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Substituent Effects in Unimolecular Ion Decompositions. III. Elucidation of Competing Alternative Pathways for the Formation of a Particular Ion.[1]

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Abstract: Substituent effects may be used to indicate the existence of two pathways for the formation of an ion in mass spectra. For example, the $C_6H_5^+$ ion in the mass spectra of substituted benzophenones is indicated to be formed by two pathways: directly from the molecular ion, and also through the intermediacy of the benzoyl ion. This mechanism is confirmed by elimination of the first process at low voltages. Similar data are found for the $C_3H_7^+$ ion in the spectra of substituted butyrophenones. Further use of the low-voltage technique is demonstrated in the determination of the origin of the $C_2H_3O^+$ ion in m- and p-t-butylacetophenone.

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(1) Presented in part at the 150th National Meeting, American Chemical Society, Atlantic City, N.J., Sept. 1965.

Substituent effects offer promise in the unraveling of the structural detail of ions formed in the mass spectrometer and of the kinetic processes relating them. The sigma constants of Hammett[2] have been shown to correlate the appearance potentials of ions from aromatic species.[3,4] A significant correlation with such sigma constants obtained

(2) L. P. Hammett, Physical Organic Chemistry, McGraw-Hill Book Company, Inc., New York, N.Y., 1940, Chapter VII.

(3) A. Streitwieser, Jr., Prog. Phys. Org. Chem., 1, 1 (1963).

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(4) A. Foffani, S. Pignataro, B. Cantone, and F. Grasso, Z. physik. Chem. (Frankfurt), 42, 221 (1964).

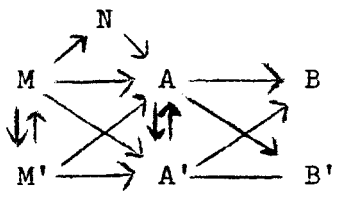
in solution indicates similarity in the structure of the gas phase ion to that of species found in solution chemistry, both for ion abundance data[5] and for appearance potentials.[6,7]

(5) M. M. Bursey and F. W. McLafferty, J. Am. Chem. Soc., 88, 529 (1966).

(6) J. M. S. Tait, T. W. Shannon, and A. G. Harrison, J. Am. Chem. Soc., 84, 4 (1962).

(7) F. Meyer and A. G. Harrison, Can. J. Chem., 42, 1762 (1964).

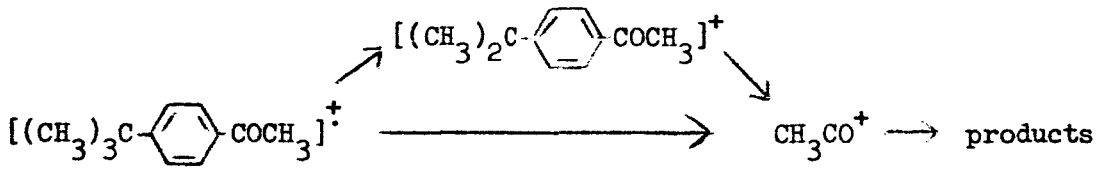
In the previous paper of this series,[5] ion abundance data were demonstrated to yield useful information about the structures of ions and transition states in the formation of acyl ions from substituted acylbenzenes: m- or p-Y-C_6H_4-COR → Y-C_6H_4· + COR^+. This simple case was ideal for study, since there are no alternative pathways for the formation of the acyl ion, nor is there a substituent effect on further decomposition of this ion. Of all the possible routes for formation of this ion (A) from the molecular ion (M) shown in the generalized scheme (I), only the process M ⟶ A is important as a formation route for A, which then decomposes to various B. The present paper extends this technique to the more complex system in which a particular product



Scheme I

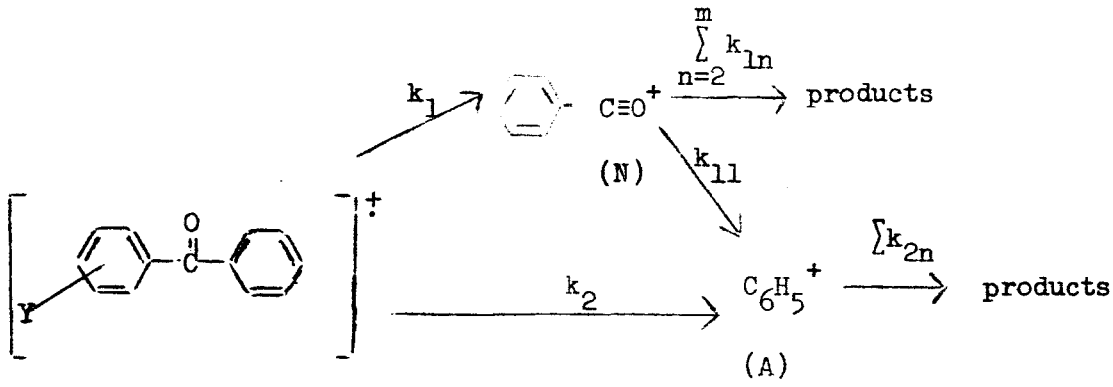
ion (A) can be formed from a particular precursor ion (M) by competing reaction paths ($M \longrightarrow A$ and $M \longrightarrow N \longrightarrow A$). To our knowledge no techniques for the study of such a situation have been discussed previously; isotopic labelling will not distinguish these pathways, as both produce ions of identical formulas.

A simple example of this situation was suggested[5] to be the intervention of a rearrangement or a loss of some fragment from the molecular ion; in the formation of acetyl ion from m- and p-t-butylacetophenone, part of the acetyl ion is produced from the intermediate in which a methyl radical has been lost, as in scheme II.



Scheme II

A system more amenable to study by substituent effects is the formation of the $C_6H_5^+$ ion from substituted benzophenone ions, for which the pathways depicted in scheme III are probable.



