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 ¹³C NMR spectra of acylium ions and concluded that ketenelike resonance structures (e.g., I) are important.⁷ The ¹³C 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 aryldialkoxy-carbonium ions has been reported.²³ However, a ¹³C 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

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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 N2) 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 SOCl₂.

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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-1,3diphenyl-2-propen-1-one, 1704-15-0; cyclohexanecarbonyl chloride, 2719-27-9; acetyl chloride, 75-36-5; benzoyl chloride, 98-88-4; 1,1,1trimethoxyethane, 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.

Solvent Effects in the Nitration of Nitrobenzene

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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 = -8.5, n = 10, n = -8.5, n = 10, n = -8.5, n = 10, n = -8.5, n0.99), 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

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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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This paper deals with the effects of the hydrogen bonding on the reactivity of nitrobenzene, which cannot be protonated in 80-98.5% sulfuric acid.⁶

Experimental Section

Materials. Spectroscopic grade nitromethane and methylene chloride were dried with molecular sieves. Commercial nitrobenzene, methyl phenyl sulfone, isomers of dinitrobenzene, 1,2,3,4-tetrachlorobenzene, and octachloropropane were used without further purification. 1.3.5-Trinitrobenzene was employed after recrystallization. Nitronium hexafluorophosphate was purchased from Ozark-Mahoning Co. and purified by the method described previously.⁷ Pure nitric acid was prepared by distillation under reduced pressure of 98% nitric acid with an equal volume of 98% sulfuric acid and stored at -10 °C. The compositions of aqueous and fuming sulfuric acid solutions were determined by titration with a 0.1 N standard solution of sodium hydroxide.

Isomer Proportions for the Nitration in Aqueous and Fuming Sulfuric Acid. Solutions of nitrobenzene (0.06 M) and nitric acid (0.24 M) in 98.5% sulfuric acid (10 mL) were placed in a two-legged tube at 25 °C. After being mixed, the reaction mixture was kept for 10 half-lives and then quenched in ice-water (200 mL). The mixture was extracted with methylene chloride, washed with 5% aqueous sodium carbonate and water, and dried with magnesium sulfate. The removal of the solvent gave dinitrobenzenes. Similar experiments were carried out by using 80-103% sulfuric acid as the reaction medium.

Isomer proportions of dinitrobenzene were determined by gas-liquid chromatography with a Yanagimoto Model G800 gas chromatograph equipped with a thermal conductivity detector and a 5 m \times 3 mm diameter silicone DC QF-1 column. Before these experiments, a similar experiment was carried out with 1.0 g of nitrobenzene. The yield of dinitrobenzenes, which were the sole substances isolated, was more than 95%.

Isomer Proportions for the Nitration with Nitronium Hexafluorophosphate in Nitromethane. A nitromethane solution (2 mL) of nitronium salt (0.12 M) was added dropwise to another nitromethane solution (2 mL) of nitrobenzene (0.67 M) with shaking in a drybox at room temperature. After 10 min, 10 mL of diethyl ether was poured onto the reaction solution, and the etheral layer was washed with water and dried with magnesium sulfate. Similar experiments were carried out for methyl phenyl sulfone. The products from nitrobenzene were isolated by the same procedure as described above. For the determination of isomer proportions of the nitrated methyl phenyl sulfone, NMR spectra of the products dissolved in acetone- d_6 were recorded on a JEOL-PS100 with Me₄Si as an internal standard.

Relative Rates for the Nitration with Nitronium Salt in Nitromethane. A Union Giken Co. Model MX-7 was used for mixing the substrates and the nitronium salt in nitromethane solutions. Nitrobenzene (0.8 mmol) and 1,2,3,4-tetrachlorobenzene (0.5 mmol) with octachloropropane (0.3 mmol) as an internal standard were dissolved in 10 mL of nitromethane. Another reactant solution was prepared by dissolving the nitronium salt (0.2 mmol) in 2 mL of nitromethane. These solutions were prepared and used in a drybox containing phosphorus pentoxide as a drying agent. Samples (0.625 mL) of each of the solution were taken from resorvoirs into syringes and ejected into the flasks. The reaction solution was treated as before and analyzed for products.

The competitive nitration of methyl phenyl sulfone with 1,2,3,4-tetrachlorobenzene in the presence of 1,3,5-trinitrobenzene as an internal standard was carried out similarly.

