For other trajectories, the $^{13}CH_3^+$ strips a C from the C_2H_4, and only dissociations to the left are allowed. This model envisions a potential surface of two reaction paths with very similar scrambling and energy partioning features. It is also similar to model IV in using reaction 2 data for the theory rather than using the theory to fit the reaction 2 data. The closeness of the original model I fit to the reaction 2 data, however, means the revised model outlined here has no significant effect on the predicted cross sections for reactions 3 and 5.

Of the two model I mechanisms, the revised version just presented rests upon the more reasonable assumptions. The existence of two mechanisms with similar net results seems more likely than the reversal of C atom momenta with each proton jump. Yet, without the experimental kinematic information, the original static version of model I would have been acceptable and simpler. This reaction thus illustrates the importance of examining the experimental reaction dynamics when considering simplified models for a reaction, and warns of the danger of viewing a reactive event in terms of static intermediates.

V. Conclusions

1. The reaction takes place via a direct mechanism, although considerable C and H scrambling occurs. All ionic products are predominantly formed forward of the center of mass.

2. In our energy range, the isotopic scrambling can be accounted for by a simple model involving linear intermediates.

3. Despite any scrambling processes, or the likelihood of two separate mechanisms, the kinematics of all products are similar. This behavior is more clearly illustrated by reaction 1 than the previously studied methyl cation–methane reaction,[19] but may prove typical for many reactions in which scrambling occurs. Experiments on other carbonium ion reactions are in progress. In addition, theoretical trajectory studies of this or similar reactions,[20] while difficult, might clarify the puzzling behavior of this system.

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(18) The rotational period can be calculated from the angular momentum, estimated by $L = \mu bg$ where μ is the reduced mass of the colliding reactants, g is the relative collisional velocity, and b is the maximum impact parameter leading to reaction, estimated from the cross section by $b = (\sigma/\pi)^{1/2}$. Then $\tau = 2\pi I/L$ where $I \approx \frac{1}{2}\mu b^2$.
(19) Consider the reaction of ref 5, $CH_3^+ + CH_4 \rightarrow C_2X_5^+ + X_2$, in which the majority of all isotopic ion products are forward scattered. This occurs regardless of the end of the $C_2H_7^+$ complex from which the X_2 dissociates.
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Gaseous Ionic Acetylation of Cresols

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Abstract: Rates of the ion–molecule reaction of o-, m-, and p-cresol with $CH_3COCO(COCH_3)CH_3^+$, $CH_3CO(COCH_3)CH_3^+$, and CH_3CO^+ were measured by ion cyclotron resonance and compared with calculated results. The relative insensitivity of the rate to the choice of neutral isomer was duplicated, but only modest agreement was found on examining sensitivity to the choice of ionic acetylating species.

There have been several approaches to the study of reactions resembling electrophilic aromatic substitutions in the gas phase. One approach has been through the ion cyclotron resonance technique.[3-5] The other has been through high-energy ion chemistry.[6-8] In addition, the acylation of oxygen-containing compounds has been studied by ion cyclotron resonance with the use of a variety of precursors.[9,10]

In connection with these studies, and in an attempt to explore the applicability of accepted theories of ion–molecule reaction rates to very complex organic reactions, we have now studied the rates of acetylation of the three isomeric cresols using two different precursors of the acetyl ion, acetone and biacetyl. Conventional ion cyclotron resonance (ICR) techniques were used.

Experimental Section

A Varian V-5900 ICR spectrometer was used for all experiments. It was equipped with a standard (1.27 × 2.54 × 14 cm)

three-section cell, grid modulation, split drift voltages, and a 20 l/s Noble Ion pump. Pulsed double resonance experiments were conducted while observing the usual precautions of low emission current (<100 nA) and small irradiating field strengths (<40 mV/cm).[11] Double resonance experiments were normally confirmed by lowering the emission current and the irradiating field strength to the lower limit of detection of the instrument. Ion ejection experiments were performed on ions of a given mass that double resonance experiments had indicated were precursor ions to products. Radiofrequency irradiation of 1200 mV/cm was applied to the upper source drift plate at the proper frequency and the magnetic field was scanned over the secondary or tertiary ion of interest. The difference in signal intensity with and without the double resonance irradiation is equal to the contribution of that particular precursor ion to the overall formation of the product ion under observation. In the case of the complex kinetic scheme where the ions are related by the two pathways $A^+ \rightarrow B^+ \rightarrow C^+$ and $A^+ \rightarrow C^+$ (which, it will be seen, is not pertinent to the present example but might have been), only ejection of B^+ gives an easily interpreted measure of the relative contributions of the two direct precursors A^+ and B^+ to C^+; ejection of A^+ reduces the amount of B^+ present too, and so increases the dependence of the intensity of C^+ on A^+ beyond the simple relationship.

