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(24) Isomerization of $[RXA^+]$ is an extensive process depending upon the exothermicity of its formation reaction. The extent of isomerization of $[RXA^+]$ and the consequent isomeric distribution have been thoroughly investigated and will be presented in a separate paper.

(25) In agreement with thermochemical calculations on molecules structurally related to those of the present study, the unimolecular dissociation of $[RXA^+]_{exc}$, excited by the exothermicity of its formation process, is energetically allowed, except when the gaseous acid is $CH_3FCH_3^+$. The extent of unimolecular dissociation in analogous ionic intermediates has been extensively investigated by mass spectrometry and found to be related to the proton affinity of the leaving group. (a) Reference 18b. (b) Jardine, I.; Fenselau, C. *J. Am. Chem. Soc.* **1976**, *98*, 5086.

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Gas-Phase Acylation Reactions. Substrate and Positional Selectivity of Free Acetylium Ions toward Methylbenzenes

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Abstract: Free acetylium ions, obtained in the diluted gas state from the γ radiolysis of CH_3F–CO mixtures, have been allowed to react with methylbenzenes, in the pressure range 380–760 Torr, and in the presence of a gaseous base (NH_3). The gaseous cation has been confirmed to be unreactive toward benzene and toluene, whereas it acetylates the xylenes and the other selected polymethylated benzenes. The relative rates of acetylation have been determined in competition experiments, using mesitylene as the reference substrate. The mechanism of acetylation and subsequent isomerization is discussed, and the substrate and positional selectivity of the free CH_3CO^+ ion are evaluated, together with its intrinsic steric requirements. Comparison of the gas-phase results with those of related condensed-phase reactions, involving CH_3CO^+ salts as one of the reactive species, reveals no basic mechanistic differences. Some observed reactivity and selectivity discrepancies, in particular those concerning acetylation of toluene, *o*- and *m*-xylene, and hemimellitene, are outlined and their possible causes considered.

Introduction

In a previous paper, the application of specifically designed radiolytic and nuclear methods to generate free acetylium (CH_3CO^+) ions in the diluted gas state has been reported.[1] It has been shown that, independently of their origin, gaseous acetylium ions display features typical of a mild electrophile, as evidenced by their unreactivity toward unactivated π-type substrates, such as benzene and toluene. Only n-donor nucleophiles (aliphatic alcohols) and activated arenes (anisole and phenol) undergo attack by thermal CH_3CO^+ ions, yielding the corresponding acetylated derivatives. Gas-phase condensation reactions between ground-state[2] CH_3CO^+ and the abovementioned substrates could not be observed in independent ICR experiments.[3,4]

The growing interest attached to directive effects in the gas-phase aromatic substitutions, i.e., in the absence of solvation, ion pairing, etc.,[5] has stimulated further work aimed to assess the *intrinsic* reactivity and selectivity of a well-defined gaseous cation, the CH_3CO^+ ion, toward increasingly substituted and activated arenes, in order to determine the reactivity limits of the electrophile and its positional selectivity.

The resulting information is expected to contribute to the rationalization of condensed-phase acetylation reactions, usually complicated by the diverse mechanisms occurring simultaneously in such systems and by the largely variable reactivity and steric requirements attributed to the postulated acetylation reactants.[6]

In the present paper, we describe the results of related

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studies of the gas-phase attack of CH_3CO^+ ions, from the γ radiolysis of CH_3F-CO mixtures, on representative methylbenzenes, in order to characterize the variables affecting their reactivity order and directive properties toward the electrophile.

We hope thereby to delineate the mechanistic details of the gas-phase acetylation reaction and to compare them with their condensed-phase counterparts.

Experimental Section

Materials. Methyl fluoride, carbon monoxide, oxygen, and ammonia were high-purity gases from Matheson Co., used without further purification. Methanol, ethanol, ethyl acetate, and the selected aromatic substrates (Fluka AG) were analyzed by GLC to check the absence of any acetylated and methylated derivatives. The isomeric acetylated substrates used in this investigation are known compounds and all were prepared by established procedures and purified by preparative GLC and their identities were checked by IR, NMR, and GC-mass spectrometry.

