

The linear least-squares correlations of relaxation rates with ρ for the deuterons are:

$$\begin{aligned} 1/T_{ax} &= 27.57\rho + 1.546 \\ 1/T_{eq} &= 15.50\rho + 1.686 \end{aligned} \quad (5)$$

with standard deviations of 0.158 and 0.101 s⁻¹ respectively for axial and equatorial relaxation rates. The estimate of the ratios of T_1 values (T_{ax}/T_{eq}) in the uncomplexed and complexed compound can be estimated by setting $\rho = 0$ and $\rho = 1$, respectively. Using standard statistical procedures¹⁷ for estimating uncertainties of the extrapolated values, the ratios (90% confidence interval) are:

$$\begin{aligned} T_{ax}/T_{eq} &= 1.09 \pm 0.08 \quad (\text{uncomplexed molecule}) \\ T_{ax}/T_{eq} &= 0.59 \pm 0.05 \quad (\text{complexed molecule}) \end{aligned} \quad (6)$$

The experimental value of 1.09 for T_{ax}/T_{eq} of the uncomplexed molecule agrees with the theoretical value of 1.093.¹⁸ Comparison of $T_{ax}/T_{eq} = 0.59$ for the complexed molecule with the above value of 1.09 shows that the inversion of T_{ax}/T_{eq} upon addition of shift reagent occurs as is predicted from theory for a bent C=O—M angle. A comparison of 0.59 with the theoretical values in Table I would suggest even a more bent C=O—M angle (~150°) than the value ~160° proposed by Schneider and Weigand.² However, because of the approximations involved, this should not be viewed as a serious discrepancy. As in the previously reported case,¹ the paramagnetic dipolar relaxation effects usually associated with shift reagents appear to be completely dominated by the quadrupolar relaxation mechanism as verified by separate experiments employing the diamagnetic La(fod)₃ reagent.

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- The program STRAIN (Cf. E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 8005 (1973), and J. D. Andose and K. Mislou, *ibid.*, **96**, 2168 (1974)) was kindly provided by Professor Kurt Mislou. Results of the calculation which are particularly critical to the evaluation of T_{ax}/T_{eq} for the shift reagent complex of **1** are the bond distances and bond angles associated with the carbonyl group and its attached methylene groups. Bond distances (denoted by r) are $r_{CO} = 1.224$ Å, $r_{CC} = 1.507$ Å, $r_{CH} = 1.098$ Å; bond angles are $\angle CCO = 122.8^\circ$, $\angle CCH(\text{axial}) = 106.5^\circ$, $\angle CCH(\text{equatorial}) = 106.4^\circ$; and dihedral angles are $\angle HCCO(\text{axial}) = 115.2^\circ$, $\angle HCCO(\text{equatorial}) = -1.0^\circ$.
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- In separate experiments in which ca. 5% deuteriochloroform was employed as an internal reference a ratio of T_{ax}/T_{eq} of 1.06 was obtained. Although deuteriochloroform may affect the absolute magnitudes of T_1 of both deuterons this value for the ratio of relaxation times also indicated $T_{ax} > T_{eq}$.

Gaseous Ionic Acetylation of Some Substituted Anisoles. Evidence for an Intermediate π Complex

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Abstract: Rates of reaction of CH_3CO^+ , $\text{CH}_3\text{CO}(\text{COCH}_3)\text{CH}_3^+$, and $\text{CH}_3\text{COCO}(\text{COCH}_3)\text{CH}_3^+$ with methyl- and halogen-substituted anisoles were measured. The rates are not always less than the ADO limit, but for the methylanisoles and the cresols reported previously an excellent linear relation between rates for different reagent ions holds for unsubstituted and para-substituted neutrals. For the more closely substituted neutrals, a different relation holds. The interpretation totally consistent with results requires a π complex with transfer to oxygen. The halogenated anisoles react with these ions too slowly to measure, behaving similarly to other halogenated aromatics; ions corresponding to the mass of the products expected from them were shown in some cases to be products of reactions of ions derived from the aromatic compound.

The nature of interactions in the collision complex between an ion and a molecule when both are moderately complex has not been greatly explored. When molecules approach the size of interest to the physical organic chemist, however, relationships not seen in reactions of very simple species have been observed. We wish to report a striking example detected in the last set of compounds from a large series which we have investigated over the past several years.