The pressures generally employed for these studies were: acetone or biacetyl, 40×10^{-6} Torr; cresol, 2×10^{-6} Torr. Pressures of all compounds were corrected by calibration of the ion pump with a Datametrics Barocel capacitance manometer whose hysteresis was found to be <3% in the pressure region where its scale and the useful range of the ion pump overlapped. The pumping speeds of biacetyl, acetone, and a variety of simple mono- and disubstituted aromatic compounds were in the ratio 1.0:1.1:1.0 (±6%); this lack of equality may introduce a small error because of selective pumping of mixtures. A measure of the accuracy of the calibration may be estimated from the fact that the rate of the reaction

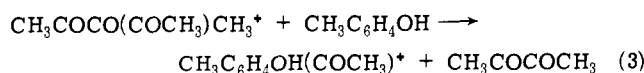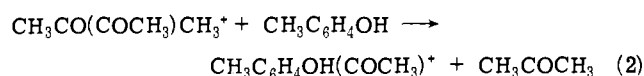$$CH_4\cdot^+ + CH_4 \longrightarrow CH_5^+ + CH_3\cdot \qquad (1)$$
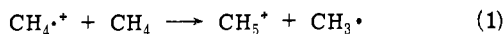
measured in this laboratory was within 8% of the most widely accepted value.

The compounds used were reagent grade commercial samples showing no impurities by mass spectrometric or chromatographic techniques. They were used as received, except for biacetyl, which was distilled shortly before usage.
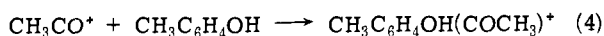
Results and Discussion

At 15 eV ionizing energy the ICR spectra of the cresols are simple; the molecular ion dominates the spectrum, and small $(M - 1)$ and $(M + 1)$ ions are also present. Mixtures of biacetyl and cresol give, in addition, the peaks at m/e 43, 86, and 129 due to biacetyl[9] and a peak at m/e 151 corresponding to acetylated cresol. Mixtures of acetone and cresol give peaks at m/e 43, 58, 59, and 101 due to acetone[12] and m/e 151. The protonation of cresol is not significant with respect to the acetylation of cresol under the conditions employed for the rate study, as will be noted.
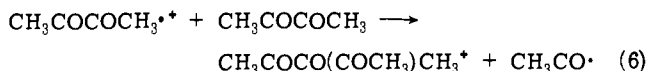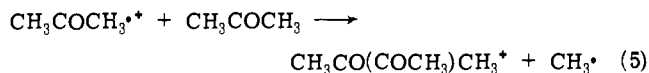
Except for the mixture of o-cresol and biacetyl, double resonance experiments indicated that at the pressures quoted in the Experimental Section the reaction pathway for acetylation of the cresols comes entirely from the transfer of CH_3CO^+ by acetylated ketone ions (eq 2 and 3). In the one

$$CH_3CO(COCH_3)CH_3^+ + CH_3C_6H_4OH \longrightarrow$$
$$CH_3C_6H_4OH(COCH_3)^+ + CH_3COCH_3 \quad (2)$$

$$CH_3COCO(COCH_3)CH_3^+ + CH_3C_6H_4OH \longrightarrow$$
$$CH_3C_6H_4OH(COCH_3)^+ + CH_3COCOCH_3 \quad (3)$$

exception, acetylation by CH_3CO^+ is also observed (eq 4).

$$CH_3CO^+ + CH_3C_6H_4OH \longrightarrow CH_3C_6H_4OH(COCH_3)^+ \quad (4)$$

This may be a consequence of a different energy content or distribution of states in CH_3CO^+ as a function of its origin. The rate constants for formation of the reagent ions (eq 5

$$CH_3COCH_3\cdot^+ + CH_3COCH_3 \longrightarrow$$
$$CH_3CO(COCH_3)CH_3^+ + CH_3\cdot \quad (5)$$

$$CH_3COCOCH_3\cdot^+ + CH_3COCOCH_3 \longrightarrow$$
$$CH_3COCO(COCH_3)CH_3^+ + CH_3CO\cdot \quad (6)$$

and 6) were determined by measuring the extent of the reaction as the pressure was varied.[13] The value of 7.5×10^{-10} cm³/(molecule sec) for eq 6 was determined separately by Dunbar and ourselves and reported before.[14] Our value of 2.0×10^{-10} cm³/(molecule sec) for eq 5 is in good agreement with the value of 1.9×10^{-10} cm³/(molecule sec) reported by MacNeil and Futrell.[12]

In principle one may solve for the rate constants for eq 2 and 3 by use of an exact method.[14,15] The conditions of our experiment, however, are such that simplifying assumptions may be made.

