Comparison of the Effect of Methyl and Phenyl Substituents on the Stabilities of Some Carboxonium Ions. Stability Decreases Associated with Increasing Charge Delocalization

John W. Larsen,* P. A. Bouis, and Charles A. Riddle

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916

The effect of the phenyl and methyl groups on the stabilities of acylium ions in FSO_3H and dialkoxycarbonium ions in sulfuric acid has been measured calorimetrically. As with other alkoxycarbonium ions previously studied, the formation of the methyl-substituted cations is more exothermic than the formation of phenyl-substituted cations. Resonance stabilization of the starting molecules is ruled out as an explanation. Whatever the reason, all carboxonium ions studied are more stable when methyl substituted than when phenyl substituted.

One of the basic tenets of organic chemistry is that increasing delocalization of charge results in increasing stability of ions, other factors being equal. If increasing delocalization did not result in a stability increase, there would be no driving force for delocalization, and it would not occur. Systems in which increasing charge delocalization does not result in increasing stability are important and interesting because they violate this important tenet. We have measured the relative stabilities of a series of methyl- and phenyl-substituted delocalized carbocations and have learned that for this pair of substituents, a stability decrease *always* occurs when methyl is replaced by phenyl. The stabilities of the ions are decreased by a phenyl substituent which delocalizes the charge more than does a methyl substituent. This is a clear violation of the principle that increasing delocalization leads to increasing stability. This behavior is always observed when the ion system being studied is itself delocalized. It may be that the only carbocations in which replacing methyl by phenyl leads to a stability increase are the simple, trivalent carbonium ions (R_3C^+).

We previously measured the relative stabilities of several families of cations in which the positive charge was delocalized over carbon and oxygen (for references see Table I). In general, substituent effects were as expected, good Hammett plots were observed,[1] and alkyl substituents showed the Baker–Nathan order. A glaring exception to our expectations was that the phenyl-substituted cations were less stable than the methyl-substituted cations (see Table I). In all cases, resonance stabilization of the cation by the aromatic ring is expected. There being no obvious factors which would prevent resonance interactions of the aromatic ring with the cationic center, a normal substituent effect is expected; i.e., phenyl-substituted cations should be more stable than methyl-substituted ones. As will be discussed, there is ample NMR evidence for delocalization of the positive charge into the ring. Increasing charge delocalization should result in increasing stability. Thus there is every reason to expect the phenyl-substituted cations to be more stable than their methyl analogues, yet the opposite substituent effect was observed. Further exploration of this substituent effect is the subject of this paper.[2]

Results

Data were obtained for two more families of ions and are shown in Table II. As before,[1,3-6] the enthalpy change occurring when a neutral molecule is converted to a stable ion in an acidic solvent was measured calorimetrically. Use of this technique has ample precedent. It does require independent evidence for the structure and kinetic stability of the ions formed. The acylium ions reported in Table II have been characterized by a variety of techniques including both ^{13}C and ^1H NMR studies by Olah.[7] Our own ^1H NMR studies of these ions are in general agreement with his and showed very clean ion formation, with no peaks due to side products or starting material being detected. The dialkoxycarbonium ions are quite stable, well-studied ions. Good surveys of their formation and chemistry can be found in Perst's reviews.[8,9] A great deal of NMR work has been done, with much emphasis on rates of rotation about the carbon–oxygen partial double bond. References can be found in Perst's book.[10] Our NMR studies indicated that all ions were formed cleanly from the ortho esters and, except for formates, were stable. It is obvious from the data in Table II that the formation of these ions is more exothermic with a methyl substituent than with a phenyl substituent.

Discussion

The quantity being measured is the enthalpy change when a molecule is converted to a cation in strong acid. A substituent change will affect both the starting molecule and the ion, and so effects on both must be considered. The methyl and phenyl groups differ in many respects, and the net results of the substituent change can be treated as the sum of a number of "effects", each effect originating from a difference between phenyl and methyl. The two groups differ in size, resonance interactions, inductive effects, and polarizabilities, all of which will have a predictable effect on the transformation being studied. The impact of each of these on the ionization process will be considered in an attempt to rationalize these data.