Others have noted that the rates of gas-phase reactions of aromatic compounds with the $(\text{CH}_3\text{CO})_2^+$ ion may be correlated roughly with the Hammett σ function, the substituent of the aromatic compound influencing the rate in a way

suggesting an electrophilic attack upon the ring.¹ The range of observed rates is rather small, about two, in comparison to the range of effects in solution, which may be many orders of magnitude larger. The absolute values of these rate constants were not reported, but the rate of attack of $(\text{CH}_3\text{CO})_2^+$ on pyrrole was found to be 4.3×10^{-10} cm³ molecule⁻¹ s⁻¹,² which is about 30% of the calculated³ rate; many other rates of acetylation of aromatic compounds are no more than two orders of magnitude less than the calculated rate of collision.

Likewise, it was found that proton transfer from toluene to allyl anion in the gas phase, which has a rate constant of 7.5

Table I. Rates of Acetylation of Substituted Anisoles^a

Substituent	CH ₃ CO ⁺							
	Exptl		Calcd	CH ₃ CO(COCH ₃)CH ₃ ⁺		CH ₃ COCO(COCH ₃)-CH ₃ ⁺		
	From CH ₃ COCH ₃	From CH ₃ COCOCH ₃		Exptl	Calcd	Exptl	Calcd	
H	0	0	1.79	0.29	1.37	1.4	1.29	
<i>o</i> -CH ₃	0.20	1.9	1.74	0.40	1.32	0.95	1.24	
<i>m</i> -CH ₃	0	0.18	1.77	0.54	1.34	1.6	1.26	
<i>p</i> -CH ₃	0	0.35	1.80	0.30	1.37	1.6	1.29	
<i>p</i> -C ₂ H ₅	0	0	1.65	0.37	1.24	2.5	1.16	

^a Units of 10⁻⁹ cm³/molecule s.

× 10⁻¹¹ cm³ molecule⁻¹ s⁻¹, may be catalyzed by the introduction of methanol.⁴ In this case the proton transfer from methanol to allyl anion has a rate constant of 2.5 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ and that from toluene to methoxide anion has one of 2.0 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹. Thus the catalysis of the reaction by supplying a reagent which interacts differently with aromatic systems increases the rate only by a factor of three, but nevertheless the overall rate is well within two orders of magnitude of the theoretical limit.

Finally, we note that changes in rates of attachment of acetyl ion to isomers of ketones and esters can be made by changing only the stereochemistry of the functional group.^{5,6} Again, even though the rate constants are within two orders of magnitude of the theoretical limit for these processes, details of the interactions in the collision complex play an important role in the overall rate of reaction. Here the effects produce no greater effect than a factor of three to seven.

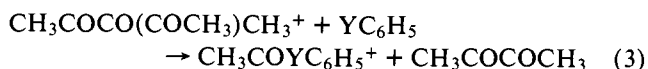
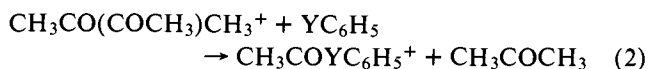
It therefore is apparent that there are interactions in collision complexes which play a qualitatively predictable role in making changes in reaction-rate constants for ion-molecule reactions, even though these rate constants are fairly close to the theoretical limit. Nevertheless, the observed magnitude of these changes is less than an order of magnitude. At such an approach to the limit, there is difficulty even with the concept of an activation energy⁷ and the interpretation of correlations with the Hammett equation, catalysis, and steric inhibition to reaction must be explored from other directions. We wish to report data for the acetylation of substituted anisoles, which conclude our investigations of these reactions and which indicate that these kinds of unexpected results, qualitatively similar to solution chemistry, are now extended to quantitative relationships.

Experimental Section

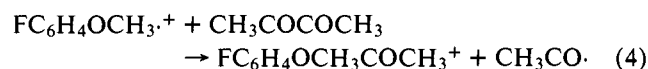
Details of the experimental technique, the rationale for estimation of the experimental error in rate constants, and the analysis of the kinetic scheme used are given in a previous paper in this series.⁸ The only new experimental data to be added here are results of experiments to establish the relative pumping speeds of the components. They are: acetone, 1.00; 2,3-butanedione, 1.1; anisole, 1.2; *o*-methylanisole, 1.0; *m*-methylanisole, 1.0; *p*-methylanisole, 1.0; *o*-fluoroanisole, 1.1. As before, we estimate absolute error as ±20%, but relative error as ±3%.

Results and Discussion

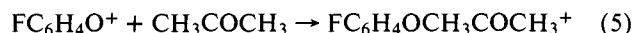
The reactions indicated in the equations



are generally the only important reactions observed in mixtures of alkylanisoles and either acetone (eq 2) or 2,3-butanedione (eq 3). Unlike other systems noted previously,^{9,10} there are no adducts formed with acetone; indeed, there are no ion-molecule products observed save the ions of interest, the M + 43 ions. However, in two cases of halogen-substituted anisoles these ions are formed by pathways not previously noted. In the case of *o*-fluoroanisole, the acetylated product is formed by a reaction of the molecular ion of the aromatic compound with neutral 2,3-butanedione.