Procedure. The gaseous reaction mixtures were prepared according to standard vacuum techniques, introducing each bulk constituent of the system (CO or CH_3F) into separate, break-seal-tipped, Pyrex cylindrical containers having a capacity of 150–850 mL. All of the reaction vessels were previously evacuated and carefully outgassed. The other required gaseous additives (O_2, NH_3, together with fragile weighed glass ampoules containing the aromatic substrates) were always introduced into the container with CH_3F. The two components of the reaction vessel were then sealed to each other in such a way that the total volume of the reactor was made equal to 1 L for all systems. After careful outgassing the whole apparatus was sealed off. Once equilibrated, the gaseous samples were irradiated in a cobalt-60 220 Gammacell from Nuclear Canada Ltd., at a temperature of 37.5 °C and a dose rate of 0.4 Mrad h^{-1}, as determined by a Fricke dosimeter.

After receiving a constant dose of 4.8 Mrad, the irradiated samples were analyzed on a Hewlett-Packard Model 5700 A gas chromatograph, equipped with a FID unit, after careful washing of the vessel walls with methanol, as required by the relatively low volatility of the products, whose yields were determined from the areas of the corresponding elution peaks, using appropriate calibration factors. In some cases, aliquots of the irradiated samples were analyzed on a VG 7070 gas chromatograph mass spectrometer, and the irradiation products were identified by comparison of their fragmentation pattern with those of authentic samples.

The constancy of the yields from different analyses of the same reaction vessel was within 1%. The reported 10% scatter refers to the data from different experiments and is mainly due to the difficulty in reproducing the composition of the system.

Results

Acetylation of Ethanol. A set of experiments, involving ethanol, as substrate, has been performed in order to select the experimental conditions suited to maximize the formation of the acetylium ions from γ radiolysis of CH_3F-CO systems. To this purpose, gaseous CH_3F-CO mixtures prepared at constant total pressure (760 Torr), but containing variable concentration of the two components, have been irradiated in the presence of small constant amounts of substrate (4.0 Torr) and of a thermal radical scavenger (O_2; 4 Torr).

As illustrated in Figure 1 and in qualitative agreement with previous data,[1] acetylation and methylation of the substrate represent the two major channels, each accounting for over 25% of the recovered products.[7] The absolute product yields, given as $G_{(M)}$ values, are differently biased by the sample composition, so that, while the acetylation yield rapidly reaches a maximum and then slowly decreases, the methylation G value increases monotonically by increasing the molar fraction of CH_3F (X_{CH_3F}). Overall acetylation *plus* methylation product yield maintains a constant value ($G_{(M)} = 3.3 \pm 0.5$) independently of the system composition. This value coincides, within the experimental uncertainty, with the dimethyl ether yield ($G_{(M)} = 3.4 \pm 0.4$) from methylation of CH_3OH by the $CH_3FCH_3^+$ ions generated by γ radiolysis of pure gaseous CH_3F (at 760 Torr).[8a] The typical ionic character of both the acetylation and the methylation reactions is demonstrated by the sharp decrease of the acetylated and methylated product yields (ranging from 60 to 90%), by addition of a certain amount (5 Torr) of an efficient ion trapper, such as ammonia, to the gaseous mixtures.[8]

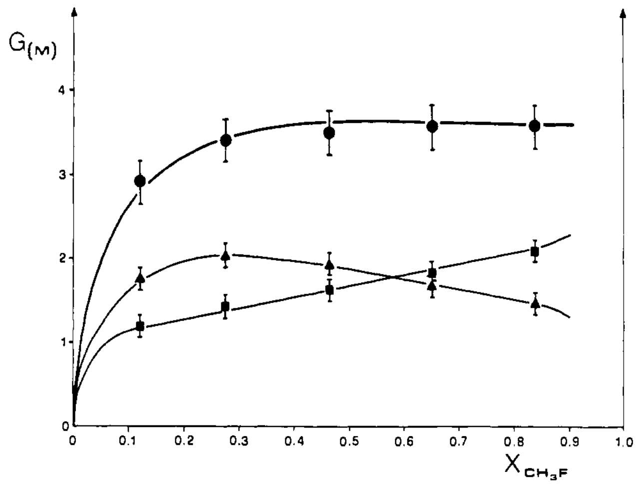


Figure 1. System: $CH_3F + CO + C_2H_5OH + O_2$. Dependence of $G_{(M)}$ values on the molar fraction of CH_3F (X_{CH_3F}): ▲, ethyl acetate; ■, ethyl methyl ether; ●, ethyl acetate + ethyl methyl ether.