Calculations⁸

In order to get information on the reactivities of complexes of nitrobenzene and solvent molecules, some semiempirical all-valence-electron MO calculations were carried out. The reactivities of monosubstituted benzene

Table I.	Electron Densities on Benzyl Protons $(Q_{H(2,3)})$
and	Estimated Partial Rate Factors (prf's) for
	Approximate Models of Nitrobenzene

<u> </u>		estim	estim log prf	
model	$Q_{H(2,3)}^{a}$	1 ^b	2^c	log prf
benzene	0.9973		0	
m-NB	0.9899		-6.03	-5.73
p-NB	0.9890		-6.76	-7.09
$m - NB \cdot H_2O$	0.9889		-6.84	
p-NB·H ₂ O	0.9880		-7.58	
m-NB-HSO	0.9976		+0.28	
$p \cdot \text{NB} \cdot \text{HSO}_{4}$	0.9955		-1.44	
$m - NB \cdot H_2 SO_4$	0.9849		-10.12	
p-NB·H ₂ SO ₄	0.9833		-11.43	
$m \cdot NB \cdot H_2O \cdot H_2SO_4$	0.9863		8.97	
p-NB·H ₂ O·H ₂ SO ₄	0.9849		- 10.12	
m-NB·H ₃ O ⁺	0.9752	-29.17	-18.06	
$p - NB \cdot H_3O^+$	0.9712	-31.32	-21.34	
$m - NB \cdot H_5O_2^+$	0.9762	-27.92	-17.25	
p-NBH _s O ₂ ⁺	0.9723	-29.90	-20.44	
$a Q_{\rm III}(x) = (Q_{\rm III}(x) +$	Q_{TT}	^b Estin	nated by	L^+ c Es-

 $(2_{\rm H(2)} + Q_{\rm H(3)})/2.$ Estimated by L^{*} . timated by $\Delta Q_{H(2,3)}$.

have been known to correlate well with a CNDO/2 proton-localization energy (L^+) .⁹ Unfortunately, the calculations do not converge for any complexes such as $PhNO_2 \cdot H_2SO_4$ and $PhNO_2 \cdot H_2O \cdot H_2SO_4$.

Instead of the localization energy, electron densities of the benzyl protons of monosubstituted toluene were employed as reactivity indices for the complexes. The average electron densities $(Q_{H(2,3)})$ of two benzyl protons, H(2) and H(3), of approximate models I and II were linearly cor-



related with L^+ for free and complexed nitrobenzenes.⁸ Therefore, prf's for the important complexes of nitrobenzene were estimated also from $Q_{H(2,3)}$. The results are listed in Table I.

Results

Isomer Proportions. The results for the nitration of nitrobenzene with nitric acid in 80-98.5% sulfuric acid and in oleum and with nitronium salt in nitromethane are given in Table II along with those by Tillett et al.¹⁰ and Olah et al.11

Relative Rates. The relative rates of nitrobenzene and methyl phenyl sulfone to 1,2,3,4-tetrachlorobenzene for the nitration with the nitronium salt in nitromethane are also listed in Table II. The relative rates of the substrates over benzene were calculated from the above data and the relative rates⁴ of 1,2,3,4-tetrachlorobenzene over benzene for the nitration with nitric acid in aqueous sulfuric acid.

Discussion

Species Undergoing Nitration in Sulfuric Acid. The rates of nitration of most compounds involving ni-

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Table II.	Isomer Proportions and	Relative	Rates for the	Nitration of N	Nitrobenzene and	Methyl Phenyl	Sulfone at 25 °C
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		isomer proportions, %		rel ra	ite	
nitrating agent	solvent	0	m	p	1ª	2 ^b
		Niti	robenzene	5		
NO, *PF, *	MeNO,	11.1	86.9	1.9	0.45	$7.2 imes 10^{-7}$
	-	10.0	88.5	1.5^{c}		
NO, PF	96% H ₂ SO ₄	7.1	91.5	1.4^{c}		
HNÔ, °	85.2-98.5% H ₁ SO₄	6.7	91.8	1.6		
HNO	80.2-90.0% H _{SO} (50 °C)	9.4	88.3	2.2		
HNO,	oleum (102,5%)	4.9	93.0	2.1		
HNO ³	H ₂ SO ₄	6.12	91.8	2.06^{d}		
		Methyl F	henyl Su	lfone		
NO ₂ ⁺ PF ₆	MeNO ₂	10.8	89	0.2^e	3.1	$5.0 imes 10^{-6}$

^a Rate relative to 1,2,3,4-tetrachlorobenzene. ^b Rate relative to benzene. $k_{\text{TCB}}/k_{\text{B}} = 1.6 \times 10^{-64}$ was used. ^c Data obtained by Olah et al.¹¹ ^d Data obtained by Tillett et al.¹⁰ ^e Meta and para isomers could not be separated. The para isomer was neglected in the calculations for the prf's.