Scheme III

Absence of other pathways involving the substituent in the formation of the benzoyl ion, N, has been demonstrated, as has the substituent dependence of the rate k_1. One way to simplify the study of the formation of M from A is to eliminate one of the two pathways. If one has a sufficiently higher energy requirement, it may be possible to remove this path by lowering the ionizing voltage.

Low voltage studies. - It is a fairly common practice in the analysis of complex spectra to free them of the confusing profusion of small peaks by recording them at low voltage; such techniques may be made quantitative, so that ionization potentials and appearance potentials may be determined for electron impact processes.[8,9]

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(8) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N.Y., 1957, p. 26.

(9) R. W. Kiser, "Introduction to Mass Spectrometry," Prentice-Hall, Inc., Englewood Cliffs, N.J., 1965, p. 162.

The distinction in the present case is that the interfering fragment ion is identical (or at least has the same elemental composition) as the fragment ion of lower energy.

The predicted substituent effect for the two-step process M -> N A is based on the information that k_1 is determined by the Hammett equation[2] and that k_{11} is independent of substituent.[5] With the steady-state approximation, eqs 1 and 2 are written for the relations governing the concentrations of M, N, and A in the ion source. If the bombarding electron energy is sufficiently low so that no ions appear below m/e 77 in the spectrum, then $\sum k_{2n} = 0$ and $\sum k_{1n} = k_{11}$ for our purposes.

$$0 = \frac{d[A]}{dt} = k_{11}[N] - \left(\sum k_{2n} + \sum k'_{inst}\right)[A] \qquad (1)$$

$$0 = \frac{d[N]}{dt} = k_1[M] - \left(\sum k_{1n} + \sum k'_{inst}\right)[N] \qquad (2)$$

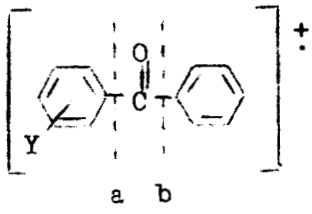
Irrespective of this, combination of these equations yields eq 3 for the ratio of [A] to [M], which is designated Z, the ratio of the intensities

$$Z = \frac{[A]}{[M]} = \frac{k_{11}k_1}{\left(\sum k_{1n} + \sum k'_{inst} \quad \sum k_{2n} + \quad k'_{inst}\right)} \qquad (3)$$

of the ions. The substituent effect on the ratio of intensities is then the same as the effect on k_1, because all the other rates are independent of substituent; but the substituent effect on k_1 has been shown to be predicted by the Hammett equation,[5] so that for the two-step process, eq 4 holds.

$$\frac{Z}{Z_0} = \frac{k_1}{k_1^0} = \exp\,(1.01\sigma/2.3) \qquad (4)$$

On the other hand, the prediction of the substituent effect on the assumption of only the one-step process requires some argument. In the molecular ion I, an electron-withdrawing substituent should weaken bond b



I

and produce more $C_6H_5^+$ ions than in the parent compound, but because of the additional bond and cross-conjugation of the carbonyl group between the substituent and the reaction site, the magnitude of the substituent effect would be quite small in comparison with the effect on the cleavage of bond a. If the Hammett equation holds, as it does for the cleavage of bond a, the reaction constant ρ is small and positive, and eq 5 is followed. The relation of Z ratios to rate constants under

$$\frac{k_2}{k_2^0} = \exp\,(\rho\sigma/2.3), \text{ where } 0 < \rho << 1.01 \tag{5}$$

this assumption follows directly from eqs 6 and 7; since the denominator is constant for all substituents, eq 8 yields the desired expression

$$0 = \frac{d[A]}{dt} = k_2[M] - \left(\sum k_{2n} + \sum k'_{inst}\right)[A] \tag{6}$$

$$Z = \frac{[A]}{[M]} = \frac{k_2}{\sum k_{2n} + \sum k'_{inst}} \tag{7}$$

$$\frac{Z}{Z_0} = \frac{k_2}{k_2^0} = \exp\,(\rho\sigma/2.3) \approx 1. \tag{8}$$

for the substituent effect on the one-step process.

The correlation of substituent effect data recorded at an ionizing energy of 19 volts with Hammett sigma values is shown in Figure 1. It is apparent from the slope of the line that the two-step process, not the direct mechanism, applies, for the substituent effects are within

Figure 1. Correlation of substituent effects on the formation of $C_6H_5^+$ ions from substituted benzophenones at 19 volts with Hammett sigma constants.[10] The line is the correlation line determined previously for benzophenones,[5] with $\rho_I = 1.01$.

(10) Values tabulated by C. D. Ritchie and W. F. Sager, Prog. Phys. Org. Chem., 2, 323 (1964) were used.

experimental error to those found for the production of benzoyl ion.[5]

Further, the establishment of the two-step process as the one of lower activation energy is supported by metastable ion formation. The "metastable" ion for the loss of CO from benzoyl ion (calcd. 56.5, observed 56.5) in the spectra of the compounds studied is still present at 19 volts and indicates that the process N $\longrightarrow$ A is still important. There is no similar evidence that it is the only process, since no metastable for the direct formation of $C_6H_5^+$ from the molecular ion exists even at normal ionizing voltages; only the substituent effect data indicate this.

Data at Normal Ionizing Voltages. - The kinetic scheme for substituent effects at normal ionizing voltages is complicated by the duality of origin of the $C_6H_5^+$ ion. The rate of its appearance is given by eq 9, while the rate of appearance of the benzoyl ion is still given by eq 2. Combining these expressions gives eq 10 for the rate dependence of the

$$0 = \frac{d[A]}{dt} = k_2[M] + k_{11}[N] - \left(\sum k_{2n} + \sum k'_{inst}\right)[A] \qquad (9)$$

ion intensity ratios. For a series of ratios, eq 11 holds, since the denominator is constant for all substituents.

$$\frac{Z}{Z_0} = \frac{k_{11}k_1 + \left(\sum k_{1n} + \sum k'_{inst}\right) k_2}{k_{11}k_1^0 + \left(\sum k_{1n} + \sum k'_{inst}\right) k_2^0} \qquad (11)$$

