where $\%E_0$, $\%E_t$, and $\%E_\infty$ represent $[\mathbf{5}E]/([\mathbf{5}E] + [\mathbf{5}Z])$ at times $t = 0$, $t = t$, and $t = \infty$; and $\%Z_0$, $\%Z_t$, and $\%Z_\infty$ represent $[\mathbf{5}Z]/([\mathbf{5}E] + [\mathbf{5}Z])$ at times $t = 0$, $t = t$, and $t = \infty$; n_t = radioactivity incorporated in **5** at time t = t; and n_∞ = radioactivity in **5** at time $t = \infty$.

Acknowledgment. We are indebted to Prof. C. F. Bernasconi for sending us ref 21 and to Prof. Y. Apeloig and Dr. M. Karni for discussions and calculations. This paper was supported by a grant from the United States–Israel Binational Science Foundation (BSF), Jerusalem, Israel, to whom we are grateful.

---

[24] Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*, 3rd ed.; Wiley: New York, 1981; (a) p 304, (b) p 311.

Methyltriarylphosphonium Arenesulfonates. Preparation and Characterization by ^{1}H, ^{31}P, and ^{17}O FTNMR, Cyclic Voltammetry, and Molecular Orbital Calculations

D. E. Bugner

Copy Products—Research and Development, Eastman Kodak Company, Rochester, New York 14650-1714

Received September 12, 1988

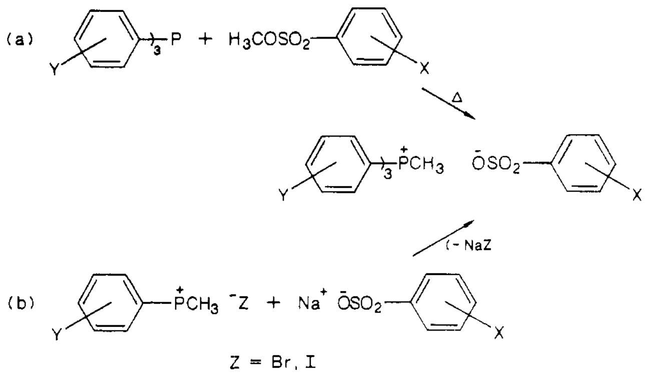
Two series of methyltriarylphosphonium arenesulfonates (**1a–i**, **2a–g**) were prepared in which either the anion or the cation is systematically varied. The frontier molecular orbitals of these salts were evaluated by a combination of spectroscopic, electrochemical, and theoretical techniques. For the cation variations, irreversible reductions are observed by cyclic voltammetry, which correlate well with substituent electronegativities. ^{1}H NMR (for the *P*-methyl group) and ^{31}P NMR (for the phosphorus itself) data also correlate well with substituent constants. For the anion variations, irreversible oxidations are observed which correlate better with σ than with σ°, implying that the aromatic π-system is involved in the oxidation. ^{17}O NMR chemical shifts for the sulfonate group, on the other hand, yield a better correlation with σ°, as would be expected for a purely inductive effect. Semiempirical molecular orbital calculations at the AM1 level were also performed on both series of ions. The calculations are consistent with the expectation that, for a given phosphonium sulfonate salt, the LUMO is on the cation and the HOMO is on the anion. Both HOMO and LUMO energies exhibit very good linear correlations with substituent constants. While the LUMO energies also correlate well with the cathodic peak potentials, the HOMO energies give a substantially poorer correlation with the anodic peak potentials. However, by using the energies calculated for the highest occupied π-orbitals (HOPO's) for the anions, a much improved correlation is observed. This is also consistent with the removal of an electron from the aromatic π-system rather than the charge-bearing sulfonate group.

Introduction

The phenomenon of triboelectrification plays a critical role in the electrostatic charging of dry electrophotographic developers of the type commonly used in office copying machines.[1-3] A two-component developer consists of toner and carrier. The toner is comprised of a thermoplastic binder, a colorant, and a charge-control agent (charge-agent).[3] The toner becomes triboelectrically charged (tribocharged) through frictional contact with the carrier. The charged toner particles are then used to develop the electrostatic latent image on the photoconductor. The carrier consists of polymer-coated magnetic particles, which attain an electrostatic charge opposite that of the toner. Carrier is retained in the machine by virtue of its magnetism. The charge-agent is used to control the magnitude and polarity of the electrostatic charge on the toner.[3] Quaternary ammonium and phosphonium salts are commonly used for positively charging toners.[4] These salts can be envisioned to function as electron donors (via the highest occupied molecular orbital (HOMO) of the anion) and/or electron acceptors (via the lowest unoccupied molecular orbital (LUMO) of the cation).[1,5] To test this model we have subtly and systematically perturbed the HOMO and LUMO energies by preparing a series of methyltriarylphosphonium arenesulfonates (**1a–i**, **2a–g**) in which the electronegativities of the substituents on either the cation or the anion are varied over a wide range. By keeping either the anion or cation constant and varying the respective counterion, we can independently adjust either the HOMO or LUMO energies of the salts.

In this paper we describe the preparation and characterization of the phosphonium sulfonates listed in Table

Scheme I



---

[1] Portions of this work have been previously communicated: (a) Anderson, J. H.; Bugner, D. E. 17th Northeast Regional Meeting of the American Chemical Society; Rochester, NY, November 8–11, 1987. (b) Anderson, J. H.; Bugner, D. E. 4th International Congress on Non-Impact Printing Technologies; New Orleans, LA, March 20–25, 1988.

[2] Jewett, W. S. IAS '77 Annual, 557 (1977).

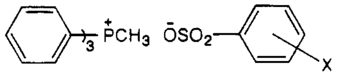
[3] Schaffert, R. M. In *Electrophotography*; John Wiley and Sons: New York, 1975; p 71.

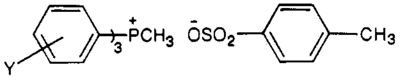
[4] (a) Jadwin, T. A.; Mutz, A. N.; Rubin, B. J. USP no. 3,893,935, July 8, 1975. (b) Wilson, J. C.; DeMejo, L. P.; Jadwin, T. A.; Merrill, S. H. USP no. 4,496,643, January 29, 1985.

[5] (a) Gibson, H. W. *Polymer* **1984**, *25*, 1. (b) Gibson, H. W.; Bailey, F. C. *Chem. Phys. Lett.* **1977**, *51*, 352.