A change in substituent size is expected to affect the observed heats for two reasons. This topic has been discussed in detail[3] and will be covered here succinctly. As

(1) J. W. Larsen and P. A. Bouis, *J. Am. Chem. Soc.*, 97, 4418 (1975).

(2) This effect has been observed in other systems containing delocalized carbocations and has often passed without comment. Some examples appear in Table III.

(3) E. M. Arnett, R. P. Quirk, and J. W. Larsen, *J. Am. Chem. Soc.*, 92, 3977 (1970).

(4) J. W. Larsen, *J. Am. Chem. Soc.*, 92, 5136 (1970).

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(6) J. W. Larsen and S. Ewing, *J. Am. Chem. Soc.*, 93, 5107 (1971).

(7) G. A. Olah and P. W. Westerman, *J. Am. Chem. Soc.*, 95, 3706 (1973).

(8) H. Perst, "Oxonium Ions In Organic Chemistry", Academic Press, New York, 1971.

(9) H. Perst in "Carbonium Ions", Vol. V, G. A. Olah and P. v. R. Schleyer, Eds., Wiley, New York, 1976.

(10) Reference 8, p 176 ff.

Table I. Substituent Effect on the Relative Heats of Formation of Some Carboxonium Ions

substituent					
R¹	R²	$\Delta \bar{H}_{s,CCl_4}$, kcal/mol	$\Delta \bar{H}_{s,acid}$, kcal/mol	$\Delta \bar{H}_{R^+}$, kcal/mol	ref

$$\underset{R^1CR^2}{\overset{O}{\|}} + HSO_3F \xrightarrow{25\ ^\circ C} \underset{R^1CR^2}{\overset{^+OH}{\|}} + SO_3F^-$$

Me	Me	0.79 ± 0.02	−18.3 ± 0.1	−19.1 ± 0.1	3
C₆H₅	Me	0.79 ± 0.01	−18.1 ± 0.2	−18.9 ± 0.2	
C₆H₅	C₆H₅	5.26 ± 0.25	−11.6 ± 0.2	−16.9 ± 0.3	

$$\underset{R^1COEt}{\overset{O}{\|}} + HSO_3F \xrightarrow{25\ ^\circ C} \underset{R^1C^+OEt}{\overset{OH}{|}} + SO_3F^-$$

Me		0.014 ± 0.004	−17.4 ± 0.1	−17.4 ± 0.1	3
C₆H₅		0.36 ± 0.02	−14.1 ± 0.1	−14.5 ± 0.1	4

$$\underset{R^1COEt}{\overset{O}{\|}} + H_2SO_4 \xrightarrow{25\ ^\circ C} \underset{R^1C^+OEt}{\overset{OH}{|}} + HSO_4^-$$

Me		0.05 ± 0.02	−12.0 ± 0.5	−12.0 ± 0.1	
C₆H₅		0.28 ± 0.04	−8.64 ± 0.14	−8.97 ± 0.16	4

$$R^1COCH_2\underset{CH_3}{\overset{O}{C}}=CH_2 + H_2SO_4 \xrightarrow{25\ ^\circ C} \text{(dioxolanylium)} + HSO_4^-$$

Me		0.72 ± 0.03	−23.0 ± 0.2	−23.7 ± 0.2	5, 6
C₆H₅		0.62 ± 0.11	−21.5 ± 0.2	−22.1 ± 0.3	

$$R^1COCH_2\underset{CH_3}{\overset{O}{C}}=CH_2 + HSO_3F \xrightarrow{25\ ^\circ C} \text{(dioxolanylium)} + SO_3F^-$$

Me		0.72 ± 0.3	−30.8 ± 0.4	−31.5 ± 0.4	
C₆H₅		0.62 ± 0.11	−28.0 ± 0.1	−28.6 ± 0.2	

$$\underset{R^1C=CHCR^2}{\overset{OH \quad\ O}{|\qquad \|}} + H_2SO_4 \xrightarrow{25\ ^\circ C} \underset{R^1C=CHC^+R^2}{\overset{OH \quad OH}{|\qquad |}} + HSO_4^-$$