Consider the overall reaction scheme for the formation of acetylated cresol ion, MAc^+, to be
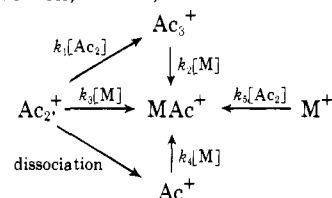
where Ac_2 is biacetyl (or more generally the acetylating agent) and M cresol (or more generally the neutral reaction); k_1 is the rate constant defined for eq 5 and 6, k_2 for eq 2 and 3, and k_4 for eq 4. In the present case some of these rate constants are too small to measure, but the general case is appropriate for discussion. Anicich and Bowers have derived an expression for secondary ion formation, e.g., for the formation of MAc^+ from Ac^+,[16] which may be expressed as

$$k_4 = \frac{A(MAc^+)}{A(Ac^+)\left[\frac{m(MAc^+)}{m(Ac^+)}\right]^2 + \left[\frac{t_S + (2t_A/3)}{t_S + (t_A/3)}\right]A(MAc^+)} \times$$
$$\frac{1}{[M]}\frac{1}{t_S + (t_A/3)} \quad (7)$$

where $A(MAc^+)$ is the power absorption of the ion MAc^+, $A(Ac^+)$ is the power absorption of the ion Ac^+, $m(MAc^+)$ is the m/e ratio of the acetylated product MAc^+, $m(Ac^+)$ is the m/e ratio of the ion Ac^+, t_S is the source residence time, t_A is the analyzer residence time, and $[M]$ is the concentration of neutral M. A similar expression may be written for k_1 when k_3 is negligible:

$$k_1 = \frac{A(Ac_3^+)}{A(Ac_2^+)\left[\frac{m(Ac_3^+)}{m(Ac_2^+)}\right]^2 + \left[\frac{t_S + (2t_A/3)}{t_S + (t_A/3)}\right]A(Ac_3^+)} \times$$
$$\frac{1}{[Ac_2]}\frac{1}{t_S + (t_A/3)} \quad (8)$$

Because k_1 is known, it is convenient to combine eq 7 and 8 in order to obtain k_4 in terms of k_1. Recalling that drift times are proportional to the m/e ratio of the ion, we write:

$$k_4 = k_1 \frac{C_1}{C_4} \frac{A(MAc^+)}{A(Ac_3^+)} \frac{[Ac_2]}{[M]} \frac{M(Ac_2^+)}{M(Ac^+)} \quad (9)$$

where

$$C_1 = A(Ac_2^+)\left[\frac{M(Ac_3^+)}{M(Ac_2^+)}\right]^2 + A(Ac_3^+)\left[\frac{t_S + (2t_A/3)}{t_S + (t_A/3)}\right] \quad (10)$$

$$C_4 = A(Ac^+)\left[\frac{M(MAc^+)}{M(Ac^+)}\right]^2 + A(MAc^+)\left[\frac{t_S + (2t_A/3)}{t_S + (t_A/3)}\right] \quad (11)$$

Table I. Observed and Calculated Rate Constants for Acetylation of the Cresols $(cm^3/(molecule\ sec))^a$

	Exptl	Gioumousis–Stevenson	Locked dipole	ADO
o-Cresol, eq 2	5.8×10^{-10}	1.14×10^{-9}	2.98×10^{-9}	1.42×10^{-9}
m-Cresol, eq 2	6.1×10^{-10}	1.14×10^{-9}	3.18×10^{-9}	1.45×10^{-9}
p-Cresol, eq 2	4.6×10^{-10}	1.14×10^{-9}	3.23×10^{-9}	1.45×10^{-9}
o-Cresol, eq 3	4.8×10^{-9}	1.08×10^{-9}	2.81×10^{-9}	1.34×10^{-9}
m-Cresol, eq 3	4.9×10^{-9}	1.08×10^{-9}	3.00×10^{-9}	1.37×10^{-9}
p-Cresol, eq 3	4.9×10^{-9}	1.08×10^{-9}	3.04×10^{-9}	1.37×10^{-9}
o-Cresol, eq 4	5.6×10^{-10}	1.49×10^{-9}	3.88×10^{-9}	1.85×10^{-9}

^{a} Estimated error as discussed in the text for differential pumping, calibration hysteresis, and inaccuracy of model, +10% and −15%.

