the unlabeled adduct[7] and are as follows: $H_{2,5} = \delta$ 3.34; $H_{1,6}$ = 4.02; $H_{7,8}$ = 6.485; $J_{7,8}$ = 8.0; $J_{1,8} = J_{6,7}$ = 6.6; $J_{2,5}$ = 6.0; $J_{1,2} = J_{5,6}$ = 3.5; $J_{1,7} = J_{6,8}$ = 1.2; $J_{1,6} = J_{2,8} = J_{5,7}$ = 0.5 Hz; and all other coupling constants equal zero.
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Formation and Reactivity of Gaseous Acetylium Ions from the Methylation of Carbon Monoxide

Pierluigi Giacomello*[1a] **and Maurizio Speranza***[1b]

Contribution from the Institut für Chemie der Kernforschungsanlage Jülich GmbH, Institut 1: Nuklearchemie, D-5170 Jülich, Federal Republic of Germany, and the Laboratorio di Chimica Nucleare del C.N.R., 00016 Monterotondo Stazione, Rome, Italy. *Received February 18, 1977*

Abstract: Free acetylium ions have been prepared in the diluted gas state at atmospheric pressure, via two different routes, i.e., the methylation of carbon monoxide by CT_3^+ ions from the decay of fully tritiated methane, and the nucleophilic displacement by CO on CH_3M^+ (M = HF, CH_3F) ions, produced from the γ-radiolysis of methyl fluoride. Independently of the preparation methods, the acetyl cation displays a much higher reactivity toward n-type than toward π-type nucleophiles. The reaction of thermalyzed CH_3CO^+ ions with alcohols or phenols yields the corresponding acetates, while no acylation of benzene and toluene was detected. Low yields of ring-acetylated products were obtained from the attack of acetylium ions on anisole and phenol, the reactivity being, however, strongly biased (83.8%) in favor of the oxygen atom of the latter substrate. From these results it appears that the intrinsic intramolecular selectivity of the free acetylium ion, measured in the gas phase, in the absence of the complicating phenomena, such as solvation and ion pairing, invariably affecting solution-chemistry studies, is characterized by a high ortho/para ratio in the acylated products.

In recent years, the gas-phase acetylation of organic compounds by various ionic reagents has been extensively studied in the limited pressure range accessible to mass spectrometric and ICR methods,[2-8] disclosing intriguing features that were not previously observed in ion-molecule reactions of simpler species and cannot be explained by even the most advanced physical models of ion-molecule interactions, but rather recall the complexity and the multifaceted problems of traditional solution chemistry.

In the mass spectrometric investigations the acylating agents are produced by electron impact on molecules such as acetone and 2,3-butanedione,[2-5,8] and species other than CH_3CO^+ ions can be formed, whose efficient acetyl transfer reactions to the substrate may obscure[7] the direct contribution of the free acetylium ion to the adduct formation. Furthermore, an inherent and obvious limitation of these otherwise so powerful and enlightening techniques is the lack of information on the site of attachment of the reacting ion,[3,4] as the isomeric species formed cannot be directly identified. On the other hand, solution chemistry studies[9] suggested that the electrophilic attack of free acylium ions on aromatic substrates represents only one of the conceivable and partly verified mechanisms of Friedel-Crafts acylation reactions. In fact, the nature of the acylating agent and its inherent reactivity and selectivity toward the substrate are strongly affected by several factors—the solvating properties of the environment, the specific features of the catalyst, and the nature of the substituent bound to the carbonyl group—so that the free-ion character of the acylating agent and, consequently, the steric and electronic requirements of the reaction are remarkably variable.[10]

The present paper deals with the formation of the acetylium ion and its reactivity toward some typical organic substrates, studied in the diluted gas state at atmospheric pressure, using the radiolytic[11-14] and the decay[15-17] techniques recently applied to the study of aromatic electrophilic substitutions. Both these approaches are suitable to evaluate the properties of the acylium ion in the absence of the complicating phenomena occurring in solution chemistry, allowing, in addition, the isolation and the identification of *final neutral products*, and their exploitation represents an attempt to establish links, and to substantiate correlations between low-pressure mass spectrometric data and the condensed-phase results.