trobenzene increase with an increase of the concentration of sulfuric acid up to ca. 90% sulfuric acid.¹² As the rate of nitration of nitrobenzene in 80% sulfuric acid at 25 °C was too slow, in 80-90% sulfuric acid, it was nitrated at 50 °C. No change in both the isomer proportions in 85-98.5% sulfuric acid at 25 °C and those in 80-90% sulfuric acid at 50 °C was observed. It means that the proportions do not vary in 80-98.5% sulfuric acid. As far as methyl phenyl sulfone was concerned, the isomer proportions changed with the concentration of sulfuric acid.⁵ However, the isomer proportions in sulfuric acid of both substrates were different from those in nitromethane. This suggests that the species undergoing nitration or the nitrating agents in these solvents are different in reactivity. If the reactivities of nitrating agents are different in these solvents, the nitrating agents in aqueous sulfuric acid should be weaker than that in nitromethane, as discussed by Olah et al.,¹¹ because the positional selectivity in the former solvent is higher than that in the latter. If the nitrating agent (NO_2^+) in more diluted sulfuric acid interacts with water to form a weaker nitrating agent, the positional selectivities of the above substrates should become higher with decreasing acidity, and the tendency in variation of the positional selectivities with acidity should be independent of the substrates. However, this was not the case. The experimental results suggest that the species undergoing nitration are different in the two solvents.

Free substrates could not be important as species undergoing nitration in 80-98.5% sulfuric acid as described later in the Hammett relationship section.

Species such as H_2SO_4 , $H_2O \cdot H_2SO_4$, H_2O , HSO_4^- , H_3O^+ , $H_5O_2^+$, and $H_3SO_4^+$ are known to be present in 80–98% sulfuric acid,¹³ and the crystal structure of $H_2O \cdot H_2SO_4$ has been determined.¹⁴ Also, the adducts of nitrobenzene with $H_2SO_4^{15}$ and H_2O^{16} are reported. The possibility of the formation of a hydrogen-bonded complex between pchloronitrobenzene and sulfuric acid has been reported by Gillespie et al.¹⁷ Hence, nitrobenzene in sulfuric acid is expected to form hydrogen-bonded complexes with some of the above-mentioned species. Concentration and reactivity determine whether it plays important roles in nitration.

The estimated prf's of PhNO₂·H₃O⁺ and PhNO₂·H₅O₂⁺ are too low to compete with other coexisting neutral species (Table I). Similarly, it is reasonable that $PhNO_{2}H_{3}SO_{4}^{+}$ may be excluded from the species undergoing nitration.

The reactivity of PhNO₂·HSO₄⁻ was estimated to be higher than that of free nitrobenzene and similar to that of benzene. However, it may not be a species which undergoes nitration for the following reasons. The solubility of nitrobenzene in very dilute sulfuric acid (0-60%) does not increase with an increase in acidity.¹⁸ in spite of an increase in the concentration of bisulfate ions. And the CNDO/S calculations¹⁹ indicate that the UV maximum absorption of PhNO₂·HSO₄⁻ was calculated at shorter wavelength (250.7 nm) than that for $PhNO_2$ (252 nm) or for $PhNO_2 \cdot nH_2O$ (n = 1 and 2) (258 and 264 nm, respectively), while the UV maximum absorption of nitrobenzene in aqueous sulfuric acid shifts in the red direction with an increase in acidity. Therefore, it could be present in only very low concentration.

The estimated reactivities of the remaining species decrease in the following order: $PhNO_2 \cdot H_2O > PhNO_2 \cdot H_2O \cdot H_2SO_4 > PhNO_2 \cdot H_2SO_4$ (Table I). As the concentrations of H_2O and $H_2O \cdot H_2SO_4$ in oleum and the estimated prf's of protonated nitrobenzene are extremely low, only the reaction of PhNO₂·H₂SO₄ will be observed in oleum. The isomer proportions of dinitrobenzenes which were observed in oleum were different from those in aqueous sulfuric acid (Table II). This discussion makes it possible to exclude the participation of $PhNO_2 H_2SO_4$ in the nitration in 80-98.5% sulfuric acid.

Unfortunately, we have no information available for the concentrations of $PhNO_2 \cdot H_2O$ and $PhNO_2 \cdot H_2O \cdot H_2SO_4$. It is therefore difficult to determine which of them is more important as the species undergoing nitration in aqueous sulfuric acid.

So far, the decrease in the nitration rate of nitrobenzene with >90% sulfuric acid has been explained in terms of "a variation of the activity of the reactant or the transition state while the concentration of the reactant is unchanged".²¹ Now we would like to explain the decrease in the rate in >90% sulfuric acid by the decrease in the concentration of the species undergoing nitration

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Figure 1. Relationship between the selected partial rate factors for nitration and σ^+ : 1; p-Me, 2; m-Me, 3; H, 4; p-Cl, 5; p-Br, 6; m-F 7; m-Cl, 8; m-Br, 9; m-SO₂Me, 10; m-NO₂, 11; p-NO₂.