One may also solve for k_5 and k_3 in terms of k_1 in like fashion

$$k_5 = k_1 \frac{C_1}{C_5} \frac{A(MAc^+)}{A(Ac_3^+)} \frac{M(Ac_2^+)}{M(M^+)} \quad (12)$$

where

$$C_5 = A(M^+)\left[\frac{M(MAc^+)}{M(M^+)}\right]^2 + A(MAc^+)\left[\frac{t_S + (2t_A/3)}{t_S + (t_A/3)}\right] \quad (13)$$

and where the concentration of Ac_2^+ ions is not seriously depleted by either competitive reaction

$$k_3 = k_1 \frac{C_1}{C_3} \frac{A(MAc^+)}{A(Ac_3^+)} \frac{[Ac_2]}{[M]} \quad (14)$$

where

$$C_3 = A(Ac_2^+)\left[\frac{M(MAc^+)}{M(Ac_2^+)}\right]^2 +$$
$$A(MAc^+)\left[\frac{t_S + (2t_A/3)}{t_S + (t_A/3)}\right] \quad (15)$$

Under the conditions of the present set of experiments, however, a special case exists. The source and analyzer drift times, as calculated by the method of McMahon and Beauchamp,[17] are such that about 30 half-lives of the primary ion at 40 μ Torr occur in the cell, 92% of these being in the analyzer. The underestimation of the rate constant based upon the assumption that $CH_3COCO(COCH_3)CH_3^+$ is formed immediately from its precursor will be about 40% for the sum of the first 3 half-lives and less than 1% during the sum of the remaining half-lives by simple consideration of the pseudo-first-order rate law obeyed here at constant pressure. Overall, then, the underestimation of the rate constant will be by slightly more than 4%. We make only this slight error, then, in treating $CH_3COCO(COCH_3)CH_3^+$ as a primary ion. An additional indication of the safety of this assumption is that the experimental rate constant measured in this way was not noticeably sensitive to modest variations in analyzer drift voltages nor to pressure changes. The depletion of $CH_3COCO(COCH_3)CH_3^+$ by cresol (M) is also small, about 5% at most. Using the same approach as before, we therefore write:

$$k_2 = k_1 \frac{C_1}{C_2} \frac{A(MAc^+)}{A(Ac_3^+)} \frac{[Ac_2]}{[M]} \frac{M(Ac_2^+)}{M(Ac_3^+)} \quad (16)$$

where

$$C_2 = A(Ac_3^+)\left[\frac{M(MAc^+)}{M(Ac_3^+)}\right]^2 +$$
$$A(MAc^+)\left[\frac{t_S + (2t_A/3)}{t_S + (t_A/3)}\right] \quad (17)$$

Acetylation by CH_3CO^+ was not observed with acetone as the reagent gas. This pathway for acetylation was observed, however, when biacetyl was the reagent gas. The relative amounts of acetylation by CH_3CO^+ and by $CH_3COCO(COCH_3)CH_3^+$ in mixtures of cresol and biacetyl were determined by ion ejection experiments. After the

appropriate [MAc$^+$] was identified in this manner, eq 9 was used to solve for k_4, and eq 16 to solve for k_2. In the other cases, where double resonance indicated only one precursor, [MAc$^+$] as read from the spectrum was used directly in eq 16. The rate constants obtained from this scheme are given in Table I. They refer to ambient temperature, 300°K, and are compared with results of the more common theoretical models of physical theory. The first of these is the model of Gioumousis and Stevenson,[18] which involves only the orbiting collision of a simple ion and a nonpolar, polarizable molecule. The second is the locked-dipole model of Moran and Hamill,[19] which takes account of the interaction of a dipole and a charge by assuming a fixed orientation of the dipole with respect to the ion as one orbits the other. The third is a method which assumes only partial orientation of the dipole with respect to the ion, the resulting interaction originally[20] being found empirically to reduce the full ion-dipole interaction by about 85%. This reduction corresponds to a partial orientation of the dipole over time (average dipole orientation, ADO, theory), so that one may think of the dipole as librating in the field of the ion. Finally, the factor corresponding to the empirical reduction has been evaluated in terms of the dipole moment and polarizability of the molecule in an attempt to justify its inclusion in the ADO theory.[21] Calculated results for each of these are shown in Table I; the factor from theory[21] and the empirical factor[20] for the ADO theory are coincidentally 0.15 in these cases. There are several interesting observations which can be made about these numbers. In any reaction, the rates for the three compounds are similar, within a given model for the reaction. This is a result of their very similar polarizabilities (they are isomers) and their dipole moments, which are within 12% of each other. Also, comparing the different acetylating agents, we note that the ion derived from acetone (eq 2) is always faster than the ion derived from biacetyl (eq 3); this result is a consequence of a reduced-mass term in the theoretical expressions.

