with the product of the s electron densities at the coupled nuclei. However, the noncontact contributions are also expected to be important especially in unsaturated compounds where a π-electronic system is well defined.[20] It is generally accepted that while calculations are able to qualitatively reproduce some of the observed trends, they are still of limited reliability at the present time.

In our present study, we have attempted to demonstrate the scope and utility of measuring one-bond carbon coupling constants and believe that these results will help understand the mechanism of ^{13}C spin interactions. We hope that, perhaps, the experimental data provided in our study will also stimulate theoretical interest to gain a more quantitative understanding of the effect of substituents on one bond ^{13}C–^{13}C coupling constants.

Experimental Section

Regular ^{13}C and ^{13}C satellite spectra were recorded at 50.3 MHz using a Varian XL-200 superconducting NMR spectrometer equipped with a variable temperature broad-band probe.

All the benzophenones used were either commercially available with 99% purity or prepared from the correspondig 4-substituted bromobenzene by standard literature procedures. The benzoyl chlorides and methyl benzoates were prepared from the corresponding, commercially available, acid precursors. The former was freshly distilled before use. All compounds used gave satisfactory spectral characteristics.

The INADEQUATE spectra were all recorded at ambient temperatures in $CDCl_3$ solutions. Concentration of solutions were typically in the order of ~30% for the methyl benzoates and benzoyl chlorides. In the case of benzophenones they varied from 8% to 15% and needed the presence of trace amounts of Cr(acac)$_3$.

The pulse sequences used for the ^{13}C satellite spectra, based on Freeman et al.[4], is $90°(x)–\tau–180°(\pm y)–\tau–90°(x)–\Delta–90°(\phi)–$Acq.$(\psi)$, where $\tau = (2n + 1)/4J_{CC}$, Δ is a very short delay (~ 10 μs) needed to reset the radiofrequency phase during which time double quantum coherence evolves and ϕ and ψ are the phase of the last 90° "read" pulse and the receiver reference phase, respectively. Optimum setting for direct coupling is when $n = 0$ and thus set at 3.5 ms for benzoyl chlorides and methyl benzoates, and at 4.5 ms for the benzophenones. Repetition rate of this sequence is 15 s for the former and 2 s for the latter which contained Cr(acac)$_3$. Reasonable signal to noise ratio was achieved in 12–20 h of acquisition. Errors in the $^1J_{C,C}$ measurements are estimated to be ±0.3 Hz.

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Registry No. 1 (R = 4-OCH_3), 121-98-2; 1 (R = 4-CH_3), 99-75-2; 1 (R = H), 93-58-3; 1 (R = 4-F), 403-33-8; 1 (R = 4-Cl), 1126-46-1; 1 (R = 4-Br), 619-42-1; 1 (R = 4-CF_3), 2967-66-0; 2 (R = 4-OCH_3), 100-07-2; 2 (R = 4-CH_3), 874-60-2; 2 (R = H), 98-88-4; 2 (R = 4-F), 403-43-0; 2 (R = 4-Cl), 122-01-0; 2 (R = 4-CF_3), 329-15-7; 2 (R = 3,5-$(CF_3)_2$), 785-56-8; 3 (R = 4-OCH_3), 90-96-0; 3 (R = 4-CH_3), 611-97-2; 3 (R = H), 119-61-9; 3 (R = 4-F), 345-92-6; 3 (R = 4-Cl), 90-98-2.

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Solvolysis of Allyl Arenesulfonates. Cautionary Comments concerning the N_{OTs} Scale of Solvent Nucleophilicities

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The rates of solvolysis of five allyl arenesulfonates are analyzed in terms of the extended Grunwald–Winstein equation. The l values are constant but the m values decrease slightly as the nucleofugality of the leaving group increases. The solvent nucleophilicity (N_{OTs}) values presently available in the literature are based upon a m value for methyl p-toluenesulfonate (tosylate) solvolysis of 0.3; it is demonstrated that a value of 0.55 is more appropriate. The previously reported l values and correlation coefficients for tosylate ester solvolyses are accurate and the "apparent" sensitivities to solvent ionizing power (m values) are easily corrected. However, for use in conjunction with solvent ionizing power scales for other leaving groups, N_{OTs} values based on the appropriate m value or, alternatively, $N_{Et_3O^+}$ values (based on triethyloxonium ion solvolysis) are required.

