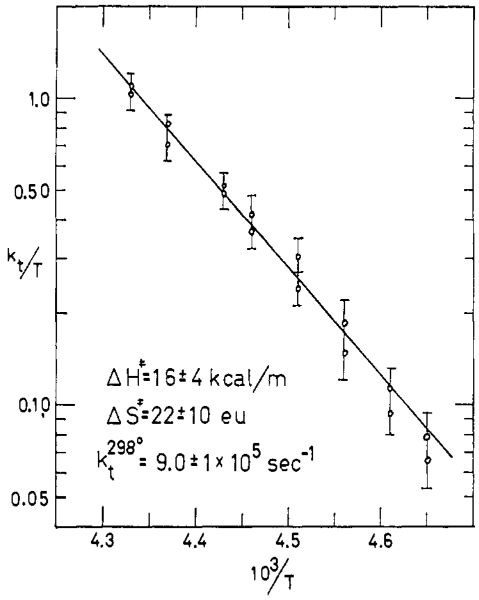

Figure 2. Plot of log $(k_t/T)$ *vs.* $1/T$. The individual points represent line-width measurements of the *meta*-1 and *meta*-2 peaks.

change conditions[17,18] using the relation, $T_2^{-1} = T_{2t}^{-1} + \tau_t^{-1}$, where $(\pi T_2)^{-1}$ is the observed line width (at half-maximum), $(\pi T_{2t})^{-1}$ is the line width in the absence of exchange (obtained as a function of temperature in both fast and slow exchange regions), and $\tau_t$ is the average lifetime of a proton in the tetrahedral species. Figure 2 shows a plot of log $(k_t/T)$ *vs.* $1/T$ ($k_t = 1/\tau_t$) which yields the activation parameters $\Delta H_t^{\ddagger} = 16 \pm 4$ cal/mole and $\Delta S^{\ddagger} = 22 \pm 10$ eu and an extrapolated rate constant at 25° of $k_t^{25°} = 9 \pm 1 \times 10^5$ sec$^{-1}$. The mean lifetime for the over-all exchange process, $\tau$, may be derived from the relation[17] $\tau = (1 - N_t)\tau_t$. This yields an over-all average rate constant, $k = 1/\tau$, of $k^{25°} = 2.4 \pm 0.2 \times 10^6$ sec$^{-1}$. A similar analysis of the chloride system was impossible owing to the much smaller percentage of tetrahedral species present. An investigation of the factors which affect rates of planar-tetrahedral equilibria is in progress.

**Diastereoisomeric Doubling. Catalyzed Oxidation of Phosphines to Phosphine Oxides.** Recent experiments with the iodide complex have shown that the multiplicity of peaks attributed[10] to diastereoisomeric doubling (separate resonances for active and *meso* complexes) is in fact due to a mixture of bis phosphine and phosphine-phosphine oxide complexes in solution of the type $Ni(PR_1R_2R_3)(OPR_1R_2R_3)I_2$. When the iodide complexes were synthesized and solutions prepared under rigorously oxygen-free conditions, only a single set of resonances was observed. Spectra were identical for complexes made from racemic and active phosphines. Admission of air or oxygen to the solutions caused the additional set of resonances to grow in; the new peaks are phosphine proton resonances in the mixed phosphine-phosphine oxide complexes. Chemical shift differences of the order of 2 ppm at −5° are observed[10] for corresponding resonances. Additional peaks near the diamagnetic position from coordinated phosphine oxide for which isotropic shifts are small are also detectable in solution. Confirmation is provided by experiments with the nickel iodide complex of achiral *n*-butyldiphenylphosphine. Aerial oxidation of chloroform solutions of $Ni[P(C_6H_5)_2(C_4H_9)]_2I_2$ produced additional shifted peaks in exact analogy with the results for the dissymmetric phosphine complexes. Infrared spectra of mixtures of nickel iodide, triphenylphosphine, and molecular oxygen in chloroform and benzene showed the presence of significant quantities of triphenylphosphine oxide. No observable oxidation of triphenylphosphine occurred in the absence of nickel iodide under otherwise identical experimental conditions. Molecular oxygen does not affect significantly the chloride and bromide complexes of methylphenyl-*p*-anisylphosphine. Nickel iodide apparently catalyzes the oxidation of phosphines to phosphine oxides in these systems. It is possible that a nickel(0) species is responsible since these are known to be effective catalysts for such oxidations.[19]