0022-3263/89/1954-2580$01.50/0 © 1989 American Chemical Society

Table I. Methyltriarylphosphonium Arenesulfonates and Their Appropriate Substituent Constants: Methyltriphenylphosphonium Arenesulfonates and Methyltriarylphosphonium Tosylates





compd	X	σ	σ°	compd	Y	σ
1a	4-NH_2	–0.66	–0.38	**2a**	4-$N(CH_3)_2$	–0.83
1b	4-CH_3	–0.17	–0.15	**2b**	4-OCH_3	–0.268
1c	4-OCH_3	–0.268	–0.12	**2c**	4-CH_3	–0.17
1d	H	0	0	**1b**	H	0
1e	4-Cl	0.227	0.27	**2d**	4-Cl	0.227
1f	3-NO_2	0.71	0.70	**2e**	4-CO_2CH_3	0.39
1g	4-NO_2	0.778	0.82	**2f**	3-CF_3	0.43
1h	3,5-$(CO_2CH_3)_2$	0.78[a]		**2g**	4-CF_3	0.54
1i	3-NO_2, 4-Cl	1.00[a]				

[a] $\Sigma\sigma$ para.[8]

I. Several key physical properties are correlated with the electronegativities of the substituents within each series. Results of molecular orbital calculations are also presented and discussed. In a separate paper we will relate the electronic properties of these salts to the charging properties of powdered electrophotographic developers in which they are incorporated.[6]

Results and Discussion

A. Preparation of Materials. The syntheses of the phosphonium salts (**1a–i**, **2a–g**) were achieved by either (a) quaternizing a triarylphosphine with a methyl arenesulfonate or (b) converting a methyltriarylphosphonium halide into an arenesulfonate by ion-exchanging with a sodium arenesulfonate (Scheme I). The methyl arenesulfonate quaternizations were carried out by heating the triarylphosphine with a slight excess of the methyl arenesulfonate in the absence of solvent. The methyl iodide quaternizations were run in refluxing 2-butanone. The crude products were purified by recrystallization from an appropriate solvent system. The salts were characterized by a combination of nuclear magnetic resonance spectroscopy (NMR), infrared spectroscopy (IR), electronic spectroscopy (UV–vis), cyclic voltammetry (CV), melting point, and combustion analysis.

Using these procedures, we were able to obtain a series of derivatives in which either the anions or cations possess substituents spanning a wide range of electronegativities. For the series of anion variations (Table I), we correlated our results with the usual Hammett constants (σ), as well as the Taft constants (σ°).[7] The latter are proposed for situations in which direct conjugation between the substituent and the active site is unlikely. If an electron is being transferred from one of the sulfonate oxygens, then one might expect a better correlation with the Taft substituent constants. For the disubstituted arenesulfonates (**1h–i**) the sum of σ(para) was used as an estimate of the effective Hammett constant.[8] For the cation series (Table I), Hammett constants are used exclusively.

B. Evaluation of Relative Donor/Acceptor Abilities. Overview. Our overall goal in this work is to relate the electronic properties of phosphonium sulfonate charge-control agents to the triboelectric behavior of electrophotographic toners which contain these materials. We were therefore especially interested in evaluating their frontier molecular orbitals. Gibson[8] has shown that the HOMO and LUMO energies can be directly related to the substituent constants for a series of neutral aromatic derivatives. However, in an effort to forge a more fundamental understanding of the mechanism of tribocharging, we felt it worthwhile to attempt to independently evaluate the energies of the frontier molecular orbitals for the series of methyltriarylphosphonium arenesulfonates used for this study, either on a relative or on an absolute scale.

Techniques for the direct determination of ionization potentials (IP's) and electron affinities (EA's), which to a first approximation[9] are equal to $-E_{\mathrm{HOMO}}$ and E_{LUMO}, respectively, are not particularly amenable to the nonvolatile nature of the compounds employed for this study. A spectroscopic technique that directly relates to differences in the frontier molecular orbital energies is UV–vis spectroscopy. Unfortunately, there are difficulties in using UV–vis spectroscopy to evaluate the HOMO–LUMO energy gap for these salts, since the anion and cation behave as independent chromophores. Thus, transitions between the HOMO on the anion and the LUMO on the cation are not observed. Instead we see two transitions: one between the HOMO of the anion and the LUMO of the anion and one between the HOMO and LUMO of the cation. Moreover, these absorptions overlap. We have therefore turned to a combination of cyclic voltammetry (CV) and nuclear magnetic resonance (NMR) spectroscopy as indirect measures of the relative frontier molecular orbital energies of these compounds. We have also carried out molecular orbital calculations on each of the ions using the MOPAC molecular orbital software package.[10]

Evaluation of the Cations. An indirect method of measuring IP's and EA's is to first measure the solution electrochemical oxidation and reduction potentials, which can then be used to calculate the gas-phase IPs and EAs by an empirically derived equation.[11] Inherent in these relationships, however, is the assumption that the solvation energies for the series of compounds of interest remain constant or, at worst, vary linearly with the redox potentials. Although this appears to be satisfied in the case of neutral aromatic compounds, to our knowledge it has not been demonstrated for ionic species.

---

(6) Anderson, J. A.; Bugner, D. E. Proceedings of the 4th International Congress on Advances in Non-Impact Printing Technologies; New Orleans, LA, March 20–25, 1988.

(7) Taft (σ°) and Hammett (σ) substituent constants are taken from tables found in *The Chemist's Companion*; Gordon, A. J., Ford, R. A., Eds.; John Wiley and Sons: New York, 1972; pp 144–155.

(8) (a) Gibson, H. W. *Can. J. Chem.* **1973**, *51*, 3065. (b) Gibson, H. W. *J. Am. Chem. Soc.* **1975**, *97*, 3832.

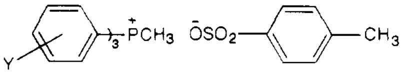
(9) Koopman, T. *Physica* **1933**, *1*, 104.

(10) Stewart, J. J. P. Quantum Chemistry Program Exchange No. 455.

(11) (a) Loufty, R. O.; Hsiao, C. K.; Ong, B. S.; Keoshkerian, B. *Can. J. Chem.* **1984**, *62*, 1877 and references cited therein. (b) Miller, L. L.; Nordblom, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972**, *37*, 916. (c) Dewar, M. J. S.; Hashmall, J. A.; Trinajstic, N. *J. Am. Chem. Soc.* **1970**, *92*, 5555.

(12) All electrochemical measurements were referenced to internal ferrocene (fc). For the conditions listed for Table II, $E_{1/2}$ (fc/fc$^+$) = +429 ± 6 mV, the average of eight measurements. For the conditions listed under Table III, $E_{1/2}$ (fc/fc$^+$) = +423 ± 10 mV, the average of 16 measurements.

Table II. Cyclic Voltammetry[12] and NMR Data for the Methyltriarylphosphonium Tosylates



compd	Y	E_{pc},[a] V	$\delta_{^1H}$ (P^+CH_3), ppm	$\delta_{^{31}P}$ (P^+CH_3), ppm
2a	4-$N(CH_3)_2$	-2.45	2.52	15.87
2b	4-OCH_3	-2.12	2.84	18.83
2c	4-CH_3	-2.08	3.00	20.34
1b	H	-1.97	3.10	21.69
2d	4-Cl	-1.71	3.27	22.86
2e	4-CO_2CH_3	-1.41	3.45	23.63
2f	3-CF_3	-1.60	3.55	24.93
2g	4-CF_3	-1.51	3.58	24.20

[a] At 25 °C in CH_3CN; working electrode, glassy carbon; auxillary electrode, Pt; reference electrode, SSCE; supporting electrolyte, 0.1 M tetrabutylammonium tetrafluoroborate; phosphonium concentration, ~1.5 mM; scan rate, 100 mV/s; all reductions are irreversible.

