

added, c_{DI_2} will increase, but owing to nonspecific effects, γ_{I_2} may vary also. It can be shown that in very dilute solutions both c_{DI_2} and γ_{I_2} (or its reciprocal) vary linearly with donor concentration;^{13,14} therefore, the total solubility increase reflects both specific and nonspecific effects. It should be obvious from eq 1 that knowledge of γ_{I_2} would permit the unambiguous determination of c_{I_2} and, by difference, c_{DI_2} ; knowledge of c_{DI_2} permits determination of the concentration of uncomplexed donor (c_D). Therefore, if γ_{I_2} were known as a function of c_D , it would be possible to obtain values of $c_{DI_2}/(c_D c_{I_2})$ in the very dilute concentration region and to extrapolate these values to infinite dilution to obtain the thermodynamic equilibrium constant K_c .

The equations of solubility parameter theory (for a mixed solvent)¹⁵ may be used to estimate γ_{I_2} as a function of c_D for several aromatic donor-iodine systems for which K_c has been determined by both the polyiodide solubility method and the Benesi-Hildebrand (BH) spectral technique.¹⁶ Table I shows values of K_c

Table I. Equilibrium Constants for Several Donor-Iodine Complexes in Heptane at 25°C^a

Donor	$K_c^{(s)},^b$ l. mol ⁻¹	$K_c^{(corr),^c}$ l. mol ⁻¹	$K_c^{(BH),^d}$ l. mol ⁻¹
Benzene	0.37	0.15	0.20
Toluene	0.50	0.28	0.32
<i>o</i> -Xylene	0.64	0.37	0.42
<i>p</i> -Xylene	0.64	0.40	0.41
<i>m</i> -Xylene	0.70	0.46	0.54
Mesitylene	0.98	0.71	0.74

^a From ref 5b. ^b $K_c^{(s)}$ values are obtained directly from the polyiodide solubility results, assuming $\gamma_{I_2} = 1$. ^c $K_c^{(corr)}$ values have been corrected for γ_{I_2} , estimated from solubility parameter theory. ^d $K_c^{(BH)}$ values have been inferred using the Benesi-Hildebrand analysis, assuming $\gamma_{DA} = \gamma_D \gamma_A$.

obtained directly from the uncorrected solubility method, values corrected for changes in γ_{I_2} , and values obtained using the BH analysis of spectral data for more concentrated solutions. The agreement between the corrected solubility results and the BH results is remarkably good, indicating that $\gamma_{DI_2} \approx \gamma_D \gamma_{I_2}$ in these systems. This is not to suggest that activity coefficient effects will in general cancel so neatly, but, at least in the case of the important aromatic hydrocarbon complexes, the spectral and solubility results can be brought into near agreement by estimating γ_{I_2} from simple nonelectrolyte solution theory.

Finally, it should be noted that properties of the electronic spectral bands of donor-iodine complexes inferred from the uncorrected solubility results (ignoring activity coefficient effects) are in better agreement with trends predicted from the Mulliken theory^{1,17} than are results inferred from the BH or corrected solubility

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methods.^{5,18} In the case of relatively weak complexes it may be argued that the total effect of donor-iodine interactions (random plus specific) should be considered in relating spectral intensities and frequency shifts to donor strength. Since the uncorrected solubility results comprise both types of effects, they should therefore be simpler to interpret theoretically. This point of view is not very different from that expressed by Orgel and Mulliken,² who introduced the concept of "contact charge transfer" to explain the anomalous variation of spectral band intensities with donor strength for weak complexes which had been investigated with the BH technique.