Despite the absence of diastereoisomeric doubling in the bis(methylphenyl-*p*-anisylphosphine) complex of nickel iodide, the present results demonstrate this effect in the nickel bromide complex. Two isotropically shifted *para* proton resonances separated by 1 ppm are observed at −57° for the complex synthesized from racemic phosphine (Figure 1), while only a single *para* proton resonance is evident for the complex made from optically active phosphine. No doublings were detected for any of the other resonances. Since the doubling is observed only in the slow-exchange region, it must be attributable to a difference $\Delta a_i$ in the hyperfine interaction constants for the *para* protons between the two diasterioisomers. The splitting in the present case is small, only 4% of the total isotropic shift.

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(17) L. H. Piette and W. A. Anderson, *J. Chem. Phys.*, **30**, 899 (1959).

(18) L. H. Pignolet and W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, **90**, 922 (1968).

(19) G. Wilke, H. Schott, and P. Heimbach, *Angew. Chem. Intern Ed. Engl.*, 6, 92 (1967).

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## Hammett Correlations in Mass Spectrometry

*Sir:*

Following the first demonstration[1] of a correlation between intensities of ions in a mass spectrum and Hammett $\sigma$ values, there has been an increasing number of studies dealing with this topic.[2] It seems now to be assumed that because of these correlations, the structures of the molecular ions undergoing fragmentation can be directly equated with the structures of the molecules before ionization and, therefore, that deductions may be drawn about the mechanisms of fragmentations. From thermochemical arguments we wish to suggest that one of the factors responsible for the correlations has major importance and has little to do with the reaction mechanism. All mass spectrometric fragmentation processes are at least two step (counting ionization as one step), and it is difficult to interpret Hammett correlations in multistep reactions. To illustrate this point we consider one of the simplest types of mass spectrometric

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(1) F. W. McLafferty, *Anal. Chem.*, **31**, 477 (1959).

(2) For leading references see M. M. Bursey, *Org. Mass Spectry.*, 1, 31 (1968).

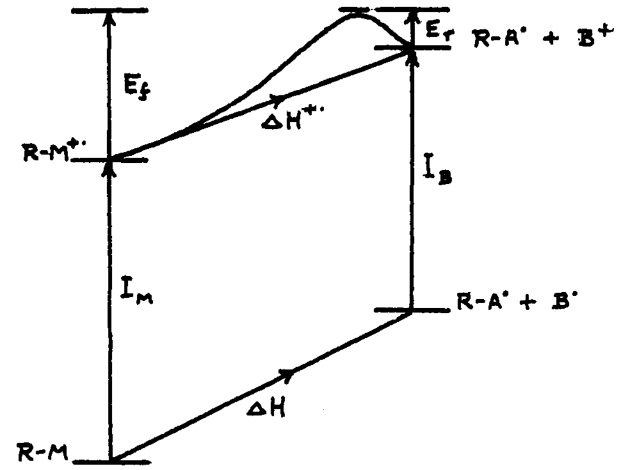

Figure 1.