Acetylation of Methylbenzenes. To the specific purposes of the present study, all of the experimental results reported below concern experiments carried out under conditions wherein the acetylation to methylation yield ratio is expected to be maximized, namely for $X_{CH_3F} = 0.13$. In addition, for the sake of clarity, methylation data have not been included in Table I, which therefore reports only the acetylation results of competition experiments involving the selected methylbenzenes and mesitylene, as the reference substrate. The *relative* yields of acetylated products, their isomeric composition, and the apparent rate constant ratios, measured at different total pressures and in the presence of ammonia, are given. The *absolute* yields of acetylated substrates do not appear in Table I because of their limited significance, mainly due to the fact that the aromatic substrate is only one of the nucleophiles, either initially present in the gaseous mixture or formed from its radiolysis, which compete for the gaseous CH_3CO^+ ion.[7] Furthermore, there is still some uncertainty about the acetylium-ion yield and its pressure dependence in the range of interest.

The major features of the gas-phase acetylation of methylbenzenes can be summarized as follows: (i) as previously observed,[1] the CH_3CO^+ ion attack on benzene and toluene does not lead to any observable neutral condensation products, whereas acetyl derivatives of *p*- and *o*-xylene are just perceptible by the analytical methods used; (ii) mesitylene is the most reactive substrate among the selected methylbenzenes, as indicated by the apparent k_s/k_m ratios; (iii) the observed reactivity order and the isomeric distribution of products are in agreement with the electrophilic character of the acetylating species; (iv) a distinct influence of the total pressure of the system and the presence of ammonia on the measured rate constant ratios and on the isomeric distribution of products is observable; (v) as expected, acetylation-induced intra- and intermolecular methyl-group transfers have never been observed under the present experimental conditions.

Discussion

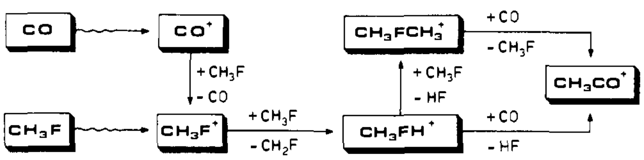
Nature and Reactivity of the Acetylating Species. As previously discussed[1] and in agreement with the observed effects

Table I. Competitive Gas-Phase Acetylation of Methylbenzenes

system composition, Torr						isomeric composition of products, %,[b]
CH_3F	CO	NH_3	substrate (S)	mesitylene, M	$(k_s/k_m)_{app}$[a]	methyl acetophenones[c]
100	650	2	benzene, 2.3	0.8	$<7.10^{-4}$	
100	650	2	toluene, 1.0	0.6	$<7.10^{-4}$	
100	650	2	*p*-xylene, 0.4	0.4	0.01	100 (2, 5)
100	650		*p*-xylene, 0.3	0.4	0.01	100 (2, 5)
50	330		*p*-xylene, 0.4	0.4	0.03	100 (2,5)
100	650	2	*m*-xylene, 0.6	0.4	0.17	20.5 (2, 6); 65.3 (2, 4); 14.2 (3, 5)
100	650		*m*-xylene, 0.8	0.5	0.23	7.8 (2, 6); 87.3 (2, 4); 4.9 (3, 5)
50	330		*m*-xylene, 0.4	0.4	0.39	3.9 (2, 6); 95.2 (2, 4); 1.9 (3, 5)
100	650	2	*o*-xylene, 0.5	0.4	0.05	77.0 (3, 4); 23.0 (2, 3)
100	650		*o*-xylene, 0.8	0.8	0.07	79.4 (3, 4); 20.6 (2, 3)
50	330		*o*-xylene, 0.6	0.7	0.09	86.4 (3, 4); 13.6 (2, 3)
100	650	2	hemimellitene, 0.3	0.5	0.07	69.6 (2, 3, 4); 30.4 (3, 4, 5)
100	650		hemimellitene, 0.9	0.9	0.10	69.4 (2, 3, 4); 30.6 (3, 4, 5)
50	330		hemimellitene, 0.2	0.3	0.07	90.3 (2, 3, 4); 9.7 (3, 4, 5)
100	650	2	mesitylene, 0.8	0.8	1.00	100 (2, 4, 6)
100	650	2	prehnitene, 0.5	0.5	0.35	100 (2, 3, 4, 5)
100	650		prehnitene, 0.4	0.4	0.30	100 (2, 3, 4, 5)
50	330		prehnitene, 0.6	0.4	0.18	100 (2, 3, 4, 5)

[a] $(k_s/k_m)_{app} = [S - Ac]/S)/([M - Ac]/M)$. Standard deviation of the k_s/k_m ratio, ~20%. [b] Standard deviation of data, ~10%. [c] The bracketed numbers refer to the position of the methyl groups within the acetophenone aromatic ring.