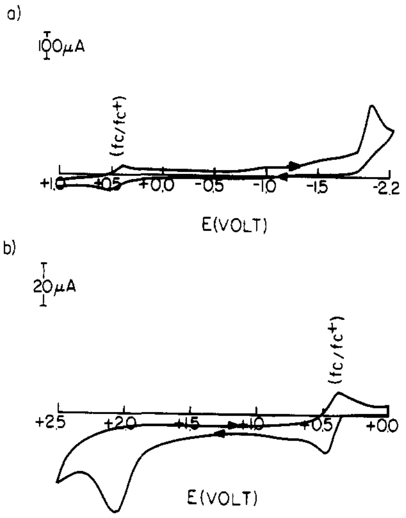
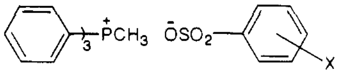


Figure 1. Cyclic voltammograms for (a) reduction and (b) oxidation of **1b**. Conditions given in Tables II and III.

Table III. Cyclic Voltammetry[12] and NMR Data for the Methyltriphenylphosphonium Arenesulfonates



compd	X	E_{pa},[a] V	$\delta_{^{17}O}$ (SO_3^-), ppm	$\delta_{^{31}P}$ (P^+CH_3), ppm
1a	4-NH_2	0.93	*b*	*b*
1b	4-CH_3	2.04	176.73	21.69
1c	4-OCH_3	1.79	176.20	21.68
1d	H	2.23	177.40	21.67
1e	4-Cl	2.33	178.04	21.64
1f	3-NO_2	2.48	178.62	*c*
1g	4-NO_2	2.52	178.80	21.53
1h	3,5-$(CO_2CH_3)_2$	2.49	177.87	*c*
1i	3-NO_2, 4-Cl	2.53	178.96	*c*

[a] Same conditions as Table III, except working electrode, Pt disk; all oxidations are irreversible. [b] Insoluble. [c] Not measured.

With this caveat in mind, attempts were made to measure the reduction potentials for the methyltriarylphosphonium *p*-toluenesulfonates (**1b**, **2a–g**) by cyclic voltammetry. Irreversible reductions attributable to the methyltriarylphosphonium cation were observed for all of the derivatives (Table II). The cathodic peak potential of -1.97 V observed for methyltriphenylphosphonium tosylate (Figure 1a) is consistent with the value reported for the corresponding bromide (-1.86 V) by polarography.[13] The observed irreversibility of these reductions is also consistent with previous reports on phosphonium reductions.[13]

While irreversible cathodic peak potentials are no substitute for reversible half-wave potentials, it is nevertheless interesting to note the correlation between the observed E_{pc}'s and the corresponding Hammett substituent constants (eq 1). The slope of the line is analogous to the

$$E_{pc} = 0.758(\sigma) - 1.887 \qquad (r = 0.971) \qquad (1)$$

Hammett reaction constant.[14] A positive slope is consistent with the expectation that more electronegative substituents should make the cation easier to reduce. This also implies a decrease in the LUMO energy, E_{LUMO}, resulting from substituents with higher positive values of σ.

It is known that irreversible peak potentials determined by cyclic voltammetry at solid electrodes can be strongly influenced by kinetic factors.[15] Our assumption is that, for a series of structurally similar compounds run under identical conditions, the observed trends in the cathodic peak potentials are valid indicators of the relative propensity for these cations to be reduced. The strong correlation indicated by eq 1 is consistent with this assumption.

As we had already characterized all of the salts by NMR, we felt it worthwhile to also look for correlations between the chemical shifts of pertinent nuclei and the substituent constants for **1b** and **2a–g**. Two convenient signals to monitor are for the protons on the methyl group bonded to phosphorus (by ^1H NMR) and for the phosphorus itself (by ^{31}P NMR) (Table II). Linear regression of both the ^1H and ^{31}P chemical shifts vs the substituent constants for the various derivatives results in the following equations:

$$\delta_{^1H} = 0.807(\sigma) + 3.13 \qquad (r = 0.991) \qquad (2)$$

$$\delta_{^{31}P} = 6.62(\sigma) + 21.28 \qquad (r = 0.986) \qquad (3)$$

The trends for both are in the expected direction: more electronegative substituents more strongly deshield the ^{31}P or ^1H nucleus, and the respective signal is shifted further downfield. Thus, the electronegativities of the substituents on the benzene rings have a direct and predictable effect on the magnetic environment of the nuclei in the phosphorus-centered cation.

The cathodic peak potentials and the ^1H NMR data can also be fit to the following equation:

$$E_{pc} = 0.93(\delta_{CH_3}) - 4.80 \qquad (r = 0.969) \qquad (4)$$

The correlation coefficient is nearly identical with that given by eq 1, further supporting our assumption that the observed E_{pc}'s are valid indicators of the relative reducibilities of this series of cations.

Evaluation of the Anions. The various anion derivatives were likewise evaluated by a combination of CV and NMR (Table III). To our knowledge, there have been no reports in the literature of arenesulfonate oxidation potentials. Indeed, when initial attempts were made to measure the oxidation potential of the tosylate derivative,

---

[13] (a) Horner, L.; Haufe, J. *J. Electroanal. Chem.* **1969**, *20*, 245. (b) Allen, D. W.; Ebdon, L. *Phosphorus Sulfur* **1979**, *7*, 161. (c) Saveant, J. M.; Binh, S. K. *J. Org. Chem.* **1977**, *42*, 1242.

[14] Zuman, P. *Substituent Effects in Organic Polarography*; Plenum: New York, 1967.

[15] See for example: Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; p 223.

1b, using conditions identical to those employed for Figure 1a, no anodic peaks were observed out to the solvent cutoff near +2.8 V. However, by switching to a platinum disk working electrode, the CV shown in Figure 1b was recorded. The observed anodic peak potentials for all of the derivatives are listed in Table III. The oxidations are all irreversible, and for arenesulfonates with more positive values of σ (and more positive E_{pa}'s), the peaks become quite broad. The sulfinilate derivative (**1a**) appears to interact with the ferrocene present as internal standard. In the presence of **1a**, the ferrocene wave itself becomes irreversible, and when the sample is swept anodically a second time, the sulfinilate peak disappears. As a consequence the E_{pa} reported in Table III for **1a** should be viewed with caution.

Taken together, these observations are clear warnings that unusual kinetic factors may be involved in these anodic processes. Nevertheless, the trends are again consistent with expectations.[14] Linear regression for E_{pa} (monosubstituted derivatives only, except **1a**) vs σ° and σ results in the following equations:

$$E_{pa} = 0.585\sigma^\circ + 2.084 \qquad (r = 0.886) \tag{5}$$

$$E_{pa} = 0.580\sigma + 2.108 \qquad (r = 0.928) \tag{6}$$

It can be seen that σ gives a significantly better correlation that σ°, despite the fact that direct conjugation between the charge-bearing oxygens and the substituents is not possible. The magnitude of the slope is comparable to that reported above for the reduction of the methyltriarylphosphonium cations. It is also comparable to those reported for similar studies on neutral aromatic compounds where actual reversible half-wave potentials were measured.[14,16] The curvature in the raw data is uncannily similar to these same previous studies.[14,16] These similarities with reversible oxidations which clearly involve an aromatic π-molecular orbital, coupled with a better correlation with σ than with σ°, suggest that the observed oxidations may involve the aromatic π-system rather than the nonbonding orbitals on the oxygens. This interesting implication will be discussed further in the context of the molecular orbital calculations presented below.