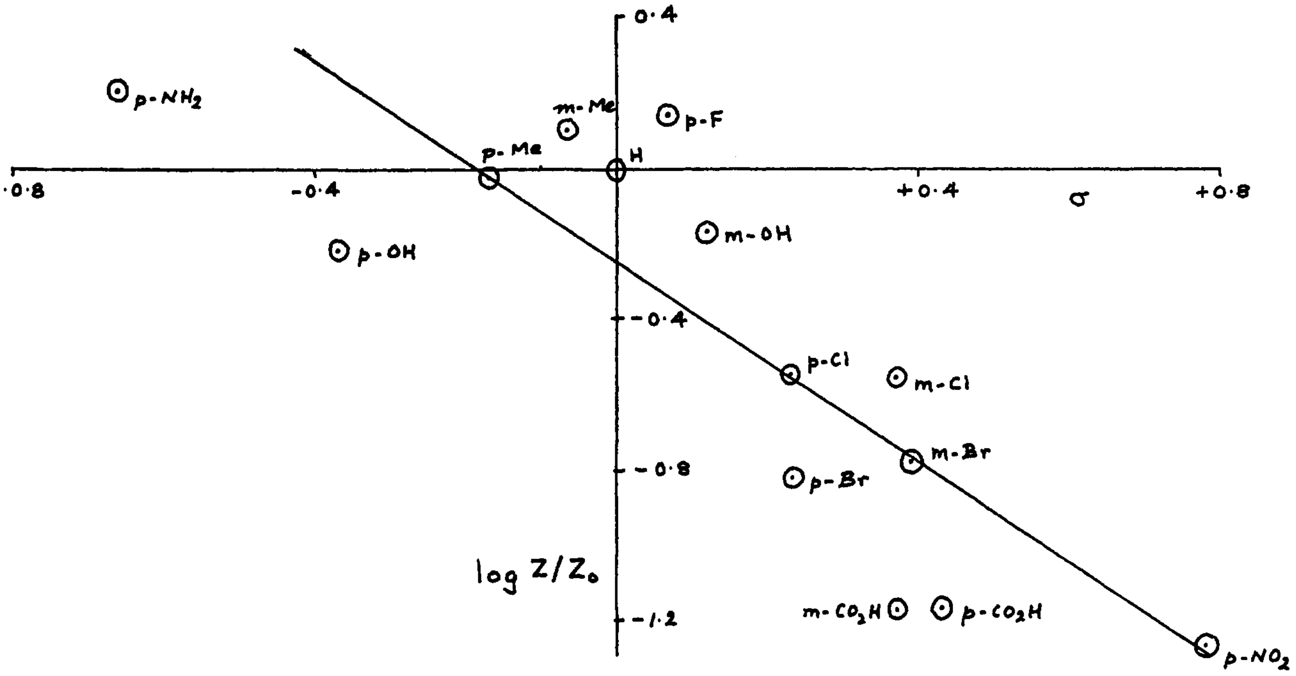

Figure 2.

fragmentations, bond cleavage, exemplified by reaction 1 in which R represents a *meta* or *para* substituent in a benzenoid molecular ion ($M^+$) and the cleavage fragments are a radical ($A\cdot$) and an ion ($B^+$). Ignoring

$$R\text{–}M\cdot^+ \longrightarrow R\text{–}A\cdot + B^+ \tag{1}$$

effects like kinetic shifts and possible electronically excited states which would modify any correlation, the essential energy terms are illustrated in Figure 1.

The bond dissociation energy ($\Delta H\cdot^+$) for reaction 1 is given by $\Delta H\cdot^+ = E_f - E_r = \Delta H + I_B - I_M$. The activation energy for the reverse reaction ($E_r$) can be shown to be small for many mass spectrometric processes[3] and is generally assumed to be nearly zero for simple cleavage as might be expected by comparison with ordinary solution chemistry. Therefore, for $E_r \ll E_f$, we can write $E_f = \Delta H\cdot^+ = \Delta H + I_B - I_M$, and for a substituent (R) compared with hydrogen (H) the simplified rate equation[4] gives

$$k_R = \nu_R[(E_R - E_R^0)/E_R]^{N_R-1}$$
$$k_H = \nu_H[(E_H - E_H^0)/E_H]^{N_H-1}$$

whence

$$\log (k_R/k_H) = (N_R - 1) \log \nu_R[(E_R - E_R^0)/E_R] - (N_H - 1) \log \nu_H[(E_H - E_H^0)/E_H] \tag{2}$$

For the usual substituents, the effective numbers of oscillators ($N_R$, $N_H$) may be considered equal without significant error, as also the frequency factors ($\nu_R$, $\nu_H$) for any particular reaction. Hence, eq 2 reduces to

$$\log (k_R/k_H) \cong (N - 1) \times \log [(1 - E_R^0/E_R)/(1 - E_H^0/E_H)] \tag{3}$$