Incorporation of the substituent dependence of k_1 and k_2 (eqs 4 and 5) permits writing of an equation relating substituent constants to the expected behavior of the $C_6H_5^+$ ion (eq 12). This is simplified to eq 13 for further discussion. The shape of the correlation line is therefore

$$\frac{Z}{Z_0} = \frac{k_{11}k_1^0 \exp\,(1.01\sigma/2.3) + \left(\sum k_{1n} + \sum k'_{inst}\right) k_2^0 \exp\,(\rho\sigma/2.3)}{k_{11}k_1^0 + \left(\sum k_{1n} + \sum k'_{inst}\right) k_2^0} \qquad (12)$$

$$\frac{Z}{Z_0} = A\exp\,(1.01\sigma/2.3) + B\exp\,(\rho\sigma/2.3) \qquad (13)$$

a function of k_1^0, k_2^0, k_{11}, $\sum k_{1n}$ and both rho values. In Figure 2, several cases are illustrated in which one rho value is maintained equal to 1. For sufficiently different rho values and sufficiently similar A and B, the observed ratio (which is the sum of the two contributions represented by the two lines below it) does not correlate linearly with Hammett substituent constants, but curves instead.

Figure 2. Hypothetical examples of eq 13: (a), A = B, ρ = 1; (b), A = B, ρ = 0; (c), A = B, ρ = -1; (d), A = 10B, ρ = 1; (e) A = 10B, ρ = 0; (f) A = 10B, ρ = -1. The heavy lines are the sum of the contributions from the two lighter lines.

The relative intensities of the $C_6H_5^+$ ion in the mass spectra of substituted benzophenones at 75 eV are plotted vs Hammett sigma constants[2,10] in Figure 3.

Figure 3. Correlation of substituted effects on the formation of $C_6H_5^+$ ions from substituted benzophenones at 75 volts with the sum of predicted contributions from two reaction pathways.

An approximate fit to the data may be obtained with the curved line, which is the logarithm of the sum of the Z/Z_0 values of the two straight lines below it, and which resembles the curve of Figure 2b. The slope of one line corresponds to the value found for the formation of $C_6H_5^+$ ion at 19 volts; the other has a slope of approximately zero and corresponds to the direct formation of the $C_6H_5^+$ from the molecular ion. As expected, the small slope of the latter reflects the very slight influence of substituents on the strength of the bond being broken in the direct process, because of the intervention of cross conjugation. By comparison to Figure 2b again, the coefficients A and B are nearly the same; a graphical solution yields the relation A = 1.2B. The chief product of decomposition of $C_6H_5CO^+$ is logically $C_6H_5^+$, so that k_{11} accounts for most of $\sum k_{1n}$; a conservative lower limit is 50%. If $\sum k'_{inst}$ is small compared to $\sum k_{1n}$, it follows that $1.2 < k_1^0/k_2^0 < 2.4$ at 75 volts. In compounds substituted by electron-donating groups, the preponderance of the product is formed by the one-step process. On the other hand, for compounds with electron-withdrawing substituents, formation of benzoyl ion from the molecular ion is so greatly accelerated that the two-step process overwhelms the one-step process.

Deviations of substituents from solution behavior. - Certain substituents were proposed to have undergone structural rearrangements in discussion of the correlation of benzoyl ion intensities,[5] because they deviated markedly from the correlation line found to predict the effects of most substituents on this reaction. A simple test of the applicability of similar reasoning to the present case involves the correlation of the data for $C_6H_5^+$ with those for $C_6H_5CO^+$. Figure 4 illustrates the improvement in correlation anticipated for such a plot over the correlation in Figure 3. The conclusion is that substituents exert the same

Figure 4. Correlation of the formation of $C_6H_5^+$ and $C_6H_5CO^+$ ions from substituted benzophenones.

effect in both reactions: most are not detectably different in structure from what they are in solution. The deviations of the nitro and cyano substituents in Figure 3 parallel those effects found on the rate of formation of benzoyl ion; the cause again may be a partial isomerization of the molecular ion to a similar extent.

Just as no other contributions to the formation of benzoyl ion from other pathways were detected by substituent effects,[5] so also it may be deduced that the contributions of other pathways for individual substituents to the formation of $C_6H_5^+$ are not large, for they are significant only to the extent of deviation of individual points from the correlation line of Figure 4. Only the p-methoxy substituent gives much more $C_6H_5^+$ than is predicted. This substituent has been noted to yield anomalous substituent effects: in the formation of

substituted C_7 ions from substituted toluenes, the p-methoxy substituent appears to prevent skeletal rearrangement, in contrast to the other substituents examined.[6] The cause of this behavior has been suggested as localization of charge on the oxygen; establishment of an alternate reaction site would therefore provide an additional source of $C_6H_5^+$ ion. The process involving the intermediacy of $CH_3OC_6H_4^+$ (Scheme IV)

$$CH_3OC_6H_4COC_6H_5^{+\cdot} \longrightarrow \underset{107}{CH_3OC_6H_4^+} \longrightarrow \underset{77}{C_6H_5^+}$$

Scheme IV

is supported by a metastable (calcd. 55.4, found 55.5). The existence of a metastable does not rule out other pathways, nor indicate the importance of this route relative to other possibilities. The substituent effect can do these, however. Other routes (e.g., Schemes V and VI) are also analogous to the expulsion of the elements of formaldehyde from anisole,[11] but these should have given rise to abnormal amounts

(11) C. S. Barnes and J. L. Occolowitz, Austral. J. Chem., 16, 219 (1963).

$$CH_3OC_6H_4COC_6H_5^+ \longrightarrow CH_3OC_6H_4CO^+ \longrightarrow C_6H_5CO^+ \longrightarrow C_6H_5^+$$

Scheme V

$$CH_3OC_6H_4COC_6H_5^{+\cdot} \longrightarrow C_6H_5COC_6H_5^{+\cdot} \begin{cases} \nearrow C_6H_5CO^+ \\ \searrow C_6H_5^+ \end{cases}$$

Scheme VI

of $C_6H_5CO^+$ as well.