In some respects, the predicted trends are matched by the actual results found in Table I. In both eq 2 and eq 3, the rates are very nearly the same for the three isomers, as would be expected in the absence of a steric effect of the alkyl group. It is known that a methyl group adjacent to a phenolic hydroxyl group does not seriously affect the rate of attack by qualitative comparisons of alkylated phenols.[22] The results for m- and p-cresol are in serious disagreement with predictions of the Hammett equation, which would call for substantially more rapid reaction of the para isomer in a situation involving formation of a positively charged species from a neutral; while examples of applicability of the Hammett equations to reactions of gaseous ions are known,[23] there is no reason to assume its applicability here. Thus the physical theory is more satisfactory in explaining this aspect of the results.

However, when one compares the absolute value of the rate constant obtained by experiment with the theoretical value, there is not good agreement. The rates calculated for eq 2 are too large by a factor of 2. Since the physical theory

may be interpreted as a theory predicting the rate of collision (irrespective of whether the collisions always result in reaction), this may be taken to indicate that not every collision results in reaction. On the other hand, the rates calculated for eq 3 are too small. The theory perhaps requires another term to overcome this objection; one may speculate that the most probable form of the ion in eq 3 is **1**, as seems

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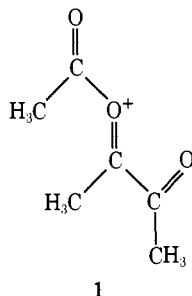
likely from the mechanism of reaction.[24] This ion is unlike others used in tests of ion–molecule theory; according to molecular-orbital (INDO) calculations, the charge is distributed over all of the heavy atoms to a great extent, and the highest filled orbital is a π orbital made up of contributions of p orbitals on all the heavy atoms.[25] Theory has not yet taken into account the effect of the polarizability of the ion nor the effect of a nonpoint charge. These omissions seem particularly striking in the present example and may account for the large difference between calculated and observed rates because of close-range interactions. The charge distribution and π system in **2**, the most likely structure of

2
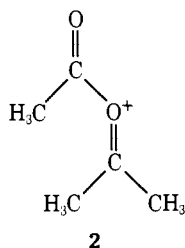
the reagent in eq 2, are less extensive. Additionally, one finds from inspection of models that **1** is geometrically able to form a π complex with the aromatic ring involving four ring atoms, while such an extensive interaction is not possible with **2**; this effect may affect reactivity upon collision. Whatever the nature of the cause of the difference in reactivity, it seems to be general; in studies of several dozen aromatic compounds, **1** reacts faster than **2** by factors ranging from 2 to 10.[26]

Thus, some of the factors recognized by organic chemists in complicated systems may be of importance here. However, there are not immediate and obvious analogies with the solution reactivity of cresols to be explored here. For example, from the viewpoint of differences in reactivity of the cresols, acetylation upon the oxygen atoms is subject to larger difference in rate. In ethyl acetate solvent, the reaction rate of the cresols varies by a factor of more than 4 as one goes from *p*-cresol to the slower *o*-cresol.[27] On the other hand, rate studies of the acylation of cresols on carbon do not appear to have been carried out. The Friedel–Crafts reaction of cresols in the presence of either strong proton donors or Lewis acids is a well-known high-yield reaction for both alkylation[28] and acylation,[29] and RCO$^+$ is sometimes invoked as the acylating species in the latter case.[30] Thus some retardation of the rate in the ortho compound is known for at least *O*-alkylation, but since we cannot test yet whether ionic acetylation in the gas phase occurs on oxygen

or carbon in the cresols, the correlation is of little value. The protonation of the cresols in superacid media has been shown to occur on both carbon and oxygen as a function of solvent,[31-34] and we have found that the isomeric acetylated ions with the acetyl group on ring carbons and on oxygen of a cresol molecule are often of similar energy according to INDO calculations.[25] Accordingly, there may be several channels into which the ion–molecule collision complex may collapse, leading to several products of the same mass.

It is clear that much work remains to be done on reactivity of simple aromatic systems toward electrophiles in the gas phase. We have accumulated a large amount of data on acetylation under these conditions which we shall report in subsequent articles.

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