This pathway has not been observed for any other aromatic compound we have studied. Additionally, for the mixture of acetone with either of the fluoroanisoles studied, the M + 43 peak has the (M - 15)⁺ ion of the aromatic compound as its precursor. This also has no precedent



and it is possible that the product of this reaction does not have the same structure as the acetylated ions formed by eq 1-3. The formation of an ionic product with no neutral product by eq 5 suggests that the aromatic π system is able to absorb the energy of the reaction; this parallels other reactions of aromatic systems, for example eq 1, where there is also no neutral product.¹¹ Equation 4 was determined by our previously used method to have a rate constant of 3.7 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ and eq 5 was found to have a rate constant of 1.2 × 10⁻¹¹ for the ortho isomer and 1.0 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ for the para. All of these are significantly less than even the Langevin model predicts. It is therefore concluded that the reactant ion and neutral undergo many unreactive collisions for each reactive collision that occurs.

The main effort of this study, however, is directed towards examples of eq 1-3. Results of these studies are given in Table I, along with results from parametrized average dipole orientation (ADO) theory using average polarizabilities.³ This provides a reasonably advanced form of theory, the theory for ion-quadrupole interactions¹² not yet being developed for molecules of low symmetry. It may be taken as a useful guide to the number of collisions (whether reactive or not) to be expected when the only interactions are the polarization of the molecule and the partial orientation of its dipole by the approaching ion, although it should be noted that rates in considerable excess of the calculated limit have been observed in our studies.

Reactions of CH₃CO⁺ with Anisoles. Among the substituted anisoles, the most reactive is *o*-methylanisole, the only compound here which reacts with acetyl ion from both sources. It recently was suggested that it would be difficult to find a reagent which distinguished ortho isomers from others,¹³ but

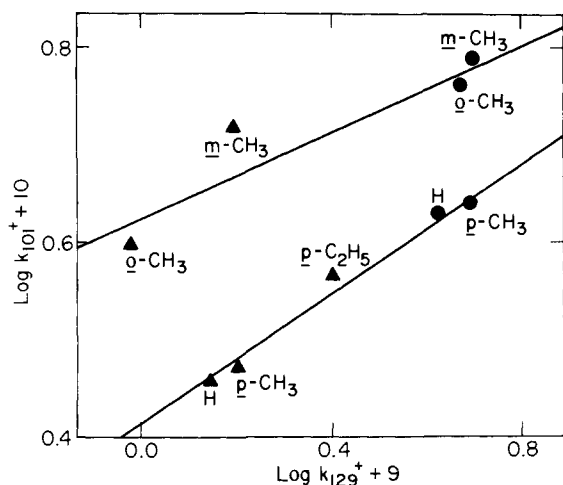


Figure 1. Correlations between the rate of acetylation of phenols (●) and their methyl ethers (▲) by m/e 129 ($\text{CH}_3\text{COCO}(\text{COCH}_3)\text{CH}_3^+$, eq 2) and 101 ($\text{CH}_3\text{CO}(\text{COCH}_3)\text{CH}_3^+$, eq 3). Upper line, $r = 0.90$, is for ortho- and meta-substituted compounds; lower line, $r = 0.99$, is for unsubstituted and para-substituted compounds. Relative error of data $< 6\%$.^{10,11}

CH_3CO^+ , especially from acetone, is clearly an example of a reagent ion which does so, not only distinguishing *o*-methylanisole by its reactivity, but also *o*-xylene,¹¹ *o*-cresol,⁸ and *o*-nitrotoluene¹⁰ from their isomers as well. We do not claim this to be a predictable result on the basis of our present understanding, however, and suggest only that specific interactions at close range between the ion and the molecule may govern reactivity. Theoretical studies of the most favorable site of attachment of a positive ion to some of these molecules have been completed. The process for achieving this most stable ion may be complex, however.

With the ion derived from 2,3-butanedione, all three isomers of methyl anisole were found to be reactive and in one case the rate is similar to that predicted by ADO theory. In other cases, collision is much less efficient and leads to reaction in only 10–20% of the cases.

