to be a rigid matrix, decreasing the size of the solvent channel "squeezes" the nitroxide from the channel interior onto the polymer–water interface where it feels the influence of the rigid nonpolar resin. If the polymer is considered mobile, decreasing the water content decreases the mole fraction of water and increases the internal viscosity. Based upon EPR and chemical studies, it is now clear that, for solvent-swelled cross-linked polystyrene, both pendant groups and the polymer backbone have significant mobility.[9,10] Resin **1** appears to have similar properties and we, therefore, prefer to adopt the cosolvent model.[11]

Although we expected little difference between a_N for **2** imbibed as a toluene solution in **1**, with that measured for **2** in pure toluene or 1,2-dimethoxyethane, we have observed a slightly higher value under conditions of low swelling (entry 4). This difference may result in part from trace amounts of tenaciously bound water in **1**. Comparison of entry 4 with 7 strongly suggests that imbibed water can contribute to the polarity of the environment experienced by **2**. Control experiments carried out in which unfunctionalized polystyrene was swelled with limited amounts of water-saturated toluene containing **2** indicate a large degree of immobilization of the probe but no significant change in the polarity of its environment (entries 2 and 5).

Triphase Conditions. When **1** was swelled with an excess of both water and toluene and the external liquid phases removed by rapid suction filtration, the polarity within the polymer as revealed by **2** was equivalent to that of $X_{H_2O} = 0.25$ for water–1,2-dimethoxyethane (entry 6). In contrast, **3** indicated that, for a similarly swelled resin, the internal polarity is comparable to $X_{H_2O} = 0.97$ (entry 14). These data clearly establish the existence of relatively fluid polar and nonpolar zones within the polymer. Additional support for this conclusion comes from the EPR spectrum of 3-carbamoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy imbibed in **1** under similar triphase conditions. Here, spectral distortion not found in **2** and **3** is readily apparent (most notably, the high field peak is replaced by two lines). This distortion is undoubtedly derived from the nitroxide located in two regions of significantly different polarity; in addition, exchange between the zones must be slow relative to the EPR time scale.[12,13] With the water content constant, decreasing the amount of toluene results in a steady increase in a_N and W values for **2** (entries 6–8). Although time averaging of signals of **2** partitioned between polar and nonpolar zones accounts for this trend, the very large increase in W clearly indicates that the spin probe is not relocating completely into the fluid interior of the polar zone (compare entry 8 with 16).[14] When the toluene content is constant and the amount of water is reduced, a_N decreases and W increases for nitroxide **3** (entries 14 and 15). These data are consistent with (a) contraction of the nonpolar (polar) zone "squeezing" **2** (**3**) onto a polar–nonpolar interface[15] and/or (b) the polarity and viscosity of the interior of the polar and nonpolar zones being variable. At present we cannot assess the importance of each of these possibilities.

Experiments now in progress are aimed at correlating EPR measurements of the type described here with catalytic activity of a series of related resins for both displacement and hydrolysis reactions in an effort to gain a better understanding of the nature of the catalysis.

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(11) EPR measurements made of a polymer similar to **1** containing a low concentration of covalently bonded 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl[9] indicated very rapid tumbling of the spin label under both biphase and triphase conditions.

(12) When equilibrated with equal volumes of water and toluene, ~7% of 3-carbamoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy partitioned into the toluene phase.

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(14) For labels **2** and **3** dissolved in a mixture of water–1,2-dimethoxyethane where $X_{H_2O} = 0.54$, measured W values are 0.06 and 0.10, respectively.

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(16) Toluene content was measured by washing the swelled resin with a large volume of ethyl ether and analyzing the filtrate by GLC using an internal standard. Water content was determined by the difference in weight of total imbibed solvent and that of toluene.

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Simple Prediction of Substituent Sensitivity (ρ^+) for Carbocations[1]

Sir:

The "tool of increasing electron demand", which has been developed and used extensively by Tanida,[3a] Gassman,[3b] and Brown,[4] has proven to be an important probe of internal participation during solvolyses and of the electron demand of the incipient carbonium ions. The method is generally applied to the solvolyses of a series of tertiary, aryl *p*-nitrobenzoates. By varying the substituents on the aryl ring, the sensitivity of the reaction to the substituents is revealed in the slope (ρ^+) of a Hammett-Brown plot of the logarithm of the rates vs. σ^+. A very negative ρ^+ indicates the solvolysis is greatly influenced by substituents and that the incipient carbonium ion has high electron demand, e.g., for 7-aryl-7-norbornyl *p*-nitrobenzoates, $\rho^+ = -5.27$.[3b] Less negative values of ρ^+ are often symptomatic of carbonium ions whose electron demand is diminished by internal charge delocalization, e.g., for *syn*-7-aryl-*anti*-7-norbornenyl *p*-nitrobenzoates, $\rho^+ = -2.30$.[3b]

We present here a straightforward theoretical method for estimating ρ^+'s using MO calculations in conjunction with a simple perturbation theory expression. The agreement between theory and experiment establishes that the key factors governing the electron demand of a carbonium ion are the delocalization and energy of the cation's LUMO.