Recently, we used[1] the extended Grunwald–Winstein equation[2-4] (eq 1) to analyze the kinetic data of Sendega and co-workers for the solvolyses of allyl arenesulfonates[5-7] (eq 2). In eq 1, k and k_0 are the specific rates of solvolysis in the solvent under consideration, and in the standard (80% ethanol) solvent, l represents the sensitivity to solvent nucleophilicity values (N) and m represents the sensitivity to solvent ionizing power values (Y). The specific rates of solvolysis were correlated for a combination of ethanol, aqueous methanol, aqueous dioxane, and aqueous acetone systems.

$$\log (k/k_0) = lN + mY \tag{1}$$

$$CH_2{=}CHCH_2OSO_2Ar + SOH \rightarrow CH_2{=}CHCH_2OS + ArSO_3H \tag{2}$$

Using N_{KL} values based on triethyloxonium ion solvolysis[8] and Y values based on *tert*-butyl chloride solvolysis,[9] it was found that as the nucleofugality of the arene-

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Table I. First-Order Rate Coefficients for the Solvolysis of Allyl Arenesulfonates[a] at 50.0 °C as a Function of the Ring Substituent

	10^5k, s^{-1} [b]			
solv[c]	none	*p*-Cl	*m*-NO_2	*p*-NO_2
MeOH	24.6	58.1	288	262
EtOH	9.27	23.1	145	122
80% EtOH	42.5	117	646	627
60% EtOH	106	273	1270	1428
97% TFE	3.25	4.86	26.8	27.0
80% TFE[d]	14.5	27.6	135	137
HCO_2H	41.0	71.9	261	266
CH_3CO_2H	0.257	0.542	3.07	2.81

[a] Solvolysis of ca. 0.008 M ester in a solvent consisting of 98% of the indicated composition plus 2% dioxane; all runs performed in duplicate. [b] Standard deviations for *k* were within 4% of reported values. [c] On a volume–volume basis, at 25.0 °C, and with water as the other component, except for the TFE–H_2O mixtures, which are on a weight-percentage basis. [d] Values for N'_{OTs} of −1.72 and for Y_{OTs} of +1.94 obtained by interpolation within the data of ref 13.

Table II. Correlation of Specific Solvolysis Rates[a] (at 50.0 °C) of Allyl Arenesulfonates with $N_{Et_3O^+}$ or N'_{OTs} and Y_{OTs} Values

	$N_{Et_3O^+}$, Y_{OTs}			N'_{OTs},[b] Y_{OTs}		
substituent	*l*	*m*	*r*[c]	*l*	*m*′[d]	*r*[c]
p-CH_3[e]	1.127	0.745	0.983	0.814	0.529	0.982
none[f]	1.097	0.717	0.979	0.796	0.509	0.982
p-Cl[f]	1.168	0.716	0.976	0.854	0.498	0.988
m-NO_2[f]	1.125	0.660	0.966	0.834	0.455	0.990
p-NO_2[f]	1.137	0.684	0.962	0.848	0.479	0.992

[a] The eight solvents are listed in Table I. [b] The literature values[13] based on eq 5 ($y = 0.3$). [c] Correlation coefficient. [d] Apparent *m* value. [e] Using specific solvolysis rates reported in ref 1. [f] Using specific solvolysis rates from Table I.

sulfonate leaving group increased, both *l* and *m* fell in value. It was suggested that the transition states became looser, but the resulting increase in *m* values was outweighed by a decrease due to a reduced solvation, accompanying improved internal charge dispersion.