Reactions of Anisoles with $\text{CH}_3\text{CO}(\text{COCH}_3)\text{CH}_3^+$ and $\text{CH}_3\text{COCO}(\text{COCH}_3)\text{CH}_3^+$. Table I suggests that reaction with the secondary ions in eq 3 and 4 follows trends noted before. On taking account of the usual 20% error in the experimental data, we find for those compounds which react with these acetylating agents that the rates are within the limit imposed by the average dipole orientation theory, except for the *p*-ethyl compound. The locked dipole model can resolve this conflict. Interesting trends which parallel, for the most part, trends in data for phenol⁹ and the cresols⁸ can be found. For example: the addition of a methyl group to phenol is observed to increase its rate of acetylation by 10–40%, irrespective of the substituent. So we find here with the anisoles that substitution by a methyl group in any position usually increases its rate of acetylation. For both the phenols and the anisoles, the substituent effects follow the same trend with position: for reaction with $\text{CH}_3\text{CO}(\text{COCH}_3)\text{CH}_3^+$ the rate increases in the order para $<$ ortho $<$ meta. For reaction with $\text{CH}_3\text{COCO}(\text{COCH}_3)\text{CH}_3^+$ the rate increases in the order ortho \approx meta \approx para. For reaction with both ions, relative reactivity of the ortho compound is suppressed among the anisoles compared to its relative reactivity among the cresols, and the suppression is especially dramatic for the larger ion, $\text{CH}_3\text{COCO}(\text{COCH}_3)\text{CH}_3^+$.

The reactivity of *o*-fluoroanisole, *p*-fluoroanisole, *o*-chloroanisole, and *p*-chloroanisole is so low that it could not be measured. The lowering of reactivity parallels the lowering of reactivity of the simple halobenzenes vs. that of benzene itself towards acetylating agents,⁹ but the reason may be more

complex. The reaction may simply be insufficiently exothermic to be seen. Alternatively, if the maximum tensor elements of the polarizability tensor are no longer oriented in the direction of the ether functional group but toward the halogen atom, any lock-in with the ion might direct the ion to an unreactive site in the molecule, even though the reaction might be sufficiently exothermic at other, less favored sites.

The unusually great reactivity of the *p*-ethylanisole is matched in aromatic systems by unusual reactivity of acetophenone, phenol, and the cresols. Possible explanations for this behavior have been discussed. There is no apparent structural relation between the aromatic compounds which react at an abnormally fast rate.

These results allow a testing of a common hypothesis in physical organic chemistry applied to these compounds. First of all, the rates of the reactions observed here do not fit the predictions of the best applicable physical theory of ion-molecule reactions, which predicts the ion-molecule reaction rates of simpler systems very well. Because of this failing, the controlling factors governing these reaction rates must be sought elsewhere besides the simple attraction between ions and polar molecules. They presumably lie in the close-range interactions between the ion and the molecule and manifest themselves in a complex intermolecular potential. Such a potential, in general, must be related to the structure of ion and neutral, for the proposed mechanism of catalysis of proton transfer noted earlier⁴ requires special interactions, the observation of the steric influence of both neutral⁵ and ionic¹⁴ reactant indicates such a sensitivity to structure, and observed correlations of rates with the electron-donating and -withdrawing properties of aromatic substituents¹ suggests a further type of correlation beyond simple steric parameters.

Conversion to an energy scale and comparison of the data in Table I with each other and with data drawn from previous work leads to the remarkably good correlations found in Figure 1, the size of the circles indicating relative error. These data comprise the largest set of ion-molecule reactions of moderately complex substances yet examined to uncover this sort of trend and the division of data into two sets is unmistakable. Within each set, the correlation is the best ever obtained for gaseous ionic reactions and is the first which may be considered quantitative. However, the results in no way are intended to constitute a correlation with Hammett parameters. The ortho substituents do not have Hammett constants and there is no general way to compare two classes of compound in the same plot in a Hammett correlation as is done here. The plot is a more general example of an energy correlation. The choice of compound is nevertheless extremely limited and one cannot expect the correlation to be of major predictive value; from our previous experience, major steric parameters will begin to influence the patterns upon extension to larger alkyl substituents and the lack of reactivity of compounds with other substituents, as noted above, makes it impossible to include them in the plot. In short, these are all the data expected to bear on the problem.

