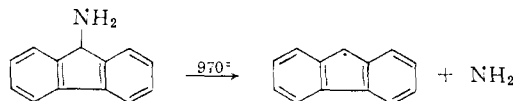


The identity of this radical was confirmed by measuring the ionization potential of indenyl radicals produced by the pyrolysis of indenyl bromide



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.

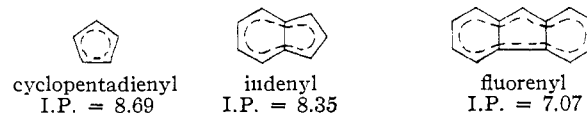
Materials.—Fluoro-, chloro- and bromoanisole, anisonitrile, *p*-methylanisole, *p*-anisidine, 4-methoxystyrene, 1-methoxynaphthalene, *p*-methoxyphenol and *m*- and *p*-dimethoxybenzene were commercial samples of good purity. Indenyl bromide was prepared from indene using *N*-bromosuccinimide in CCl_4 solution,⁹ followed by bulb-to-bulb vacuum distillation. 9-Amino-

fluorene 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 $\text{CH}=\text{CH}_2$ 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 σ -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 σ -values,^{11,12} the lower graph a plot against σ^+ -values,¹³ the *para* values being used in both cases. The value of σ 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 σ -value, the scatter of points is so great that no quantitative relationship can be obtained. The lower graph, ionization potential as a function of σ^+ , 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_6H_4 to give the indenyl and fluorenyl radicals



Substitution by the first C_6H_4 group brings about a reduction of 0.34 v., but substitution by the second C_6H_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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