We also evaluated the series of anions by NMR spectroscopy. Unfortunately, the ^{1}H NMR spectrum is not particularly useful for these ions. The protons on the aromatic ring give rise to multiplets of varying complexities, which are often obscured by the more intense signals arising from the aromatic protons on the cation. We were successful, however, in measuring the more pertinent ^{17}O chemical shifts for the sulfonate group for this series of compounds (Table III). The least-squares lines for the chemical shifts of the sulfonate oxygens as a function of either σ° or σ were calculated by using the data for the monosubstituted derivatives:

$$\delta_{^{17}O} = 1.91\sigma^\circ + 177.31 \qquad (r = 0.972) \tag{7}$$

$$\delta_{^{17}O} = 1.78\sigma + 177.42 \qquad (r = 0.956) \tag{8}$$

A plot of the ^{17}O chemical shifts vs σ° for all the derivatives is shown in Figure 2 along with the calculated line.

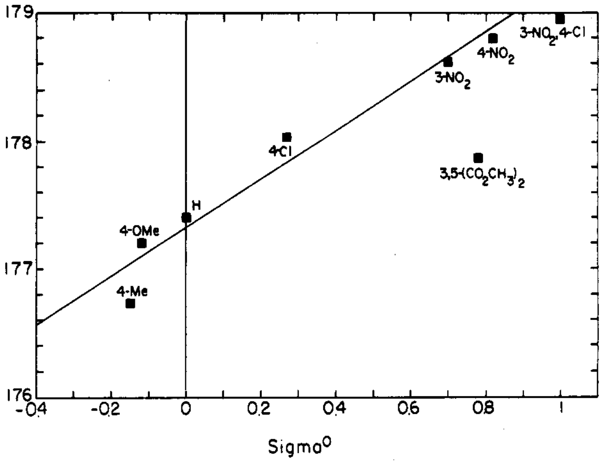


Figure 2. A plot of ^{17}O FTNMR chemical shift vs substituent constant for **1a–i**.

In comparing eq 7 or 8 with eq 2 or 3, it is evident that the correlation is not as good, and that the relative magnitude of the interaction is substantially less than that displayed for the ^{31}P and ^{1}H NMR spectra of the cations. The relative weakness of the effect of substituent electronegativity on the ^{17}O chemical shift can be rationalized as follows. For the anions, the substituent effect is strictly inductive and is being shared by three oxygens. On the other hand, each phosphorus-centered cation feels both inductive and resonance effects from three substituents. The weakness of the interaction, as well as the stronger correlation with σ°, stand in marked contrast to the electrochemical data presented above. Again, the implication is that the oxidative electron is emanating from the aromatic ring rather than the sulfonate oxygens.

Recently it has been reported that ^{33}S NMR chemical shifts for a series of ionized arenesulfonic acids in water display a linear correlation with both substituent constants and pK_a's.[17] As one might expect, the extent of the interaction between the substituent and the sulfur is much greater than that observed by us for oxygen. When the ^{33}S chemical shifts are plotted against normal Hammett σ values, a correlation coefficient of 0.986 is calculated. Interestingly, the effect of a more electronegative substituent is an upfield shift in the ^{33}S signal. This has been explained as resulting from increased backbonding between the attached oxygens and the d orbitals on sulfur.[17] This net result is to shift electron density from the oxygens to the sulfur, i.e., to deshield the oxygens and to shield the sulfur. Our data are consistent with this explanation.

Out of curiosity, we also measured the ^{31}P chemical shifts for several of the anion variations. Interestingly, the ^{31}P chemical shift for the methyltriphenylphosphonium cation displays a definite correlation with the substituent constants for the groups on the sulfonate anion:

$$\delta_{^{31}P} = -0.161(\sigma^\circ) + 21.67 \qquad (r = 0.990) \tag{9}$$

This implies at least a finite degree of electronic communication between the anion and cation. Compared to eq 3, however, the extent of interaction is quite small: 0.16 ppm per σ° unit vs 6.6 ppm per σ unit. To a first approximation, therefore, we can treat the anion and cation as separate electronic entities.

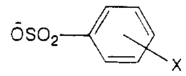
C. Molecular Orbital Calculations. An alternative to the analytical methods discussed above for evaluating E_{HOMO} and E_{LUMO} is to carry out molecular orbital calculations. This is conveniently accomplished by using the MOPAC molecular orbital software package.[10] Upon inputting the approximate atomic coordinates (most conveniently achieved by using available molecular modeling software), MOPAC will implement either MNDO or MNDO/3 Hamiltonians and calculate, among other things,

---

[16] Cressman, P. J.; Hartmann, G. C.; Kuder, J. E.; Saeva, F. D.; Wychick, D. *J. Chem. Phys.* **1974**, *61*, 2740.

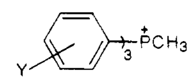
[17] Crumrine, D. S.; Shankweiler, J. M.; Hoffman, R. V. *J. Org. Chem.* **1986**, *51*, 5013.

Table IV. Molecular Orbital Calculations for the Anions



entry	X	E_{HOMO}, eV	E_{LUMO}, eV
1	4-NH_2	−5.59	3.40
2	4-CH_3	−5.97	3.08
3	4-OCH_3	−6.06	2.94
4	H	−5.94	3.23
5	4-Cl	−6.22	2.71
6	3-NO_2	−6.58	1.70
7	4-NO_2	−6.65	1.43
8	3,5-$(CO_2CH_3)_2$	−6.71	1.99
9	3-NO_2, 4-Cl	−6.80	1.33

Table V. Molecular Orbital Calculations for the Cations



entry	Y	E_{HOMO}, eV	E_{LUMO}, eV
1	4-$N(CH_3)_2$	−11.45	−4.15
2	4-OCH_3	−12.57	−4.60
3	4-CH_3	−12.81	−4.55
4	H	−12.89	−4.65
5	4-Cl	−13.19	−5.02
6	4-CO_2CH_3	−11.02	−5.12
7	3-CF_3	−13.82	−5.47
8	4-CF_3	−13.80	−5.58

the eigenvectors, the localized orbitals, and the molecular orbitals of the molecule, ion, or radical of interest. While E_{HOMO} and E_{LUMO} determined by this method are no substitute for direct or indirect physical measurements, and while care should be taken not to put too much emphasis on the absolute values of the energies as calculated, they are useful in comparing and predicting the properties of members of a structurally similar series. For our calculations we employed the MNDO Hamiltonian, and the calculations were allowed to proceed until optimized geometries were obtained. To improve the efficiency of the calculations, the geometries of the unsubstituted ions were optimized first, i.e., benzenesulfonate and methyltriphenylphosphonium. Then ions of either series were input using these base geometries, and the calculations were carried out with reoptimization only within the vicinity of the substituent. Each ion was calculated as a separate moiety rather than in the presence of the counterion. Although the ^{31}P NMR data for the anion series imply a measurable degree of electronic interaction with the counterions, the assumption here is that any perturbation by a given ion, e.g., methyltriphenylphosphonium or p-toluenesulfonate, on a series of similar counterions is a constant. Each optimized geometry was visually inspected to verify that the bond lengths and angles for a given group of adjacent atoms were in the expected ranges. For example, a comparison of the calculated geometry for the methyltriphenylphosphonium cation with that determined by X-ray crystal structure[18] reveals virtually identical bond lengths and angles as well as the propeller-like arrangement of the phenyl rings.

