

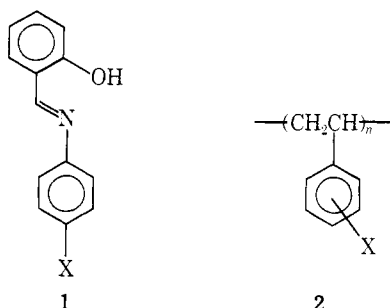
## Linear Free Energy Relationships. V. 1-4 Trielectric Charging of Organic Solids

Sir:

Electrical charging by contact, either frictional (triboelectrification) or nonfrictional, of dissimilar materials has been known since about 600 B.C.<sup>5-7</sup> This electrification phenomenon is a necessary component for the process of xerography,<sup>8,9</sup> for the electrostatic separation of materials,<sup>10</sup> for the behavior of self-clinging wrapping materials, and for electrostatic paint application. However, the production of electric charges by contact of human footwear with carpeting is a nuisance; the triboelectrification of flammable fuels by flow through pipes is an extreme hazard. Yet in spite of the importance of the phenomenon, no relationship between the sign and magnitude of charging and chemical structure has been reported; some qualitative rankings of materials have appeared, however.<sup>11</sup>

We now wish to report the first quantitative correlation of solid state triboelectric charging and molecular structure.

On the assumption that charge exchange between dissimilar bodies might constitute a molecular electrochemical phenomenon, subject to the same structural rules that generally govern the reactivity of organic species, several homologous series of compounds were chosen for examination in order to apply linear free energy relationships to the elucidation, control, and prediction of triboelectric charging. The monomeric salicylaldehyde anils, **1**, chosen because they are well characterized,<sup>3</sup> were recrystallized several times to analytical purity.<sup>3</sup> The substituted polystyrenes, **2**, the simplest homologous aromatic polymer series, were likewise purified by repeated precipitations. Films  $\sim 10 \mu$  thick



were cast from solution or applied from the melt onto aluminum substrates, dried in vacuo ( $< 1$  Torr) at room temperature for 60 hr, and examined using the simple device depicted in Figure 1. This is an adaptation<sup>12</sup> of a device reported for the charging of glasses and minerals.<sup>10</sup> The entire apparatus was contained in a drybox maintained at constant relative humidity by means of air circulation through desiccant scrubbers or saturated salt solutions. The films were 9 in. long and were mounted at a  $30^\circ$  angle to the horizontal. The hopper was mounted 1 cm above the film.<sup>13</sup> Steel beads ( $250 \mu$ ) or zinc powder (Baker C.P.) that has been washed with tetrahydrofuran and dried in vacuo at  $100^\circ$  for 4 hr was employed;<sup>14</sup> from 5 to 30 g were used per measurement. An average of at least three measurements was taken. The quantity determined is  $Q/M$ , the ratio of charge (in nanocoulombs) to mass of the metallic beads, since the charge acquired by the films is directly related to the mass of beads employed up to a certain saturation level.<sup>10</sup> The precision of the determination is 5-10% of the average value.

The experimental results of this study are shown in Figure 2, where  $\log(Q/M)$  is shown as a function of the Hammett substituent constant,  $\sigma_x$ . As can be seen good linear correlations exist for the anils **1** and for the polystyrenes **2**.

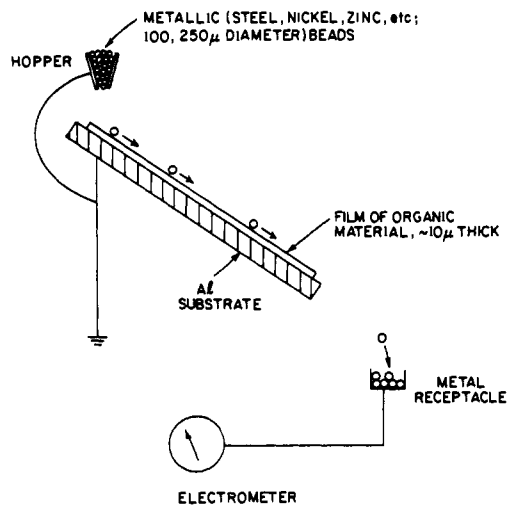


Figure 1. Device for determination of triboelectric charging of organic solids.