Methods of Formation. Two different synthetic approaches have been designed for the preparation of gaseous $C_2H_3O^+$ ions, namely, the condensation reaction of CO with the CT_3^+ cations from the β decay of fully tritiated methane, and the nucleophilic displacement by carbon monoxide of HF or CH_3F molecules from CH_3FH^+ and respectively $(CH_3)_2F^+$ ions, produced in the γ-radiolysis of gaseous mixtures containing methyl fluoride.

A. Decay Synthesis. Methyl cations are known, from theoretical[17] and mass spectrometric[19] studies, to be the predominant (>80%) charged species formed from the β decay of a radioactive atom of tritiated methane. Tracer activities of multitritiated methane of known isotopic composition (CT_4 60.4 ± 0.5%, CHT_3 29.4%, CH_2T_2 8.1%, CH_3T 2.0%), prepared and purified according to Cacace and Schüller,[20] were allowed to decay in the presence of a large excess of carbon monoxide and smaller amounts of the organic substrates.

In these conditions, the $C_2T_3O^+$ ions formed from the process

$$CT_3^+ + CO \rightarrow (C_2T_3O^+)_{exc} \tag{1}$$

and excited by its exothermicity, roughly estimated around 80 kcal mol^{-1}, are expected to yield eventually, irrespective of the original site of attack of the methyl cation to the CO molecule, the most stable[21,22] acetylium ion $CT_3\text{-}CO^+$, subsequently thermalized by a large number of unreactive collisions with carbon monoxide before reacting with the substrate molecules.

B. Radiolytic Preparation. The second method for the production of gaseous acetylium cations is based upon the extension to high-pressure systems of the nucleophilic displacement reaction

$$CO + CH_3M^+ \rightarrow CH_3CO^+ + M \; (M = HF, CH_3F) \tag{2}$$

studied by ICR methods by Beauchamp and co-workers.[23] For this purpose, gaseous mixtures, containing a large excess of CH_3F and CO, were exposed at room temperature to the γ radiation of a ^{60}Co source, in the presence of traces of O_2, as a thermal radical scavenger, and of the organic substrates. According to previous reports,[24,26] the primary ions produced by the radiolysis of the mixtures are expected to be essentially[27] those summarized in eq 3 and 4.

$$CH_3F \rightsquigarrow CH_3F^+ + e \tag{3}$$

$$CO \rightsquigarrow CO^+ + e \tag{4}$$

The CH_3M^+ species (eq 2) are efficiently formed in the processes shown in eq 5 and 6, at the expense of CH_3F^+ ions,

$$CH_3F^+ + CH_3F \rightarrow CH_3FH^+ + CH_2F \tag{5}$$

$$CH_3FH^+ + CH_3F \rightarrow CH_3F^+CH_3 + HF \tag{6}$$

which could also arise from a charge-transfer reaction between the primary CO^+ ions (IP (CO) = 14.01 eV) and the parent CH_3F molecules (IP (CH_3F) = 12.85 eV).[28]

Both acetylium and dimethylfluoronium ions, in concentrations depending on the relative amounts of CO and CH_3F within the irradiated system, are expected to be eventually formed in the gas, leading to acetylation as well as methylation processes.

A common feature of both decay and radiolytic method is the production of a single acetylating ionic reagent, which, irrespective of the formation processes, is efficiently thermalized by a large number of unreactive collisions with the bulk of the gaseous system before reacting with the diluted organic substrate.

Experimental Section

Materials. Methane CT_4 was prepared and purified according to known methods,[20,29] and diluted with CH_4 to a specific activity of 224 Ci mol^{-1}. Methyl fluoride, carbon monoxide, and oxygen were high-purity gases from Matheson Co., used without further purification. All the organic substrates and the reference compounds used in the GLC analyses were reagent grade products from Merck Co. The starting materials contained no detectable traces of the possible products of the acylation reaction, as checked by GLC on the same columns used in the final analyses.