Frontier orbital theory predicts that the important stabilizing interaction for a substituted carbonium ion occurs between the HOMO of the electron donating substituent and the LUMO of the carbonium ion. For an aryl group the appro-

Table I. LUMO Charges and Energies, Sensitivity Factors, and ρ^+'s

R^+	$Q_L{}^{a,b}$	$-\epsilon_L{}^{a,c}$	f^{+d}	$-\rho^+_{\text{exptl}}$	$-\rho^+_{\text{calcd}}{}^e$
Coates'[s]	0.409	3.51	0.061	2.05[f]	2.01
7-Norbornenyl[p]	0.428	3.66	0.065	2.30[g] (1.75)[r]	2.07
2-Cyclohexenyl	0.445	6.53	0.121	2.52[h]	2.83
α-Methylcyclopropyl carbinyl	0.596	6.08	0.145	2.78[i]	3.15
3-Nortricyclyl	0.621	5.88	0.144	3.27[j] (3.02)[r]	3.14
2-Norbornyl	0.753	6.47	0.202	3.79[k,q] (3.965)[r]	3.93
Cyclopentyl	0.769	6.88	0.232	3.82[l] (4.16)[r]	4.33
3-Cyclopentenyl	0.773	6.89	0.234	3.92[l] (4.32)[r]	4.36
Bicyclo[2.1.1]hex-2-yl	0.738	6.52	0.201	4.31[m]	3.91
Cyclohexyl	0.759	6.62	0.212	4.60[h]	4.06
Isopropyl	0.758	7.15	0.249	4.72[n]	4.56
Cyclobutyl	0.782	7.13	0.255	4.92[n]	4.64
Cyclopropyl	0.798	7.47	0.292	5.15[n,o]	5.15

[a] MINDO/3 results with complete geometry optimization. [b] Single electron population for the carbonium carbon in the LUMO. [c] LUMO energy in eV. [d] Sensitivity factor defined in eq 4 with $\epsilon_H = -10.2$ eV. [e] Calculated from eq 5 with $a = -13.58$ and $b = 1.184$. Mean error is 0.27 ρ^+ units. [f] H. C. Brown and M. Ravindranathan, *J. Am. Chem. Soc.*, **99**, 299 (1977). [g] P. G. Gassman and A. F. Fentiman, Jr., *ibid.*, **92**, 2549 (1970). [h] H. C. Brown, M. Ravindranathan, and M. M. Rho, *ibid.*, **98**, 4216 (1976). [i] E. N. Peters and H. C. Brown, *ibid.*, **95**, 2397 (1973). [j] H. C. Brown and E. N. Peters, *ibid.*, **97**, 1927 (1975). [k] H. C. Brown, K. Takeuchi, and M. Ravindranathan, *ibid.*, in press. [l] E. N. Peters and H. C. Brown, *ibid.*, **97**, 7454 (1975). [m] H. C. Brown, M. Ravindranathan, and C. G. Rao, *ibid.*, **99**, 2359 (1977). [n] H. C. Brown, M. Ravindranathan, E. N. Peters, C. G. Rao, and M. M. Rho, *ibid.*, in press. [o] Extrapolated from data for *p*-H and *p*-CH_3 derivatives in C. H. DePuy, L. G. Schnack, and J. W. Hausser, *ibid.*, **88**, 3343 (1966), corrected to 25 °C. [p] The NLUMO (the *n*ext MO above the LUMO in energy) is the appropriate orbital with *S* symmetry in this case. [q] Average of exo (−3.83) and endo (−3.75). Results from ref 12. [s] 9-Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonyl.