Since there is no abnormal amount of benzoyl ion detected in p-methoxybenzophenone,[5] these alternate pathways are not important. The excess $C_6H_5^+$ from pathway IV amounts to 1.1 times that from the direct process, according to this reasoning.

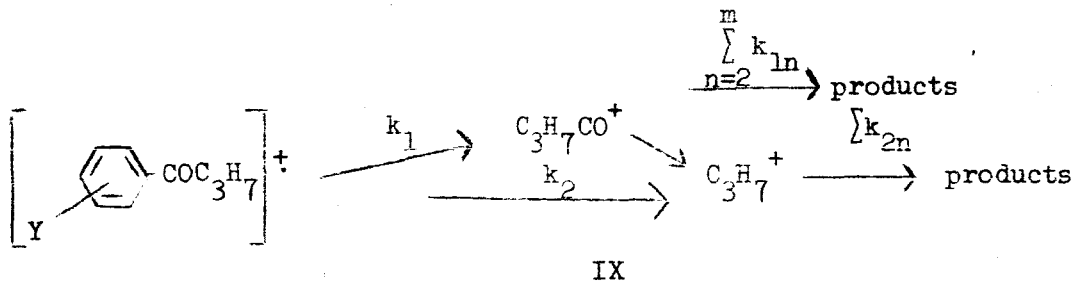
Other Systems. - The applicability of this approach to study ions arising from several sources in other sets of compounds is illustrated by the analysis of the intensity of the $C_3H_7^+$ ion in the mass spectra of substituted n-butyrophenones. (Figure 5). Although the data points

Figure 5. Correlation of the relative intensities of $C_3H_7^+$ ions in the mass spectra of substituted n-butyrophenones with Hammett sigma constants.[10]

are somewhat scattered, the same characteristics are observed: the apparent decrease in the effect of electron-donating substituents on the intensity of the product produces a curve indicating a similar mechanism of formation to that for the $C_6H_5^+$ ion in the benzophenones. The correlation of $C_3H_7^+$ to $C_3H_7CO^+$ is not indicated; there is significant scatter in it, probably related to the surprisingly low intensity of the $C_3H_7CO^+$ ion in these spectra, and to possible contributions from alternate structures connected with rearrangements.[12] The pertinent

(12) F. W. McLafferty, Anal. Chem., 31, 82 (1959).

scheme is given in IX. Since the butyryl ion is so weak (2% of molecular-ion intensity in n-butyrophenone), k_{11} is apparently large; the product possesses especial stability and may be cationated cyclopropane.[13]



(13) P. N. Rylander and S. Meyerson, J. Am. Chem. Soc., 78, 5799 (1956).

Because both processes are important in determining the intensity of $C_3H_7^+$ in n-butyrophenone, we may use these data from the more intense $C_3H_7^+$ to comment on the substituent dependence of the formation of the much weaker n-butyryl ion exclusive of rearrangement products which may obscure its true substituent dependence; and by analysis of the relative contributions of the two pathways, the relative importance of k_1 and k_2 may be assessed. Thus, for direct formation of $C_3H_7^+$ from substituted butyrophenones, rho equals 0, and for the formation of butyryl ion, rho equals 1.8, and $k_1^0 = 3.2\ k_2^0$ if $k_{11} = 0.50\ \sum k_{1n}$ and $\sum k'_{inst} << \sum k_{1n}$.

Alternately, the problem of the lower energy path in the intervention of decomposition of the t-butyl substituent in Scheme II is easily solved. Elimination of the two-step process at low voltage induces a return of the substituent effect to its normal solution value; elimination of the one-step pathway would occur simultaneously in the substituted compound and acetophenone itself, so that the Z/Z_0 value would increase as the ionizing voltage is lowered. The data in Table I support the latter alternative.

Table I

Y	σ value[14]	log Z/Z_0 at 75 volts	log Z/Z_0 at 16.3 volts
m-$(CH_3)_3C$	-0.10	0.72	1.02
p-$(CH_3)_3C$	-0.20	0.69	0.97

(14) Values tabulated by D. H. McDaniel and H. C. Brown, J. Org. Chem., 23, 420 (1958).

Application of Substituent Effects to Appearance Potential Studies. - The different character of the substituent profile of more complex reactions near the appearance potential of the product raises comment on the interpretation of appearance potential data for ions for which a multiplicity of modes of formation is possible. Many methods of calculating appearance potentials call for determination of fractional intensities, i.e., intensities relative to the intensity at some higher voltage.[9] This is admittedly an arbitrary process, and the present work indicates that it can lead to error.[15] The intensity of $C_6H_5^+$

(15) For an alternate reason for error -- a high-voltage decomposition leading to depletion of the molecular ion -- see C. Lifschitz and F. A. Long, J. Chem. Phys., 41, 2468 (1964).

in p-aminobenzophenone at 19 volts is about 1.5% of its value at 75 volts; but only about 10% of the intensity at normal ionizing voltage is from a process kinetically significant near the appearance potential, according to our interpretation. Thus the value at 19 volts is more

properly 15% of its relevant intensity at 75 volts. If these data were to be compared with those for p-nitrobenzophenone, where about 90% of the 75-volt value is attributable to the process measured at low voltage, an error of several tenths of an e.v. in the difference between the appearance potentials of $C_6H_5^+$ in the two cases would result from failure to recognize the kinetic complexity of the high-voltage process of formation. In processes where substituent effects are demonstrable, it appears advisable to make similar studies of processes which may arise by several routes and to combine these data with raw appearance potential data before comparison of results.

Conclusions. - Substituent effects may be used to detect and evaluate two routes of formation for a particular ion, if the effects are sufficiently different; and third processes may be detected for a particular derivative by the deviation from the expected substituent behavior. Analysis of complex curves leads to evaluation of relative magnitudes of competing rates of decomposition for the molecular ion. Substituent dependences of these rates seem to be predicted by the usual arguments relative to interposition of resonating groups to determine rho values, and Hammett substituent constants appear to be generally useful in such analyses. Even for such complex competing reactions rho values and relative base rate constants may be collected for analysis of unresolved systems. Such studies on more complex systems will be continued in this series.