Table I. Products Yield in the Gas-Phase Reactions of Decay Formed CT_3CO^+ Ions

System composition (Torr)	Products (activity, %)[a,b]
CO (720)	EtOAc (90.6)
EtOH (9.8)	MeOAc (5.2)
Methane (0.19)	EtOH[c] (2.4)
	Unknowns (2.0)
CO (720)	Acetophenone[d]
Benzene (3.0)	Benzene (80.4)
Methane (0.19)	Toluene (8.2)
	MeOAc (5.6)
	Unknowns (5.8)

[a] Standard deviation of data ca. 10%. [b] The total activity recovered in the products accounts for 35% of the theoretical yield in the case of EtOH and for 15% in the case of C_6H_6. [c] This yield is not significant owing to labile hydrogen atoms exchange with GC columns. [d] Not detectable.

Procedure. The gaseous mixtures were prepared according to the vacuum techniques described in detail elsewhere.[11-14] The irradiations were carried out at a dose of 4.8 Mrad, at a dose rate of 0.4 Mrad h^{-1}, in a 220 Gammacell from Nuclear Canada Ltd., at a temperature of 25 °C. The 280-mL bulbs for the decay experiments, containing an activity of 0.6 mCi of CT_4, were stored in the dark at 22 °C for a 9-month period, and analyzed by radio GLC using a Hewlett-Packard Model 7620A chromatograph, equipped with a hot wire detector in series with a 10-mL internal-flow proportional counter from Berthold Co., heated at 150 °C.

The counter yield was 4.4% at a flow rate of 125 mL min^{-1}.

The irradiated samples were analyzed on a Hewlett-Packard Model 5700A chromatograph, equipped with FID unit, after careful washing of the vessel walls with diethyl ether when required by the relatively low volatility of products, whose yields were determined from the areas of the corresponding elution peaks, using appropriate calibration factors.

For the decay experiments the following gas chromatographic glass columns were employed: 3 m Porapak Q + 3 m Porapak S, operated at 200 °C, and 12 m Igepal Co 880 on Chromosorb W AW DMCS, operated at 90 and 100 °C. The radiolytic mixtures were analyzed on the following phases: 4 and 6 m Porapak Q operated from 70 °C up to 190 °C, 2 m Chromosorb 102 operated at 160 °C, 4 and 6 m diisodecyl phthalate, operated from 70 to 120 °C, 2 m E 301 from 25 to 120 °C, 4 m OS 550 at 120 °C, 4 m TCP at 70 °C. All liquid phases used were absorbed on Chromosorb W.

Results

Table I summarizes the relative yields of the products obtained from the reactions of decay-formed methyl cations in gaseous systems consisting of carbon monoxide as the bulk constituent, with traces of ethanol or benzene as the organic substrates.

The total activity recovered in the products accounts for 35% of the theoretical yield in the case of ethanol and for 15% in the case of benzene. It is evident from the data that extensive acetylation of ethanol leads to high yields of ethyl acetate, while no acetophenone is produced, indicating that the acetylium cations are unable to acylate benzene. In the latter case, in fact, mainly labeled benzene is formed together with traces of toluene, whose yield is much lower than from the direct methylation of C_6H_6.[17,30]

The results of radiolytic experiments carried out at a constant dose of 4.8 Mrad are listed in Table II. Products yields are given as $G_{(M)}$ values, i.e., as the number of molecules produced per 100 eV absorbed energy.

As in the preceding set of experiments, the acetylium cation, produced via a different pathway, but again under conditions

Table II. Product Yields in the Gas-Phase Reactions of Radiolytically Formed CH_3CO^+ Ions

System composition,[a] Torr				Products, $G_{(M)}$[b]			
CH_3F	CO	Substrate		Acetylation		Methylation	
100	650	MeOH	2.5	MeOAc,	1.32	[c]	
200	550	EtOH	4.3	EtOAc,	0.93	EtOMe	0.75
100	650	EtOH	4.7	EtOAc,	1.68	EtOMe	1.21
100 + H_2, 550	100	EtOH	4.9	EtOAc,	0.98	EtOMe	1.00
100	650	*n*-PrOH	1.2	*n*-PrOAc,	1.65	[c]	
100	650	*i*-PrOH	1.3	*i*-PrOAc,	1.44	[c]	
200	550	Benzene	2.4	Ring		[c]	
100	650	Toluene	0.8	Ring		Xylenes	0.015
100	650	Anisole	1.1	Ring,	0.013	Methylanisole	0.19
100	650	Phenol	0.5	Ring,	0.052	Cresols, negligible	
				PhOAc,	0.27	Anisole	0.30

[a] O_2, 4 Torr, present in each experiment. Radiation dose 4.8 Mrad. [b] Standard deviation of data ca. 10%. [c] Not measured.