Scheme I



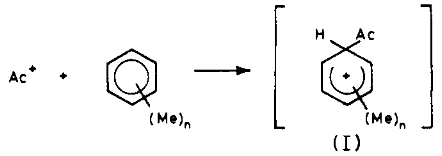
of NH_3 and of the system composition (see Figure 1) on the products yields, γ radiolysis of CH_3F-CO gaseous mixtures leads to the formation of CO^+ and CH_3F^+ as the most abundant primary species, which immediately initiate the sequence shown in Scheme I by reacting with their parent molecules. Since CO and CH_3F are isoelectronic molecules with comparable ionization potentials [IP(CO) = 14.01 eV; IP(CH_3F) = 12.85 eV],[9] the total ion-pair yield from irradiation of gaseous CH_3F-CO systems is expected to be quite insensitive to the mixture composition. According to mass spectrometric data,[10] the efficiency of the elementary steps of the network of Scheme I is very high; thus only a few collisions between the primary ionic species and the parent molecules are sufficient to establish steady-state concentrations of thermalized CH_3CO^+ and $CH_3FCH_3^+$ ions, whose combined yield is therefore largely independent of the system composition. The relative constancy of the overall G values, observed in Figure 1, is therefore a direct consequence of the mechanism of formation of CH_3CO^+ and $CH_3FCH_3^+$ and of their high reactivity toward n bases, such as ethanol.[8] While CH_3CO^+ is completely unreactive toward the parent molecules (CH_3F and CO),[10] $CH_3FCH_3^+$ ions may undergo an exothermic CO for CH_3F displacement process contributing to the formation of CH_3CO^+. However, this further channel is slow, when compared with the parallel CO for HF substitution on CH_3FH^+,[11] which represents the main source of CH_3CO^+ ions. In fact, if the two displacement processes take place at comparable rates, the steady-state concentration of $CH_3FCH_3^+$ would be comparatively very small, on account of the large excess of CO with respect to the present substrate (EtOH). Consequently, the acetylation-methylation yield ratios would have to be far greater than 1 and somewhat independent on X_{CH_3F}.[12] On the contrary, the $G_{(CH_3COOC_2H_5)}/G_{(CH_3OC_2H_5)}$ ratio ranges from 1.7 ($X_{CH_3F} = 0.13$) to 0.7 ($X_{CH_3F} = 0.87$), excluding therefore $CH_3FCH_3^+$ as significant source of CH_3CO^+ ions. In conclusion, γ radiolysis of CH_3F-CO mixtures produces a steady-state concentration of CH_3CO^+, accompanied by a comparable amount of $CH_3FCH_3^+$ ions in proportions that approximately follow the composition of the gaseous mixture.

Radiolytic acetylium ion ($\Delta H_f^\circ = 160 \pm 2$ kcal mol^{-1})[13] is thermalized by a large number of unreactive collisions with the parent molecules before reacting with the substrate. Methylation excepted,[1,2c] the energetically allowed acetylium-ion attack on methylbenzenes[14] represents the predominant ionic pathway in the irradiated samples, since other conceivable ionic processes, such as protonation (eq 1) and hydride-ion abstraction (eq 2), can be safely ruled out on energetic and kinetic grounds.[16] Hence the reactivity ratios arising from the competition experiments of Table I refer exclusively to the acetylation channel, providing a measure of the nucleophilic reactivity of the selected arenes toward CH_3CO^+.