Me	Me	0.80 ± 0.05		−17.0 ± 0.2	4
C₆H₅	Me	0.35 ± 0.14		−15.4 ± 0.2	
C₆H₅	C₆H₅	5.95 ± 0.30		−11.2 ± 0.5	

$$\underset{R^1C=CHCR^2}{\overset{OH \quad\ O}{|\qquad \|}} + HSO_3F \xrightarrow{25\ ^\circ C} \underset{R^1C=CHC^+R^2}{\overset{OH \quad OH}{|\qquad |}} + SO_3F^-$$

Me	Me	0.80 ± 0.05		−22.5 ± 0.4	
C₆H₅	Me	0.35 ± 0.14		−22.2 ± 0.2	
C₆H₅	C₆H₅	5.95 ± 0.30		−18.6 ± 0.4	

Table II. Substituent Effect on the Relative Heats of Formation of Some Acylium and Dialkoxycarbonium Ions

substituent			$\Delta \bar{H}_{s,CH_3NO_2}$,		
R¹	R²	$\Delta \bar{H}_{s,CCl_4}$, kcal/mol	kcal/mol	$\Delta \bar{H}_{s,acid}$, kcal/mol	$\Delta \bar{H}_{R^+}$, kcal/mol

$$\underset{R^1CCl}{\overset{O}{\|}} + FSO_3H\ (11.5\ mol/SbF_5\ (7.0\ mol) \xrightarrow{25\ ^\circ C} R^1C^+=O + \text{mixture of anions}$$

cyclohexyl		0.64 ± 0.01		−18.7 ± 0.5	−19.4 ± 0.5
Me		0.96 ± 0.01	0.25 ± 0.02	−20.3 ± 0.2	−21.3 ± 0.2
C₆H₅		0.69 ± 0.03		−15.2 ± 0.3	−15.9 ± 0.3

$$R^1C(OR^2)_3 + H_2SO_4 \xrightarrow{25\ ^\circ C} \underset{OR^2}{\overset{OR^2}{R^1C^+}} + R^2OH + HSO_4^-$$

Me	Me	−0.37 ± 0.01		−30.3 ± 0.6	−29.9 ± 0.6
C₆H₅	Me	−0.18 ± 0.05		−26.3 ± 0.9	−26.1 ± 0.9
Me	Et	−0.35 ± 0.02	0.82 ± 0.16	−32.3 ± 1.2	−32.0 ± 1.2
Et	Et	−0.17 ± 0.01		−33.2 ± 0.5	−33.0 ± 0.2
C₆H₅	Et	−0.42 ± 0.04	2.20 ± 0.19	−27.8 ± 0.2	−27.4 ± 0.2

the size of an ion increases, its stabilization by Born solvation decreases, so it is expected that, in the absence of any other effects, the size increase on passing from methyl to phenyl would result in an endothermic contribution to

the ion stability, due to a decrease in solvation. Another endothermic contribution derives from the fact that the heats reported are heats of transfer from a solvent of low cohesive energy (CCl_4) to one of high cohesive energy (the acid). The larger the molecule transferred, the larger will be the enthalpy cost of creating the cavity which contains the molecule.

The data in Table II indicate that these effects are small. The most convincing demonstration of this is that the formation of $C_6H_{11}C^+=O$ is only 2 kcal/mol more endothermic than the formation of $CH_3C^+=O$ and 3.5 kcal/mol more exothermic than formation of the benzoylium ion. The cyclohexyl-substituted and phenyl-substituted ions are of approximately equal size. Another less conclusive approach leads to the same conclusion. If the reference solvent has the same cohesive energy as the acid, this size effect will disappear. Nitromethane has a cohesive energy density nearly as high as that of sulfuric acid,[11] and if it is used as the reference solvent, the 4.6-kcal/mol difference between the phenyldiethoxycarbonium ion and the methyldiethoxycarbonium ion is reduced to 3.1 kcal/mol. Again, there is a visible effect due simply to the size difference, but it is not enough.