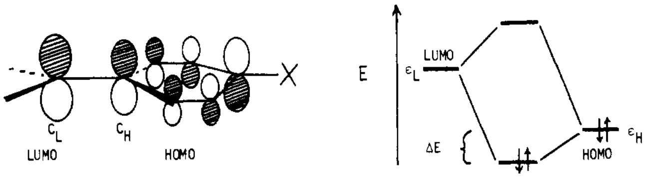

Figure 1. The important frontier interaction between the LUMO of the carbonium ion and HOMO of the aryl substituent.

priate HOMO is the $1e_{1g}$ benzene-like orbital with *S* symmetry (Figure 1) while for a methyl group it is the π_{CH_3} group orbital with *S* symmetry.[6] For a given substituent, the energy of the HOMO-LUMO interaction should be a measure of the electron demand of the carbonium ion. A strong interaction implies that the carbonium ion is very sensitive to substitution and corresponds to more negative values of ρ^+ for generating the ion. Thus, a direct relationship can be expected between ρ^+, a log *k* term, and the stabilization energy of a carbonium ion by a substituent.

The interaction energy (ΔE) between the aryl HOMO and the LUMO of a simple carbonium ion, e.g., isopropyl, may be estimated from the second-order perturbation theory expression.

$$\Delta E = \frac{H_{HL}{}^2}{\epsilon_L - \epsilon_H} \approx \frac{(C_H C_L \beta)^2}{\epsilon_L - \epsilon_H} \tag{1}$$

The coefficient on the carbonium carbon in the cation's LUMO, C_L, is less than one except for methyl due to hyperconjugation. Equation 1 may also be rewritten as

$$\Delta E \approx \frac{Q_H Q_L \beta^2}{\epsilon_L - \epsilon_H} \tag{2}$$

where $Q_H(C_H{}^2)$ is the one electron density at the site of attachment in the aryl HOMO and $Q_L(C_L{}^2)$ is the population at the carbonium carbon in the LUMO, if it were occupied by one electron. However, not all carbonium ions are planar at the carbonium carbon, particularly homoaromatic ones, so for greater generality we take Q_L to be the sum of all the AO coefficients on the carbonium carbon in the LUMO squared (eq 3).

$$Q_L = \sum_i^{\text{AO's on C}^+} C_{iL}{}^2 \tag{3}$$

For our purposes, interaction with a generalized substituent will be considered for which Q_H, β, and ϵ_H can be treated as constants which may be optimized. ΔE is then proportional to the term in eq 4 which is defined as f^+, the theoretical sensitivity factor for the carbonium ion.

$$\Delta E \propto \frac{Q_L}{\epsilon_L - \epsilon_H} \equiv f^+ \tag{4}$$

Finally, a linear relationship between f^+ and ρ^+ may be anticipated, i.e., eq 5 where *a* and *b* are constants.[13]

$$\rho^+ = af^+ + b \tag{5}$$

To test this theory, MINDO/3[7] calculations were performed with complete geometry optimization on 13 *secondary* carbonium ions for which experimental ρ^+'s have been determined for the corresponding tertiary, aryl *p*-nitrobenzoates.[5] The MINDO/3 results were used to provide the Q_L and ϵ_L values recorded in Table I. ϵ_H was then treated as a parameter and computed by least-squares procedures along with *a* and *b* to fit eq 5 to the experimental ρ^+'s. The best fit was found for $\epsilon_H = -10.2$ eV, which is close to the MINDO/3 ϵ_H for benzene (−9.2 eV), $a = -13.58$ and $b = -1.184$. The results for f^+ and ρ^+_{calcd} are compared with the experimental ρ^+'s in Table I and Figure 2. The mean deviation of the calculated ρ^+'s from the experimental ones for the 13 points is 0.27 ρ^+ units over a range of 3.10 ρ^+ units. Although the agreement is certainly not perfect, it is sufficient to establish the utility of this remarkably simple procedure and to confirm the importance of the delocalization parameter, Q_L, and the LUMO energy in determining substituent sensitivity. The significance of these two factors has been noted more qualitatively in the past.[2,8] Linear correlations of ρ^+ with either factor alone yield significantly larger mean deviations, ca. 0.35 ρ^+ units. Correlating ρ^+ with the calculated charge density (q) at the carbonium carbon in the secondary ions ($\rho^+ = aq + b$) gives an even greater error (0.43).

The potential sources of disagreement between the calcu-

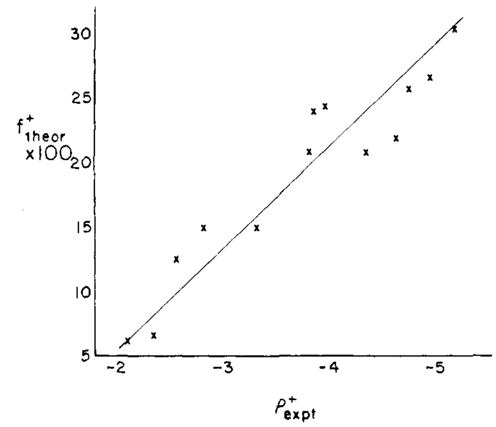

Figure 2. Correlation of theoretical f^+ (eq 4) with experimental ρ^+ for carbonium ions in Table I.