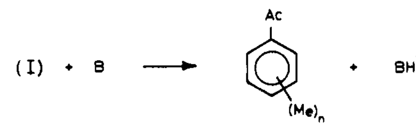
$$CH_3CO^+ + ArCH_3 \rightarrow CH_2CO + HArCH_3^+ \quad (1)$$

$$CH_3CO^+ + ArCH_3 \rightarrow CH_3CHO + ArCH_2^+ \quad (2)$$

Gas-Phase Acetylation Mechanism. The experimental features of gas-phase acetylium-ion attack on methylbenzenes



(3)



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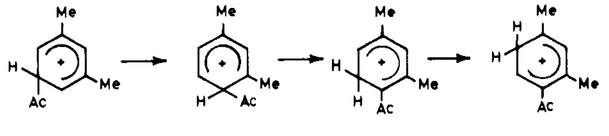

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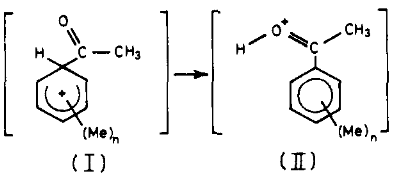


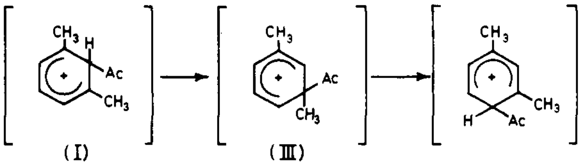
(6)

Table II. Relative Rates of Acetylation of Methylbenzenes

electrophile	substrate								source
	benzene	toluene	*p*-xylene	*o*-xylene	*m*-xylene	hemimellitene	mesitylene	prehnitene	
$CH_3COCl/AlCl_3$ $C_2H_4Cl_2$ at 25 °C	3.4×10^{-4}	0.043	0.008	0.72	0.12	0.81	1.00	2.48	ref 22a
$CH_3COCl/AlCl_3$ CH_3NO_2 at 25 °C	4.4×10^{-4}	0.060	0.010	0.61	0.39		1.00		ref 22b
$CH_3CO^+SbF_6^-$ CH_3NO_2 at 25 °C	9.1×10^{-4}	0.114	0.021	1.14	0.59		1.00		ref 22c
$CH_3CO^+SbCl_6^-$ CH_3NO_2 at 25 °C	9.8×10^{-4}	0.119	0.021	1.19	0.41		1.00		ref 22c
$CH_3CO^+SbCl_6^-$ $C_6H_5NO_2$ at 25 °C	8.5×10^{-4}	0.106	0.106	0.60	0.41		1.00		ref 22c
CH_3CO^+ gas phase at 37.5 °C	$<7 \times 10^{-4}$	$<7 \times 10^{-4}$	0.010	0.05	0.17	0.07	1.00	0.35	this work

are consistent with a mechanism involving as the first step the electrophilic attack of CH_3CO^+ (Ac^+) on the ring electrons of the aromatic substrate, yielding isomeric arenium ions (I), excited by the exothermicity of the process (eq 3).[14] Collisional quenching of the excited intermediates (I), followed by proton loss to a gaseous base B,[17] provides a direct route to the acetylated neutral products (eq 4). Before thermalization, the excited arenium ions (I) tend to isomerize toward the thermodynamically most stable isomer(s), for instance, eq 5. The yields and the isomeric composition of the acetylated products reflect only the extent of acetyl-group shifts in ions I and, therefore, the accompanying intramolecular 1,2-hydrogen transfers that are likely to occur at comparatively higher rates[18] will not be further considered. However, intramolecular proton transfer (eq 6) between the two basic (π and n type) sites of I may represent an additional isomerization channel leading to the very stable O-protonated isomer II[19] preventing further acetyl-group shifts. Inconclusive evidence on the nature of process 6 is provided by the data summarized in Table I, whose only firm indication, related to the increased yields of 4-acetylated products at low pressures, conflicts with the occurrence of eq 6 at rates higher than those of the competitive channels (eq 5).