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(18) A puzzling result of the BH spectral studies is that in a series of weak complexes such as those between the aromatic donors and iodine the molar absorptivities of the charge-transfer band do not increase uniformly as the donor strength increases;^{1,2} in fact, there is an abrupt drop in absorptivity in the series benzene·I₂-toluene·I₂-xylene·I₂, and the absorptivity rises again as more highly alkylated donors are employed. The polyiodide solubility results yield absorptivity values which are all in the range 6900 ± 1200 l. mol⁻¹ cm⁻¹ for the complexes listed in Table I.^{5b} Moreover, the uncorrected solubility results lead to simple correlations between complex stability and the intensities and frequency shifts of the blue-shifted iodine bands of the aromatic donor complexes.^{5b}

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Substituent Effects in Gas-Phase Ionic Nitration and Acetylation of Aromatics

Sir:

We report the observation using ion cyclotron resonance (icr) spectroscopy of marked substituent effects on the gas-phase reaction rates of (NO₂)⁺ and (CH₃CO)⁺ transfer to a variety of substituted benzenes and heteroaromatic compounds. Although substituent effects in gas-phase ionic reactions have never been examined under conditions comparable to those employed in this work a number of studies have dealt with ion-molecule reactions involving aromatic compounds.¹⁻¹⁰ Of particular interest are the results of Cacace,^{4,5} *et al.*, on tritiation by strong Brønsted acids, in which a substantial positional selectivity is observed, but little rate selectivity.

(1) S. A. Benzra, M. K. Hoffman, and M. M. Bursey, *J. Amer. Chem. Soc.*, **92**, 7501 (1970); M. K. Hoffman and M. M. Bursey, *Tetrahedron Lett.*, 2539 (1971).

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(5) F. Cacace, R. Cipollini, and G. Occhiucci, *J. Chem. Soc., Perkin Trans. 2*, 84 (1972).

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We have examined substituent effects for reactions 1 and 2 using a Varian Associates ICR-9 spectrometer.



Rather than attempting absolute rate determinations, the rates of the reactions were determined relative to the rates for benzene by competition experiments. The $\text{CH}_2\text{ONO}_2^+$ reactant ion was generated by electron bombardment at 14 eV from ethyl nitrate and was allowed to react competitively at about 5×10^{-5} Torr with a mixture of two aromatic species, with the relative peak heights of the two possible product ions (corrected for mass discrimination) giving the relative reaction rates for the two aromatic substrates. In contrast to the analogous competition techniques in solution, no uncertainties can arise from incomplete mixing, since mixing is rapid and depletion of the neutral reactants is negligible, so that the relative intensities of the product ions should be a true measure of the relative reaction rates. A similar procedure was followed using $(\text{CH}_3\text{CO})_2^+$ generated from biacetyl at 14 eV. Neutral reactant concentrations were determined from low-pressure icr spectra with appropriate calibration and standardization.

Bursey, *et al.*,¹ have investigated the ionic reactions of benzene with ethyl nitrate at an ionizing voltage of 30 eV. We find that at 14 eV only three primary ions are formed with significant abundance, NO_2^+ and $\text{CH}_2\text{ONO}_2^+$ from ethyl nitrate, and C_6H_6^+ from benzene. The only significant secondary ions formed are $\text{C}_2\text{H}_5\text{ONO}_2\text{NO}_2^+$ (m/e 136), $\text{C}_6\text{H}_6\text{O}^+$ (m/e 94), and $\text{C}_6\text{H}_6\text{NO}_2^+$ (m/e 108). In agreement with Bursey, *et al.*,¹ we find by ion cyclotron double resonance that $\text{C}_6\text{H}_6\text{O}^+$ has NO_2^+ as its precursor. Therefore, in the present study the only ion arising from reaction of benzene with $\text{CH}_2\text{ONO}_2^+$ is $\text{C}_6\text{H}_6\text{NO}_2^+$. This reaction was confirmed by double resonance. This was found to be true for all aromatic substrates investigated: attack on the aromatic molecule by $\text{CH}_2\text{ONO}_2^+$ either followed reaction 1 or gave no product at all. The aromatic parent cations were also shown by double resonance not to yield significant ArHNO_2^+ .