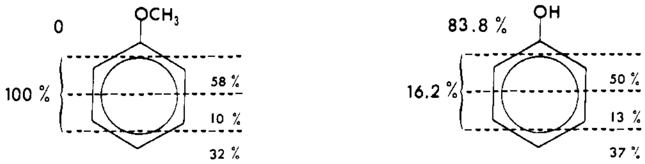


Figure 1. Selectivity of the electrophilic attack of CH_3CO^+ cation on aromatic substrates.

ensuring its efficient thermalization by unreactive collisions, displays a remarkable reactivity toward the substrates containing at least one n-type center, but it fails to condensate with nucleophiles carrying only a π-type system.

When ambident aromatic substrates, strongly activated in the ring, such as phenol and anisole, are allowed to react with acetylium ion, low yields of ring-acylated products are detected. It is also apparent from Table II that methylation yields invariably parallel acetylation yields, as expected by the extrapolation to high-pressure systems of the reactivity data measured in the mass spectrometric experiments.[24-26]

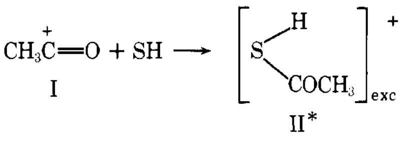
Further evidence that reactions 2 and 6 of CH_3FH^+ ions take place under these conditions is provided by those experiments where an excess of H_2 was radiolyzed in the presence of CH_3F and CO. In fact, formation of H_3^+ in these systems,[31] and its subsequent protonation of methyl fluoride, provide an additional, direct route to CH_3FH^+, leading to comparable yields of the same products as in the other experiments. The acetylium cation displays a marked selectivity in its attack on phenol and anisole, as shown by inspection of Figure 1, where both the extent of O- vs. ring acetylation and the isomeric composition of products from the electrophilic aromatic substitution are illustrated.

Discussion

A. The Reagent and Its Formation. The nature of the neutral products identified, and the composition of the systems studied, suggest that, in both decay and radiolysis experiments, acylium cations of the same structure and with comparable excitation energy distributions are formed. In fact, even though the energetics of the two formation processes, ca. 80 kcal mol^{-1} in the decay experiments and from 22 to 45 kcal mol^{-1} in the radiolytic systems, are quite different, the large molar fraction of carbon monoxide, compared to the trace concentrations of the organic substrate(s), ensures in both cases the efficient thermalization of the electrophile by unreactive collisions before its attack on the substrate. Moreover, the composition of the systems is such that side processes, e.g., the direct attack of the primary decay ions on the substrate, or its direct radiolysis can be safely neglected.

The efficient condensation reaction (1) of the methyl cations with CO is well known from solution studies, where the formation of acetylium ions was directly detected by NMR spectroscopy.[32,33] On the other hand, the extension of mass spectrometric results to the interpretation of the reactions occurring in irradiated systems at substantially higher pressure has been widely exploited in earlier studies[11-14,34] and the present results confirm its usefulness.

Finally, several theoretical studies[21,22] indicate that the acetylium ion of C_{3v} symmetry is the most stable among the possible isomers. These considerations, together with the fact that no condensation product different from those containing the CH_3CO moiety was observed, indicate that, in the present study, the formation of acetylated compounds must be traced to the attack (7) of acetylium ions (I) on the organic substrates,



$$\underset{\mathrm{I}}{CH_3\overset{+}{C}{=}O} + SH \longrightarrow \underset{\mathrm{II}^*}{\left[S\begin{matrix} H \\ COCH_3 \end{matrix} \right]^{+}_{\mathrm{exc}}} \qquad (7)$$

yielding ions of the general structure II, which subsequently undergo collisional deactivation and are eventually quenched by intra- and/or intermolecular proton transfer to gaseous bases, either deliberately added to the system, or generated by its radiolysis.[35]

B. Reactivity and Selectivity of the Reagent. The reactivity of the acetylium cation displays features that are typical of a very mild electrophile, and its behavior in high-pressure systems closely recalls the ICR results[2-8] and appears very sensitive to energetic constraints.