Concerning the inter- or intramolecular character of the isomerization process 5, some indication can be deduced from the acetylation data of *m*-xylene. The effect of decreasing the total pressure of the gaseous CH_3F-CO mixture on the yields of 2,6-dimethylacetophenone from *m*-xylene is comparable with that observed for other products wherein the acetyl group is not flanked by two methyl groups, e.g., 3,4-dimethylacetophenone from *o*-xylene. This observation is hardly consistent with any isomerization pathway involving *exclusively* intramolecular 1,2-acetyl shifts. In fact, intramolecular migration of the acetyl group within the ionic precursor of the abovementioned product necessarily requires the intermediacy of the ipso substituted species III, particularly unfavored on energetic grounds.[20] As a consequence, pathway 7 should be much slower, under identical experimental conditions, than, for instance, the process shown in eq 8. The particular isomerization pattern observed in the acetylation of *m*-xylene, coupled with the appreciable dependence of the apparent k_s/k_m ratios on the experimental conditions, is consistent with a *reversible* acetylation mechanism, particularly evident when occurring on the hindered position(s) of the substrate and, therefore, attributable to the *intrinsic* steric requirements of the gaseous acetylium ion.[21] Accordingly, collisional quenching and fast deprotonation of I are expected to prevent deacetylation and, therefore, to increase comparatively the yields of the most encumbered acetyl derivatives. Thus, at high pressure and in the presence of ammonia, the highest yield of 2,6-dimethylacetophenone is measured from *m*-xylene, concurrently with the lowest apparent k_s/k_m ratio. In conclusion, it appears that kinetically significant relative *k* values can be evaluated only under conditions (high pressure and presence of NH_3) minimizing deacetylation.



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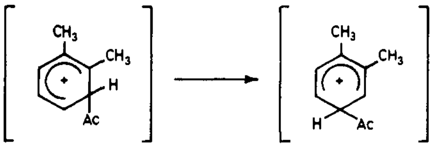

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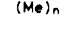

(9)

Under such conditions, the gas-phase CH_3CO^+ ion attack on methylbenzenes follows closely a pattern typical of electrophilic aromatic substitutions, giving acetylated products only from sufficiently activated substrates. At least two factors affect the positional and substrate selectivity of gaseous acetylium ions: (i) the *intrinsic* orienting properties of the aromatic toward the electrophile and (ii) the possibility of readily forming acetylated intermediate(s), sufficiently stable to prevent acetyl-group transfer. Only when activated by at least two methyl groups does the aromatic substrate undergo acetylation. The combined activating effects of two methyl groups ortho to a given ring position overcome the limited steric requirements of free CH_3CO^+ ions, conferring to the position a reactivity comparable with that activated by two methyl groups, one meta, the other ortho or para. Finally, the presence of three activating methyl groups in mesitylene confers to the substrate a reactivity even higher than that of prehnitene, overwhelming, therefore, any possible steric hindrance toward the electrophile.

Comparison with Solution Chemistry Data. While the proposed gas-phase acetylation mechanism of methylbenzenes follows the general pattern of electrophilic acetylation processes occurring in solution, the present results suggest that the gas-phase reactivity and selectivity of free acetylium ions do not have any defined counterpart in solution. This point is particularly evident from the k_s/k_m ratios measured in the gas-phase and compared (in Table II) with those observed in Friedel-Crafts systems, wherein the formation of the CH_3CO^+ counterion pairs has been detected. The listed figures confirm that the apparent reactivity trends of condensed-phase experiments can be mostly ascribed to pronounced effects of the solvent, the counterion, and the catalyst. In fact, while in solution, toluene and xylenes display a comparable affinity toward the electrophile; the xylenes represent the gas-phase reactivity onset of CH_3CO^+ toward methylbenzenes. Furthermore, the high discrepancy between gas-phase and solution reactivity data concerning *o*-xylene and hemimellitene arises probably from the steric hindrance of the encumbered reference mesitylene toward acetylation from the bulky *solvated* Friedel-Crafts acetylating species, whereas, in the gas-phase, the intrinsic steric requirements of the CH_3CO^+ ion do not cause such large reactivity deviations.

A further support to this conclusion is provided by the positional selectivity of the gaseous acetylium ions toward *m*-xylene. In particular, the appreciable yields of 2,6-dimethylacetophenone, not formed under Friedel-Crafts conditions, suggest that the observed difference in positional selectivity is due to the diverse nature of the acetylating species or, at least, to the solvation shell of the electrophile, enhancing its limited intrinsic steric requirements. Besides, the observed distribution of the isomeric acetylhemimellitene (4:69%; 5:31%) in the gas phase, incidentally very similar to that (4:65%; 5:35%) calculated from the partial rate factors obtained from the Friedel-Crafts acetylation of toluene,[22] reveals the preferred 4-orienting effect of hemimellitene toward "naked" CH_3CO^+. The extremely variable isomeric composition obtained in the condensed-phase acetylation of hemimellitene[23] can be therefore ascribed to several environmental factors, influencing inter alia the very nature of the electrophile, its degree of solvation, and the lifetime of the σ complex. In fact, gas-phase results indicate that long-lived ions I can undergo extensive acetyl-group transfer, in contrast to the generally accepted view[24] against isomerization involving acetyl group shifts and, therefore, assuming the observed isomeric distribution as a measure of the actual positional selectivity of the acetylating species. In this connection, a close correspondence does exist between the gas-phase intermolecular isomerization pattern and the Gore's reversibility theory of Friedel-Crafts acylation reactions,[25] while the kinetic demonstration of the rate-determining proton-transfer step (eq 4) in condensed-phase experiments[22c] represents a further supportive analogy to the conclusion reached in the present study on the importance and the consequences of reversible deacetylation occurring within gaseous encumbered intermediate ions (I).