In mixtures of biacetyl with aromatics, acetyl ion, biacetyl ion, and triacetyl ion were all observed in agreement with Bursey, *et al.*² Double resonance showed that acetyl ion did not give acetylated product, but both biacetyl ion and triacetyl ion gave the ArHCOCH_3^+ product.

Double resonance showed small contributions of aromatic parent cations to the acetylated products, and corrections were made to the rates to allow for these contributions.

For benzene and toluene, double resonance showed that the triacetyl ion was not a significant precursor. For aniline, anisole, and nitrobenzene, the very large product peaks (ranging from 34 to 140 times as large as in benzene) were found to be largely due to triacetyl ion, and because of masking of the biacetyl ion reaction by the much faster triacetyl ion reaction, and the strong reactive coupling between biacetyl and triacetyl ions, no rate could be determined for the biacetyl ion reactions under the present conditions.¹¹ For pyrrole, the bi-

acetyl ion reaction was determined to be about one-tenth as fast as the triacetyl ion reaction.¹²

Table I shows the relative rates determined for re-

Table I. Relative Reaction Rates^a for Substituted Benzenes and Heteroaromatic Compounds

Neutral reactant	Ionic reactant	
	$\text{CH}_2\text{ONO}_2^+$	$(\text{CH}_3\text{CO})_2^+$
Benzene	1.0	1.0
Benzene- <i>d</i> ₆	1.0	1.0
Aniline	0	<i>b</i>
Anisole	0	<i>b</i>
Nitrobenzene	10	<i>b</i>
Pyrrole	0	~1.5 ^c
Ethylbenzene	0	
Toluene	0.3	1.5
Cyclopropylbenzene	0	
Chlorobenzene	0.25	
α,α,α -Trifluorotoluene	0.3	0
Pyridine	0.3	
Fluorobenzene	0.55	0
Xylene (<i>o</i> , <i>m</i> , or <i>p</i>)	0	0
<i>o</i> -Difluorobenzene	0.25	0
<i>m</i> -Difluorobenzene	0.3	0
<i>p</i> -Difluorobenzene	0	0
Pentafluorobenzene	0	0
<i>p</i> -Bromoanisole	0	0
1,3,4-Trimethoxybenzene	0	0.05

^a Uncertain to about ± 0.05 . ^b The rate of the biacetyl cation reaction could not be determined because of masking by a very fast reaction with triacetyl cation reactant. ^c Corrected for contribution of triacetyl cation reaction to the product. Probably uncertain to ± 0.2 .

actions 1 and 2 for various aromatic substrates. The substituent effects are large, in contrast to the theoretical prediction of the simple Stevenson-Gioumoussis model,¹⁰ and also in contrast to previous gas-phase results (using conditions and reactants substantially different from those of the present study), and it is evident that specific chemical effects are particularly prominent under the mild conditions of the icr experiments. While direct attachment to the ring substituent cannot be ruled out, the observation that the rates decline drastically for reactions of difluorobenzene, pentafluorobenzene, xylene, bromoanisole, and trimethoxybenzene relative to corresponding monosubstituted compounds suggests that attachment to the fluoro, methyl, anilino, and methoxy groups at least is not important.

The rates for reaction 2 indicate the influence of normal inductive substituent effects, and the rates qualitatively parallel the substituent effects in solution-phase electrophilic substitution. Thus, for example, toluene is slightly faster than benzene and α,α,α -trifluorotoluene is immeasurably slow. It appears that $(\text{CH}_3\text{CO})^+$ transfer in the gas phase is an electrophilic reaction corresponding to solution-phase aromatic acetylation, but with the degree of selectivity considera-

triacetyl ion reactions, obtained using source irradiation in a flat icr cell, were in disagreement with his own results on the same systems, and were in fact erroneous. The double resonance results reported here were obtained using analyzer irradiation in a square icr cell.