The point of finding the correlations is in resolving a portion of the mechanism of transfer of acetyl ion to these compounds. Of several hypotheses we have formulated, only one seems generally consistent with all of the details of the data. Discarding the others, we interpret the correlation to mean that the major reason for acceleration of the reaction with the $\text{CH}_3\text{COCO}(\text{COCH}_3)\text{CH}_3^+$ ion from biacetyl is the formation of a π complex at an intermediate stage of the reactive collision. We have commented before that the extended π system of this ion is more extended than that of the $\text{CH}_3\text{CO}(\text{COCH}_3)\text{CH}_3^+$ ion from acetone and that the generally greater reactivity of the former with aromatic systems is somehow related to the extended system.⁸ The data presented in Figure 1 reveal a much more detailed picture. First, the meta- and ortho-sub-

$\Delta\epsilon_F/\epsilon_F$ directly as a function of wavelength.¹⁵ This method has been successful in CD calculations of polynucleotides.¹⁶ The equation is

$$\frac{\Delta\epsilon_F}{\epsilon_F} = -\frac{2\pi}{\lambda} \frac{\sum_i \sum_{j \neq i} \phi_i \text{Im} A_{ij} \mathbf{R}_{ij} \cdot \mathbf{e}_i \times \mathbf{e}_j}{\sum_i \sum_{j \neq i} \phi_i \text{Im} A_{ij} \mathbf{e}_i \cdot \mathbf{e}_j} \quad (22)$$

$$A_{ij} = \left[\frac{\delta_{ij}}{\alpha_i(\lambda)} + G_{ij} \right]^{-1}$$

where λ is the wavelength and \mathbf{R}_{ij} is the distance between groups i and j . A_{ij} is the inverse of a matrix which has wavelength dependent complex polarizabilities, $\alpha_i(\lambda)$, on the diagonal and interaction terms ($G_{ij} = V_{ij}/|\mu_i||\mu_j|$) off the diagonal. Unit vectors \mathbf{e}_i and \mathbf{e}_j specify the directions of the one-dimensional polarizability tensors corresponding to each transition. The real and imaginary parts of the polarizability correspond to the refraction and absorption of the transition. Note that each transition is weighted by its effective fluorescence quantum yield, ϕ_i . The effective quantum yield characterizes the relative contribution of each transition to the measured fluorescence. It can take into account energy transfer and different efficiencies of detection for different fluorophores in the system.

The fluorescence quantum yield weighting of the transitions is particularly interesting for nonrigid molecules. The usual

CD measures the average over all conformations; FDCD measures the average over fluorescent conformations. Comparison of the two measurements will allow a better assessment of what conformations are present in the molecules.

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Studies in the Chiroptical Properties of Selenoamino Acids¹

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Abstract: The circular dichroism (CD) spectra of four selenium-containing amino acids were investigated and compared with those of their sulfur and methylene analogues. In the region 190–250 nm, positive Cotton effects of carboxyl and selenide (or sulfide) chromophores always correlate with L (= S) or L,L (= S,S) absolute configurations. The additive nature of such Cotton effects was demonstrated by a "difference curve" method, which permits the chiroptical properties of the Se (or S) chromophore to be determined. Results suggest that the C–Se–C selenide chromophore has three optically active transitions in the near uv range at approximately 225, 210, and 195–200 nm. The absolute configuration of natural (+)-selenocystathionine has been established spectroscopically to be L,L (= S,S), in agreement with enzymatic results.

Selenoamino acids first attracted interest during the latter part of the 1930's when it was shown that a cattle disease known as "alkali disease", found in parts of the United States, was closely connected with the selenium content of the soil, that plants were capable of accumulating selenium, and that the selenium so incorporated occurred in the protein fraction of the plants.^{3,4} Selenoamino acids were isolated from the plant material⁵ and proved to be highly toxic.⁶

These findings led to the synthesis of selenoamino acids by Fredga⁷ and by Zdansky.⁸ Walter and Roy⁹ have reviewed the selenopeptides and selenoproteins, an undiscovered territory only a decade ago.

Optically active selenocystathionine (**2**) has been isolated from plant material^{10,11} and was found to possess biological effects. Its absolute configuration was assigned as L on the basis of the lack of reactivity with D-amino acid oxidase.¹¹ However, the selenium compound could have inhibited the enzyme.

Since no chiroptical studies of selenoamino acids have been made, we decided to investigate this subject. Among the physical methods used for obtaining information on chiroptical properties, the technique of circular dichroism (CD) measurement is the most efficient since it gives precise data on the chirality of specific transitions. The acids under investigation contain two chromophores which absorb in the near-uv region: COOH and C–Se–C. References on simple carboxyl absorption indicate that the $n \rightarrow \pi^*$ transition occurs at approximately 210 nm and a $\pi \rightarrow \pi^*$ transition below 190 nm.¹² However, few literature references exist for the C–Se–C selenide chromophore. The solution spectrum (hexane) of diethylselenide¹³ reveals an absorption band at 250 nm (ϵ_{max} 50). In the similarly constituted dialkyl sulfides, the C–S–C sulfide chromophore has recently been shown^{14,15} to have several electronic transitions between 198 and 255 nm. The $n \rightarrow \sigma^*$ transitions of the C–Se–C chromophore may therefore be