The results of these calculations are summarized in Tables IV and V. The calculations are consistent with our assumption that the LUMO's of the salts are located on the cations and the HOMO's are on the anions. As far as we know, no independent data exist for the ionization potentials or electron affinities of these ions. It is thus difficult to comment on the accuracy of the calculated values. Correlations between these calculated energies and the appropriate substituent constants are surprisingly good (eq 10 and 11) considering that the calculations assume

$$\text{(anions) } E_{HOMO} = 0.74(\sigma) + 6.09 \qquad (r = 0.981) \qquad (10)$$

$$\text{(cations) } -E_{LUMO} = 1.02(\sigma) + 4.85 \qquad (r = 0.950) \qquad (11)$$

the gas phase, whereas the substituent constants were empirically derived from solution measurements. The trends are consistent with the electrochemical data: more electronegative substituents result in greater stabilization of the respective MO's.

The calculated HOMO and LUMO energies reported here for the isolated ions in the gas phase are most likely exaggerated relative to the same ions in the presence of their counterions and solvent. The fact that good linear correlations are observed for eq 10 and 11 implies that the calculated values are at least valid in a relative sense. In fact, by using a constant scaling factor to adjust our calculated values of E_{HOMO} and E_{LUMO} to more realistic condensed phase values, the triboelectric behavior of toners containing these salts as charge-agents can be accurately modeled using Fermi–Dirac statistics.[6]

Further insights can be gained by examining the relationship between the calculated energies and the measured CV peak potentials. The data for the anions were fit to the following equation:

$$E_{pa} = 1.05(-E_{HOMO}) - 4.46 \qquad (r = 0.851) \qquad (12)$$

Considering the aforementioned caveats concerning the MO calculations and the irreversible peak potentials, we were surprised that the correlation was as high as indicated. However, further examination of MO calculations reveals the following: (a) The HOMO for the sulfinilate anion (X = NH_2) is π in nature and includes the nonbonding $2p_z$ orbital on the nitrogen atom. (b) For all the other arenesulfonates, the HOMO results from the combinations of the oxygen 2p atomic orbitals and is localized on the sulfonate group. (c) For these same anions, however, there are several MO's with varying degrees of π-character[19] within 0.2–1.0 eV in energy below the HOMO. It not unlikely, then, that electrochemical oxidation of the aromatic π-system may be thermodynamically and/or kinetically favored over the nonbonding orbital on the sulfonate group. This is certainly consistent with the observations reported above concerning the dependence of E_{pa} on substituent constants. By correlating the peak potentials with the energies of the highest occupied π-orbitals (HOPO's), the following least-squares line is obtained:

$$E_{pa} = 1.07(-E_{HOPO}) - 4.81 \qquad (r = 0.931) \qquad (13)$$

The significant improvement in the correlation provides further support for our hypothesis that the aromatic π-system is directly involved in these oxidations.

In a similar manner, the phosphonium LUMO has been examined in greater detail. The LUMO appears to be σ-antibonding (σ^*) in nature, localized between the phosphorus 3s orbital, the sp^2 hybrid orbitals on the three adjacent aromatic carbons, and the sp^3 orbital on the adjacent methyl carbon. The strongest antibonding interaction is between the phosphorus and the methyl carbon. This is in complete agreement with the observed cleavage of the phosphorus–alkyl carbon bond when salts such as

---

[18] Wing, R. M. J. Am. Chem. Soc. 1968, 90, 4828.

[19] The π-character of the orbitals was estimated by summing the squares of the coefficients for the benzene C $2p_z$ atomic orbitals. Substituent atoms with $2p_z$ orbitals capable of overlap with the benzene π-system were included in the estimate.

these are electrochemically reduced.[13]

The correlation between E_{pc} and $-E_{LUMO}$ is described by eq 14. Once again, all things considered, we are quite satisfied with the correlation, and we are comfortable in using the calculated LUMO energies as relative indicators of the actual electron affinities of this series of ions.

$$E_{pc} = 0.67(-E_{LUMO}) - 5.13 \qquad (r = 0.920) \qquad (14)$$

Summary and Conclusions

Current hypotheses of the origin of triboelectrification of electrophotographic toner particles postulate the transfer of electrons between the toner and carrier.[1,5,6] We have attempted to relate this model to the electronic properties of the charge-agents present in such toners. To this end we have prepared a series of methyltriarylphosphonium arenesulfonates in which substituents on both the anion and cation are systematically varied over a wide range of electronegativities. We have shown through a combination of ^{1}H, ^{31}P, and ^{17}O NMR, cyclic voltammetry, and molecular orbital calculations that the HOMO and LUMO energies of quaternary phosphonium sulfonate charge-agents can be directly related to the electronegativity of substituents on the anions and cations, respectively. Ideally, one would like to be able to directly measure the IP's and EA's for this series of compounds. As yet we have been unsuccessful in these endeavors. Nevertheless, the results reported here have allowed us to corroborate our assumptions (and those of others[5,8]) that E_{HOMO} and E_{LUMO} can be directly related to substituent electronegativities.

Experimental Section

General. Triphenylphosphine, tris(4-methylphenyl)phosphine, tris(4-methoxyphenyl)phosphine, methyltriphenylphosphonium bromide, sodium tosylate, sodium 3-nitrobenzenesulfonate, methyl tosylate, and methyl benzenesulfonate were obtained from Eastman Kodak Laboratory Chemicals. Sodium 3-nitro-4-chlorobenzenesulfonate and methyl 4-nitrobenzenesulfonate were obtained from Aldrich Chemical Co. Tris(4-chlorophenyl)phosphine was a product of Alfa Chemical Co. All of the above were used without further treatment unless otherwise specified. Methyl 4-methoxybenzenesulfonate and methyl 4-chlorobenzenesulfonate were prepared from the respective sulfonyl chlorides and sodium methoxide in anhydrous methanol.[20] Tris(3-(trifluoromethyl)phenyl)phosphine and tris(4-(trifluoromethyl)phenyl)phosphine were prepared from phosphorus trichloride and the appropriate (trifluoromethyl)bromobenzene.[21] Methyltris(4-(dimethylamino)phenyl)phosphonium tosylate (**2a**), methyltris(4-(methoxycarbonyl)phenyl)phosphonium tosylate (**2e**), methyltriphenylphosphonium 3,5-bis(methoxycarbonyl)benzenesulfonate (**1h**), and methyltriphenylphosphonium 4-aminobenzenesulfonate (**1a**) were kindly provided by J. Wilson.[4b] The intermediate methyltriarylphosphonium iodides were prepared by treating the corresponding triphenylphosphine with methyl iodide in 2-butanone, followed by recrystallization of the crude precipitate.

Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer 297 or 298 spectrophotometer; Fourier transform infrared (FTIR) spectra were obtained with a Nicolet 5DXC instrument equipped with a diffuse reflectance cell. Nuclear magnetic resonance (NMR) spectra were obtained as follows. (a) ^{1}H: General Electric QE-300, referenced to internal tetramethylsilane. (b) ^{31}P: Nicolet NT-200, 0.05 M in $CDCl_3$, 25 °C, referenced to external 85% phosphoric acid. (c) ^{17}O: Bruker AM-500, 33 °C, referenced to external dioxane, only chemical shifts for SO_3^- are reported. Electronic (UV–vis) spectra were recorded on a Perkin-Elmer Lambda 5 spectrophotometer. Cyclic voltammetry (CV) measurements were made on a BioAnalytical Systems Model 100 electrochemical analyzer, using the conditions given in Tables II and III. The platinum disk and glassy carbon working electrodes were freshly polished just prior to making each measurement. The solutions were degassed by bubbling argon through them for 10 min with vigorous stirring. The stirrer was switched off, and a couple of minutes elapsed before each scan was initiated.

General Procedure for the Direct Quaternization of Methyltriarylphosphines with Methyl Arenesulfonates. A mixture of the triarylphosphine and an excess of the methyl arenesulfonate were mixed without solvent under an inert atmosphere. The mixture was heated as indicated below and then allowed to cool. The resulting solids were crytallized by treating with ether. The crystals were filtered and were washed well with ether. Analytically pure products were obtained by recrystallization from an appropriate solvent system.

Methyltriphenylphosphonium Tosylate (1b). A mixture of 11.8 g (45.0 mmol) of triphenylphosphine and 8.40 g (45.1 mmol) of methyl tosylate was allowed to react for 2 h at 130 °C. A total of 19.9 g (44.4 mmol, 98.6%) of methyltriphenylphosphonium tosylate was obtained. The product was further purified by stirring overnight in 95:5 ether–acetonitrile, filtering, and drying in a vacuum oven. Analyses: mp 147.0–149.0 °C; ^{1}H NMR ($CDCl_3$) δ 2.29 (s, 3 H), 3.10 (d, 3 H, J = 13.3 Hz), 7.03 (d, 2 H) and 7.6–7.9 pm (m, 17 H); ^{31}P NMR ($CDCl_3$) δ 21.69 ppm; ^{17}O NMR ($CDCl_3$) δ 176.73 ppm; IR (KBr) ν 1588, 1486, 1439, 1417, 1330, 1219, 1203, 1161, 1114, 1030, 1009, 997, 897, 833, 768, 748, 716, 695, and 677 cm^{-1}; UV–vis (H_2O) λ (log ϵ) 226 (4.56), 254 (sh), 266 (3.57), and 273 nm (3.50). *Anal.* Found: C, 69.5; H, 5.7; P, 7.0; S, 7.0. Calcd for $C_{26}H_{25}O_3PS$ (448.52): C, 69.6; H, 5.6; P, 6.9; S, 7.1.

Methyltriphenylphosphonium 4-Methoxybenzenesulfonate (1c). A mixture of 8.89 g (44.0 mmol) of triphenylphosphine and 11.2 g (42.7 mmol) methyl 4-methoxybenzenesulfonate was allowed to react for 2 h at 140 °C. A total of 18.0 g (38.7 mmol, 90.7%) of **1c** was obtained. It was further purified by recrystallization from 90:10 toluene–acetonitrile. Analyses: mp 96.0–98.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.11 (d, 3 H, J = 13.3 Hz), 3.77 (s, 3 H), 6.76 (d, 2 H), and 7.6–7.9 ppm (m, 17 H); ^{31}P NMR ($CDCl_3$) δ 21.68 ppm; ^{17}O NMR ($CDCl_3$) δ 177.20 ppm; IR (KBr) ν 1596, 1493, 1439, 1298, 1248, 1221, 1198, 1160, 1115, 1028, 1002, 992, 920, 904, 828, 799, 749, 718, 690, and 678 cm^{-1}; UV–vis (H_2O) λ (log ϵ) 226 (4.56), 254 (sh), 261 (sh), 266 (3.54), and 273 nm (3.45). Anal. Found: C, 67.1; H, 5.6; P, 6.7; S, 6.9. Calcd for $C_{26}H_{25}O_4PS$ (464.52): C, 67.2; H, 5.4; P, 6.7; S, 6.9.

Methyltriphenylphosphonium Benzenesulfonate (1d). A mixture of 19.2 g (73.2 mmol) of triphenylphosphine and 12.6 g (73.2 mmol) of methyl benzenesulfonate was allowed to react for 2 h at 130 °C. A total of 27.6 g (63.5 mmol, 86.8%) of **1d** was obtained after recrystallization from 75:25 toluene–acetonitrile. Analyses: mp 147.6–149.7 °C; ^{1}H NMR ($CDCl_3$) δ 3.08 (d, 3 H, J = 13.3 Hz), 7.2–7.9 ppm (m, 20 H); ^{31}P NMR ($CDCl_3$) δ 21.67 ppm; ^{17}O NMR ($CDCl_3$) δ 177.40 ppm; IR (KBr) ν 1589, 1485, 1439, 1322, 1218, 1202, 1160, 1120, 1031, 1016, 997, 920, 903, 759, 722, 714, 691, and 609 cm^{-1}; UV–vis (H_2O) λ (log ϵ) 220 (sh), 261 (sh), 266 (3.52), and 273 nm (3.42). Anal. Found: C, 69.2; H, 5.3; P, 7.1; S, 7.3. Calcd for $C_{25}H_{23}O_3PS$ (434.49): C, 69.1; H, 5.3; P, 7.1; S, 7.4.

Methyltriphenylphosphonium 4-Chlorobenzenesulfonate (1e). A mixture of 11.0 g (41.9 mmol) of triphenylphosphine and 9.16 g (44.4 mmol) of 4-chlorobenzenesulfonate was allowed to react for 2 h at 140 °C. A total of 16.4 g (35.0 mmol, 83.5%) of **1e** was obtained. It was further purified by recrystallization from 95:5 toluene–acetonitrile. Analyses: mp 123.2–125.2 °C; ^{1}H NMR ($CDCl_3$) δ 3.08 (d, 3 H, J = 13.3 Hz), 7.20 (d, 2 H), and 7.6–7.9 ppm (m, 17 H); ^{31}P NMR ($CDCl_3$) δ 21.64 ppm; ^{17}O NMR ($CDCl_3$) δ 178.04 ppm; IR (KBr) ν 1586, 1483, 1474, 1438, 1419, 1390, 1338, 1328, 1275, 1225, 1205, 1162, 1114, 1082, 1029, 1003, 994, 899, 890, 850, 838, 825, 783, 780, 748, 742, 714, 691, and 642 cm^{-1}; UV–vis (H_2O) λ (log ϵ) 224 (4.64), 253 (sh), 260 (sh), 266 (3.54), and 273 nm (3.45). Anal. Found: C, 63.8; H, 4.9; P, 6.8; Cl, 7.5; S, 7.0. Calcd for $C_{25}H_{22}ClO_3PS$ (468.94): C, 64.0; H, 4.7; P, 6.6; Cl, 7.6; S, 6.8.

Methyltriphenylphosphonium 4-Nitrobenzenesulfonate (1g). A mixture of 5.83 g (22.2 mmol) of triphenylphosphine and

---

[20] Morgan, M. S.; Cretcher, L. H. *J. Am. Chem. Soc.* **1948**, *70*, 375.