There were, however, features of the analysis that suggested the need for further consideration. From an experimental standpoint, the report[5] of "normal" behavior in methanol and ethanol for the *p*- and *m*-nitro derivatives (the para derivative with the larger Hammett σ value[10] reacting faster) is contrary to other reports[11,12] of the specific rates of alcoholysis of arenesulfonate esters. Faster solvolyses of the *m*-nitro derivative have been observed for esters ranging from methyl[11] (model S_N2) to adamantyl[12] (model S_N1). From the standpoint of multiple regression analysis, the range of *N* values was rather restricted. For the *p*-toluenesulfonate (tosylate) ester, 11 additional solvents, chosen so as to extend the range of *N* values, were studied, and appreciable changes were observed in both *l* and *m* values. The wider range of *N* values should be incorporated into the analyses of the rates of solvolysis of the other allyl arenesulfonates.

It was demonstrated[1] that a limited number (eight) of well-chosen solvents gave *l* and *m* values essentially identical with those obtained from a consideration of the full range of 28 solvents. These eight solvents have been used in the present extension of the allyl tosylate study.

Results and Discussion

The solvolyses of allyl benzenesulfonate and the *p*-chloro, *m*-nitro, and *p*-nitro derivatives have been studied, at 50.0 °C, in methanol, ethanol, 80% ethanol, 60% ethanol, 97% 2,2,2-trifluoroethanol (TFE), 80% TFE, formic acid, and acetic acid. The first-order rate coefficients are reported within Table I.

For methanolysis and ethanolysis, comparisons can be made with previously reported[5] values. The specific solvolysis rates for unsubstituted and *p*-chloro-substituted esters are in reasonable agreement. However, we observed, as expected,[12] the fastest reaction with the *m*-nitro derivative rather than with the *p*-nitro derivative.[5] In methanol, our values for 10^5k of 288 and 262 s^{-1} can be compared with values of 224 and 323 s^{-1}, and, in ethanol, our values of 145 and 122 s^{-1} can be compared with values of 118 and 178 s^{-1}. The cause of these discrepancies is not known.

The results of two analyses of our data in terms of the extended Grunwald–Winstein equation (eq 1) are presented in Table II. Both analyses use a scale of solvent ionizing power based on 2-adamantyl tosylate solvolysis (Y_{OTs}).[13] The scale of solvent nucleophilicity was either the $N_{Et_3O^+}$ scale[14] or the N_{OTs} scale,[13] based upon methyl tosylate solvolysis and defined as in eq 3 with a value of

$$N_{OTs} = \log (k/k_0)_{MeOTs} - mY_{OTs} \tag{3}$$

0.3 chosen for *m*. The procedure used to arrive at the value of 0.3 has been criticized,[8,15] and, by comparison with the N_{KL} scale, it was suggested[8] that a value of 0.5 would be more appropriate. Despite these criticisms, the N_{OTs} scale has continued to be employed[16] and new N_{OTs} values based on eq 3 have been reported.[16b,17,18] It is important to realize that the very reasonable *l* values and the very good to excellent correlation coefficients (*r*) obtained[13] when the reported N_{OTs} and Y_{OTs} values have been employed[13,16a] cannot be considered to give support to the choice of a value of 0.3 for use within eq 3. Indeed, it can readily be shown that *the l values and the "goodness of fit" for solvolysis of a tosylate ester are independent of the value for the sensitivity of methyl tosylate solvolysis toward solvent ionizing power which is incorporated into eq 3.*

Let us assume that the scale of solvent nucleophilicities based on methyl tosylate solvolysis is accurately defined as in eq 4, but it can also be arbitrarily defined as in eq 5. Eliminating $\log (k/k_0)_{MeOTs}$ between eq 4 and 5, one

$$N_{OTs} = \log (k/k_0)_{MeOTs} - xY_{OTs} \tag{4}$$

$$N'_{OTs} = \log (k/k_0)_{MeOTs} - yY_{OTs} \tag{5}$$

$$N_{OTs} = N'_{OTs} + (y - x)Y_{OTs} \tag{6}$$

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$$\log (k/k_0) = lN'_{\mathrm{OTs}} + [m + (y - x)l]Y_{\mathrm{OTs}} \qquad (7)$$

arrives at eq 6. Substituting eq 6 within eq 1 and using Y_{OTs} values within the mY term, one arrives at eq 7. Any arbitrary N'_{OTs} scale, derived from eq 5, will accurately generate l values and will lead to an apparent m value (m') greater than the true m value by the quantity $(y - x)l$. The correlation of the data will be equally good for any value that might be chosen for y.