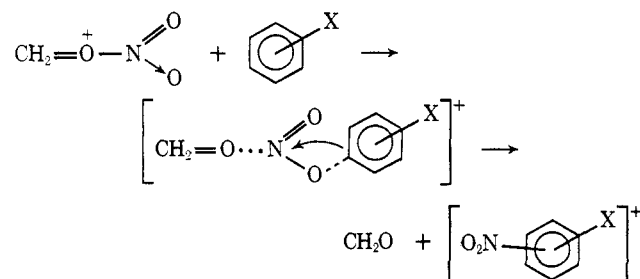
(12) The comparison of the rates of the biacetyl and triacetyl ion reactions in the presence of the strong reactive coupling between biacetyl and triacetyl ions was accomplished using a triple resonance experiment in which the triacetyl ions were totally ejected from the cell by cyclotron ejection,¹³ while the reactive coupling between biacetyl and acetylated pyrrole was simultaneously determined by normal double resonance.

(13) R. C. Dunbar, *J. Amer. Chem. Soc.*, **93**, 4354 (1971).

(11) We are greatly indebted to Professor Maurice Bursey for pointing out to us that our double resonance comparisons between biacetyl and

bly lower due to the high reactivity of the gaseous cations.

Reaction 1, by contrast, shows an inverted order of relative rates. Thus, for instance, fluorobenzene and α,α,α -trifluorotoluene react as fast or faster than toluene and aniline. There is qualitatively an inverse correlation between the gas-phase relative rates of reaction 1 and the relative rates of solution-phase electrophilic reactions, and this strongly suggests that reaction 1 in the gas phase is nucleophilic in character, and thus does not correspond at all to solution-phase electrophilic nitration by the NO_2^+ ion. We tentatively suggest as a possible rationalization of this unexpected result that reaction 1 involves primary electrostatic interaction of the aromatic substrate with the nucleophilic terminal oxygen of the $\text{CH}_2\text{ONO}_2^+$ cation, followed by displacement by the aromatic ring on nitrogen, with simultaneous elimination of formaldehyde.



We believe this to be the first clearcut case in which two gas-phase cation-molecule reactions with aromatic substrates have been observed with one reaction showing nucleophilic, the other electrophilic substituent effects on the reaction rates.

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Electrophilic Reaction at Single Bonds. XIII.¹ Chlorination and Chlorolysis of Alkanes in $\text{SbF}_5\text{-Cl}_2\text{-SO}_2\text{ClF}$ Solution at Low Temperature

Sir:

In preceding studies, we have shown the reactivity of alkanes in typical electrophilic reactions such as protolytic processes (isomerization, hydrogen-deuterium exchange, protolysis),² alkylation,³ and nitration.⁴ We presently would like to report the chlorination and chlorolysis⁵ of alkanes in $\text{SbF}_5\text{-Cl}_2\text{-SO}_2\text{ClF}$ solution,⁶ a powerful new electrophilic chlorinating system.⁷

(1) Part XII: G. A. Olah, Y. Halpern, J. Shen, and Y. K. Mo, *J. Amer. Chem. Soc.*, submitted for publication.

(2) G. A. Olah, Y. Halpern, J. Shen, and Y. K. Mo, *ibid.*, **93**, 1251 (1971).

(3) (a) G. A. Olah and J. A. Olah, *ibid.*, **93**, 1256 (1971); (b) G. A. Olah, Y. K. Mo, and J. A. Olah, *ibid.*, submitted for publication.