Acknowledgments. - The donation of samples by Dr. Herbert C. Brown, Dr. Saul G. Cohen, Dr. Thomas DeVries, and Dr. Paul G. Ricca is noted with thanks. This work was supported by grants from the National Science Foundation (GP 4335) and the National Aeronautics and Space Administration. (NGR 15-005-021).

Experimental Section

Samples were either commercial samples or gifts, and did not contain any impurities detectable by mass spectrometry.

Spectra were recorded at least in duplicate on a Hitachi RMU-6A single-focusing instrument with inlet at 185° ± 5° C and source at 160 ± 10° C. Ionizing current for high-voltage spectra was 80 μA; electron energy was 75 volts.

The low voltage spectra of the benzophenones were recorded under similar temperature conditions, with repellers tied at 1.5 volts and trap current at 2 μA. The voltage was standardized against an Ar sample; it was adjusted until the intensity of the Ar^+ ion was 10% of its value at 48 volts (max voltage on low-voltage scale) and the entire spectrum was recorded. Although it is subjective to choose a point of departure for voltages based on peak intensities of a standard, the 10% value for Ar^+ occurs 3.2 volts higher than its 1% value, which was arbitrarily taken as 15.8 volts, the literature appearance potential.[16,17]

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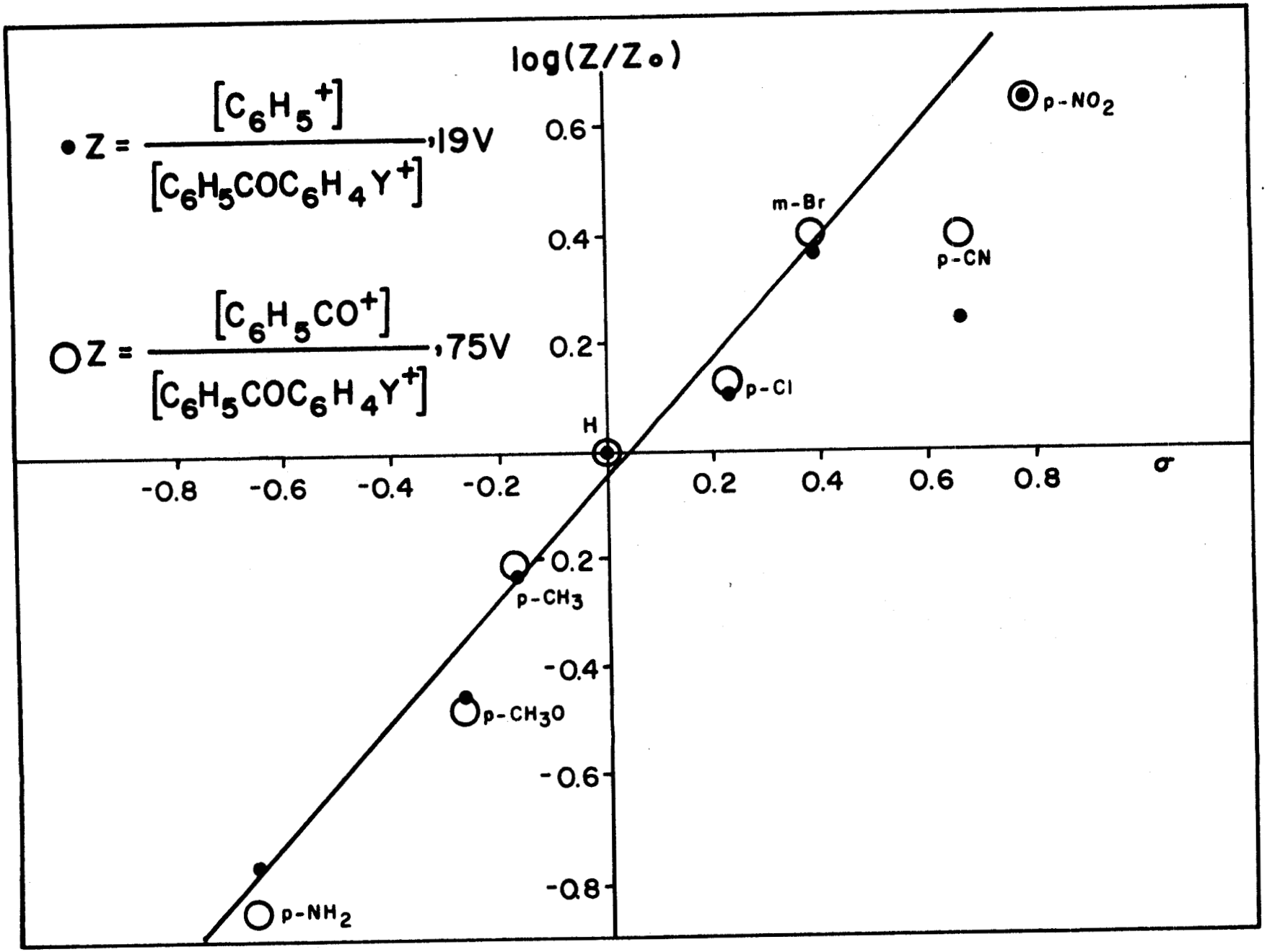
(16) W. Bleakney, Phys. Rev., 35, 1303 (1930).