 $(PhNO_2 \cdot H_2O \text{ or } PhNO_2 \cdot H_2O \cdot H_2SO_4)$, which is mainly due to the increase in the concentration of $PhNO_2 \cdot H_2SO_4$.

As far as methyl phenyl sulfone was concerned, it was assumed in a previous paper⁵ that the change in isomer proportion with acidity was due to a hydrogen-bonded complex. The contrast of isomer proportion in nitromethane with those in sulfuric acid⁵ supports this assumption. However, we cannot give a more detailed discussion except to say that free methyl phenyl sulfone is not important in the nitration in sulfuric acid, because it is too complicated to determine what are the species undergoing nitration by the same treatment as that for nitrobenzene.

Hammett Relationship for the Nitration of Nitrobenzene and Methyl Phenyl Sulfone. As pointed out earlier, the prf's of nitrobenzene and methyl phenyl sulfone for the nitration in aqueous sulfuric acid were lower than expected.^{4,5} It can be explained in terms of the above discussion.

If we use the selected prf's for nitration, a good Hammett relationship is obtained as shown in Figure 1 (ρ = -8.5, n = 11, r = 0.99). The prf's used for nitrobenzene and methyl phenyl sulfone were calculated from the values listed in Table II. For the relative rate of toluene, the value of 79 was adopted. It was obtained by Ridd et al.²² as the intrinsic one by comparing the relative rate for nitration with that for bromination. Other prf's come from the report of Coombes et al.⁴ A better linearity of the points on σ^+ plots may be due to the fact that the species undergoing nitration for these substrates are kinetically free substrates, and the rates are not influenced by the solvation under the experimental conditions used. Supposing this speculation is right, the observed ortho isomers (11.1%)and 10.8% yields) are the results of the nitration of "free" nitrobenzene and methyl phenyl sulfone.

Registry No. Nitrobenzene, 98-95-3; methyl phenyl sulfone, 3112-85-4; nitronium hexafluorophosphate, 19200-21-6.

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Sesterterpenes from Spongia idia

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The sponge Spongia idia (=Leiosella idia) from Pt. Loma, San Diego, contained both linear and pentacyclic sesterterpenes. The linear sesterterpenes were identified as furospinulosin-1 (1) and idiadione (2). The pentacyclic sesterterpenes were heteronemin (3), 12-epideoxoscalarin (4), 12-deacetyl-12,18-diepiscalaradial (5), scalarafuran (6), and scalarolide (7). The structures of idiadione (2), scalarafuran (6), and scalarolide (7) were determined from spectral data and chemical interconversions. An ecological function for these molecules is proposed.

It has generally been assumed that the production of secondary metabolites by a marine sponge contributes to the survival of the sponge. We are investigating the hypothesis that certain sponge metabolites act to deter potential predators and/or prevent surface overgrowth. Spongia idia de Laubenfels (=Leiosella idia) was one of the most commonly encountered sponges in a spongedominated assemblage at an ecological study site off Pt. Loma, San Diego. S. idia did not appear to suffer predation, except by a specific dorid nudibranch, and its surface was rarely overgrown. We have therefore isolated and identified the major secondary metabolites from S. *idia* and have shown that some of these metabolites were active in bioassays employing adult and larval forms of common marine algae and invertebrates.

Sponges of the order Dictyoceratida, of which Spongia *idia* is an example, are known as a source of sesterterpenes, an otherwise rare group of terpenoids. Linear sesterterpenes have been isolated from various Ircinia species¹ while pentacyclic sesterterpenes, often referred to as the scalarins, have been isolated from Cacospongia scalaris,² C. mollior,³ Spongia nitens,⁴ and Heteronema erecta.⁵ In this paper, we report the unusual occurrence of both linear and pentacyclic sesterterpenes from Spongia idia.

The hexane-soluble material extracted from the lyophilized sponge was chromatographed on silica gel to obtain two linear sesterterpenes, furospinulosin-1 (1; 0.4% dry weight) and idiadione (2; 1.2% dry weight), and five pentacyclic sesterterpenes: heteronemin (3; 1.7% dry weight), 12-epideoxoscalarin (4; 0.7% dry weight), 12-deacetyl-12,18-diepiscalaradial (5; 0.2% dry weight), scalarafuran (6; 0.2% dry weight), and scalarolide (7; 0.3% dry weight) (see Chart I). Furospinulosin-1 (1),^{1a} heteronemin

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