Because of uncertainty as to whether the N_{OTs} scale is best defined by using the m value of 0.3, the "traditional" N_{OTs} scale,[13] which is used in one of the analyses reported within Table II, will be designed as N'_{OTs} ($y = 0.3$). Due to compression of an N scale based upon an ethyl derivative relative to one based upon a methyl derivative,[8] higher l values are obtained from the analysis with the $N_{\mathrm{Et_3O^+}}$ scale, the ratio of the l values for each of the five substrates are 1.385, 1.378, 1.368, 1.349, and 1.341. Despite the use of the same Y scale and the very good to excellent correlations obtained for both analyses, there are appreciable differences between the two sets of m values obtained. If it is accepted that the m values in the $N_{\mathrm{Et_3O^+}}$ plus Y_{OTs} analysis approximate the true values (no mY correction needed in deriving the $N_{\mathrm{Et_3O^+}}$ scale), we can calculate the x value of eq 4 from the relationship $m = m' + (x - 0.3)l$. The x values obtained for the five substrates are 0.565, 0.562, 0.555, 0.546, and 0.542. The average values for the ratio of the l values (1.364) and for the x value (0.554) are consistent with the l value of 1.336 and the m value of 0.543 ($r = 0.944$) obtained when, at 50.0 °C, the specific rates of methyl tosylate solvolysis[13] in the same solvents (except that 70% TFE is substituted for 80% TFE) are correlated against $N_{\mathrm{Et_3O^+}}$ and Y_{OTs} values.

In summary, for tosylate ester solvolyses, the previously reported l and r values are meaningful but the "apparent" m values (m') need correction. If 0.55 is accepted as the x value of eq 4, then $m = m' + 0.25l$.

A word of caution is in order concerning the claim[19] that N'_{OTs} ($y = 0.3$) values can be used in conjunction with Y scales (Y_{X}) based upon other anionic leaving groups. This requires a linear relationship between Y_{X} and Y_{OTs}. In general, eq 8 will be required. For these situations, $N_{\mathrm{Et_3O^+}}$

$$\log (k/k_0)_{\mathrm{RX}} = lN'_{\mathrm{OTs}} + l(y - x)Y_{\mathrm{OTs}} + mY_{\mathrm{X}} \qquad (8)$$

or N_{OTs} ($y = x$) values are strongly recommended. *In principle*, multiple regression analysis of $\log (k/k_0)_{\mathrm{RX}}$ against N'_{OTs}, Y_{OTs}, and Y_{X} would allow an independent determination of x.

For allyl arenesulfonate solvolysis, it can be seen (Table II) that the m values vary in the manner reported earlier,[1] but the l values are now found to be essentially independent of the nature of the leaving group, consistent with observations for other leaving group variations.[8] For the tosylate ester, the two analyses have essentially identical correlation coefficients. Since the Y_{OTs} scale was established with a tosylate ester,[13] one would expect the correlations to become less precise (reduced correlation coefficient) as the arenesulfonate leaving group becomes less like the tosylate. This prediction is followed for the correlations against $N_{\mathrm{Et_3O^+}}$ and Y_{OTs}, but, surprisingly, the correlation coefficient rises in value as one moves away from the tosylate for correlations against N'_{OTs} and Y_{OTs}.