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References and Notes

(1) Giacomello, P.; Speranza, M. *J. Am. Chem. Soc.* **1977**, *99*, 7918.

(2) As a matter of fact, excited CH_3CO^+ from electron impact on butane-2,3-dione has been observed to add slowly to toluene in a ICR source. However, the same process involving the less excited CH_3CO^+ from acetone could not be observed under the same experimental conditions.[3c]

(3) (a) Bursey, M. M.; Elwood, T. A.; Hoffman, M. K.; Lehman, T. A.; Tesarek, J. M. *Anal. Chem.* **1970**, *42*, 1370. (b) Benezra S. A.; Bursey, M. M. *J. Am. Chem. Soc.* **1972**, *94* 1024. (c) Chatfield, D. A.; Bursey, M. M. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72* 417. (d) Chatfield, D. A.; Bursey, M. M. *J. Am. Chem. Soc.* **1975**, *97*, 3600. (e) Chatfield, D. A.; Bursey, M. M. *Ibid.* **1976**, *98* 6492. (f) Dunbar, R. C.; Shen, J.; Olah, G. A. *Ibid.* **1972**, *94*, 6862. (g) Chatfield, D. A.; Bursey, M. M. *Int. J. Mass Spectrom. Ion Phys.* **1975**, *18*, 239.

(4) Lehman, T. A.; Bursey, M. M. "Ion Cyclotron Resonance Spectrometry"; Wiley: New York, 1976; p 39.

(5) For a recent review, see Cacace F. "Kinetics of Ion-Molecule Reactions", Ausloos, P., Ed.; Plenum Press: New York, 1979.

(6) For a review, see Gore P. H. "Friedel-Crafts and Related Reactions", Olah, G. A. Ed.; Wiley-Interscience: New York, 1964; Vol. III, Part 1, p 64.

(7) The remaining fraction of the recovered products is largely due to the direct radiolysis of the $CH_3F-CO-O_2$ system, as evidenced by the product spectra of blank runs carried out in the absence of substrate (EtOH). The total, acetylation and methylation, absolute yield slightly increases with the molar fraction of the substrate and at low radiation doses, i.e., at low concentrations of radiolytically formed nucleophiles. This behavior indicates that the added substrate is only one of the nucleophiles competing for the present ionic species. On the other hand, for any given initial $CH_3F-CO-O_2$ composition of the system, the acetylation/methylation ratio is reasonably constant within wide ranges of radiation dose and substrate concentration. Thus, under the present experimental conditions, parasitic reactions of the present electrophiles with nucleophiles other than EtOH do not interfere to a different extent in the acetylation and methylation competing processes.

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(9) Vedeneyev, V. I.; Gurvich, L. V.; Kondrat'yev, V. N.; Medvedev, V. A.; Frankevich, Ye. L. "Bond Energies, Ionization Potentials and Electron Affinities"; Edward Arnold: London, 1966.

(10) Holtz, D.; Beauchamp, J. L. *Nature (London), Phys. Sci.* **1971**, *231*, 204.

(11) Both processes are energetically allowed, being exothermic for 22 and 45 kcal mol^{-1}, respectively.

(12) This conclusion would not be any longer correct if CH_3CO^+, in contrast to what was previously *observed*,[1] *were* also a good methylating *agent*.

(13) (a) Ausloos, P.; Lias, S. G. *Chem. Phys. Lett.* **1977**, *51*, 53. (b) Davidson, W. R.; Lau, Y. K.; Kebarle, P. *Can. J. Chem.* **1978**, *56*, 1016. (c) Vogt, J.; Williamson, A. D.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 3478. (d) Debrou, G. B.; Fulford, J. E.; Lewars, E. G.; March, R. E. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *26*, 345.