The lack of reactivity toward benzene and toluene is confirmed by the present results, strongly suggesting that an energy barrier either in the form of an activation energy, or, more likely, due to the endothermicity of the process,[36] does in fact prevent a condensation reaction. The striking contrast of the gas-phase evidence with the Lewis acids catalyzed acetylation of arenes occurring in solution can be rationalized by taking into account the higher degree of solvation of the arenium ion with respect to that of the acylating agent, which is likely to play a determining role in the condensed phase.

The formation of methyl acetate in the decay experiments cannot be satisfactorily explained by the present data, as well as the labeling of benzene.[37] Taking into account the composition of the system, the minor yield of toluene is likely to originate from the exothermic methyl transfer from the acetylium cations to benzene, and/or from a less probable direct methylation of the arene by CT_3^+ ions. On the other hand, the expected parallel methylation (see above) has been observed in radiolytic experiments, and will be discussed elsewhere.[38]

As shown by inspection of Table II, the reactivity of the acetylium ion toward the aliphatic alcohols is greater than toward the phenolic OH group, in qualitative agreement with the parallel trend observed in the methylation reaction.

Whereas a meaningful quantitative comparison is not allowed by the present data, the general reactivity of the substrates toward CH_3CO^+ appears roughly to match their nucleophilic character, confirming the electrophilic nature of the attack.

The reagent displays a relevant positional selectivity in its attack to phenol, O-acetylation exceeding ring acetylation by a factor of 5. This result closely agrees with the behavior observed in the case of another mild gaseous cation, the t-$C_4H_9^+$ ion,[39] which gives a ratio of O-alkylation to ring alkylation of 8:1, under kinetically controlled conditions.

The isomeric compositions of ring-substituted products are very similar for anisole and phenol, indicating a prevalent ortho/para acylation, and leading to para/meta ratios of 6.4 and 5.7, respectively. In addition, the gas-phase results show the ability of the free acetylium ion to yield high ortho/para ratios, in contrast with the para substitution generally prevailing in solution.[9] Thus, whereas not directly comparable with the widespread and frequently conflicting evidence from condensed-phase acylation studies, the present gas-phase results may hopefully prove of some value for separating intrinsic reactivity features associated with the very nature of the electrophile–substrate interaction from those arising from the influence of the environment, in particular solvation and ion pairing.

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(1) (a) Visiting chemist of KFA, Jülich. Università di Roma, 00100 Rome, Italy. (b) Laboratorio di Chimica Nucleare del C.N.R.

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(35) A conceivable additional route for the acetylation of the hydroxyl group might involve the intermediacy of ketene, which is known to undergo efficient condensation with alcohols (cf. G. M. Breuer, F. J. Grieman, and K. C. Edward, *J. Phys. Chem.*, **79**, 542 (1975)), and could be generated by proton transfer between CH_3CO^+ ions and a base. However, on the grounds of the available thermochemical data (J. Long, and B. Munson, *J. Am. Chem. Soc.*, **95**, 2427 (1973)), the formation of ketene (PA 201 kcal mol^{-1}) should be endothermic in our experiments, suggesting a negligible, if any, contribution of this channel to the esters formation. This assumption is strengthened by the ICR results,[7] indicating that protonation by quasi-thermal $C_2H_3O^+$ and/or $CH_3COCOCH_3^+$ is observed only with substrates, e.g., phenetole, benzaldehyde, or acetophenone, that are significantly more basic than ours.

(36) Assuming for CH_3CO^+ ion one of the reported $\Delta H_f°$ values (see J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions", National Bureau of Standards Publication No. NSRDS-NBS-26, U.S. Government Printing Office, Washington D.C., 1969), still even a rough estimate of the $\Delta H_f°$ for the ipso-protonated acetophenone is impossible on the ground of available data, preventing any more precise statement.

(37) Even though the tritium exchange in benzene appears the major reaction channel in the $CT_4/CO/C_6H_6$ experiment, nevertheless it accounts only for ca. 12% of the overall activity of decay ions. In this case the contribution of labeled species[19] (ions and radicals), other than CT_3^+ ions, formed in the decay process could be significant.

(38) M. Speranza et al., to be published.

(39) M. Attina, F. Cacace, G. Ciranni, and P. Giacomello, *J. Am. Chem. Soc.*, in press.