For homolytic bond cleavage, $\Delta H_R \cong \Delta H_H$ within about 1 kcal mole$^{-1}$, as can be seen from bond dissociation energies α or β to a substituted phenyl ring.[5] If it is assumed that $E_R = E_H = E$, the excess internal energy,[6] eq 3 gives (4) after the substitution $E_0 = E_f$ and approximating the right-hand-side logarithm in the usual way.

$$\log (k_R/k_H) \cong [(N - 1)/E][I_M^R - I_M^H] \tag{4}$$

If, as with Bursey and McLafferty[6] and despite some objections on instrumental grounds,[7] we put $k_R/k_H = Z/Z_0$, and since for simple substituted benzenes it is known[8] that $[I_M^R - I_M^H] = k\sigma$ ($k$, a constant), we ob-

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(3) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957, Chapter IV.

(4) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Natl. Acad. Sci. U. S.*, **38**, 667 (1952).

(5) V. I. Vedeneyev, L. V. Gurvich, V. N. Kondratyev, V. A. Medvedev, and Ye. L. Frankevich, "Bond Energies, Ionisation Potentials, and Electron Affinities," Edward Arnold, Ltd., London, 1966.

(6) M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.*, **88**, 529 (1966).

(7) I. Howe and D. H. Williams, *Chem. Commun.*, 220 (1968); M. M. Bursey and D. Rosenthal, *ibid.*, 1010 (1968).

(8) A. Streitwieser, Jr., *Progr. Phys. Org. Chem.*, 1, 27 (1963).