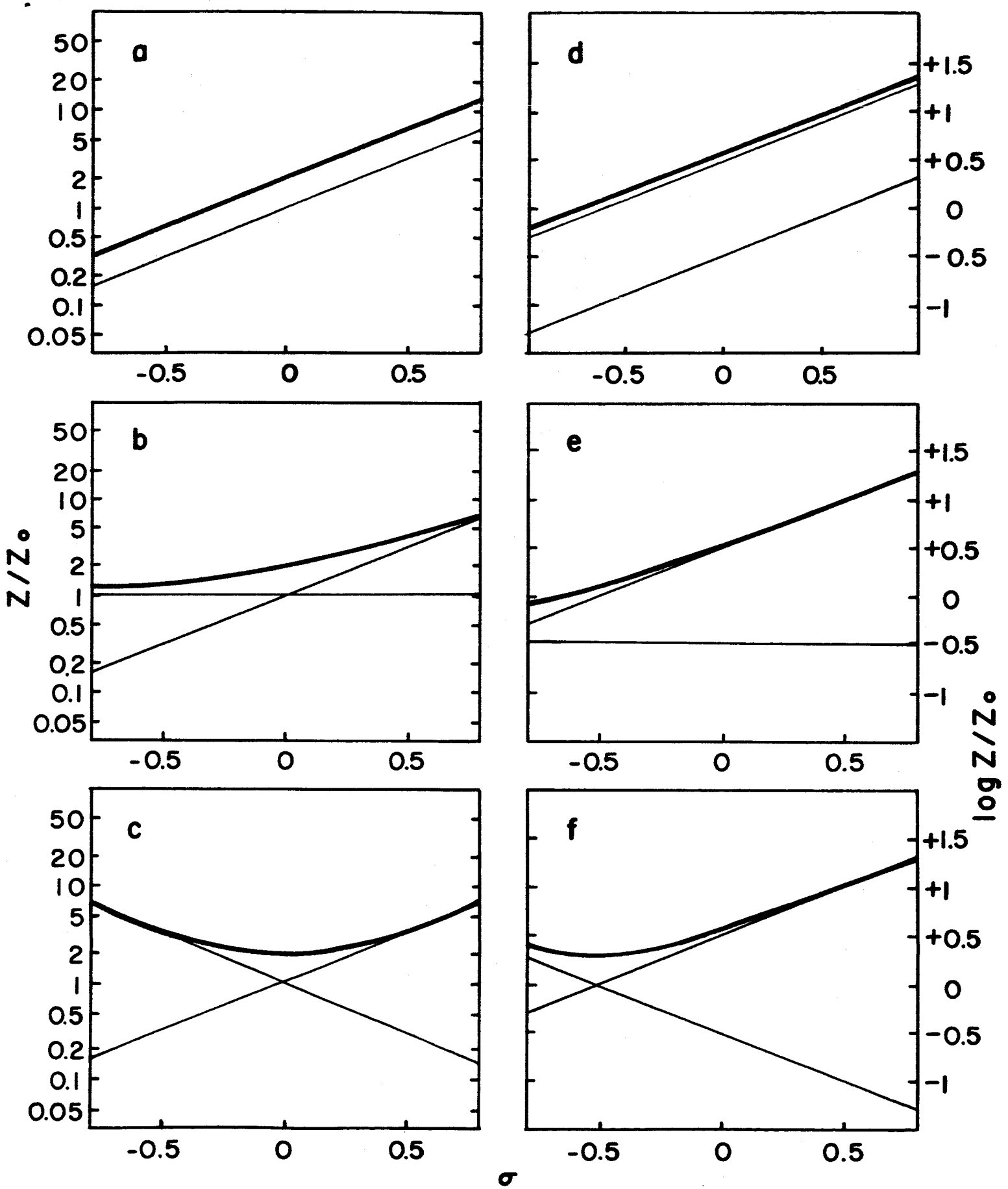
(17) R. E. Honig, J. Chem. Phys., 16, 105 (1948).

Data for the acetophenones were recorded at a voltage at which the intensity of the m/e 43 ion of acetophenone was equal to 4% of its value at 75 volts; this value was 2.6 volts above the energy at which the m/e 43 ion is 1% of its high-voltage value. The voltage for the 1% value again was arbitrarily taken to equal the literature appearance potential, 13.7 volts.[18] Data for various compounds were compared after

(18) J. R. Majer, C. R. Patrick, and J. C. Robb, Trans. Faraday Soc., 57, 14 (1961).

standardization against the relative intensity of the $C_2Cl_3^+$ ion of tetrachloroethylene, which attains 20% of its intensity at 75 volts at this voltage.


log(Z/Z₀)
• Z = [C6H5+] / [C6H5COC6H4Y+] ,19V
○ Z = [C6H5CO+] / [C6H5COC6H4Y+] ,75V
0.6
0.4
0.2
-0.2
-0.4
-0.6
-0.8
-0.8
-0.6
-0.4
-0.2
0.2
0.4
0.6
0.8
σ
p-NO2
m-Br
p-CN
p-Cl
H
p-CH3
p-CH3O
p-NH2