The next topic is polarizability, which is particularly evident in the gas phase.[12] It is not expected to dominate in solution and does not. It predicts greater stabilization by phenyl, and the reverse is observed.

On first glance, resonance effects also make the wrong prediction. Phenyl groups are known to stabilize cations by resonance, and our data indicate less stabilization by phenyl. However, there is a way around this difficulty which, regretfully, we suggested might be a rationalization of much of the data in Table I.[6] Briefly, if the resonance interactions of the phenyl group with the neutral ion precursor are greater (more stabilizing) than its resonance interactions with the ion, then the observed behavior is predicted. This is the familiar case of resonance stabilization of the ground state applied to yet another system.

The ortho ester ionization was studied to test this explanation. In the ortho esters, resonance stabilization of the ion precursor is impossible; the central carbon is sp^3 hybridized. Resonance stabilization of the ion is possible. Thus, if resonance stabilization of the ground state is the correct explanation, the destabilization by phenyl relative to methyl should not be observed with cations derived from an ortho ester. As shown in Table II, destabilization by phenyl is observed, and this explanation must be rejected.

One additional possibility must be considered. This is that the effect of replacing a methyl by a phenyl is in different directions when measured by ΔG than when measured by ΔH. In other words, even though this change has an unfavorable ΔH, it may have a favorable ΔG. This would mean a large favorable ΔS change upon substitution. One can visualize this happening as follows. Charge is much more delocalized in the phenyl-substituted ion. The solvation requirements at the cation center are reduced, and the molecule is less tightly solvated or specifically solvated by fewer solvent molecules. This might provide the requisite favorable ΔS. One argument against this picture is the good linearity between ΔG and ΔH observed in several systems by Arnett and co-workers[3,13,14] and by

Katritzky.[15] The explanation outlined above would require that the parallel increases in both ΔG and ΔH observed in several systems be reversed. There is no reason for expecting a reversal in these systems. A number of the ion systems studied are not capable of hydrogen bond donation to the solvent and both Arnett[16] and Taft[17] have shown that solvent interactions of such charged-delocalized cations are small and similar. Thus solvent–solute interactions capable of causing the effect observed here would be exceptional.

Another argument for the unimportance of solvent effects can be made. Numerous examples of the destabilization of cations by phenyl relative to methyl exist in the literature. Some selected examples appear in Table III. It is clear from the heats of complexation of ketones with Lewis acids that there is nothing special about the proton causing this effect. Its observation with cyclopropenyl and cyclopentenyl cations shows that the presence of heteroatoms is not necessary. Most importantly, its existence in a very wide range of solvents, from benzene and carbon tetrachloride through water to superacids, argues strongly against specific solvation as an important factor in this effect. If solvation is playing a role, it is the very generalized role of stabilizing the cations by surrounding them with a dielectric medium. This will reduce the stabilizing effect of phenyl due to polarizability and resonance interactions by providing additional stabilization of the cation over that found in the gas phase. It is possible that the demand for stabilization by these cations in the gas phase will be enough higher to increase resonance and polarization stabilization by phenyl to the extent that the "normal" order is seen. The only way to discern the role of general nonspecific solvation is to compare gas-phase data with solution measurements. We hope the results reported here will lead to appropriate gas-phase measurements by some of our colleagues equipped to do them. Without gas-phase measurements we cannot rule out solvation. We can, however, claim that if solvation is involved in the observed effect, it is of a very nonspecific variety.

All that remains to be considered is the difference in inductive effects. Phenyl is electron withdrawing by induction compared to methyl, and this is expected, in the absence of other effects, to result in a destabilization as observed. In resonance terminology, the stability gained by resonance interactions with phenyl is overwhelmed by the inductive electron-withdrawing effect. The observed destabilization by phenyl would then be the result of two competing interactions, inductive destabilization and resonance stabilization. Since resonance delocalization is stabilizing, the observed charge delocalization occurs. Since the overall stability is dominated by the destabilizing inductive effect, the result is increasing charge delocalization coupled with decreasing stability.