[21] Eapen, K. C.; Tamborski, C. *J. Fluorine Chem.* **1980**, *15*, 239.

5.00 g (23.0 mmol) and methyl 4-nitrobenzenesulfonate was allowed to react for 2 h at 145 °C. A total of 10.3 g (21.5 mmol, 96.8%) of **1h** was obtained, which was further purified by recrystallization from 90:10 toluene–acetonitrile. Analyses: mp 127.0–128.6 °C; ^{1}H NMR ($CDCl_3$) δ 3.11 (d, 3 H, J = 13.4 Hz), 7.2–8.2 ppm (m, 19 H); ^{31}P NMR ($CDCl_3$) δ 21.53 ppm; ^{17}O NMR ($CDCl_3$): δ 178.80 ppm; IR (KBr) ν 1604, 1590, 1520, 1487, 1440, 1349, 1225 (sh), 1211, 1117, 1030, 1009, 993, 906, 853, 748, 738, 719, 689, and 636 cm^{-1}; UV–vis (H_2O) λ (log ϵ) 223 (4.47), 253 (sh), 261 (sh), 266 (4.13), and 273 nm (4.08). Anal. Found: N, 2.9; C, 62.7; H, 4.7; P, 6.4; S, 6.5. Calcd for $C_{25}H_{22}NO_5PS$ (479.49): N, 2.9; C, 62.6; H, 4.6; P, 6.5; S, 6.7.

Methyltris(4-methoxyphenyl)phosphonium Tosylate (2b). A mixture of 5.37 g (15.2 mmol) of tris(4-methoxyphenyl)phosphine and 2.95 g (15.8 mmol) of methyl tosylate was allowed to react for 1 h at 135 °C. A total of 5.96 g (11.1 mmol, 73.0%) of **2b** was obtained, which was further purified by recrystallization from 97:3 toluene–ethanol. Analyses: mp 100.6–105.4 °C; ^{1}H NMR ($CDCl_3$) δ 2.28 (s, 3 H), 2.84 (d, 3 H, J = 13.3 Hz), 3.86 (s, 9 H), 7.10 (m, 6 H), 7.39 (aa′mm′, 4 H), and 7.55 ppm (m, 6 H); ^{31}P NMR ($CDCl_3$) δ 18.83 ppm; IR (film) ν 1596, 1569, 1503, 1462, 1444, 1415, 1300, 1269, 1220, 1191, 1123, 1036, 1015, 905, 836, 819, 806, and 682 cm^{-1}; UV–vis (H_2O) λ (log ϵ) 223 (sh), 229 (sh), 248 (4.68), 270 (sh), and 279 nm (sh). Anal. Found: C, 64.6; H, 5.8; P, 5.7; S, 5.8. Calcd for $C_{29}H_{31}O_6PS$ (538.60): C, 64.7; H, 5.8; P, 5.8; S, 6.0.

Methyltris(4-methylphenyl)phosphonium Tosylate (2c). A mixture of 2.38 g (7.82 mmol) of tris(4-methylphenyl)phosphine and 1.53 g (8.22 mmol) of methyl tosylate was allowed to react for 1 h at 130 °C. A total of 2.38 g (4.85 mmol, 62.0%) of **2c** was obtained, which was further purified by recrystallization from 97:3 toluene–ethanol. Analyses: mp 103.4–137.1 °C; ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 3 H), 2.45 (s, 9 H), 3.00 (d, 3 H, J = 13.2 Hz), 7.3–7.6 (m, 12 H), and 7.42 ppm (aa′mm′, 4 H); ^{31}P NMR ($CDCl_3$) δ 20.34 ppm; IR (KBr) ν 1600, 1504, 1450, 1403, 1324, 1205 (broad), 1108, 1089, 1032, 1011, 922, 902, 812, 769, 709, 679, and 652 cm^{-1}; UV–vis (H_2O): λ (log ϵ) 229 (4.59), 263 (3.52), and 274 nm (3.29). Anal. Found: C, 69.5; H, 6.3; P, 6.3; S, 6.6. Calcd for $C_{29}H_{31}O_3PS$ (490.60): C, 71.0; H, 6.4; P, 6.3; S, 6.5.

Methyltris(4-chlorophenyl)phosphonium Tosylate (2d). A mixture of 2.08 g (5.69 mmol) of tris(4-chlorophenyl)phosphine and 1.03 g (5.53 mmol) of methyl tosylate was allowed to react for 1 h at 125 °C. A total of 2.80 g (5.07 mmol, 91.7%) of **2d** was obtained, which was further purified by recrystallization from 97:3 toluene–ethanol. Analyses: mp 176.5–177.5 °C; ^{1}H NMR ($CDCl_3$) δ 2.31 (s, 3 H), 3.27 (d, 3 H, J = 14.0 Hz), 7.21 (aa′mm′, 4 H), and 7.5–7.8 ppm (m, 12 H); ^{31}P NMR ($CDCl_3$) δ 22.86 ppm; IR (film) ν 1590, 1496, 1402, 1222 (sh), 1210, 1194, 1028, 997, 931, 920, 817, 800, 764, and 689 cm^{-1}; UV–vis (H_2O) λ (log ϵ) 231 (4.68), 252 (sh), 259 (3.55), and 270 nm (3.29). Anal. Found: C, 57.1; H, 4.1; O, 8.4; Cl, 19.5; S, 5.9. Calcd for $C_{26}H_{22}Cl_3O_3PS$ (551.86): C, 56.6; H, 4.0; O, 8.7; Cl, 19.3; S, 5.8.

Methyltris(3-(trifluoromethyl)phenyl)phosphonium Tosylate (2f). A mixture of 6.20 g (13.3 mmol) of tris(3-(trifluoromethyl)phenyl)phosphine and 2.94 g (15.8 mmol) of methyl tosylate was allowed to react for 3 h at 140 °C. A total of 7.64 g (11.7 mmol, 88.0%) of **2f** was obtained, which was further purified by recrystallization from toluene–ethanol. Analyses: mp 176.0–178.6 °C; ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 3 H), 3.55 (d, 3 H, J = 14.0 Hz), 7.22 (aa′mm′, 4 H), 7.66 (d, 3 H), 7.85 (m, 3 H), 7.99 (d, 3 H), and 8.40 ppm (m, 3 H); ^{31}P NMR ($CDCl_3$) δ 24.93 ppm; IR (KBr) ν 1603, 1428, 1320, 1278, 1204, 1170, 1118, 1069, 1030, 1009, 991, 918, 896, 809, 690, 676, and 645 cm^{-1}; UV–vis (H_2O) λ (log ϵ) 221 (4.62), 255 (sh), 260 (sh), 267 (3.45), and 274 nm (3.35). Anal. Found: C, 53.2; H, 3.4; P, 5.0; F, 26.5; S, 5.0. Calcd for $C_{29}H_{22}F_9O_3PS$ (652.51): C, 53.4; H, 3.4; P, 4.7; F, 26.2; S, 4.9.