Table III. Hammett ρ Values for the Solvolyses of Allyl Benzenesulfonate[a] and *p*-Methyl,[b] *p*-Chloro,[a] *m*-Nitro,[a] and *p*-Nitro[a] Derivatives at 50.0 °C

solv	ρ^c	r^d	$\rho^{c,e}$	r^d
MeOH	1.36 ± 0.07	0.996	1.35 ± 0.03	0.999
EtOH	1.47 ± 0.10	0.994	1.48 ± 0.05	0.998
80% EtOH	1.48 ± 0.08	0.996	1.48 ± 0.06	0.998
60% EtOH	1.41 ± 0.05	0.998	1.40 ± 0.05[f]	0.998
97% TFE	1.25 ± 0.07	0.995		
80% TFE	1.23 ± 0.07	0.996		
HCO_2H	1.01 ± 0.06	0.995		
CH_3CO_2H	1.38 ± 0.07	0.996	1.38 ± 0.03[g]	0.999

[a] Using first-order rate coefficients from Table I. [b] Using first-order rate coefficients from ref 1. [c] Using Hammett σ values from ref 10 and with associated standard errors. [d] Correlation coefficient. [e] Substituting the modified σ values for *m*-NO_2 and *p*-NO_2 substituents reported in ref 12. [f] The modified σ values for nitro substituents obtained by interpolation. [g] Averages of the three pairs of modified σ values for nitro substituents (ref 12) used.

The specific solvolysis rates can also be submitted to a Hammett $\rho\sigma$ treatment,[10,20] with a consideration of the effect of varying the ring substituent made for each of the eight solvents. The Hammett ρ values obtained by using the five allyl arenesulfonates of this study are reported in Table III. For those solvents for which σ values for nitro substituents as corrected for solvation effects are available,[12] the ρ values have been calculated both with the traditional values and with the values determined in the appropriate solvent. The ρ values are independent of the choice of σ values, but the standard errors are reduced and the correlation coefficients increased by use of the modified values.

The ρ values obtained are consistent with previous considerations of arenesulfonate esters.[12,20] The value of 1.48 in ethanol is similar to the value for the isopropyl ester of 1.55 (at 70 °C) and intermediate between the values of 1.32 for methyl esters (at 70 °C) and 1.81 for 2-adamantyl esters (at 55 °C). In methanol, the value of 1.36 is virtually identical with the value of 1.37 for isopropyl esters. As regards the effect of solvent upon the magnitude of the ρ value, it is generally accepted[21] that the susceptibility to substituent effects, reflected in the magnitude of the ρ values, increases as the ability of the solvent to stabilize charge by solvation decreases. Indeed a plot of the ρ values from Table III against the Y_{OTs} values for the solvents[13] is approximately linear ($r = -0.847$). An outstanding correlation would not be expected because solvent ionizing power can be considered only as a rough approximation of the ability to disperse charge through solvation.

Experimental Section

The commercially available solvents were purified by previously outlined procedures.[8,22] Allyl bromide was purified by distillation. Silver arenesulfonates were prepared by the interaction of the arenesulfonyl chloride with a slight excess of silver oxide in boiling water.[23] The corresponding allyl arenesulfonates were synthesized by the heterogeneous interaction of a ca. 0.40 M solution of allyl bromide in dioxane with a fourfold excess of the silver salt. After vigorous stirring for 2 days at room temperature, silver bromide and excess silver arenesulfonate were removed by filtration.

Kinetics procedures exactly paralleled those previously outlined for the study of the solvolysis of the tosylate ester.[1]

Acknowledgment. Partial support was provided by the Graduate School Fund of Northern Illinois University.

Registry No. $PhSO_2OCH_2CH{=}CH_2$, 7575-57-7; *p*-$ClC_6H_4SO_2OCH_2CH{=}CH_2$, 6165-74-8; *m*-$NO_2C_6H_4SO_2OCH_2$-$CH{=}CH_2$, 20443-61-2; *p*-$NO_2C_6H_4SO_2OCH_2CH{=}CH_2$, 33420-11-0; *p*-$MeC_6H_4SO_2OCH_2CH{=}CH_2$, 4873-09-0.

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