(14) This statement arises from the thermochemical balance of the depicted cycle, where S is the substrate, Ac_3^+, Ac_2^+, Ac^+, and Ac are triacetyl, biacetyl, and acetyl cation, and acetyl radical, respectively, and Ac_2 is neutral biacetyl. Step 1 is 14 kcal mol^{-1} exothermic on the grounds of the

$$\begin{tikzcd}
\overset{+}{Ac_2} + Ac_2 + S \arrow[r, "\Delta H_2 < 0"] & \overset{+}{Ac_3} + Ac + S \arrow[d, "\Delta H_3 < 0"] \\
Ac^+ + Ac + Ac_2 + S \arrow[u, "\Delta H_1 = -14 \text{ kcal mol}^{-1}"] \arrow[r, "\Delta H_0 < 0"] & AcS^+ + Ac_2 + Ac
\end{tikzcd}$$

standard heats of formation of Ac^+ (160 ± 2 kcal mol^{-1}), Ac_2^+ (135 kcal mol^{-1}),[15] and Ac (−11 kcal mol^{-1}).[9] Both steps 2 and 3 are very efficient exothermic processes, when S = benzene, toluene,[3] and presumably polymethylated benzenes, so that the CH_3CO^+ ion attack on S (step 0) is an exothermic process too.

(15) Franklin, J. L.; Dillard, J. G.; Rosenstock, H. M.; Herron, J. L.; Draxl, K.; Field, F. H. "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions"; U.S. Government Printing Office: Washington, D.C., 1969; NBS Publ. No. NSRDS-NBS-26.

(16) From available thermochemical data (Chong, S. L.; Franklin, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 6630; Devlin J. L., III; Wolf, J. F.; Taft, R. W.; Hehre, W. J. *Ibid.* **1976**, *98*, 1990) for most of the selected substrates both processes 1 and 2 are slightly endothermic. However, ICR data[3] showed that, even when energetically allowed, both reactions do not take place under those conditions.

(17) The base B can be either a species deliberately added to the system (e.g., NH_3 or the substrate itself) and byproducts from the γ radiolysis of the batch gases. The basic centers of the glass walls of the bulb can behave as good proton acceptors too.

(18) Intramolecular 1,2-proton transfers in arenium ions are characterized by low activation energies. See, for instance: (a) Mac Lean, C.; Mackor, E. L. *Discuss. Faraday Soc.* **1962**, *34*, 165. (b) Field, F. H. "Ion-Molecule Reactions", Franklin, J. L., Ed.; Butterworths: London, 1972; Vol. 1, p 283.

(19) (a) Lau, Y. K.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 7452. (b) Larsen, J. W. *Ibid.* **1978**, *100*, 330.

(20) Heidrich, D.; Grimmer, M.; Sommer, B. *Tetrahedron* **1976**, *32*, 2027.

(21) A similar effect has been observed for another mild gaseous electrophile, the *tert*-butyl cation (Giacomello, P.; Cacace, F. *J. Am. Chem. Soc.* **1976**, *98*, 1823) and for the much stronger isopropyl cation (Attinà, M.; Cacace, F.; Ciranni, G., Giacomello, P. *Ibid.* **1977**, *99*, 2611) toward xylenes.

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(23) Friedman, L.; Honour, R. J. *J. Am. Chem. Soc.* **1969**, *91*, 6344.

(24) See, for instance, ref 22c.

(25) (a) Girdler, R. B.; Gore, P. H.; Hoskins, J. A. *J. Chem. Soc. C* **1966**, 181. (b) Agranat, I.; Avnir, D. *J. Chem. Soc., Chem. Commun.* **1973**, 362. (c) Agranat, I.; Shih, Y. S.; Bentor, Y. *J. Am. Chem. Soc.* **1974**, *96*, 1259. (d) Andreov, A. D.; Gore, P. H.; Morris, D. F. C. *J. Chem. Soc., Chem. Commun.* **1978**, *271*. (e) Frangopol, M.; Genunche, A.; Negoita, N.; Frangopol, P. T.; Balaban, A. T. *Tetrahedron* **1967**, *23*, 841.