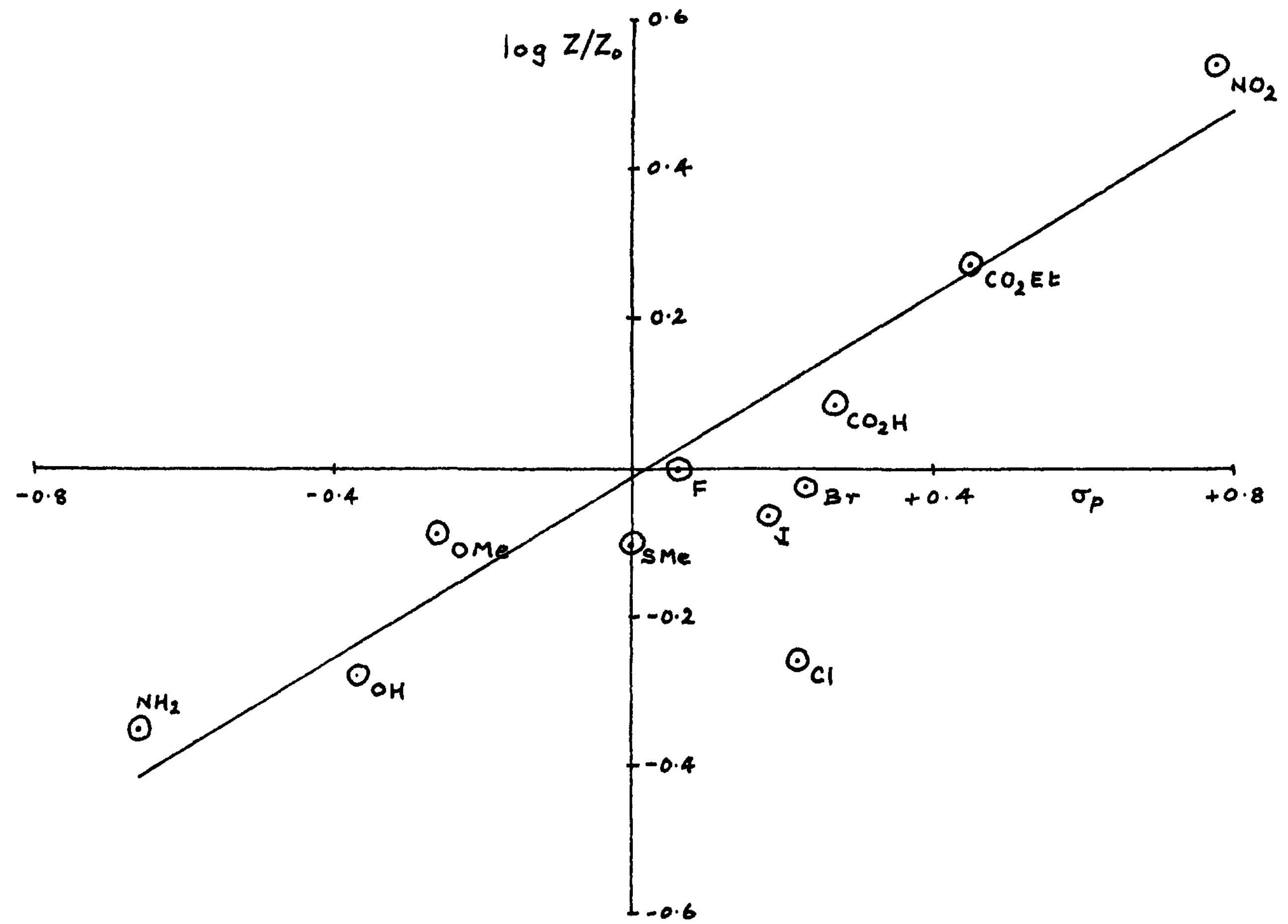

Figure 3.

tain the final result in eq 5 where $K$ is a constant.

$$\log (k_R/k_H) = \log (Z/Z_0) = K\sigma \qquad (5)$$

According to the simplified treatment given here, eq 5 shows that a correlation between log ($Z/Z_0$) and the Hammett $\sigma$ values can be deduced from the quasi-equilibrium theory, but *the correlation is due to the correlation of the molecular ionization potential with* $\sigma$ and not to the mechanism of bond cleavage.

In cases where the substituent appears in the fragment ion, the ionization potential ($I_B$) will also probably correlate with $\sigma$ and the net energy term ($I_B - I_M$) will be important. However, even in such cases, only one of the terms ($I_B$) has any connection with the reaction center and unless some attempt is made to dissect out its importance, any deductions about structure and mass spectrometric mechanisms based on log ($Z/Z_0$) experiments are suspect. Indeed, we have already stressed[9] the desirability of examining the energies involved by measurement of ionization and appearance potentials and estimates of kinetic shifts. Examples of complex mass spectrometric fragmentations in which log ($Z/Z_0$) correlates with $\sigma$ at least as closely as many previously published results are shown in Figures 2 and 3 (the values of $Z/Z_0$ were obtained from the literature[10]). The loss of CHO from substituted phenols, a specific and yet complex fragmentation involving destruction of the aromatic ring, gives the fair correlation shown in Figure 2. Even more remarkable is the correlation shown in Figure 3 which was obtained from the mass spectra of monosubstituted benzenes. In each instance of the latter, the intensity of the molecular ion was noted and then the intensity of the first major skeletal fragment ion *irrespective of the actual fragmentation involved.* Thus, in Figure 3 are included such diverse reactions as loss of HCN from aniline, of $NO_2$ from nitrobenzene, of Cl from chlorobenzene, of $C_2H_2$ from fluorobenzene, elimination of terminal $C_2H_4$ from ethyl benzoate, and of CO from phenol. We prefer not to draw any conclusions about the fragmentation mechanisms from these correlations.

The assumptions used in our mathematical treatment are similar to those used to deduce the log ($Z/Z_0$) relationship,[2] and both treatments suffer from oversimplification. Because of this it is very difficult to draw conclusions about the reaction mechanisms of fragmentation. More detailed studies are discussed in the full publication.

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## Sensitized Photolysis of Cobalticyanide Ion

*Sir:*

In aqueous acid solutions, the decomposition of potassium hexacyanocobaltate(III), $K_3Co(CN)_6$, occurs

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[9] R. A. W. Johnstone and D. W. Payling, *Chem. Commun.*, 601 (1968).

[10] American Petroleum Institute, Project 44; Uncertified Mass Spectral Data, Dow Chemical Co., Midland, Mich.