lated and experimental ρ^+'s are numerous.[9] Use of ab initio rather than MINDO/3 results could lead to even better accord.[10] In addition, the assumption of equal β (eq 1) for the different ions is suspect since variations in the carbonium carbon to aryl ring bond length are expected as well as variations in the planarity of the carbonium carbon. Ground state effects on the ionizations are also important. For example, the experimental ρ^+'s for cyclopentyl and 3-cyclopentenyl seem anomalously high compared to the calculated values and isopropyl. This may be attributed to steric acceleration that relieves eclipsing interactions in the solvolyses leading to the five-membered ring cations. The strain relief decreases the electron demand on the substituents in the transition state for solvolysis and raises ρ^+.[3a] Similarly, the calculated ρ^+ for cyclohexyl is too high probably due to steric deceleration which increases the substituent sensitivity of the transition state and lowers ρ^+. The steric effects can be compensated somewhat by using Peters' values for ρ^+ which correlate the solvolysis rates of the tertiary, aryl species with their secondary parents.[12] As shown in Table I, Peters' values (in parentheses) are in significantly better agreement with the calculated ρ^+'s than the experimental results for the tertiary species only. A new fit of eq 4 to the experimental ρ^+'s including Peters' data reduces the mean deviation between theory and experiment to 0.20 ρ^+ units. The decision on which experimental values to use is complicated by the lack of linearity observed by Peters in some of his Hammett-Brown plots, e.g., for cyclohexyl and Coates' cation.[12] We have chosen to use the consistent data base involving only the solvolyses of the tertiary, aryl p-nitrobenzoates and emphasize that the theoretical method ignores conformational effects on this reaction. It is not clear that the benefits gained by attempting to take such factors into account would offset the loss of simplicity. One element that does not appear to be affecting the results is differences in solvation for the various carbocations.[2a] This is reasonable, however, since the ρ^+'s correspond to the generation of highly delocalized, π-conjugated and/or homoaromatic carbocations. The solvation of such ions should be uniformly weak.[2,11]

Predictions of ρ^+ for some systems that have not yet been studied experimentally are recorded in Table II. The total accumulation of data permits some general observations. (1) The low f^+'s (high ρ^+'s) for the homoaromatic species result from a combination of both extensive delocalization (low Q_L) and high LUMO energy (ϵ_L). (2) The low f^+'s for π-conjugated cations are due primarily to delocalization. (3) The ρ^+'s and the ϵ_L's and Q_L's for the cyclopropylcarbinyl cations are intermediate between those of the homoaromatic and simple, classical ions. (4) It must be emphasized that the key factor for delocalization is the delocalization of the LUMO, not the actual charge delocalization which is determined by the occupied orbitals.

Table II. Calculated Sensitivity Factors and ρ^+'s for Additional Cations

R^+	$Q_L{}^{a,b}$	$-\epsilon_L{}^{a,c}$	f^{+d}	$-\rho^+_{calcd}{}^e$
Bridged 2-norbornyl	0.351	4.98	0.067	2.09
Trishomocyclopropenyl[g]	0.526	3.87	0.083	2.31
3-Bishomocyclopropenyl[f,h]	0.575	4.41	0.099	2.53
2-Cyclobutenyl	0.496	5.45	0.104	2.60
7-Norbornadienyl[f]	0.423	3.65	0.065	2.07
Bicyclo[3.1.0]hex-3-yl	0.776	6.76	0.226	4.25
Bicyclo[3.1.0]hex-2-yl	0.507	5.83	0.116	2.76
α-Methylbenzyl	0.427	6.17	0.106	2.62
1,3-Dimethylallyl	0.443	6.49	0.119	2.80

[a] MINDO/3 results with complete geometry optimization. [b] Single electron population for the carbonium carbon in the LUMO. [c] LUMO energy in eV. [d] Sensitivity factor defined in eq 4 with $\epsilon_H = -10.2$ eV. [e] Calculated from eq 5. [f] The NLUMO is the appropriate orbital with S symmetry in this case. [g] From bicyclo[3.1.0]hex-3-yl. [h] From 3-cyclopentenyl.

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Competing Triplet and Radical Pair ^{19}F Polarizations in the Electron Transfer Quenching of Triplet α,α,α-Trifluoroacetophenone

Sir:

We have applied the CIDNP technique[1] to study the interaction of photoexcited α,α,α-trifluoroacetophenone (TFA, **1**) with strong electron donors such as 1,4-diazabicyclo[2.2.2]-