It is generally accepted that the magnitude of resonance stabilization depends on "demand". A highly stable cation will derive less resonance stabilization from a phenyl group than will a less stable cation. The limiting case of this behavior would be a system so stable that no resonance or inductive stabilization is observed. The ferrocenyl cation shows this property.[18] The oxocarbonium ions show

(11) J. H. Hildebrand and R. L. Scott, "The Solubility of Non-electrolytes", 3rd ed., Dover Publications, New York, 1965.

(12) J. I. Brauman, J. M. Riveros, and L. K. Blair, *J. Am. Chem. Soc.*, **93**, 3914 (1971).

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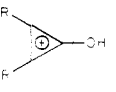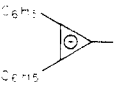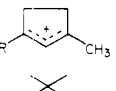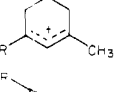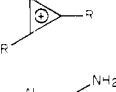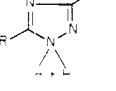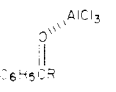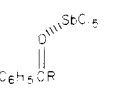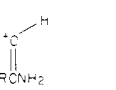
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(16) E. M. Arnett and C. Petro, *J. Am. Chem. Soc.*, **100**, 5408 (1978).

(17) J. F. Wolf, J. L. M. Abbound, and R. W. Taft, *J. Org. Chem.*, **42**, 3316 (1977).

(18) J. W. Larsen and P. Ashkenazi, *J. Am. Chem. Soc.*, **97**, 2140 (1975).

Table III. Effect of Phenyl and Methyl Substituents on the Thermodynamic Stability of Cations

ion	solvent	stability[k]		exptl technique	ref
		R = C_6H_5	R = Me		
(structure)	H_2SO_4(aq)	-2.5^l	-1.5^l	NMR	a
(structure)	50 aqueous acetonitrile	2.80^m	3.8^m	spectrophotometric titration	b
(structure)	H_2SO_4(aq)	50^n	35^n	UV acidity function	c
(structure)	H_2SO_4(aq)	52^n	50^n	UV acidity function	c
(structure)	H_2O	3.1^o	7.4^o	UV acidity function	d
(structure)	H_2O / acetone	3.65^p / 5.93^p	4.43^p / 7.69^p	titration	e
(structure)	chlorobenzene	-15.4^q	-19.2^q	calorimetric	f
(structure)	benzene	-5.9^q	-8.1^q	calorimetric	g
(structure)	H_2O (H_2SO_4) / H_2O (HCl)	-2.01^p / -1.90^p	-1.35^p / -1.35^p	UV acidity function	h
$RC{\equiv}N\|\|\|\|$ HOMe	CCl_4	153.5^r	159^r	IR	i
$RN{\equiv}C\|\|\|\|$ HOC_6H_5	CCl_4	203^s	228^s	IR	i
$RC{\equiv}^+NH$	H_2SO_4	0.069 ± 0.009^t	0.157 ± 0.014^t	conductivity	j