Methyltris(4-(trifluoromethyl)phenyl)phosphonium Tosylate (2g). A mixture of 5.25 g (11.3 mmol) of tris(4-(trifluoromethyl)phenyl)phosphine and 2.43 g (13.0 mmol) of methyl tosylate was allowed to react for 2 h at 135 °C. A total of 5.41 g (8.29 mmol, 73.4%) of **2g** was obtained, which was further purified by recrystallization from toluene–ethanol. Analyses: mp 185.0–185.8 °C; ^{1}H NMR ($CDCl_3$) δ 2.29 (s, 3 H), 3.58 (d, 3 H, J = 13.2 Hz), 7.20 (aa′mm′, 4 H), and 7.7–8.1 ppm (m, 12 H); ^{31}P NMR ($CDCl_3$) δ 24.20 ppm; IR (film) ν 1403, 1321, 1180, 1132, 1063, 1034, 1014, 918, 907, 838, 820, 806, 714, and 684 cm^{-1}; UV–vis (H_2O) λ (log ϵ) 222 (4.74), 254 (sh), 262 (sh), 270 (3.78), and 277 nm (3.74). Anal. Found: C, 53.5; H, 3.4; P, 4.7; F, 26.6; S, 5.1. Calcd for $C_{29}H_{22}F_9O_3PS$ (652.51): C, 53.4; H, 3.4; P, 4.7; F, 26.2; S, 4.9.

General Procedure for the Ion-Exchange Reaction between Methyltriphenylphosphonium Bromide and Sodium Arenesulfonates. An aqueous solution of a slight excess of the sodium arenesulfonate was added to a well-stirred aqueous solution of methyltriphenylphosphonium bromide. The products separated as either a crystalline solid (**1i**) or an oil (**1f**). They were isolated and purified as described below.

Methyltriphenylphosphonium 3-Nitrobenzenesulfonate (1f). The reaction was performed with 10.0 g (28.0 mmol) of methyltriphenylphosphonium bromide in 150 mL of water and 6.98 g (31.0 mmol, 1.11 equiv) of sodium 3-nitrobenzenesulfonate in 150 mL of water. The resulting oil was isolated by extracting with dichloromethane (2 × 50 mL). The organic phase was dried with sodium sulfate and then evaporated, yielding 11.9 g (24.8 mmol, 88.6%) of **1f** as a viscous oil. Analyses: ^{1}H NMR ($CDCl_3$) δ 3.10 (d, 3 H, J = 13 Hz), 7.46 (t, 1 H), 7.6–7.9 (m, 15 H), 8.10 (d, 1 H), 8.20 (d, 1 H), and 8.60 ppm (s, 1 H); ^{17}O NMR ($CDCl_3$) δ 178.62 ppm; IR (film) ν 1525, 1442, 1354, 1215 (sh), 1205, 1115, 1018, 910, 752, 715, 698, 688, 675, and 623 cm^{-1}. Due to the oily/gummy nature of the product, satisfactory elemental analyses could not be obtained.

Methyltriphenylphosphonium 4-Chloro-3-nitrobenzenesulfonate (1i). The reaction was performed with 10.0 g (28.0 mmol) of methyltriphenylphosphonium bromide in 75 mL of water and 13.6 g (42.0 mmol, 1.5 equiv) of sodium 4-chloro-3-nitrobenzenesulfonate in 150 mL of hot water. The product precipitated upon chilling in an ice water bath. It was collected by filtration, washed well with water, and dried to a constant weight in a vacuum oven. A total of 13.2 g (25.7 mmol, 91.8%) of **1i** was obtained, which gave satisfactory analyses: mp 169.1–171.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.04 (d, 3 H, J = 13 Hz), 7.43 (d, 1 H), 7.65–7.82 (m, 15 H), 7.96 (d, 1 H), and 8.20 ppm (s, 1 H); ^{17}O NMR ($CDCl_3$) δ 178.96 ppm; FTIR (KBr) ν 3058, 2988, 1534, 1438, 1339, 1233, 1219, 1194, 1116, 1033, 750, 720, 690, 667, 652, and 507 cm^{-1}. Anal. Found: N, 2.6; C, 58.0; H, 4.0; Cl, 7.0; P, 6.0; S, 6.3. Calcd for $C_{25}H_{21}ClNO_5PS$ (513.94): N, 2.7; C, 58.4; H, 4.1; Cl, 6.9; P, 6.0; S, 6.2.

Acknowledgment. We wish to thank John Wilson and Frank Pettrone for providing several of the charge-agents as indicated in Table I, James Whitefield and Frank Michaels for recording the ^{31}P and ^{17}O NMR spectra, and John McKelvey and Jim Eilers for providing guidance and assistance with the molecular orbital calculations.

Registry No. **1a**, 119907-85-6; **1b**, 55818-45-6; **1c**, 119907-86-7; **1d**, 95736-42-8; **1e**, 119907-87-8; **1f**, 119907-88-9; **1g**, 119907-89-0; **1h**, 117417-54-6; **1i**, 119907-90-3; **2a**, 119907-91-4; **2b**, 119907-92-5; **2c**, 119907-93-6; **2d**, 119907-94-7; **2e**, 95736-46-2; **2f**, 119907-96-9; **2g**, 120360-41-0; 4-$H_2NC_6H_4SO_3^-$, 2906-34-5; 4-$CH_3C_6H_4SO_3^-$, 16722-51-3; 4-$CH_3OC_6H_4SO_3^-$, 55735-62-1; $C_6H_5SO_3^-$, 3198-32-1; 4-$ClC_6H_4SO_3^-$, 45934-90-5; 3-$NO_2C_6H_4SO_3^-$, 30904-40-6; 4-$NO_2C_6H_4SO_3^-$, 30904-42-8; 3,5-$(CO_2CH_3)_2C_6H_3SO_3^-$, 46914-24-3; 3-NO_2-4-$ClC_6H_3SO_3^-$, 81756-03-8; (4-$(CH_3)_2NC_6H_4)_3PCH_3^+$, 80919-54-6; (4-$CH_3OC_6H_4)_3PCH_3^+$, 47468-19-9; (4-$CH_3C_6H_4)_3PCH_3^+$, 47253-43-0; $(C_6H_5)_3PCH_3^+$, 15912-74-0; (4-$ClC_6H_4)_3PCH_3^+$, 86099-75-4; (4-$CH_3OCOC_6H_4)_3PCH_3^+$, 95736-45-1; (3-$CF_3C_6H_4)_3PCH_3^+$, 119907-98-1; (4-$CF_3C_6H_4)_3PCH_3^+$, 119907-95-8; triphenylphosphine, 603-35-0; methyl tosylate, 80-48-8; methyl 4-methoxybenzenesulfonate, 6214-19-3; methyl benzenesulfonate, 80-18-2; methyl 4-chlorobenzenesulfonate, 15481-45-5; methyl 4-nitrobenzenesulfonate, 6214-20-6; tris(4-methoxyphenyl)phosphine, 855-38-9; tris(4-methylphenyl)phosphine, 1038-95-5; tris(3-(trifluoromethyl)phenyl)phosphine, 25688-46-4; tris(4-(trifluoromethyl)phenyl)phosphine, 13406-29-6; tris(4-chlorophenyl)phosphine, 1159-54-2; methyltriphenylphosphonium bromide, 1779-49-3; sodium 3-nitrobenzenesulfonate, 127-68-4; sodium 4-chloro-3-nitrobenzenesulfonate, 119907-97-0.