a
b
c
d
e
f
50
20
10
5
2
1
0.5
0.2
0.1
0.05
Z/Z₀
+1.5
+1
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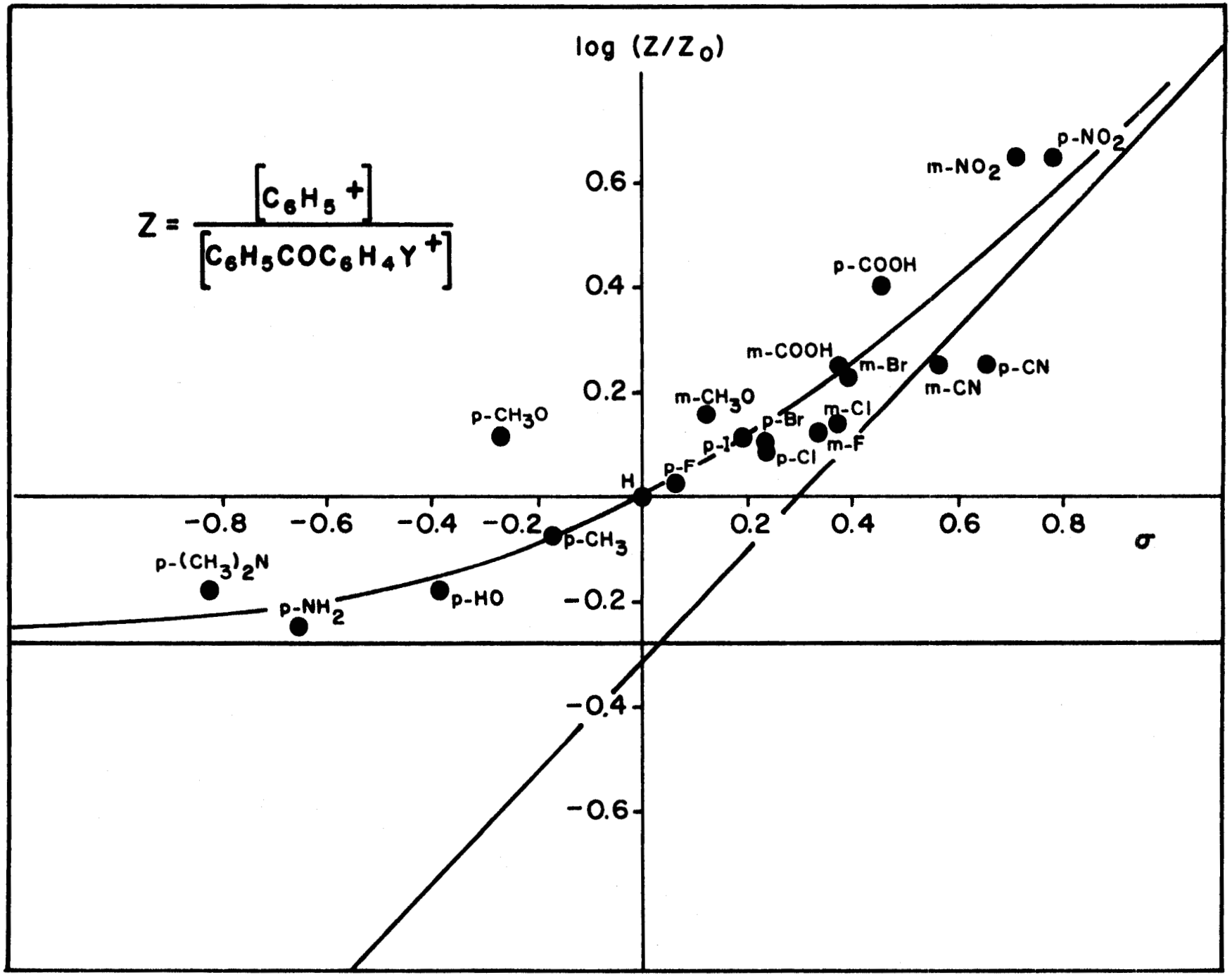
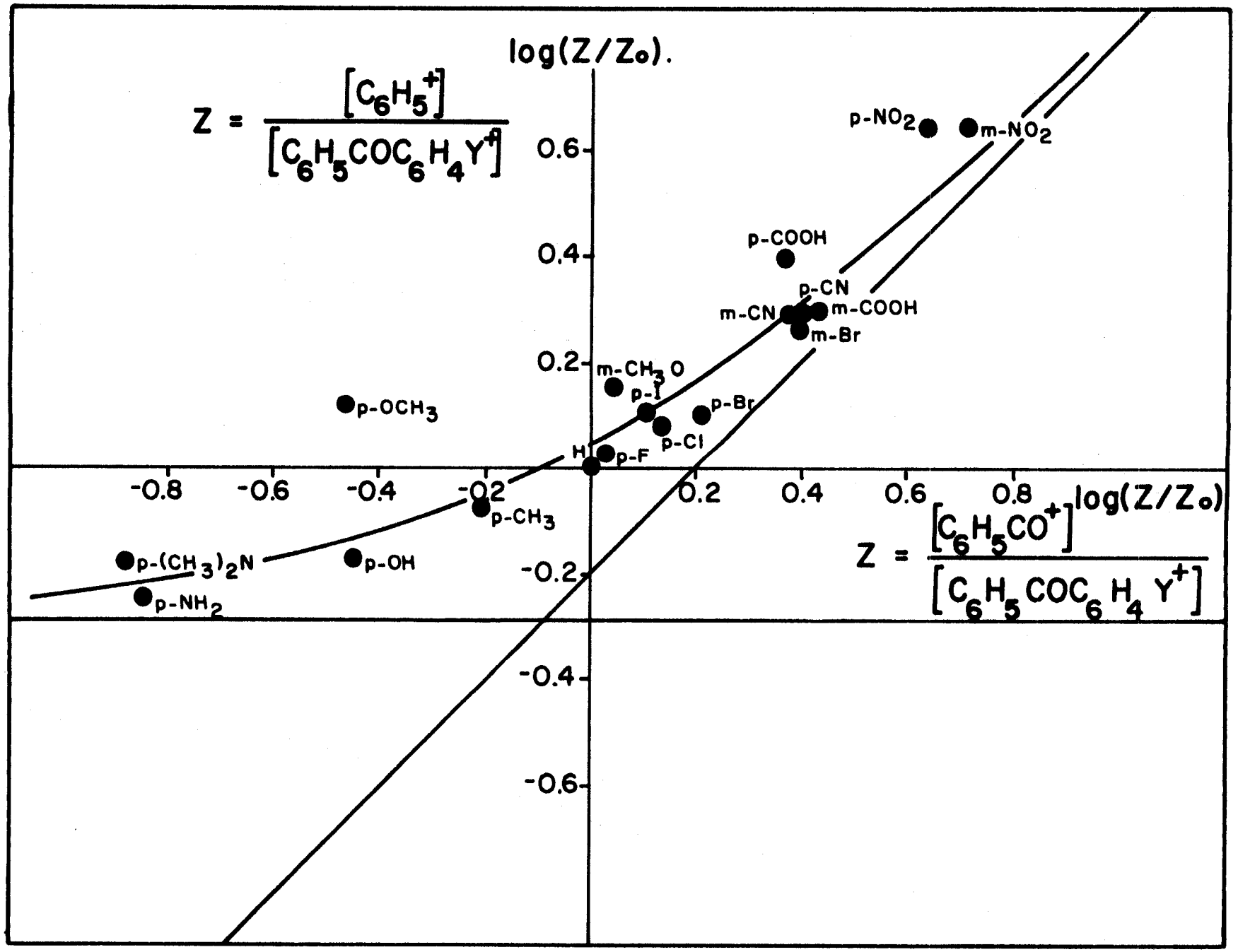
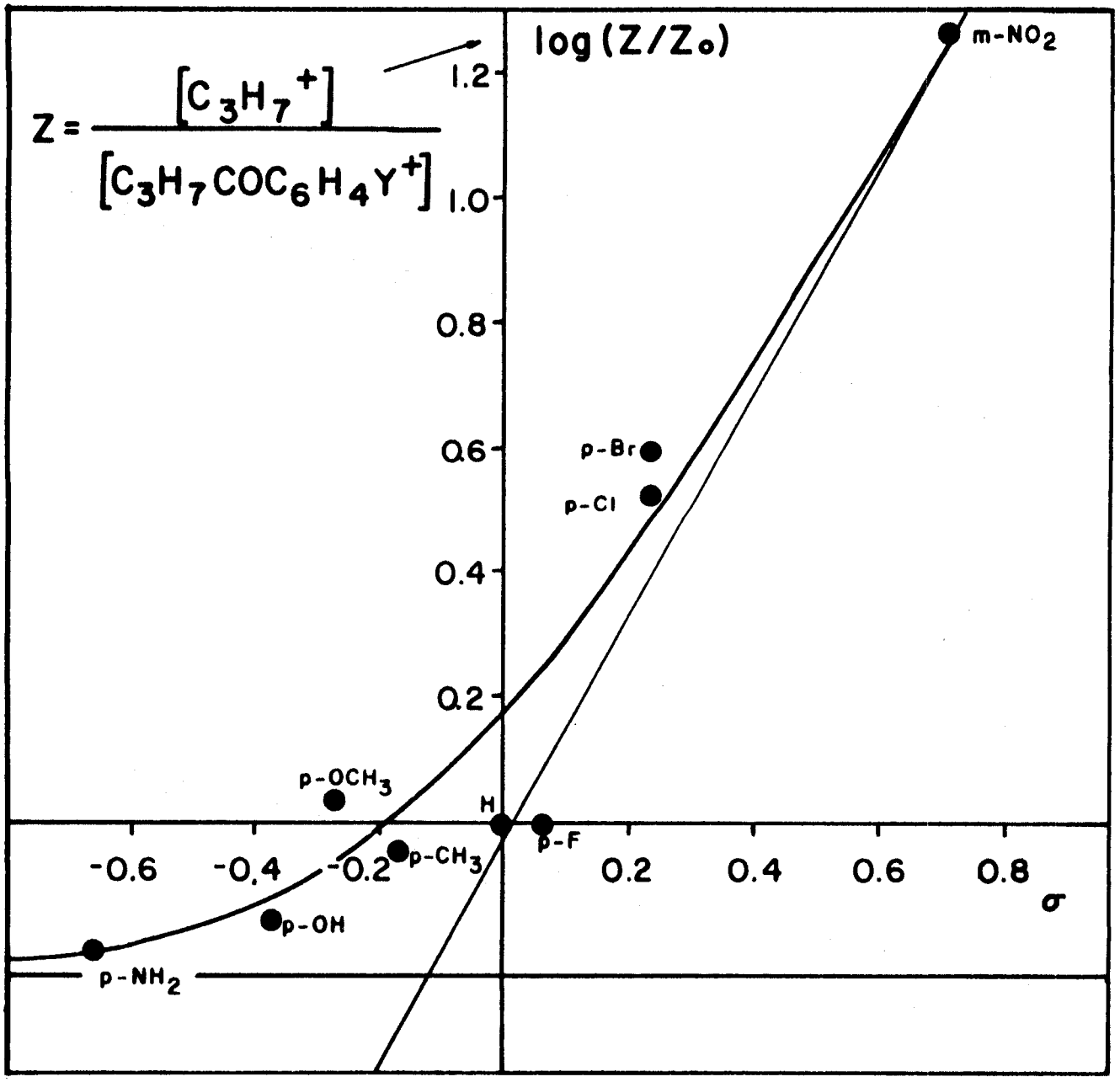
0
-0.5
-1
log Z/Z₀
-0.5
0
0.5
σ