a R. Breslow and L. J. Altman, *J. Am. Chem. Soc.*, **88**, 504 (1966). *b* R. Breslow, H. Horen, and H. W. Chang, *J. Am. Chem. Soc.*, **84**, 3168 (1962). See also R. C. Kerber and C. Hsu, *ibid.*, **95**, 3239 (1973). *c* N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *J. Am. Chem. Soc.*, **87**, 4533 (1965). *d* M. R. Wasielewski and R. Breslow, *J. Am. Chem. Soc.*, **98**, 4222 (1976). *e* M. G. Voronkov, T. V. Kashik, V. V. Makarskii, V. A. Lapyrev, S. M. Ponomareva, and E. F. Shibanova, *Dokl. Akad. Nauk. SSSR*, **227**, 282 (1976). *f* M. H. Dilke, D. C. Ely, and M. G. Shepperd, *Trans. Faraday Soc.*, **46**, 262 (1950). *g* R. C. Paul, S. C. Ahlywalia, and R. Darbosh, *Inidan J. Chem.*, **6**, 464 (1968). *h* J. T. Edwards and S. C. R. Meacoch, *J. Chem. Soc*, 2000 (1957). N. F. Hall, *J. Am. Chem. Soc.*, **52**, 5115 (1930). *i* P. v. R. Schleyer and A. Allerhand, *J. Am. Chem. Soc.*, **84**, 1322 (1962). *j* M. Liler and D. Kosanovic, *J. Chem. Soc.*, 1084 (1958). *k* The quantity measured is given in the following footnotes. *l* [HO⁻] at half-protonation. *m* pK, with *n*-Pr and not Me. *n* [H_2SO_4] at half-protonation in percent. *o* pK_{R^+}. *p* pK. *q* Heat of complexation in killocalories per mole. *r* $\Delta\nu$ (cm⁻¹) for MeO-H. *s* $\Delta\nu$ (cm⁻¹) for C_6H_5O-H. *t* K_b.

no overall dependence of this substituent effect on ion stability. Probably solvation differences are dominating the situation. The large substituent effect on the dimethoxy- and diethoxycarbonium ions deserves comment. For the acylium ions, the least stable ion studied, the difference between methyl and phenyl is 5.4 ± 0.4 kcal/mol while for the diethoxycarbonium ion this difference is 4.6 ± 1.2 kcal/mol, identical within experimental error. Stabilization should decrease with the more stable ion, yet it does not. An explanation of this behavior can be found in Kresge's work on the dimethoxycarbonium ion.

He studied the effect of a phenyl group (compared to hydrogen) on the cyclic dioxolenium ion (II) and on the open dimethoxycarbonium ion (III).[19] In the cyclic case,

(structures I, II, III)
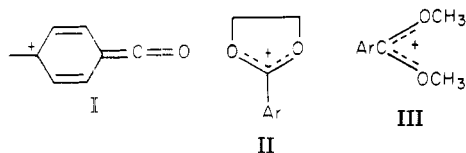
phenyl accelerated the rate of hydrolysis while in the acyclic case, it diminished it. This behavior was convincingly ascribed to steric inhibition of resonance in the acyclic case but not in the cyclic ion. For the cyclic ion in sulfuric acid, we observe a methyl–phenyl difference of 1.6 kcal/mol while the acyclic dimethoxycarbonium ion shows a difference of 3.8 kcal/mol. As mentioned, this difference is even larger with the diethoxycarbonium ion. These data are explained nicely by invoking steric inhibition of resonance in the acyclic but not in the cyclic ions, a la Kresge. With the diminution of resonance interactions, inductive effects are more obvious, and the methyl–phenyl difference increases. As the alkyl groups grow in size in the acyclic ion, the effect increases. Kresge's conclusion is supported by our data. However, this explanation should not be generalized. There is no evidence for steric inhibition of resonance in the dioxolenium ions, and it certainly cannot be invoked in the linear $ArC^+{=}O$.

(19) Y. Chiang, A. J. Kresge, P. Salomaa, and C. I. Young, *J. Am. Chem. Soc.*, **96**, 4494 (1974).

A general explanation for the destabilization of delocalized carbocations by phenyl when compared to methyl must still be sought.