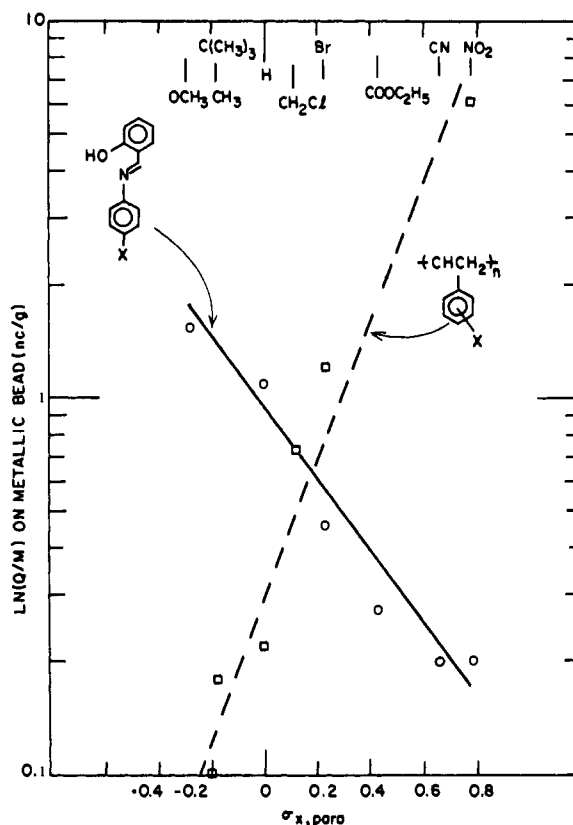


Figure 2. Triboelectric charging as a function of substituent constant for salicylaldehyde anils (**1**) using  $250 \mu$  steel beads at 0% relative humidity, organic films positively charged,  $\ln(Q/M) = -1.98\sigma_x - 0.136$  (correlation coefficient  $r = 0.966$ )  $\circ$ — $\circ$ , and substituted polystyrenes (**2**) using zinc powder (Baker) at 56% relative humidity, organic films negatively charged:  $\ln(Q/M) = 4.16\sigma_x - 1.23$  (correlation coefficient  $r = 0.978$ )  $\square$ — $\square$ .

The triboelectrification phenomenon is viewed as a solid state electrochemistry, whereby one molecule loses an electron to another. However, unlike solution electrochemistry there is no transport medium (electrolyte) and therefore the reaction depends upon physical contact.

By analogy to electrochemistry the electron exchange process may be considered to be governed in an exponential manner by the difference in the energy levels of the orbitals of the acceptor and the donor. Thus for positive charging of the organic solids  $\ln(Q/M) \propto E_{\text{HOMO}} - E_A$ , when  $E_{\text{HOMO}}$ ,

the energy of the highest occupied molecular orbital, is significantly higher than  $E_A$ , the acceptor level of the metal.<sup>15</sup> In previous work we have related molecular energy levels to structure through the use of substituent constants;<sup>1-4</sup> in particular it has been shown that the gas phase ionization potentials of mono- and disubstituted benzenes are well correlated in this way.<sup>1</sup> This seems to be general.<sup>16</sup> Therefore, for compounds **1** the ionization potentials would increase with the Hammett substituent constant,  $\sigma_x$ , and in fact their electrochemical oxidation potentials in solution indicate that this is true.<sup>3</sup> Therefore, under the assumption that this relationship also holds in the solid state, substitution of  $E_{\text{HOMO}} = -m_1\sigma_x + b_1$  ( $m_1, b_1$  are positive constants) into the equation above for positive charging of the organic compounds yields  $\ln(Q/M) \propto -m_1\sigma_x - E_A + b_1$ . Thus, for a given metallic bead acceptor<sup>17</sup> and constant experimental variables  $\ln(Q/M) \propto -\sigma_x$ . Similarly for negative charging of the organic solid  $\ln(Q/M) \propto E_D - E_{\text{LUMO}}$ , when  $E_D$ , the donor level of the metal, is significantly greater than  $E_{\text{LUMO}}$ , the energy of the lowest unoccupied molecular orbital.<sup>15</sup> Since the electron affinities, which are direct measures of  $E_{\text{LUMO}}$ , can be shown to be linear functions of the Hammett substituent constant in aromatics generally,<sup>18</sup> one can substitute  $E_{\text{LUMO}} = -m_2\sigma_x + b_2$  ( $m_2, b_2$  are positive constants). Using a given metallic donor<sup>17</sup> then  $\ln(Q/M) \propto +\sigma_x$ . This treatment therefore predicts a linear dependence of  $\ln(Q/M)$  on substituent constant, but having negative slope for positive charging of the organic and positive slope for negative charging. Thus, the relationships derived not only correctly rationalize the linear nature of the dependence of  $\ln(Q/M)$  on substituent, but also the sign of the slope relative to the sign of charging.