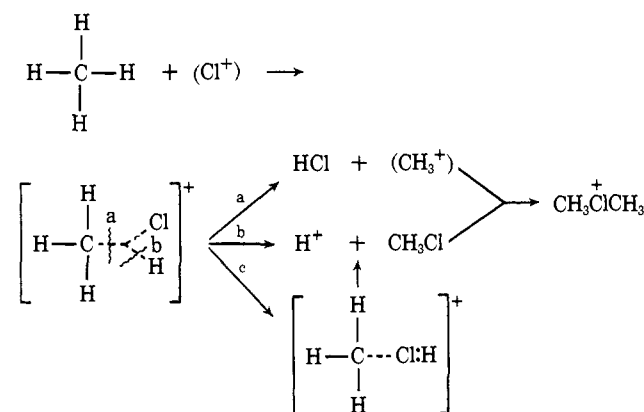
(4) G. A. Olah and H. C. Lin, *ibid.*, **93**, 1259 (1971).

(5) The terms are defined as substitution (of hydrogen for a chlorine atom) and chlorolytic cleavage (of C-C bonds), respectively.

(6) The solution was prepared by condensed excess Cl_2 in $\text{SbF}_5\text{-SO}_2\text{ClF}$ solution at -78° .

Methane reacts in $\text{SbF}_5\text{-Cl}_2\text{-SO}_2\text{ClF}$ solution at -78° to give dimethylchloronium ion exclusively. As a small amount of HF can always be present in the $\text{SbF}_5\text{-SO}_2\text{ClF}$ solution, a protolytic process of methane leading to the formation of CH_3^+ and H_2 would also seem possible. The formed methyl cation then could react with chlorine to give methyl chloride. However, methane as well as ethane, to be discussed subsequently, do not react with $\text{SbF}_5\text{-SO}_2\text{ClF}$ at -78° . In fact, protolytic cleavage of methane can be achieved only above room temperature in $\text{FSO}_3\text{H-SbF}_5$ solution to give trimethylcarbenium ion as a main product. Furthermore, both methane and ethane do not react with $\text{Cl}_2\text{-SO}_2\text{ClF}$ in the absence of SbF_5 under the same reaction conditions. Consequently, the formation of dimethylchloronium ion from methane in $\text{SbF}_5\text{-Cl}_2\text{-SO}_2\text{ClF}$ can be rationalized as depicted in Scheme I.

Scheme I



The electrophile (" $\text{Cl}^{+\cdot}$ ")⁸ attacks the C-H bond through a two-electron three-center bound transition state to give either (CH_3^+) and HCl (a route) or H^+ and CH_3Cl (b route). Under the stable ion conditions, dimethylchloronium ion is formed. It is also possible that the hydrogen involved in the three-center bond may intramolecularly shift to the n -donor chlorine site $(\text{CH}_2\text{-Cl:H})^+$ (c route), which subsequently deprotonates to methyl chloride.

Alternatively, the $\text{Cl}^{+\cdot}$ (or $\text{Cl}_2^{+\cdot}$) radical cation (*i.e.*, the triplet state) could also be involved in the reaction. If this is the case, the transition state would involve three-center three-electron bond formation cleaving to HCl and $\text{CH}_3\cdot$, the latter initiating radical chain chlorination of methane. Methyl chloride subsequently would form with SbF_5 the dimethylchloronium ion. That no radical chain chlorination is probable in the system is demonstrated when toluene is treated under identical conditions and only electrophilic (mostly ortho-para) ring-chlorinated products are obtained. When excess methane was treated with $\text{SbF}_5\text{-Cl}_2\text{-SO}_2\text{ClF}$ in a bomb at room temperature for 24 hr, it gave besides dimethylchloronium ion (in solution), methyl chloride (in gas phase). No methylene chloride is formed, indicating the absence of less selective radical chlorination.

(7) The electrophilic chlorination of aromatic systems with this reagent was reported: G. A. Olah, H. C. Lin, and Y. K. Mo, *J. Amer. Chem. Soc.*, **94**, 3667 (1972).

(8) For simplicity, we are depicting the electrophile as " $\text{Cl}^{+\cdot}$ " although there is presently no evidence for the existence of the chloronium ion, $\text{Cl}_2\text{-SbF}_5$, or any well-defined species in the system. Studies relating to the nature of the active chlorinating agent will be reported separately.