There is no question but that charge is delocalized into the aromatic ring if NMR evidence is creditable.[20] Olah has studied the ^{13}C NMR spectra of acylium ions and concluded that ketenelike resonance structures (e.g., I) are important.[7] The ^{13}C NMR spectra of the protonated ketones have recently been discussed and indicate significant charge delocalization into the benzene ring.[21] The proton chemical shifts of the methylenes of dioxolenium ions (II) are sensitive to substituents in the aromatic ring,[22] consistent with charge delocalization. However, the dependence is small. Also, a small dependence of the chemical shift of the methyl protons of a series of aryldialkoxycarbonium ions has been reported.[23] However, a ^{13}C NMR and ESCA study of the methyldialkoxycarbonium ion showed *no* charge on the methyl substituent.[24] It seems safe to conclude that the charge is delocalized into the aromatic ring and that probably the amount of delocalization decreases as the ions become more stable. Such delocalization would not occur if there were not a driving force for it. It does occur, and it must increase the stability of the system. It is likely that these systems are stabilized by resonance, but this stabilizing effect is not sufficient to overcome some other destabilizing effect introduced when methyl is replaced by phenyl. The two prime candidates are inductive electron withdrawal by the phenyl or, less likely, changes in the solvation of the ion. Our understanding of the individual factors responsible for the

stability changes observed when a phenyl group replaces a methyl group is incomplete and rudimentary.

Gas-phase measurements will permit an evaluation of the importance of solvation, and we hope such measurements will soon be made. The separation between inductive and resonance effects can be made in a number of ways. Detailed molecular orbital calculations on these systems would seem to be the most fruitful approach, and we are taking this route. The interplay between delocalization and stabilization in these systems is fascinating and hopefully will soon be understood.

Experimental Section

The calorimeter and its use have been described previously.[25,26] All ortho esters used are commercially available. They were purified by careful distillation (under N_2) onto 3-Å molecular sieves, stored under nitrogen, and used within 24 h of the distillation. The acid chlorides were either commercial products or were prepared by reacting the appropriate carboxylic acid with $SOCl_2$.

Registry No. 2-Propanone, 67-64-1; 1-phenylethanone, 98-86-2; diphenylmethanone, 119-61-9; ethyl acetate, 141-78-6; ethyl benzoate, 93-89-0; 2-methyl-2-propen-1-ol acetate, 820-71-3; 2-methyl-2-propen-1-ol benzoate, 829-53-8; 4-hydroxy-3-penten-2-one, 1522-20-9; 4-hydroxy-4-phenyl-3-buten-2-one, 1704-14-9; 3-hydroxy-1,3-diphenyl-2-propen-1-one, 1704-15-0; cyclohexanecarbonyl chloride, 2719-27-9; acetyl chloride, 75-36-5; benzoyl chloride, 98-88-4; 1,1,1-trimethoxyethane, 1445-45-0; (trimethoxymethyl)benzene, 707-07-3; 1,1,1-triethoxyethane, 78-39-7; 1,1,1-triethoxypropane, 115-80-0; (triethoxymethyl)benzene, 1663-61-2.

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Solvent Effects in the Nitration of Nitrobenzene

Kenji Fujiwara, Takayuki Andoh, Mitsuru Arai, Masamitsu Tamura, and Tadao Yoshida*

Department of Reaction Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

Results obtained from nitration of nitrobenzene and methyl phenyl sulfone with nitronium hexafluorophosphate in nitromethane gave a good Hammett relationship using σ^+ as the substituent constant ($\rho = -8.5$, $n = 11$, $r = 0.99$), in contrast to the results for the nitration with nitric acid in sulfuric acid. Different partial rate factors (prf's) and isomer proportions in both nitromethane and sulfuric acid suggested that the species undergoing nitration are different in the two solvents. Semiempirical molecular orbital calculation of reactivities of free and hydrogen-bonded complexes of nitrobenzene indicated that one of the complexes of nitrobenzene played important roles in its nitration in concentrated sulfuric acid.

The rate of aromatic nitration has been reported to obey the Hammett $\sigma^+\rho$ relationship by Brown and Okamoto.[1] However, the number of substrates suitable for determining the intrinsic prf's is limited for the nitration in aqueous sulfuric acid, because of the encounter-rate control,[2] side reactions,[3] solvent effects such as protonation

and hydrogen-bonded complex formation, and so on. For example, the points on σ^+ plots for the nitration of nitrobenzene and methyl phenyl sulfone in aqueous sulfuric acid deviate from the line obtained for other substrates,[4,5] on the order of $\sim 10^{-3}$.

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