Significantly, the present results demonstrate that triboelectric charging of solids is directly related to the *molecular* structure of the *bulk* and moreover apparently to the molecular orbital energy levels of the isolated molecules (in gas phase or solution).<sup>19</sup> In this regard the results for the polystyrenes **2** are especially noteworthy. While the relationship of triboelectrification and triboluminescence<sup>20</sup> is obscure, both clearly relate to molecular properties. A recent report from these laboratories describes similar correlations for injection of charge from amorphous solids in a less explicit but analogous manner.<sup>21</sup> The application of linear free energy relationships (and other chemical principles) to the correlation and elucidation of these and related physiochemical interactions of solids makes the processes amenable to study at the molecular level and allows molecular structural control of the phenomena.

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- (13) The charge acquired by the beads has been shown to be a function of the film length, the angle to the horizontal, and the bead drop height; these geometric factors relate to the number of bead contacts per unit length of the film (R. Menchel, O. Hauser, and M. W. Williams, Xerox Corporation, private communication). For these homologous compounds the observed number of bounces appears relatively constant. The effects of surface morphology appear to be minimal since melt coating and solution coating of films of **1** give the same results.
- (14) Metallic beads are used since they can easily be made electrically neutral. Against a film of the same metal, the charge acquired by the bead is negligible.
- (15) The restriction that  $E_{\text{HOMO}}$  be significantly greater than  $E_A$  or that  $E_D$  be significantly greater than  $E_{\text{LUMO}}$  avoids intermediate cases where the electrochemical analogy is not as straightforward. In these other cases, very low and irreproducible charging levels result.
- (16) For example we find that the first four ionization potentials of substituted pyridine *N*-oxides (data of J. P. Maier and J. F. Muller, *Tetrahedron Lett.*, 2987 (1974)) are linearly correlated (correlation coefficients  $r = 0.994, 0.995, 0.945, 0.935$ , respectively) by the sums of the  $\sigma_{\text{para}}$  substituent constants.
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## Theoretical Models for Oxidized Rubredoxin. SCF-X $\alpha$ -SW Calculations on FeS $_4^{5-}$ , Fe(SH) $_4^-$ , and Fe(SCH $_3$ ) $_4^-$

Sir:

Determination of the X-ray structure of oxidized rubredoxin to nearly small-structure accuracy<sup>1</sup> has stimulated interest in correlation of measurable properties of this iron-sulfur protein with the structural results.<sup>2</sup> Especially intriguing is the question of the reasons for and the effects of one of the four approximately tetrahedral Fe-S bonds being significantly shorter (2.05 (3) Å) than the other three (2.24 (3), 2.32 (3), and 2.34 (2) Å). Rubredoxin is also an important model for understanding the more complex ferredoxins, which contain iron-sulfur clusters with significant Fe-Fe as well as Fe-S bonding.<sup>3,4</sup> Common to rubredoxin and most ferredoxins are Fe<sup>III</sup>  $\rightarrow$  Fe<sup>II</sup> reduction potentials which are low compared to an aqueous environment,<sup>2</sup> and there is much interest<sup>3,4</sup> in how the proteins create this particular degree of stability for Fe<sup>III</sup> relative to Fe<sup>II</sup>.

We have begun a comprehensive theoretical study of models for the Fe(SR) $_4$  core in rubredoxin using the SCF-X $\alpha$  scattered wave method,<sup>5</sup> which, in the overlapping sphere modification,<sup>6,7</sup> yields quite accurate electronic structures at moderate cost.<sup>8,9</sup> The only previous calculations on rubredoxin<sup>10</sup> used the iterative extended-Hückel LCAO technique. Direct comparison of extended-Hückel and X $\alpha$ -SW methods have shown them to be comparable in speed, despite the much more approximate nature of the former.<sup>11</sup> Here we report preliminary results for FeS $_4^{5-}$ , Fe(SH) $_4^-$ , and Fe(SCH $_3$ ) $_4^-$  as models for oxidized rubredoxin. The first was calculated in  $T_d$  and the last two in  $D_{2d}$  symmetry, using Fe-S = 2.29 Å, S-H = 1.34 Å, S-C =