log (Z/Z0)
Z = [C6H5+] / [C6H5COC6H4Y+]
0.6
0.4
0.2
-0.2
-0.4
-0.6
-0.8
-0.6
-0.4
-0.2
0.2
0.4
0.6
0.8
σ
p-NO2
m-NO2
p-COOH
m-COOH
m-Br
m-CN
p-CN
m-CH3O
p-CH3O
p-Br
m-Cl
p-I
p-Cl
m-F
p-F
H
p-CH3
p-(CH3)2N
p-NH2
p-HO


log(Z/Zo).
Z = [C6H5+] / [C6H5COC6H4Y+]
0.6
0.4
0.2
-0.2
-0.4
-0.6
-0.8
-0.6
-0.4
-0.2
0.2
0.4
0.6
0.8
log(Z/Zo)
Z = [C6H5CO+] / [C6H5COC6H4Y+]
p-NO2
m-NO2
p-COOH
p-CN
m-CN
m-COOH
m-Br
m-CH3O
p-I
p-Br
p-Cl
H
p-F
p-OCH3
p-CH3
p-(CH3)2N
p-OH
p-NH2


$Z = \frac{[C_3H_7^+]}{[C_3H_7COC_6H_4Y^+]}$
log (Z/Z₀)
1.2
1.0
0.8
0.6
0.4
0.2
m-NO2
p-Br
p-Cl
p-OCH3
H
p-F
p-CH3
p-OH
p-NH2
-0.6
-0.4
-0.2
0.2
0.4
0.6
0.8
σ